PHASE TRANSITION PROPERTIES OF SOLIDS:

THE CRYOLITES, \( A_3MF_6 \)

A thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Physics in the University of Canterbury, Christchurch, New Zealand.

by

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This thesis discusses structural phase transitions that occur in various cryolite compounds. The cryolites are characterised by the chemical formula $A_3MF_6$, where $A$ and $M$ are cations with valency 1 and 3 respectively. At high temperatures these compounds tend to possess a characteristic face-centred cubic form (space group $O_h^5$). On cooling, this is often transformed to a lower symmetry structure; the particular structure assumed varies from compound to compound.

Structural transitions of this type are often associated with the reduction in frequency ("softening") of just one particular lattice vibrational mode of the high temperature form. Landau's theory of phase transitions provides a means of predicting this mode, given just the crystal structures existing on each side of the transition. A summary of the group theory of lattice dynamics is given to provide a basis for using Landau's approach. This group theory is used to derive all the vibrational modes which, according to Landau's results, can be associated with a second-order structural phase transition from the face-centred cubic cryolite form. A complete analysis is performed for a transition to the tetragonal ($D_{4h}^6$) structure; this transition is predicted to be associated with the $X^{2+}$ mode of the high temperature form.

Experimental approaches and results described in the literature are surveyed. In the current work it has been generally necessary to use powder rather than crystal samples, and the emphasis has been on appropriate X-ray diffraction methods. The design and operation of a variable temperature
A system for taking Debye-Scherrer X-ray photographs is described, as well as the development of facilities for digitizing and processing the resultant data. Previously undetected transitions, observed using differential thermal analysis (D.T.A.), are reported for \((\text{NH}_4)_3\text{VF}_6\) (three) and \((\text{NH}_4)_3\text{CrF}_6\). Some preliminary X-ray data on the low temperature structures of \((\text{NH}_4)_3\text{FeF}_6\), \((\text{NH}_4)_3\text{CrF}_6\) and \((\text{NH}_4)_3\text{AlF}_6\) are discussed.
ACKNOWLEDGEMENTS

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(3) Wave Vector $X_z$ (0 0 1)  
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CHAPTER I

INTRODUCTION

1.1 GENERAL INTRODUCTION

The study of structural phase transitions has blossomed over the past fifteen years. Two developments in particular have made this possible. The first has been the origin of the concept of the "soft mode"\(^3,27,28\), that is, the idea that a structural transition is associated with one of the crystal lattice normal modes whose frequency falls near the transition. The second has been the development of Raman spectroscopy and neutron inelastic scattering as techniques for probing the lattice dynamics of crystals.

The object of the work to be described in this thesis has been to investigate the structural phase transitions that occur in cryolites. Cryolite itself is sodium hexafluoroaluminate, \(\text{Na}_3\text{AlF}_6\). The general member of the group has the chemical formula \(\text{A}_3\text{MF}_6\), where A and M are monovalent and trivalent respectively.

Structural transitions were first observed in cryolites by Steward and Rooksby\(^{127}\) through X-ray powder photography of \(\text{Na}_3\text{AlF}_6\), \((\text{NH}_4)_3\text{AlF}_6\) and \((\text{NH}_4)_3\text{FeF}_6\). The high temperature structures obtained were all face-centred cubic with a space group \(O_h^5\) (Fm\(\overline{3}\)m), and this is a common occurrence for the cryolites as a whole. This structure (figure (1.1)) is characterised by the following atomic positions:
FIG. 1.1 COMMON CRYOLITE STRUCTURE FOR HIGH TEMPERATURES
CHEMICAL FORMULA: $A_3MF_6$
$a =$ LENGTH OF FACE CENTRED CUBIC UNIT CELL
M (4a) : (0 0 0)
A (4b) : (½ ½ ½)
A (8c) : (½ ½ ½)
F (24e) : (±x,0,0), (0,±x,0), (0,0,±x) with x ≈ 0.2.

The site labels are those of the International Tables for X-ray Crystallography.

It can be seen from figure (1.1) that each M atom sits at the centre of six fluorines, as do one third of the A atoms. The fluorine atoms, however, are generally bound far more strongly to the M's than to the A's, to the extent that the MF$_6^{3-}$ octahedron sometimes exists free in solution (see, for example, reference 76). The remaining A's are at tetrahedral sites with fluorine coordination number 12.

1.2 CHARACTERISTICS OF CRYOLITE PHASE TRANSITIONS

There are several reviews$^{5,14,17,23,33,112}$ that deal with cryolites. The transitions noted in these reviews, and a number of others from original papers, are listed in table (1.1). In the basic cryolite structure the tetrahedral A sites are significantly larger than the octahedral sites of the same atom. This allows the observed changes to the basic structure that take place as the temperature is lowered. At the phase transitions the strongly bound MF$_6^-$ octahedron tends to rotate as a unit, often with little distortion. The fluorines thus move away from the edges of the unit cell, enlarging the space available for the octahedrally coordinated A atoms. In some cases distortions of other types may occur also, lowering the symmetry still further.
Table (1.1) Transitions in Cryolites

<table>
<thead>
<tr>
<th>Compound</th>
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<tr>
<td>Li₃AlF₆</td>
<td>$\alpha$, ortho, $C_{2v}^9$ ($Pna2_1$) $\rightarrow$ $\beta$ $\rightarrow$ $\gamma$</td>
<td>B4, H1, M2</td>
</tr>
<tr>
<td>NaAlF₆</td>
<td>$\beta$, mcl, $C_{2h}^5$ ($P2_1/n$) $\rightarrow$ $\alpha$, sfcc, $O_h^5$ ($Fm3m$)</td>
<td>B1</td>
</tr>
<tr>
<td>K₃AlF₆</td>
<td>$\beta$, $t$, $D_{4h}^{17}$ ($I4/mmm$) $\rightarrow$ $\gamma$, $t$ $\rightarrow$ $\delta$, sfcc, $O_h^5$</td>
<td>B1, S1, G1, H2</td>
</tr>
<tr>
<td>Rb₃AlF₆</td>
<td>$\alpha$, $t$ $\rightarrow$ $\beta$, $c$, $O_h^5$</td>
<td>H2</td>
</tr>
<tr>
<td>Cs₃AlF₆</td>
<td>$\alpha$, $t$ $\rightarrow$ $\beta$, $c$, $O_h^5$</td>
<td>H2</td>
</tr>
<tr>
<td>(NH₄)₃AlF₆</td>
<td>$\gamma$ $\rightarrow$ $\beta$, symmetry lower than $D_{4h}^{6}$ $\rightarrow$ $\alpha$, sfcc, $O_h^5$</td>
<td>B1, G4</td>
</tr>
<tr>
<td>Li₃GaF₆</td>
<td>$\alpha$, ortho, $C_{2v}^9$ $\rightarrow$ $\beta$, mcl, $C_{2h}^6$ or $C_s^4$</td>
<td>C1, M2</td>
</tr>
<tr>
<td>Na₃GaF₆</td>
<td>$\alpha$, mcl, $C_{2h}^5$ $\rightarrow$ $\beta$</td>
<td>C1</td>
</tr>
<tr>
<td>K₃GaF₆</td>
<td>$\alpha$ $\rightarrow$ $\beta$, $c$ $\rightarrow$ $\gamma$, fcc</td>
<td>C1</td>
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<tr>
<td>Rb₃GaF₆</td>
<td>$\alpha$ $\rightarrow$ $\beta$, $c$ $\rightarrow$ $\gamma$, $t$ $\rightarrow$ $\delta$, fcc</td>
<td>C1</td>
</tr>
<tr>
<td>Cs₃GaF₆</td>
<td>$\alpha$, $t$ $\rightarrow$ $\beta$, fcc</td>
<td>C1</td>
</tr>
<tr>
<td>Tl₃GaF₆</td>
<td>$\alpha$, $t$ $\rightarrow$ $\beta$, fcc</td>
<td>C3</td>
</tr>
<tr>
<td>(NH₄)₃GaF₆</td>
<td>$\beta$ $\rightarrow$ $\alpha$, sfcc or microtwinned $T_h^6$ ($Pa3$) structure</td>
<td>S2, S3</td>
</tr>
<tr>
<td>Li₃InF₆</td>
<td>$\alpha$, $t$ $\rightarrow$ $\beta$, $c$ $\rightarrow$ $\gamma$, fcc</td>
<td>G3</td>
</tr>
<tr>
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<td>$\alpha$, mcl, $C_{2h}^5$ $\rightarrow$ $\beta$, $c$ $\rightarrow$ $\gamma$, fcc</td>
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</tr>
<tr>
<td>Rb₃InF₆</td>
<td>$\alpha$, $t$ $\rightarrow$ $\beta$, $c$ $\rightarrow$ $\gamma$, $t$ $\rightarrow$ $\delta$, fcc</td>
<td>G5</td>
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<tr>
<td>Cs₃InF₆</td>
<td>$\alpha$, $t$ $\rightarrow$ $\beta$, $c$ $\rightarrow$ $\gamma$, $t$ $\rightarrow$ $\delta$, fcc</td>
<td>G5</td>
</tr>
<tr>
<td>Tl₃InF₆</td>
<td>$\beta$, $t$ $\rightarrow$ $\alpha$, $c$ $\rightarrow$ $\gamma$, fcc</td>
<td>G5</td>
</tr>
<tr>
<td>(NH₄)₃InF₆</td>
<td>$\alpha$, $t$, $D_{4h}^{6}$ ($P4/mnc$) or $C_{2h}^5$ ($P2_1/n$) $\rightarrow$ $\beta$, $O_h^5$ or $T_h^6$</td>
<td>B1, S2</td>
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<tr>
<td>Na₃TlF₆</td>
<td>$\alpha$, mcl $\rightarrow$ $\beta$, fcc</td>
<td>G3</td>
</tr>
<tr>
<td>Na₃ScF₆</td>
<td>$\alpha$, mcl, $C_{2h}^5$ $\rightarrow$ $\beta$, sfcc</td>
<td>T1</td>
</tr>
<tr>
<td>Tl₃ScF₆</td>
<td>$\alpha$, $t$ $\rightarrow$ $\beta$, sfcc</td>
<td>C4</td>
</tr>
<tr>
<td>(NH₄)₃ScF₆</td>
<td>$\beta$, $t$, $D_{4h}^{6}$ $\rightarrow$ $\alpha$, sfcc, $O_h^5$</td>
<td>B1, B2</td>
</tr>
<tr>
<td>Li₃TlF₆</td>
<td>$\alpha$, ortho, $C_{2v}^9$ $\rightarrow$ $\beta$, mcl, $C_{2h}^6$ or $C_s^4$</td>
<td>M2</td>
</tr>
</tbody>
</table>

Transition temperatures in °C
\[(\text{NH}_4)_3\text{TiF}_6\] \[	frac{\alpha}{\beta} \xrightarrow{35} \tfrac{\beta}{100} \xrightarrow{\gamma} \text{B2}\]

\[\text{Li}_3\text{VF}_6\] \[	frac{\tfrac{\alpha}{\beta},\text{orth},c}{2v} \xrightarrow{310} \tfrac{\beta}{565} \]

\[\text{K}_3\text{VF}_6\] \[	frac{\alpha}{t} \xrightarrow{200} \tfrac{\beta}{\text{fcc}} \]

\[\text{Rb}_3\text{VF}_6\] \[	frac{\alpha}{130} \xrightarrow{258} \tfrac{\beta}{345} \xrightarrow{\delta,\text{fcc}} \text{C2}\]

\[\text{Cs}_3\text{VF}_6\] \[	frac{\alpha}{345} \xrightarrow{\beta,\text{fcc}} \text{C2}\]

\[\text{Tl}_3\text{VF}_6\] \[	frac{\alpha}{115} \xrightarrow{\beta,\text{fcc}} \text{C2}\]

\[\text{Li}_3\text{CrF}_6\] \[	frac{\tfrac{\alpha}{\beta},\text{orth},c}{2v} \xrightarrow{2} \tfrac{\beta}{\text{mcl}},c_{2h} \text{ or } c_s \]

\[\text{Rb}_3\text{CrF}_6\] \[	frac{\alpha}{410} \xrightarrow{\beta,\text{fcc}} \text{K}\]

\[\text{Tl}_3\text{CrF}_6\] \[	frac{\alpha}{212} \xrightarrow{\beta,\text{fcc}} \text{K}\]

\[\text{Li}_3\text{CrF}_6\] \[	frac{\text{CF}}{\alpha,\text{sfcc},0^5_{\text{h}}} \]

\[\text{Li}_3\text{FeF}_6\] \[	frac{\tfrac{\alpha}{\beta},\text{orth},c}{2v} \xrightarrow{500\pm20} \tfrac{\beta,\text{mcl},c_6}{2h} \text{ or } c_s \]

\[\text{Na}_3\text{FeF}_6\] \[	frac{\alpha,\text{mcl},c_5}{2h} \xrightarrow{630\pm10} \tfrac{\beta}{\text{fcc}} \]

\[\text{K}_3\text{FeF}_6\] \[	frac{\alpha}{t} \xrightarrow{140\pm10} \tfrac{\beta}{\text{fcc}} \]

\[\text{Rb}_3\text{FeF}_6\] \[	frac{\alpha,\text{t},\text{symmetry not greater than } C_4^5}{4} \xrightarrow{360\pm10} \tfrac{\beta}{\text{fcc}} \]

\[\text{Cs}_3\text{FeF}_6\] \[	frac{\alpha,\text{t},\text{symmetry not greater than } C_4^5}{4} \xrightarrow{360\pm10} \tfrac{\beta}{\text{fcc}} \]

\[\text{Ag}_3\text{FeF}_6\] \[	frac{\alpha,\text{t},\text{symmetry not greater than } C_4^5}{4} \xrightarrow{145\pm10} \tfrac{\beta}{\text{fcc}} \]

\[\text{Ag}_3\text{FeF}_6\] \[	frac{\text{CF}}{\alpha,\text{sfcc},0^5_{\text{h}}} \]

Abbreviations:

c cubic
orth orthorhombic
mcl monoclinic
fcc face-centred cubic
sfcc face-centred cubic, ideal cryolite structure
cfcc face-centred cubic, with fluorine atoms distributed randomly over one-eighth of the 192 (l) sites of the O^5_h lattice
t tetragonal
* the fluorogallate phases which are labelled by ar sterisk are isotypes
† the α- and β-phases can both exist at room temperature.
Comments:

1) All the published work on transitions has been for powders; hence the number of definite structures is limited.

2) There is data for $K_3FeF_6$ (References A, S4) which assigns to it a cubic room temperature structure. In this case the sample was prepared from aqueous solution, and a possible explanation for its being cubic is the presence of small amounts of water substituting for fluorine ions (cf. $K_{2.9}AlF_{5.9}(H_2O)^{0.1}$ which is cubic while $K_3AlF_6$ is tetragonal — reference B3).

References for Table (1.1)

C3 Chassaing, J., ibid., 269C, 774 (1969).
H2 Holm, J.L., ibid., 19, 261 (1965).
Result obtained in the course of work for this thesis.

S1 Steward, E. and Rooksby, H., Acta Crystallographica 6, 49 (1953).
S2 Schwarzmann, S., Fortschritte der Mineralogie 42, 231 (1964).
This discussion of the phase transitions in terms of the structure can be made more quantitative by defining a "tolerance factor", \( t \), similar to that used by Goldschmidt for perovskites\(^\text{55}\). For the general cryolite \( \text{A}_3\text{MF}_6 \) this will be defined as

\[
\begin{align*}
\frac{\text{Sum of radii of fluoride and tetrahedral site A ions}}{\text{Distance between their centres in the basic cubic structure}} &= t \\
&= \frac{2(R_A + R_F)}{\left[ (R_A - R_M)^2 + 2(R_A + R_M + 2R_F)^2 \right]^{1/2}} \quad (1.1)
\end{align*}
\]

The \( R \)'s in this formula represent ionic radii. In particular \( R_A \) is the radius of the A ion at the tetrahedral site and \( R_A' \) the radius of the same ion at the octahedral site.

For the basic face-centred cubic form to be stable at all, \( t \leq 1 \). As \( t \) decreases the room available for motion of the F- ions increases. The simple cryolite structure should thus be less stable, and we would expect it to transform to a lower symmetry form at a higher temperature. In this connection note that \( \frac{\partial t}{\partial R_A} \) is always negative, and also, if we take the approximation that \( R_A \cdot R_A' = 1.12 \) (the approximate ratio of radii for ions of the same type with coordination numbers 12 and 6 respectively\(^\text{155}\)), \( \frac{\partial t}{\partial R_A} \) is positive. Thus replacement of the M ion by one with a larger radius or of the A atom by a smaller one would decrease \( t \) and be expected to result in a higher transition temperature.

In figure (1.2) values of \( t \) are plotted against transition temperatures for the compounds of table (1.1). Lithium salts are omitted; their low \( t \)-values do not favour the formation of the face-centred cubic phase. Since the face-centred cubic structure is the high temperature form the highest transition
FIG. 1.2 TOLERANCE FACTOR VERSUS TRANSITION TEMPERATURE

A point labelled AM corresponds to the compound $A_3MF_6$. 
temperature has been taken when a compound has more than one transition. The ionic radii used to calculate the tolerance factor are those of Shannon and Prewitt\textsuperscript{120}, except for the ammonium ion which they do not list. This was assigned a radius of 1.48Å as given by Pauling\textsuperscript{109}. When the observed radius for the A ion in the tetrahedral site (coordination number 12) was unavailable a value was obtained by multiplying the octahedral site radius (coordination number 6) by 1.12 (as in ref. 155).

It is apparent from figure (1.2) that the tolerance factor does not satisfactorily predict transition temperatures. However, if we group the compounds together according to the A-ion some systematic behaviour is evident. For the ammonium salts there is on the whole a good correlation between decreasing t (increasing R\textsubscript{M}) and increasing transition temperature; only the fluorotitanate, (\textit{NH}_4)_3\textit{TiF}_6, is significantly against this trend, possibly because of the Jahn-Teller effect (see Section 7.3.4). The sodium cryolites also show some trend towards similar behaviour to the ammonium compounds, but this is not so for potassium, rubidium, caesium or thallium. No correlation at all is evident between R\textsubscript{A} and the transition temperature.

To go beyond this we need to consider the lattice dynamics of the cryolites in detail. Some indication of the path to follow can be gained by comparing the basic face-centred cubic cryolite structure with those of the perovskite (AMX\textsubscript{3}) and antifluorite (A\textsubscript{2}MX\textsubscript{6}) (here A and M are metals, X is oxygen or a halogen). The atomic coordinates for these are:
Perovskite: Simple cubic, space group $O_h^1$ (Pm3m)

- $M$ (1a) : (0 0 0)
- $A$ (1b) : ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$)
- $X$ (3d) : ($\frac{1}{2}$ 0 0), (0 $\frac{1}{2}$ 0), (0 0 $\frac{1}{2}$)

Antifluorite: Face-centred cubic, space group $O_h^5$ (Pm3m)

- $M$ (4a) : (0 0 0)
- $A$ (8c) : ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$)
- $X$ (24e) : (±x 0 0), (0 ±x 0), (0 0 ±x)

For comparison the plane $\alpha$-$\beta$-$\gamma$-$\delta$ of figure (1.1) is shown on the left-hand side of figure (1.3), along with the corresponding planes for the antifluorite and perovskite structures. Those $A$ atoms which are depicted by broken circles are above and below these planes. The structural similarities are evident. The cryolite structure can be obtained from the perovskite by replacing alternate $M$ atoms by $A$ atoms, or from the antifluorite by inserting $A$ atoms at the centres of the unit cell edges.

Transitions involving rotations of the $MX_6$ octahedra have been studied for both the antifluorite and perovskite structures. Some examples of these transitions are depicted on the right-hand side of figure (1.3). In each of the cases shown there is a rotation of each $MX_6$ octahedron about its (0 0 1) (four-fold) axis. For $SrTiO_3$ and $(NH_4)_3 ScF_6$ we find that as we move in the $Z$-direction the octahedra of fluorine ions about $M$ atoms in consecutive layers rotate in opposite directions but with equal angles of rotation. There is consequently a doubling of the unit cell dimension in that direction. For $K_2 ReCl_6$ all octahedra rotate in the same direction. The
FIG. 1.3 COMPARISON OF ANTIFLUORITE, PEROVSKITE AND CRYOLITE STRUCTURES
transitions of $K_2ReCl_6$ and $SrTiO_3$ are both associated with soft modes$^{105,47}$, and the similarities of structure encourage us to seek a similar explanation for cryolite transitions.

1.3 STRUCTURE OF THIS WORK

An explanation of a structural phase transition requires a discussion of the lattice dynamics of the material. Chapter II lays a foundation for this with a summary of the group theory of lattice dynamics. This summary provides the basis for discussing Landau's theory of phase transitions (Chapter III), which is then applied to the basic face-centred cubic cryolite structure described above. The manner in which Landau's work is extended to predict that structural phase transitions will have associated soft modes is indicated, and the implications of the theory's predictions for experimental work are also discussed. This leads on in Chapter IV to a review of experimental investigations carried out on cryolites. Results published in the literature are summarised, along with some preliminary data obtained in the work done for this thesis. In Chapter V the design of a variable temperature attachment for a Debye-Scherrer X-ray camera is described. This equipment enables us to investigate phase transitions in cryolite powder samples. The methods for reading and processing the resultant X-ray data are covered in Chapter VI. Finally, in Chapter VII some initial X-ray results are discussed, and the paths for further experimental work are indicated.
2.1 **INTRODUCTION**

In this chapter the group theory of lattice dynamics will be discussed in sufficient detail to provide a basis for
a) labelling the peaks obtained in infrared and Raman spectra
b) simplifying lattice dynamical calculations
c) applying the Landau theory of phase transitions.

To illustrate these group theoretical techniques, they will then be applied to the ideal cryolite structure and one of its low temperature modifications.

2.2 **SPACE GROUPS AND POINT GROUPS**

2.2.1 **Definitions**

Basic theory of groups and their representations will be assumed (see, for example, Reference 140).

The atoms in an ideal crystal vibrate about average positions given by the vectors

\[ \chi(\chi, \kappa) = \chi(\kappa) + \sum_{\ell=1}^{3} \ell \alpha_{\ell} \]  

\[ = \chi(\kappa) + \ell \]  

(2.1a)

(2.1b)

where

the \( \alpha_{\ell} \) are three primitive translation vectors that define the crystal lattice,
the \( l_i \) are integers, and thus define a particular primitive unit cell (the smallest repeating structural unit of the crystal), and \( \kappa \) is the label of a particular atom in a primitive unit cell.

The space group \( (G) \) of the crystal is the set of operations consisting of translations, rotations, inversions and combinations of these that leave the appearance of the crystal unchanged. We write these operations

\[
\{S | x(m) + \tilde{v}(S) \} \tag{2.2}
\]

where \( S \) is the rotation, inversion or combination of these, \( x(m) + \tilde{v}(S) \) is the translation which follows this operation \( S \), \( x(m) \) is that part of the translation that can be written as a lattice vector of the form of \( \tilde{l} \), and \( \tilde{v}(S) \) is a fractional translation vector associated with \( S \).

These space group operations obey the normal combination rules for groups.

The point group of the crystal \( (G_0) \) is a group consisting of the set of \( S \)'s occurring in the elements of \( G \).

2.2.2 Representations

All of the irreducible representations of the 230 space groups have been listed\(^{91} \). We will find irreducible multiplier representations (alternatively called weighted, ray, projective or loaded representations) more suited to our purposes. For these the law of multiplication of the representation matrices \( T(R) \) has the form
\[ T(R_i) T(R_j) = \phi(R_i, R_j) T(R_i R_j) \] (2.3)

\( R_i \) and \( R_j \) are elements of the group, and the scalar function \( \phi(R_i, R_j) \) is called the multiplier.

The groups we shall be using are the point groups of the wave vector (these will be discussed later). The matrices for their irreducible multiplier representations may be obtained from tables 68, 154, though caution must be exercised since some of the entries in reference 68 are incorrect. Computer programs 102, 152 which will construct these representations are also available. There is a one-to-one correspondence between these irreducible multiplier representations and the ordinary irreducible representations of the space group.

2.2.3 The Reciprocal Lattice

The basis vectors \( b_i \) (\( i = 1, 2, 3 \)) of the reciprocal lattice are defined by

\[ b_i = \frac{\zeta}{a_i \cdot (a_2 \times a_3)} (a_2 \times a_3) \] (2.4)

where the expressions for \( b_2 \) and \( b_3 \) are of similar form, and are obtained by rotating the subscripts of equation (2.4) in cyclic order. It follows that

\[ a_i \cdot b_j = \zeta \delta_{ij} \] (2.5)

where \( \delta_{ij} = 1 \) if \( i = j \) and zero otherwise. The constant \( \zeta \) is usually taken equal to 1 or \( 2\pi \), as this yields the simplest algebraic expressions. We will take \( \zeta = 1 \) unless otherwise stated.
The general point in the reciprocal lattice is

\[ b = \sum_{j=1}^{3} h_j b_j \]  

(2.6)

with the \( h_j \) integers.

2.2.4 The Group of a Reciprocal Lattice Vector

For any vector \( k = \sum_{i=1}^{\infty} v_i b_i \) (\( v_i \) arbitrary) the group of \( k \), \( G(k) \), is defined as follows: it consists of the set of operations \( \{R|k\} \) belonging to the space group \( G \) and also possessing the property that

\[ Rk \equiv k \]  

(2.7)

For the purposes of this definition the vector \((k+2\pi b)\), with \( b \) a reciprocal lattice vector, is taken as being equivalent to \( k \), i.e.

\[ k \equiv k + 2\pi b. \]  

(2.8)

\( G_0(k) \), the point group of \( k \), is the set of elements \( R \) in the operations \( \{R|k\} \) of \( G(k) \).

2.3 LATTICE DYNAMICS AND SPACE GROUP THEORY

2.3.1 Basic Theory

The application of the theory of space groups to lattice dynamics has been discussed in detail in articles by Maradudin and Vosco 84 and Warren 145,146. The starting point is the potential energy of an arbitrary crystal in the harmonic approximation:
\[ \phi = \phi_0 + \frac{1}{2} \sum_{\ell \ell'} \sum_{KK'} \phi_{\alpha \beta}(\ell K; \ell' K') \nu_\alpha(\ell K) \nu_\beta(\ell' K') \]  
\hspace{1cm} (2.9)

where

\[ \nu_\alpha(\ell K) \] is the \( \alpha \) Cartesian component of the displacement of the \( K \)th atom in the \( \ell \)th unit cell from its equilibrium position, and

\[ \phi_{\alpha \beta}(\ell K; \ell' K') \] are the atomic force constants of the crystal.

The equations of motion are thus

\[ M_\ell \ddot{\nu}_\alpha(\ell K) = -\sum_{\ell' K'} \phi_{\alpha \beta}(\ell K; \ell' K') \nu_\beta(\ell' K') \]  
\hspace{1cm} (2.10)

with \( M_\ell \) the mass of atom \( \ell \).

The potential energy and the equations of motion must be invariant under all the operations of the space group. This fact can be used to develop solutions of equations (2.10), for which the atomic displacements take the form

\[ u_\alpha(\ell K) = \frac{e_\alpha(\kappa | kj)}{M_\kappa^{1/2}} \exp\{i(k \cdot \ell - \omega(\kappa, j) t)\} \]  
\hspace{1cm} (2.11)

The label \( t \) here represents time, and \( \omega(\kappa, j) \) is an associated frequency. Notice that the vector \( k \) determines the periodicity of these displacements; it is accordingly referred to as a wave vector. The amplitude \( \left[ \frac{e_\alpha(\kappa | kj)}{M_\kappa^{1/2}} \right] \) is independent of both \( \ell \) (i.e. of the particular unit cell we are examining) and the time \( t \). The 'j' is an extra label for different solutions of equal \( \kappa \). The terms \( e_\alpha(\kappa | kj) \) are solutions of the equations

\[ \sum_{\kappa' K'} D_{\alpha \beta}(\kappa K' | kj) e_\beta(\kappa' K') = \omega_2(kj) e_\alpha(\kappa kj) \]  
\hspace{1cm} (2.12)
where the matrix $D(k)$ with elements

$$D_{\alpha \beta}(k^1 \mid k^2) = \frac{1}{(M \cdot M_{\alpha \beta})^{1/2}} \sum_{\lambda} \phi_{\alpha \beta}(\lambda k^1, \lambda k^2) \exp(-i k^2 \cdot (l - l'))$$

has dimensions $3r \times 3r$ (where $r$ is the number of atoms per primitive unit cell) and is called the Fourier-transformed dynamical matrix.

Equation (2.12) possesses non-zero solutions for the amplitudes $e_\alpha(k^1 \mid k^2)$ provided the determinant of coefficients vanishes, i.e.

$$\det\left\{ \omega^2(k^1) \delta_{k^1 k^2} \delta_{\alpha \beta} - D_{\alpha \beta}(k^1 \mid k^2) \right\} = 0 \quad (2.14)$$

There is an infinite number of possible vectors $k$ for equation (2.14). We limit this number in two ways:

(i) We demand that the displacements $u_\alpha(lk)$ obey the cyclic boundary condition; that is that they be periodic, with the period being that of a defined macrocrystal with $N$ primitive unit cells and total volume $V$. Only discrete values of $k$ are then allowed.

(ii) We note that the form of $D(k)$ indicates that

$$D(k + 2\pi b) = D(k) \quad (2.15)$$

where $b$ is a reciprocal lattice vector, defined as in equation (2.6). If we now write $k = 2\pi b$, where $b$ is any vector in reciprocal space, equation (2.15) indicates that to consider all physically distinct modes of vibration of the crystal it is sufficient to take only cases for which
\[ b_\Sigma = \sum_{i=1}^{3} \mu_i b_i \] (2.16)

where \(-\frac{1}{2} < \mu_i < \frac{1}{2}\) for all \(i\).

With no loss of generality we can choose mode frequencies \(\omega(k,j)\) and polarisation vectors \(e(k,j)\) (these are column vectors with elements \(e_\alpha(k|kj)\)) to have the periodicity of the reciprocal lattice.

The lattice space spanned by vectors of the form of equation (2.16) is called the first Brillouin zone, or just the Brillouin zone. Its shape clearly depends on the crystal lattice. Vectors \(b_\Sigma\) corresponding to allowed wave vectors \(k\) are uniformly distributed throughout this zone with density \(N/V\).

We conclude this section with three brief comments.

1) \(D(k)\) is Hermitian. Hence its eigenvalues \(\omega^2(k,j)\) are real, and its eigenvectors \(e(k,j)\) can be chosen to satisfy orthogonality and closure relations. These properties will be assumed from here on.

2) \(D^*(k) = D(-k)\),

the asterisk indicating complex conjugation. This property will be of importance when we discuss time-reversal-degeneracy.

3) The general lattice displacement with components \(v_\alpha(\ell,\kappa,t)\) is given by

\[ M_{k_\alpha} = \sum_{k} \sum_{\ell,j=1}^{BZ} w(kj)e_\alpha(\kappa|kj)\exp(-i[k,\ell-\omega(k,j)t]), \] (2.18)

where the first summation is over all allowed \(\kappa\)'s in the Brillouin zone, and the \(w(kj)\)'s are coefficients representing the contribution of each mode.
2.3.2 Effect of Symmetry on the Fourier-Transformed Dynamical Matrix and Its Eigenvectors

(1) Multiplier Representations of the Point Group of the Wave Vector

By requiring that the equations of motion of the crystal lattice when it is transformed under any of its space group operations should be unaltered, we can obtain information on the transformation properties of the eigenvectors $\psi(k\beta)$ and also on the form of $D(k)$ itself $^{34,146,151}$. This information is independent of the values of the crystal force constants.

In order to express the relevant results we define a multiplier representation $T(k,R)$ of $G_0(k)$, the point group of $k$. The elements of this are $^{146}$

$$T(k,R)_{k,\alpha;\lambda,\beta} = \delta(k,F_0(\lambda,R_i,\ell)) [R_i]_{\alpha\beta}$$

$$\times \exp\{i k \cdot [x(k) - R_i x(\lambda)]\} \quad (2.19)$$

The Cartesian indices, $\alpha$ and $\beta$, vary from 1 to 3, and the atom labels $k$ and $\lambda$ from 1 to $r$, so that the combined indices $(k,\alpha)$, with $\alpha$ varying most rapidly, go from 1 to $3r$.

$F_0(\lambda,R_i,\ell)$ is the label of the atom to whose site the atom labelled $\lambda$ is moved under the space group operation $\{R_i | y(R) + \ell\}$, the $[R_i]_{\alpha\beta}$ are the Cartesian components of the standard 3x3 rotation matrix of the vector representation of $G_0(k)$, and $\delta(k,\lambda) = 1$ for $k = \lambda$, zero otherwise.

As before, the $k^{th}$ atom in the unit cell labelled by vector $\ell$ is at $\ell + x(k)$. 
The multiplier of this representation is given by
\[ \phi(k; R_1, R_j) = \exp\{i[k-R_1^{-1}k].\gamma(R_j)\} \] (2.20)
The representation is unitary, i.e.
\[ T^+(k, R) T(k, R) = 1 \] (2.21)
Also, \( D(k) \) commutes with the \( T \)'s, i.e.
\[ T(k, R_1) D(k) T^+(k, R_1) = D(k) \] (2.22)

(2) Consequences of Symmetry

The representation \( T(k, R) \) can be decomposed into a direct sum of the irreducible multiplier representations of \( G_0(k) \) as listed by Kovalev\(^6\) and Zak et al.\(^{154}\). Symbolically we write
\[ T(k) = \sum_{\sigma} c_{\sigma} T(k, \sigma). \] (2.23)

Maradudin and Vosco\(^8\) show that eigenvalues and orthogonal eigenvectors of \( D(k) \) belong to, i.e. can be labelled by, the irreducible representations \( \tau(k, \sigma) \) contained in the above decomposition. Accordingly we replace the label \( j \) in \( \varepsilon(kj) \) by the triple label \( (\sigma, \mu, \delta) \):

\( \sigma \) is the label of the representation
\( \mu \), the multiplicity index, assumes values \( 1, 2, \ldots, c_{\sigma} \)
and \( \delta \), the degeneracy index, corresponds to the \( \delta \)th row of the representation, and assumes values from 1 to \( d_{\sigma} \), where \( d_{\sigma} \) is the dimension of the matrices \( \tau(k, \sigma) \).

Equation (2.12) can now be rewritten in matrix form:
\[ D(k)e(k, \sigma, \mu, \delta) = \omega^2(k, \sigma, \mu)e(k, \sigma, \mu, \delta) \quad (2.24) \]

Group theory can simplify the calculation of \( D(k) \) in two ways:

(i) symmetry reduction, and

(ii) block diagonalisation.

Symmetry reduction obtains mathematical relationships between different elements of \( D(k) \). It is achieved by requiring that equation (2.22) be true for all elements of \( G_0(k) \). Worlton and Warren\textsuperscript{151} have shown that a matrix \( D(k) \text{SR} \) which satisfies this condition can be constructed as follows:

\[ D(k) \text{SR} = \sum_{i=1}^{g_0(k)} T(k, R_i) A^\dagger(k, R_i) \quad (2.25) \]

where \( A \) is any Hermitian matrix, and \( g_0(k) \) is the number of elements \( R_i \) in \( G_0(k) \), the summation being over all these elements.

Block diagonalisation reduces the matrix to a more easily solved set of smaller matrices. To do this one must find a unitary transformation \( V(k) \) which simultaneously brings every matrix \( T(k, R_i) \) into block diagonal form, with the blocks being matrices of the irreducible multiplier representations. The columns of \( V(k) \) can be produced by operating on an arbitrary \( 3r \times 1 \) column vector \( \chi \) with the projection operator

\[ P(k, \sigma, \delta, \delta') = \frac{d_{\sigma}}{g_0(k)} \sum_{i=1}^{g_0(k)} \tau^*_\delta \delta'(k, \sigma, R_i) T(k, R_i) \quad (2.26) \]

where \( \tau^*_\delta \delta'(k, \sigma, R_i) \) is the complex conjugate of the \((\delta, \delta')\) element of the matrix for the operator \( R_i \) of \( G_0(k) \) in the \( \sigma \)th multiplier representation. We write our resultant vector
\[ \psi(k,\sigma,\mu,\delta) = \frac{P(k,\sigma,\delta,\delta')}{\chi} \tag{2.27} \]

Worlton and Warren\textsuperscript{151} discuss the combination of such vectors to form the columns of \( \psi(k) \). The unitary transformation \( \psi(k) \) which will block diagonalise \( \psi(k) \) is then obtained by interchanging columns of \( \psi(k) \) according to the prescription
\[ (\sigma,\mu,\delta) \rightarrow (\sigma,\delta,\mu), \]
so that \( \mu \) varies most rapidly instead of \( \delta \).

The columns of \( \psi(k) \) form a complete set of orthogonal vectors \( f(k,\sigma,\mu,\delta) \). Thus, any displacement of atoms which transforms according to the representation \( \sigma \) can be written as a linear combination of a particular set of \( c_\sigma \) columns of \( \psi(k) \):
\[ \psi(k,\sigma,\delta) = \sum_{\mu=1}^{c_\sigma} \eta(\mu)f(k,\sigma,\mu,\delta) \tag{2.28} \]

The coefficients \( \eta(\mu) \) cannot be obtained from group theory but depend on the dynamics of the system. However, if the \( \sigma \)th representation occurs once only in the decomposition (2.23), then we can write
\[ \psi(k,\sigma,1,\delta) = f(k,\sigma,1,\delta) \tag{2.29} \]

In analogy to the components of the eigenvectors we shall write the \( f \)-components in the form
\[ f_\alpha(\kappa|k\sigma\mu\delta). \tag{2.30} \]

(3) Effect of Time-Reversal-Invariance

This will provide further symmetry restrictions in certain circumstances. It can occur for a given \( \kappa \) if there is an element in the point group \( (G_0) \) of the crystal which takes
\[ \kappa \text{ into } -\kappa. \] If so, it is possible, using equation (2.17), to obtain further operators, similar to the \( T(k \cdot R) \) matrices but antiunitary in nature, which commute with \( D(k) \). Sometimes this will lead to further symmetry reduction. Maradudin and Vosco discuss methods of obtaining the appropriate matrix \( \Upsilon(k) \). These methods have been simplified by Warren. We shall not discuss details here, as application of Maradudin and Vosco's criterion (see Appendix C) indicates that time-reversal-invariance will have no effect for any cases examined in this work.

### 2.3.3 Selection Rules for Raman and Infrared Spectra

Classically speaking, infrared radiation can be absorbed by those lattice modes of a crystal which change the total dipole moment of the crystal; the Raman effect, that is the inelastic scattering of photons by phonons, occurs if the atomic displacements of the lattice mode changes the atomic polarisability of the crystal. Using these facts, one can apply group theory to predict whether or not a given normal mode will be infrared and/or Raman active (see, e.g., Ref. 151). In both cases we find that a necessary condition for activity is \( \kappa = 0 \). Supplementary rules are then

\[ \sum_{R \in G_0} \chi_{\sigma}^{(R)} \chi_{\pi}^{(R)} = 0 \quad \text{infrared forbidden} \]

\[ \sum_{R \in G_0} \chi_{\sigma}^{(R)} \chi_{\pi}^{(R)} \neq 0 \quad \text{infrared permitted} \] \hspace{1cm} (2.31)

\[ \sum_{R \in G_0} \chi_{\sigma}^{(R)} \chi_{\pi}^{(R)} = 0 \quad \text{Raman forbidden} \]

\[ \sum_{R \in G_0} \chi_{\sigma}^{(R)} \chi_{\pi}^{(R)} \neq 0 \quad \text{Raman permitted} \] \hspace{1cm} (2.32)
The $\chi_\sigma(R)$ are the characters (traces) of the matrices of the $\sigma$th representation of $G_0$ to which the mode being tested belongs. (Note that $G_0 \cong G_0(\sim)$, and ordinary and multiplier representations are in this case identical). $\chi_i(R)$ and $\chi_r(R)$ can be written:

$$\chi_i(R) = \sum_{\alpha=1}^{3} R_{\alpha\alpha} = \xi + 2\cos \theta$$  \hspace{1cm} (2.33)

$$\chi_r(R) = 2\cos \theta (\xi+2\cos \theta)$$  \hspace{1cm} (2.34)

$\theta$ is the angle of rotation for operation $R$ and $\xi = +1$ or $-1$ for proper and improper rotations respectively. (An improper rotation consists of a rotation and a reflection; thus, for example, the inversion is an improper rotation since it can be achieved by a rotation through $180^\circ$, followed by a reflection perpendicular to the rotation axis.)

To find active modes for a given crystal we perform a decomposition of the representation of $G_0$ given by equation (2.19) into irreducible representations of $G_0$, and then test each representation appearing for activity via equations (2.31) and (2.32). This method is due to Bhagavantam and Venkatarayuda.  \hspace{1cm} (10)

2.3.4 Computerised Group Theoretical Analysis

There is obviously much scope for errors and considerable tedium in an analysis of the type described above. Recently, however, T.G. Worlton and J.L. Warren have embodied the method in two Fortran IV computer programs. These programs are code named ACMI and ACMM, and can be obtained from the CPC Program Library, Queens University of Belfast, Northern Ireland.
Descriptions have been published in Computer Physics Communications\textsuperscript{151,147}. The programs will perform a full analysis for any crystal structure with up to 20 atoms per unit cell, and test for infrared and Raman activity in the $k = 0$ case.

2.4 ANALYSIS OF THE CRYOLITE STRUCTURE

2.4.1 Method

We now proceed to an illustrative example using the above theory. An analysis has been performed for the ideal (cubic) cryolite structure and for one of its observed modifications of space group $D_{4h}^6$ (P4/mnc), with various choices of $k$. The program ACMI was used. This is the earlier program of the two, and does not examine fully the effects of time-reversal-invariance as ACMM does. However, as noted before, for the modes to be examined time-reversal-invariance has no effect.

2.4.2 Units Cells and Brillouin Zones

The face-centred cubic structure is normally presented as a non-primitive cubic cell of side $a$, containing four chemical structural units (or molecules) per cell and possessing the full symmetry of the group (fig. (1.1)). For calculation we want to use the primitive cell, which possesses one structural unit. This has primitive translation vectors with Cartesian coordinates

\[
\begin{align*}
a_1 &= (0 \ 1 \ 1) \ \tau_c \\
a_2 &= (1 \ 0 \ 1) \ \tau_c \\
a_3 &= (1 \ 1 \ 0) \ \tau_c
\end{align*}
\]

where $\tau_c = a/2$. (2.35)
The X, Y and Z axes of the non-primitive unit cell are then in directions (100), (010) and (001) respectively.

The reciprocal lattice vectors conjugate to the above are

\[ b_1 = (-1 1 1)/2\tau_c \]
\[ b_2 = (1 -1 1)/2\tau_c \]
\[ b_3 = (1 1 -1)/2\tau_c \]  

(2.36)

For the sake of the discussion we shall assume that the transition from the $O_h^5$ to the $D_{4h}^6$ structure is continuous. The $D_{4h}^6$ structure is depicted in figures (1.3) and (2.3), and is derived from the $O_h^5$ structure by the rotation of the MF$_6$ octahedra about one 4-fold axis (this is taken as the Z-axis in this case). The simple tetragonal $D_{4h}^6$ unit cell possesses two structural units. In the frame of the cubic unit cell its axes lie in directions (110), (-110) and (001), the last being the long axis. The primitive translation vectors in the cubic frame are

\[ a_{T1}^T = (1 1 0)\sqrt{2} \tau_T \]
\[ a_{T2}^T = (-1 1 0)\sqrt{2} \tau_T \]
\[ a_{T3}^T = (0 0 1)2\tau_z \]  

(2.37)

where $2\tau_T = a_T$ and $2\tau_z = c_T$; $a_T$ and $c_T$ are the lengths of the sides of the tetragonal unit cell.

Reciprocal lattice vectors are now
\[ b_{1T}^{\top} = \frac{(1 1 0)}{2\sqrt{2}\tau_{T}} \]

\[ b_{2T}^{\top} = \frac{(-1 1 0)}{2\sqrt{2}\tau_{T}} \]  \hspace{1cm} (2.38)

\[ b_{3T}^{\top} = \frac{(0 0 1)}{2\tau_{T}} \]

Now, because the transition is assumed continuous, at the
transition temperature

\[ c_{T} = a \]

and \[ a_{T} = \frac{a}{\sqrt{2}} \]

We then obtain the Brillouin zones shown in figure (2.1).
With the doubling of the primitive unit cell volume in going
from \( O_{h}^{5} \) to \( D_{4h}^{6} \), the Brillouin zone volume is halved.

The capital letters in figure (2.1) are standard labels
for the vectors which will be of particular interest in the
later discussion of phase transitions. These vectors are:

For the cubic cell

\[ \Gamma : \quad \Gamma = 0 \]  \hspace{1cm} (2.39a)

\[ X : \quad X = \frac{(b_{2}+b_{3})}{2} \]

\[ = \frac{(1 0 0)}{2\tau_{c}} \]

\[ = \frac{(1 0 0)}{a} \]  \hspace{1cm} (2.39b)

\[ L : \quad L = \frac{(b_{1}+b_{2}+b_{3})}{2} \]

\[ = \frac{(1 1 1)}{4\tau_{c}} \]

\[ = \frac{(1 1 1)}{2a} \]  \hspace{1cm} (2.39c)
FIG. 2.1 BRILLOUIN ZONE FOR FACE-CENTRED CUBIC CELL WITH INSCRIBED ZONE FOR SIMPLE TETRAGONAL CELL
\[ W : \quad W = \frac{(b_1 + 3b_2 + 2b_3)}{4} \]
\[ = (1, 0, \frac{1}{2})/2\tau_c \]
\[ = (1, 0, \frac{1}{2})/a \quad (2.39d) \]

For the tetragonal cell

\[ Z_t : \quad Z_t = \frac{b_3^T}{2} \]
\[ = (0, 0, 1)/4\tau_z \quad (2.40a) \]
\[ = (0, 0, \frac{1}{2})/2\tau_c \quad \text{at the transition.} \quad (2.40b) \]

The corresponding wavevectors are obtained by multiplying these vectors by \(2\pi\). We shall write

\[ k_{Z_t} = 2\pi X, \quad (2.41) \]

and define \( k_{Z_t}, k_{Z_L}, k_{Z_W} \) and \( k_{Z_t} \) similarly.

We see that the tetragonal Brillouin zone boundary vector \( Z_t \) is precisely half way between the origin (\( \Gamma \)) and the face-centred-cubic zone boundary point \( X_Z = (001)/a \) (\( X_Z \) is not a standard label, since by symmetry the \( X_Z \) and \( X \) points are equivalent). The equivalence relationship for wavevectors (equation (2.8)) then indicates that for the tetragonal system the origin, \( \Gamma \), and point \( X_Z \) become dynamically equivalent, i.e. they both correspond to a null wave vector. Now, as pointed out before, infrared and Raman activity are possible only for normal modes of zero wave vector. Consequently, below the transition some previously inactive modes may become visible. The experimental significance of this is threefold:

a) the appearance of new infrared or Raman lines can indicate the presence of a transition.
b) one of these newly visible modes is often found to be closely associated with the cause of the transition, and can provide data on this (see Chapter III).

c) the newly visible modes can provide additional data for lattice dynamical calculations. In particular, it may be possible to introduce those of them which are not too sensitive to temperature change into calculations for the cubic structure, albeit with the normal risks of extrapolation (see, e.g., Ref. 104).

We can get a physical feeling for what is happening if we examine the form of the lattice mode. In equation (2.11) we will write $\mathbf{\ell}$ in its Cartesian coordinates: $\mathbf{\ell} = (\ell_x, \ell_y, \ell_z)$. Then for $X_z$,

$$u_\alpha (\mathbf{k}) \sim e^{i k \cdot \mathbf{\ell}} \exp[-i \omega (k, j) t]$$

$$\sim \exp \left\{ i \frac{2\pi}{2c} (001) \cdot (\ell_x, \ell_y, \ell_z) \right\} \exp[-i \omega (k, j) t]$$

$$\sim \exp \left\{ i \frac{2\pi}{2c} \frac{\ell_z}{c} \right\} \exp[-i \omega (k, j) t] \quad (2.42)$$

Thus, for $X_z$ the modes have a period of $2c = a$ in the $z$ direction. Now, the $O_h$ structure has one molecule per primitive unit cell. A vibrational mode with wave vector $k_{X_z}$ therefore corresponds to a situation where neighbouring unit cells $c$ apart are moving out of phase. In the $D_{4h}$ structure, however, with two molecules per unit cell, a vibration of the same wavelength corresponds to an internal motion of the new unit cell, with all unit cells of the crystal moving in phase. Hence the vibration has become a wave of infinite wavelength ($k = 0$).
2.4.3 Labelling of Atomic Positions in the Cryolite Structures

The labelling adopted to present the group theoretical results is shown in figures (2.2) and (2.3). To differentiate monovalent atoms at the tetragonal and octahedral sites these atoms have been called A and B respectively, so that the chemical formula is now written $A_2BMF_6$ (A and B are dynamically inequivalent). The relationship of cubic and tetragonal axes is indicated in figure (2.3). Correspondence between atoms in the cubic and tetragonal structures is indicated for the latter by adding '1' or '2' to the labels of the cubic system.

2.4.4 Group Theoretical Results

(1) Data Presentation

Analyses were performed for the cubic $\Gamma$, X (actually $X_z$), L and W points and for the tetragonal $\Gamma$ point. Character tables for all relevant irreducible multiplier representations are listed in Appendix A. Program ACMI prints out a set of orthogonal vectors which will block diagonalise the dynamical matrix; these are listed in Appendix B. The forms of the symmetry reduced and block diagonalised dynamical matrices for those of the wave vectors belonging to the cubic $O_h$ system are also indicated in this appendix; these matrices can be used to simplify lattice dynamical calculations. The matrix for the $D_{4h}^6$ $\Gamma$ point, possessing 60 rows and columns and at least 149 independent elements, has been omitted, as any dynamical analysis must start from the simpler cubic structure. For the zero wave vector modes the decompositions were checked against those obtained by hand according to Bhagavantam and Venkatarayuda's method.
FIG. 2.2 LABELLING OF ATOMS FOR GROUP THEORETICAL ANALYSIS $O_h^5$ (FACE-CENTRED CUBIC) CRYOLITE STRUCTURE
FIG. 2.3 LABELLING OF ATOMS FOR GROUP THEORETICAL ANALYSIS
\[ D_{4h}^6 \] (SIMPLE TETRAGONAL) CRYOLITE STRUCTURE
\[ \phi = \text{ROTATION ANGLE OF FLUORINE OCTAHEDRA} \]
(2) **The Γ Point for the Cubic \( \text{O}_h^5 \) Structure**

(a) **Decomposition**

The decomposition for the cubic Γ point is

\[
T(\mathbf{k}_\Gamma = 0) = \tau_1 + \tau_5 + 2\tau_7 + \tau_8 + \tau_9 + 5\tau_{10}
\]

\[\begin{array}{cccc}
R & R & R & S & S & IR \\
\end{array}\]  

(2.43)

The representation labels are as defined in Appendix A. Labels R, IR and S indicate that the related modes are, respectively, Raman active, infrared active, or silent (inactive).

(b) **Orthogonal Modes**

The forms of the cubic Γ-point orthogonal vectors \( \mathbf{f}(k_\Gamma, \sigma, \mu, \delta) \) are depicted in figure (2.4). In this figure bracketed labels \( (\sigma, \mu, \delta) \) are defined as for equation (2.24), and the unbracketed numbers indicate the mode degeneracies, i.e. the dimension of the corresponding representation \( \tau_\sigma \).

For degeneracy greater than 1 only one of the degenerate modes is shown. In the two dimensional case, \((511)\), the only other mode, \((512)\), is the complex conjugate (for a discussion of the imaginary part of a mode see the section on notation in Appendix B), while for three dimensional representations the remaining modes are obtained by cyclic interchange of the (right handed)X, Y and Z coordinates.

In general each eigenvector will be a combination of the vectors \( \mathbf{f}(k_\Gamma, \sigma, \mu, \delta) \) belonging to a particular representation \( \tau_\sigma \) (see the discussion of equation (2.28)). In the present case, for example, a simple general translation of the whole crystal consists of a combination of all vectors \( \mathbf{f}(k_\Gamma, 10 \mu \delta) \).

If we remove this motion from the system, equation (2.43) indicates that there should be four Raman and four infrared peaks observable.
FIG. 2.4 SCHEMATIC REPRESENTATIONS OF THE $k_z = 0$ MODES FOR $A_3B_{12}F_6$ (FACE-CENTRED CUBIC)
(c) **Internal Modes**

As a rule in the cryolite structure the fluorine ions are bonded much more strongly to the M than to the other ions, to the extent that the $\text{MF}_6^3$ octahedron may even go into solution as a unit. A result of this is that within the crystal the normal vibrational modes this complex possesses as an isolated unit are very little affected, and the corresponding infrared and Raman lines are often labelled by these so-called "internal modes". By convention these modes are labelled $v_1$ to $v_6$; $v_1$ corresponds to mode (111) of figure (2.4), $v_2$ to (511) and (512), $v_5$ to (711), (712) and (713) and $v_6$ to the modes of $\tau_8$. The $v_3$ and $v_4$ modes are combinations of the triply degenerate modes belonging to representation $\tau_{10}$ and are as depicted in figure (2.5).

![Internal Modes](image)

**FIG. 2.5 INTERNAL MODES $v_3$ AND $v_4$ OF $\text{MF}_6$ OCTAHEDRON**

The strong M-F bonding means that the frequencies of $v_1$ to $v_6$ will as a rule be higher than the remaining $\Gamma$ modes.

(3) **Results for Other Wave Vectors**

For the other three wave vectors of the cubic system we have the following decompositions:
X\_z\) point:
\[ T(k_{X_z} = \frac{1}{a} [001]) = 3\tau_1 + 4\tau_2 + 4\tau_3 + 4\tau_4 + 5\tau_5 + 5\tau_6 + \tau_7 + \tau_8 + 3\tau_9 + 6\tau_{10} \tag{2.44} \]

L point:
\[ T(k_{L} = \frac{1}{a} [\frac{1}{2}\frac{1}{2}\frac{1}{2}]) = 4\tau_1 + 5\tau_2 + 4\tau_4 + 5\tau_5 + 5\tau_6 \tag{2.45} \]

W point:
\[ T(k_{W} = \frac{1}{a} [10\frac{1}{2}]) = 5\tau_1 + 2\tau_2 + 5\tau_3 + 2\tau_4 + 8\tau_5 \tag{2.46} \]

For the tetragonal \(\Gamma\) point the decomposition is
\[ T(k_{\Gamma} = 0) = 3\tau_1 + 4\tau_2 + 4\tau_3 + 5\tau_4 + 3\tau_5 \]
\[
\begin{array}{cccccc}
\text{R} & \text{S} & \text{S} & \text{IR} & \text{R} \\
\end{array}
\]
\[ + 2\tau_6 + 2\tau_7 + \tau_8 + 6\tau_9 + 12\tau_{10} \tag{2.47} \]
\[
\begin{array}{cccccc}
\text{S} & \text{R} & \text{S} & \text{R} & \text{IR} \\
\end{array}
\]

This last decomposition includes translation for the whole crystal, for which the relevant representation is the direct matrix sum \((\tau_4 + \tau_{10})\).

### 2.4.5 Relationships Between Vibrational Modes of the High and Low Symmetry Structures

One could obtain these relationships by operating with the projection operators (2.27) of one structure on the modes produced by ACMI for the other structure. Direct comparison is, however, usually sufficient. As an example consider the two rotary modes (111) and (121) for the \(\Gamma\) point of the \(D_{4h}^6\) structure. Labelling them by the crystal space group and wave
vector we have (see Appendix B) in tetragonal system coordinates

\[(111)(D_{4h}^6, \Gamma) = \frac{(X F_{11} - X F_{21} + Y F_{31} - Y F_{41} - Y F_{12} + Y F_{22} + X F_{32} - X F_{42})}{\sqrt{8}}\]

\[(121)(D_{4h}^6, \Gamma) = \frac{(Y F_{11} - Y F_{21} + X F_{31} + X F_{41} + X F_{12} + X F_{22} - Y F_{32} + Y F_{42})}{\sqrt{8}}\]

The relationships for transfer between the cubic and tetragonal coordinates are

\[x_t = \frac{(x^C + y^C)}{\sqrt{2}} \quad (2.48)\]

\[y_t = \frac{(y^C - x^C)}{\sqrt{2}} \]

In cubic coordinates we find that we can then combine the above modes as follows:

\[(111)(D_{4h}^6, \Gamma) + (121)(D_{4h}^6, \Gamma) = \frac{(Y F_{11}^C - Y F_{21}^C + X F_{31}^C + X F_{41}^C - Y F_{12}^C + Y F_{22}^C + X F_{32}^C - X F_{42}^C)}{\sqrt{4}} \quad (2.49)\]

\[(111)(D_{4h}^6, \Gamma) - (121)(D_{4h}^6, \Gamma) = \frac{(X F_{11}^C - X F_{21}^C + Y F_{31}^C - Y F_{41}^C + X F_{21}^C - X F_{22}^C + Y F_{32}^C - Y F_{42}^C)}{\sqrt{4}} \quad (2.50)\]

The mode described by equation (2.49) will obviously become an X-mode in the cubic structure, since equivalent fluorine atoms around the two M-ions have opposite displacements in all cases. Similarly, (2.50) indicates a \( \Gamma \) mode.

Inspection of the mode listings in Appendix B indicates that the mode (2.49) arises from the X-mode

\[(311)(O_{h}, \chi_z) = \frac{(Y F_{1} - Y F_{2} - X F_{3} + X F_{4})}{\sqrt{4}}\]

The form of (2.50) would lead us to look for a \( \Gamma \) mode of the
form \((\text{XF}1-\text{XF}2+\text{YF}3-\text{YF}4)\). There is no immediately obvious
candidate in the \(O_{h}^{5}\) \(\Gamma\)-mode listing; the mode
\[(111)(O_{h}^{5},\Gamma) = (\text{XF}1-\text{XF}2+\text{YF}3-\text{YF}4+\text{ZF}5-\text{ZF}6)/\sqrt{6}\]
is the source; the first four terms match, and the other two
will correspond to a different mode, namely
\[(131)(D_{4h}^{6},\Gamma) = (\text{ZF}5_{1t}-\text{ZF}6_{1t}+\text{ZF}5_{2t}-\text{ZF}6_{2t})/\sqrt{4},\]
when the structure becomes tetragonal.

Since the representation \(\tau_{1}\) in \(D_{4h}^{6}\) gives Raman active
modes, it follows that the X mode \((311)\) of \(O_{h}^{5}\) will become
Raman active at the transition temperature. This is of
interest since, as will become evident in Chapter III, this
mode is a candidate for involvement in the \(O_{h}^{5} \rightarrow D_{4h}^{6}\) transition
in cryolites.

2.5 CONCLUSION

This completes the group theoretical analysis. A
discussion of the experimental observation by spectroscopic
methods of the modes derived above is given in Chapter IV.
Meanwhile we have sufficient group theoretical tools to
proceed to the discussion of Landau's theory of phase trans-
itions in Chapter III.
3.1 INTRODUCTION

The theory discussed in this chapter will be limited to that required for the treatment of solid-solid transitions only. We begin with a brief discussion of the thermodynamics of these transitions, and go on to the derivation of Landau's theory for them. We then indicate the derivation of the group theoretical results arising from this theory and discuss the resultant physical consequences, in particular the determination of possible transitions and the phenomenon of the soft mode. Experimental approaches suggested by these results are then dealt with (a fuller account for cryolites in particular will be given in Chapter IV). The limitations of the Landau theory are discussed, and the chapter is concluded by applying the theory to the space group $O_{h}^{5}$, concentrating on the cryolite transition $O_{h}^{5} \rightarrow D_{4h}^{6}$, where the $O_{h}^{5}$ phase has the structure shown in figure (1.1).

3.2 THERMODYNAMICAL THEORY

A phase transition of the type we shall be examining is normally induced experimentally by varying either the temperature ($T$) of the material or the pressure ($P$) applied to it. For convenience in the following discussion, and because it corresponds to the experimental situations which will be later discussed, we shall take the pressure as fixed and the temperature as varying.
The starting point for the relevant thermodynamical theory is the Gibbs free energy, $\phi$, of a given fixed mass of material. This is defined by

$$\phi = U - TS + PV \quad (3.1)$$

where $U$ is the internal energy of the material, $S$ the entropy, $V$ the volume, and $T$ the absolute temperature. The quantity $U$ is a function of the atomic positions in the material, so that we can write the parametric dependence of $\phi$:

$$\phi = \phi(P,T,\rho) \quad (3.2)$$

Here $\rho$ is a density function defining atomic positions. Landau's theory applies the condition for thermodynamic equilibrium of the system (namely that at fixed values of $P$ and $T$ the potential $\phi$ should be a minimum with respect to variations on $\rho$) to derive information on possible crystal structures at temperatures below the transition.

Phase transitions can be classified according to the behaviour of the function $\phi$ in the region of the transition point. The classification system, due to Ehrenfest, characterises the transition by the lowest order derivative which becomes discontinuous at the phase change. Thus, 'first-order' transitions are those exhibiting discontinuities in $V$ ($= \left[ \frac{\partial \phi}{\partial P} \right]_T$) and $S$ ($= \left[ \frac{\partial \phi}{\partial T} \right]_P$). For second-order transitions volume and entropy vary continuously, but their various derivatives, specific heat $C_P$ ($= T \left[ \frac{\partial S}{\partial T} \right]_P = -T \left[ -\frac{\partial^2 \phi}{\partial T^2} \right]_P$), compressibility $\kappa$, and coefficient of volume expansion $\alpha$, are
discontinuous at the transition. Nowadays it is common practice not to make distinctions between second and higher order transitions, but to group all under the heading of "continuous transitions"\textsuperscript{49}.

3.3 LANDAU'S THEORY OF PHASE TRANSITIONS

This theory was developed by L.D. Landau\textsuperscript{69}, and is derived in the books by Landau and Lifshitz\textsuperscript{70} and Lyubarskii\textsuperscript{81}. Consequently we will indicate only the main points of the derivation.

Landau begins by assuming that the Gibbs free energy of the system may be written

\[ \phi = \phi(P, T, \eta) \] (3.3)

where the parameter \( \eta \) is called the order parameter. In the higher symmetry phase (usually at higher temperatures) \( \eta \) has the value zero; below the transition it may be either positive or negative. Examples of \( \eta \), depending on the material, may be polarisation, strain, magnetisation, or some function of atomic positions. Thus \( \eta \) is a measure of departure from the more symmetric configuration.

A continuous transition is assumed. This means that \( \eta \) can be taken as arbitrarily small as we approach the transition, and a Taylor series expansion performed:

\[ \phi(P, T, \eta) = \phi_0 + \alpha \eta + A \eta^2 + B \eta^3 + C \eta^4 + \ldots \] (3.4)

where \( \alpha, A, B, C \) etc. are functions of \( P \) and \( T \); it is assumed that all of them are well behaved at the transition point, i.e. that none becomes infinite.
For stability $\phi$ must be minimised with respect to $\eta$:

$$\frac{\partial \phi}{\partial \eta} = 0 \quad \text{and} \quad \frac{\partial^2 \phi}{\partial \eta^2} > 0 \quad (3.5)$$

Below the transition this will determine $\eta$, and for a structural transition will define the crystal structure for given $P$ and $T$. Landau shows that necessary conditions for stability are

- $\alpha = 0$
- $A$ positive above the transition point, zero at the point and negative below it
- $B$ zero at the transition point
- $C$ positive in the immediate vicinity of that point.

The coefficient $B$ may be taken as being either pressure and temperature dependent, or as identically zero. The former case gives a transition which occurs for one particular combination of temperature and pressure only (defined by the two equations $A(P,T) = 0$ and $B(P,T) = 0$). It is usual to consider that there is a range of pressure-temperature combinations for which the transition can occur, and thus require $B$ to be zero everywhere. Then if we assume that terms beyond the fourth power in the $\eta$-expansion of $\phi$ are negligible we have

$$\phi(P,T,\eta) = \phi_0(P,T) + A(P,T)\eta^2 + C(P,T)\eta^4 \quad (3.6)$$

Now, since $A(P,T) = 0$ at the transition, let us fix the pressure and expand $A$ as a Taylor series about the transition temperature $T_C$: 
\[ A(T) = a(T-T_C) + \ldots \] (3.7)

Near the transition temperature \( T_C \), only the first term of this series need be considered. Introducing this term into equation (3.6) and applying the conditions (3.5) for stability, we have

\[ \frac{\partial \Phi}{\partial \eta} = 2a(T-T_C)\eta + 4C\eta^3 = 0 \] (3.8a)

and

\[ \frac{\partial^2 \Phi}{\partial \eta^2} = 2a(T-T_C) + 12C\eta^2 > 0 \] (3.8b)

The solutions of equation (3.8a) are

(i) \( \eta = 0 \) (3.9)

This satisfies condition (3.8b) if \( T > T_C \), i.e. it is the solution above the transition temperature.

(ii) \( \eta^2 = \frac{a}{2C}(T_C-T) \) (3.10)

The condition (3.8b) indicates that this is the valid solution below the transition, i.e. for \( T < T_C \).

The order parameter \( \eta \) can usually be determined experimentally, and the requirement (3.10) that it go as \( (T_C-T)^{1/2} \) below the transition temperature \( T_C \) provides a criterion for the validity of the Landau theory in a given case.

3.4 GROUP THEORETICAL RESULTS FOR CONTINUOUS PHASE TRANSITIONS

The results of the group theory discussed in Chapter II will now be applied to the above via a density function \( \rho(x,y,z) \) which describes the probability of finding an atom at position \((x,y,z)\). For convenience in what follows we shall just consider \( \rho \) as referring to one sort of atom; the
generalisation is straightforward (see equation (3.22) and subsequent discussion).

Let us denote the high and low symmetry structures above and below the transition by space group labels $H_0$ and $H_1$ respectively, and the corresponding density functions by $\rho_0(x,y,z)$ and $\rho(x,y,z)$. These density functions are clearly invariant under their respective space groups. Now, since the transition is continuous, near it we can write

$$\rho(x,y,z) = \rho_0(x,y,z) + \delta \rho(x,y,z) \quad (3.11)$$

It can be shown that $\delta \rho$ can be expanded as a sum of basis functions, $\phi(\xi\sigma\lambda)$, of representations of $H_0$

$$\delta \rho(x,y,z) = \sum_{\xi\sigma\lambda} C(\xi\sigma\lambda) \phi(\xi\sigma\lambda) [xyz] \quad (3.12)$$

where the sum is over all functions $\phi(\xi\sigma\lambda)$ not associated with the identity representation of $H_0$. Here, as in Chapter II, the label $(\xi\sigma)$ is a representation label; $\lambda$ is a row of that representation. Note that we are here referring to the full, not the multiplier, representations.

Since $\delta \rho$ is taken as small the Gibbs free energy can be expanded as a Taylor series in $\delta \rho$. The terms with $(\delta \rho)^n$ contain expressions of the $n$th degree in the coefficients $C(\xi\sigma\lambda)$. Now, consider operating on $\delta \rho$ with elements of $H_0$; we can regard either the basis functions $\phi$ or the coefficients $C$ as varying (equivalent to the choice of rotating either coordinates or axes). We take the functions as fixed. Then the symmetry of the system demands that the multiples of
coefficients $C(k\sigma\lambda)$ must occur in combinations which are
invariant under operations of $H_0$ (and, incidentally, of $H_1$).
The Gibbs free energy then takes the form

$$\phi(P,T,[C(k\sigma\lambda)]) = \phi_0(P,T) + \Sigma A_{\epsilon}(k\sigma)[P,T]f_{\epsilon}^{(2)}(k\sigma)$$

$$+ \Sigma B_{\epsilon}(k\sigma)[P,T]f_{\epsilon}^{(3)}(k\sigma) + ...$$

(3.13)

The coefficients $A$, $B$, etc. thus depend on $P,T$, and the basis
functions $\phi$ (now fixed). Here $k$ indicates the 'star' of
the labelling vector $k$ of a representation of $H_0$; a star is
the set of all inequivalent wavevectors formed by operation by
the elements of $H_0$ upon $k$ (all wavevectors of the same star
give the same set of representations). The function
$f_{\epsilon}^{(n)}(k\sigma)$ is the $n$th order invariant combination of the $C(k\sigma\lambda)$'s.
First order invariants of the $C(k\sigma\lambda)$'s cannot exist, and all
functions $f_{\epsilon}^{(2)}(k\sigma)$ have the form

$$f_{\epsilon}^{(2)}(k\sigma) = \Sigma_{k\sigma\lambda} |C(k\sigma\lambda)|^2$$

(3.14)

Above the transition $\delta \rho = 0$ and all coefficients $C(k\sigma\lambda)$
must be zero.

It turns out that to give a minimum in $\phi$ all the $A$'s in
(3.13) must be positive, and at least one of them must go
through zero at the transition. We argue that it is unlikely
that more than one $A = A(k_1\sigma_1)$ say - should become zero
at once. This leads to the conclusion that only the C
coefficients associated with that $A$ - i.e. with only one
irreducible representation of $H_0$ - will enter the expression for $\delta \rho$ below the transition. Thus

$$\delta \rho = \sum_{\lambda} C(k_1 \sigma_1 \lambda) \phi(k_1 \sigma_1 \lambda)$$  \hspace{1cm} (3.15)$$

The condition that $H_0$ always be the most stable phase above the transition can be used to demonstrate that the third order term in (3.13) is zero at the transition; if we take this to be so elsewhere we arrive at an expansion of $\phi$ to the fourth order as:

$$\phi(P,T) = \phi_0(P,T) + A(*)_{k_1 \sigma_1} [P,T] \sum_{\lambda} C(k_1 \sigma_1 \lambda)^2$$

$$+ \sum_{\varepsilon} [(*)_{k_1 \sigma_1} [P,T]f_{\varepsilon}^{(4)}(*)_{k_1 \sigma_1}]$$  \hspace{1cm} (3.16)$$

$$= \phi_0(P,T) + A(*)_{k_1 \sigma_1} [P,T] \eta^2 + \sum_{\varepsilon} [(*)_{k_1 \sigma_1} [P,T]f_{\varepsilon}^{(4)}(*)_{k_1 \sigma_1}]$$  \hspace{1cm} (3.17)$$

where $\eta^2 = \sum_{\lambda} |C(k_1 \sigma_1 \lambda)|^2$ and $\eta f_{\varepsilon}^{(n)}(\varepsilon) = f_{\varepsilon}^{(n)}(k_1 \sigma_1) .

The parallelism between (3.17) and (3.6) is evident.

The statement that basis functions of only one representation of $H_0$ enter into the expression for $\delta \rho$ (3.15) needs some amplification. Suppose that $\text{D}(*_{k \sigma})$ is an irreducible representation of $H_0$. Now $\delta \rho$ must be a real function, but the basis functions $\phi(k_1 \sigma_1 \lambda)$ need not be. If no unitary transformation on $\text{D}(*_{k \sigma})$ can make the $\phi$'s real they can occur in an expression for $\delta \rho$ only along with their complex conjugates $\phi^*(k_1 \sigma_1 \lambda)$. If the representation for these functions $\phi^*$ is written $\text{D}^*(*_{k \sigma})$ then the representation of the complete set of functions is written as the direct sum
\[ \mathcal{D}(\mathbf{k}\sigma) = D(\mathbf{k}\sigma) + D^*(\mathbf{k}\sigma). \] (3.18)

Such representations are called 'physically irreducible'.

The general conclusion for the Landau theory is then that the basis functions of only one real irreducible representation or of one physically irreducible representation enter into the expression (3.15) for \( \delta \rho \).

Remember that what we want to find are the structures which can arise from a given high temperature form via a continuous transition. Equation (3.15) provides the basis for this, though we still need to know the relative sizes of the coefficients \( C(\sigma_1 \lambda) \). Fortunately a further development provides us with the means. Observe that the third order term of (3.13) will automatically be zero (as required) if no third order invariants can be formed for the representation \( D(\mathbf{k}\sigma_1) \). The condition that this should be so is that the symmetric cube of this representation should not contain the identity representation (which is one dimensional with all matrices equal 1). Symbolically we write

\[ [D(\mathbf{k}\sigma_1)]^3 \cap I = 0. \] (3.19)

This is the Landau condition.

A second criterion, based on arguments of spatial homogeneity in the higher symmetry phase, is that the antisymmetric square of \( D(\mathbf{k}\sigma_1) \) should not contain the representation \( V \) of \( H_0 \), where \( V \) transforms an ordinary vector. This, the Lifshitz condition, can be written

\[ \{D(\mathbf{k}\sigma_1)\}^2 \cap V = 0. \] (3.20)
These two conditions will restrict severely the (initially infinite) number of representations of \( H_0 \) which can be involved in a continuous transition. Representations which satisfy the conditions are called 'active'.

At this point, with the possible active representations found, the usual approach has been to apply conditions for stability, i.e. to minimise \( \phi \) with respect to variation of the coefficients \( C(\kappa \sigma \lambda) \). This imposes restrictions on the \( C \)'s. When they are substituted back into (3.17) only a limited number of structures are found to be possible.

The method is straightforward but tedious. An alternative approach\(^{11,74} \) will be discussed when we come to examine the cryolite structure.

3.5 THE PHYSICAL CONTENT OF LANDAU'S THEORY

3.5.1 The Order Parameter and the Soft Mode

First, however, we shall examine briefly how the idea of the soft mode associated with a phase transition arises out of the Landau theory. The discussion follows that of Cochran\(^{31} \). The association appears as a result of the marriage of Landau's theory with lattice dynamics.

Let the \( \kappa^{th} \) atom in the \( \ell^{th} \) unit cell of the structure with space group \( H_0 \) have a mean coordinate \( \mathbf{r}(\ell \kappa) \), and under the transition let it move to \( \{ \mathbf{r}(\ell \kappa) + \mathbf{u}(\ell \kappa) \} \). The static displacements \( \mathbf{u}(\ell \kappa) \) can be written in terms of phonon coordinates:

\[
\mathbf{u}_\alpha(\ell \kappa) = \frac{1}{(NM^2)} \sum_{\kappa} Q(kj) e_\alpha(\kappa | kj) \exp[i k \cdot \mathbf{r}(\ell \kappa)]
\]  

(3.21)
(c.f. equation (2.18) for dynamic displacements). The notation is as in Chapter II. The constant N is the number of unit cells assigned to our macrocrystal. Eigenvectors (components $e_{\alpha}(\kappa|\kappa_j)$) are for the space group $H_0$, with the label $j = (\sigma, \lambda)$ running over all appropriate representations (labelled by $\sigma$) of $H_0$ and their rows (labelled $\lambda$).

Writing the density function of the $H_0$ structure

$$\rho_0(\mathbf{r}) = \sum_{\kappa} \sigma_{\kappa} [r-r(\kappa \kappa)]$$ (3.22)

where $\sigma_{\kappa}(\mathbf{r})$ is the density function of an atom of type $\kappa$, it is straightforward to deduce via equation (3.21) that for the transition the change $\delta \rho(\mathbf{r})$ in $\rho_0(\mathbf{r})$ is given by

$$\delta \rho(\mathbf{r}) = \sum_{\kappa} \phi_{\kappa} [r-r(\kappa \kappa)]$$

where the part $U_{\kappa kj}(\mathbf{r})$ has the periodicity of the high symmetry crystal lattice with space group $H_0$. Substitution of expression (3.24) into equation (3.12) gives

$$\delta \rho(\mathbf{r}) = \sum_{\kappa kj} C_{kj} \phi_{\kappa}(\mathbf{r}) \exp(ikj)$$ (3.25)
Comparing the terms of (3.25) with those of (3.23) we note that those between curly brackets both have the lattice periodicity, and so we identify the static amplitudes $Q(k_j)$ with the coefficients $C(k_j)$. The $Q(k_j)$'s are consequently called order parameters, although this definition is not precisely equivalent to that of $\eta$ (see equation (3.17)), as $\eta$ is usually a combination of $C(k_j)$'s.

The appropriate form for the Gibb's free energy $\phi$ has been considered by Cowley and Miller and Kwok. It is

$$\phi = \phi_0 + \sum_{k_j} \frac{1}{n!} \sum_{n>2} \sum_{k_1 j_1, k_2 j_2, \ldots, k_n j_n} \{v(n)^{(n)}(k_1 k_2, \ldots, k_n, j_1, \ldots, j_n) \}
\times Q(k_1 j_1) \ldots Q(k_n j_n)$$

where any coefficient $j_1$ in the summation runs over all rows of representations associated with wavevector $k_1$, and the wavevectors in $v(n)$ satisfy the condition that $k_1 + k_2 + \ldots + k_n$ be a vector of the reciprocal lattice of the $H_0$ structure. There is obviously a close parallelism between (3.26) and (3.13) and (3.16). We can see the similar function of the terms $\frac{1}{2}\omega^2(k_j)$ in (3.26) and the $A$'s in (3.13) and (3.16). We will not pursue the argument in detail, but we are led to expect that since one of the $A$'s must tend to zero at the transition, the appropriate frequency $\omega(k_j)$ should do the same. Actually, Cowley showed that the frequency $\omega(k_j)$ in (3.26) is not identical with the frequency of the corresponding vibrational mode in the crystal above the transition, but it is considered
that the two frequencies are not likely to differ greatly, particularly when $\omega(kj)$ is low. The above discussion also leads us to expect that the pattern of displacement of the atoms just below a continuous transition will be that of the eigenvector $e(kj)$ appropriate to the soft mode above the transition.

3.5.2 Indicated Experimental Approaches

From an experimental point of view it is now of obvious interest to define the order parameter of a transition and to measure the temperature variation both of that parameter and of the lattice mode frequencies. The results obtained can then be compared with predictions of the Landau theory (such as equation (3.10)) and of more sophisticated theoretical approaches.

To obtain the temperature dependence of the order parameter we need data on the crystal structure throughout the transition. X-ray analysis is an obvious means of obtaining this information (though its limited accuracy may restrict its usefulness), though other methods, in particular electron paramagnetic resonance (E.P.R.) can also be useful.

The mode frequencies can be measured by neutron, infrared and Raman spectroscopy. The first of these approaches needs large crystals which are often difficult, if not impossible, to grow. The optical methods require that the relevant soft modes should be optically active. Above the transition this will not generally be so, though below it the Landau theory indicates$^{12}$ that the soft mode will give rise to Raman-active modes. This would certainly give us a starting point, though we would prefer to observe the mode above the transition as well. The reason for this will be discussed in Section (3.6).

Experimental methods will be discussed in more detail in Chapter V.
3.6 LIMITATIONS OF THE LANDAU THEORY

By its very assumptions we do not expect the Landau theory to give a precise description of a structural phase transition. The theory depends upon the possibility of expanding the Gibbs free energy $\Phi$ in a series of powers of $(T-T_c)$ and $\eta$, and it is not clear that this is possible. In particular, $\eta$ is required to tend continuously towards its transition temperature value of zero; but since $\eta$ must therefore be small near the transition, we would expect the thermally excited time-dependent fluctuations in the atomic positions to result in the local fluctuations of $\eta$ being larger than the mean value upon which the Landau calculation is based. Deviations from Landau-like behaviour are in fact observed in this "critical region". For example, just below its $110^\circ\text{K}$ phase transition temperature strontium titanate (SrTiO$_3$) has both the order parameter of the transition and the frequency of one of its soft modes (the $A_{1g}$ mode; the other ($E_g$) soft mode frequency has not been measured accurately) varying as $(T-T_c)^{1/3}$. Further below $T_c$ the behaviour tends to a Landau-like $(T-T_c)^{1/2}$ variation. The critical region in this case extends to about $11^\circ\text{K}$ below the transition$^{126}$. Such limitations of Landau theory are discussed by Ginzburg$^{51}$.

Taking this into consideration, along with the additional fact that in any case the majority of structural transitions observed are of first order, one might well ask if indeed the Landau theory is of much practical use. In fact it is. Its quantitative predictions, such as specific heat and detailed behaviour of the order parameter near the transition, are not, on the whole, fulfilled. However, the group theoretical
applications of the theory, namely the prediction of possible crystal structures which could arise from a given high temperature structure via a transition, and also the determining of the soft modes and order parameter associated with such a transition, are generally quite successful. This turns out to be the case even for many first order transitions when a mode can often be observed with its frequency falling near the transition, although the temperature $T_c$ describing variation of parameters, e.g. $\eta \sim (T-T_c)^\beta$, is not the same as the transition temperature. Such transitions are sometimes referred to as being 'almost second order'.

The group theoretical results of Landau's theory cannot be applied when the phase transition is of the order-disorder type. There is a set of cryolites listed by Bode and Voce\textsuperscript{14} to which this limitation may apply. These possess an $O_h^5$ structure similar to the basic cryolite form (figure (1.1)), but it is disordered inasmuch as the fluorine ions do not now lie in the edge of the symmetric unit cell but are distributed over one eighth of the available sites of a particular type in a random manner. While it is possible to apply basic Landau theory to order-disorder transitions, the order parameter $\eta$ is no longer a function of the normal mode displacements, and there is no reason to expect a soft mode. The observation of such a mode in a high temperature phase, then, would argue against an order-disorder transition. This, as O'Leary points out\textsuperscript{104}, is why we need to observe a soft mode on both sides of the transition; for ordered systems possess excitations whose frequency vanishes at the temperature of transition to a
disordered state. The disappearance of magnons at the Néel point and phonons at the melting point are common examples of this behaviour.

3.7 APPLICATION OF THE LANDAU THEORY TO THE CRYOLITE STRUCTURE

3.7.1 Active Representations for Space Group \( \text{Oh}^5 \)

Now that the foundations of the theory are laid, we come to apply it to the compounds that interest us. We will start with the general results for any \( \text{Oh}^5 \) structure, and specialise later.

Directly from the Lifshitz condition (3.20) an important result follows. This is that the point group of the wavevector \( \mathbf{k} \) of an active representation must either

(a) contain an inversion centre

or (b) have all its rotation axes and reflection planes intersecting at a point.

This excludes point groups of the types \( C_n \) and \( C_{nv} \). We can check which of the wavevectors for space group \( \text{Oh}^5 \) have point groups of this sort, since symmetries of all wavevectors for all space groups have been published. It then turns out that for \( \text{Oh}^5 \) the only wavevectors left whose representations might still satisfy the Lifshitz condition are:

<table>
<thead>
<tr>
<th>Wave Vector Label</th>
<th>Vectors in Star</th>
<th>Point Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma )</td>
<td>Null Vector</td>
<td>( \text{Oh} ) (m3m)</td>
</tr>
<tr>
<td>( X )</td>
<td>( \frac{b_1+b_2}{2}, \frac{b_2+b_3}{2}, \frac{b_3+b_1}{2} )</td>
<td>( \text{D}_{4h} ) (4/mmm)</td>
</tr>
<tr>
<td>( L )</td>
<td>( \frac{b_1+b_2+b_3}{2}, \frac{b_1+b_2}{2}, b_2/2, b_3/2 )</td>
<td>( \text{D}_{3d} ) (3m)</td>
</tr>
<tr>
<td>( W )</td>
<td>( \frac{2b_1+b_2+3b_3}{4}, \frac{2b_3+b_1+3b_2}{4}, \text{etc.} )</td>
<td>( \text{D}_{2d} ) (42m)</td>
</tr>
</tbody>
</table>
The squares and cubes for important $O_h^5$ representations have all been listed\textsuperscript{25}, so that it is possible to check directly which representations possessing one of the above four wave-vectors satisfy both the Landau and Lifshitz conditions. It turns out that only the following representations can be active:

- $\Gamma$: $\Gamma^1$, $\Gamma^2$, $\Gamma^2$, $\Gamma^{12}$, $\Gamma^{15}$, $\Gamma^{15}$, $\Gamma^{25}$
- $X$: $X^1$, $X^2$, $X^2$, $X^3$, $X^4$, $X^4$, $X^5$
- $L$: $L^1$, $L^1$, $L^2$, $L^2$, $L^3$, $L^3$
- $W$: $W^1$, $W^1$, $W^2$, $W^2$

The labelling is as in Appendix A.

### 3.7.2 The $O_h^5 \rightarrow D_{4h}^6$ Transition

**1) Choice of Wavevectors of Active Representations**

From this point we shall restrict ourselves to examining transitions of the form $O_h^5 \rightarrow D_{4h}^6$. Several cryolites possessing the $D_{4h}^6$ structure have been reported\textsuperscript{5,14} and there is a considerable number of others with tetragonal structure but as yet undetermined space groups to which this analysis may also be applicable. The above transition, as will become apparent, has characteristics that make it especially amenable to experimental investigation.

As a preliminary we will apply Cochran and Zia's approach\textsuperscript{30}. This allows us to readily describe any lower symmetry structure space group $H_1$ say, in terms of the irreducible representations of the more symmetric space group, $H_0$ say, from which the structure derives. If the lower symmetry form is described by a set of non-vanishing order parameters

$$\{Q(k_{ij}), \ldots Q(k_{ij})\} \quad (c.f. \text{equation (3.23)})$$
the set of wavevectors \( \{k_1 \ldots k_m\} \) must form a subgroup (proper or improper) of a group of wavevectors \( S \). \( S \) is the set of wavevectors which are inverse lattice vectors of \( H_1 \) and which also lie in or on the boundary of the first Brillouin zone of \( H_0 \); here vector addition is the group operator, and vectors differing by an inverse lattice vector of \( H_0 \) are taken as equal. For the \( O_h^5 \rightarrow D_{4h}^6 \) transition we obtain two possible groups, viz. the full set, \( \{\Gamma, X\} \) and the subgroup \( \{\Gamma\} \). We can eliminate the case of the lone null vector, \( \{\Gamma\} \), since there are then translations not belonging to \( D_{4h}^6 \) which would leave a structure described by parameters of type \( Q(0j) \) invariant. We are left with \( \{\Gamma, X\} \); for a continuous transition the displacements due to \( \Gamma \) can represent acoustic modes and contribute to thermal expansion only, and the relevant wave-vector for the Landau theory will be \( k_X \).

(2) Derivation of the Active Representation

We now seek to apply the Landau theory. When we have an assumed transition as here, there are general results which follow from the theory which can be used to avoid the need to construct the free energy function and minimise it. These are listed below. Other results of the theory are also listed for convenience of reference.

Take the transition from space group \( H_0 \) to \( H_1 \) (lower symmetry), induced by representation \( D \) of \( H_0 \). Then for a continuous transition:

1. \( H_1 \) is a subgroup of \( H_0 \).
2. \( D \) must correspond to a physical tensor field. For a displacement transition this implies that \( D \) must occur in the vibrational representation of the \( H_0 \) compound.
3. \([D]^3 \cap I = 0\).
4. \([D]^2 \cap V = 0\).
5. \(D + H_1\), the representation obtained when \(D\) is restricted to the elements of \(H_1\), must contain the totally symmetric representation \((I_1\) say\) of \(H_1\), i.e.
\(D + H_1 \cap I_1 \neq 0\).
6. The chain subduction criterion:

If \(H_2\) is a subgroup of \(H_1\),
and \(D + H_1\) contains the identity representation \(I_1\) of \(H_1\) once only
and \(D + H_2\) contains the identity representation \(I_2\) of \(H_2\) once only
then, the transition \(H_0 \rightarrow H_2\) cannot be continuous.

Condition 2. is not in the Landau theory, but is implicitly used in most work. It is straightforward to check if a given representation occurs in a vibrational representation, but as we have already obtained the relevant decomposition this will be unnecessary. Conditions 5. and 6. were obtained by Goldrich and Birman.

Lavrenčič and Shagenari have published details of a method for applying condition 5. for any representation. Applying their method to the \(D_{4h}\) cryolite structure we discover that the only possible active representation is \(X^{2+}\) (or \(\tau_3\) in Kovalev's notation). Equation (2.44) indicates that this representation does in fact occur in the vibrational representation of the cubic cryolite form. It appears once only, and this means that the \(X^{2+}\) basis function

\[(311)(0^5_hX_z) = (YF1 - YF2 - XF3 + XF4)/\sqrt{4}\]
obtained in Chapter II is in fact an eigenvector of the dynamical matrix. It corresponds to the rotation of a fluorine octahedron about the particular four-fold axis which will become the c-axis of the $D_{4h}^6$ structure, with the octahedra in alternate X-Y planes rotating equal amounts in opposite directions, owing to modulation by the factor $\exp[2\pi i (\frac{z}{2c})]$ (c.f. equation (2.41)). From the form of this mode it is evident that $\phi$, the angle of rotation of the fluorine octahedra from their original position with the fluorines in the cubic cell edges, and the mode amplitude $Q(k_{X_z},311)$ are linearly related, at least at small angles. Thus, measuring $\phi$ is equivalent to measuring the order parameter of the transition.

Such a mode is obviously amenable to experimental investigation. E.P.R. with a paramagnetic ion substituted at the centre of the fluorine octahedron suggests itself as a possible method. Also, as noted in Chapter II, the $X^{2+}$ mode becomes Raman active below the transition (though optically inactive above it). We shall go on in the next chapter to discuss the experimental observation of such modes.
CHAPTER IV

EXPERIMENTAL INVESTIGATION OF PHASE TRANSITIONS

4.1 INTRODUCTION

The purpose of this chapter is to discuss some of the experimental methods which can be used to investigate the cryolite transitions. The preparation of the cryolites themselves is covered in Appendix D. There, it is pointed out that attempts to obtain crystals large enough for spectroscopic work were unsuccessful. Consequently we seek in particular methods by which useful information can be obtained from the material in powder form. Some preliminary experimental results are covered in the course of the discussion along with relevant data from the literature.

4.2 THERMAL INVESTIGATIONS

A model of a phase transition will generally provide an expression for the Gibbs free energy, \( \Phi \), from which the specific heat at constant pressure \( (c_p) \) can be calculated and compared with experiment:

\[
c_p = -T \left[ \frac{\partial^2 \Phi}{\partial T^2} \right]_P
\]  

(4.1)

where \( T \) represents the temperature, \( P \) the pressure. The expression for the Landau model (equation (3.6)), for example, leads to a discontinuity in the specific heat curve at the phase transition temperature \( T_c \). The height of this
discontinuity is \[ \frac{a^2 T_c}{2C \left( \frac{p_c}{T_c} \right)^2} \] (notation as for Chapter III).

Even without a model useful information can be obtained from specific heat measurements. Observation of a hysteresis effect in the transition temperature will unequivocably label a transition as first-order. In addition, experimentally defining the region of the anomalous contribution to specific heat around the transition point provides an estimate of the so-called critical region in which the detailed predictions of Landau theory are not expected to be fulfilled.

No specific heat work appears to have been thus far carried out with cryolites. One reason is evident; the best samples for specific heat experiments are complete crystals, for the low thermal conductivity of powders makes thermal equilibrium hard to achieve. Moreover, a powder sample is liable to have strains present which alter the transition temperature. The resultant smearing out of the transition temperature would tend to make a (first order) latent heat jump look like a second order transition anomaly, so that there is no guarantee that we are observing the true properties of a single crystal sample.

Differential thermal analysis is a more rapid though less informative method of checking for phase transitions. A sample and a standard material are heated or cooled under identical conditions, and the temperature difference continuously monitored to detect heat transfer from a phase transition. Powder samples of \( (NH_4)_3AlF_6 \), \( (NH_4)_3FeF_6 \), \( (NH_4)_3CrF_6 \), and \( (NH_4)_3VF_6 \) were investigated by this method, using apparatus previously described by Cunningham et al. The reference material was \( \alpha-Al_2O_3 \), and the observations were carried out.
from room to just above liquid air temperature. The new results for the chromium and vanadium salts are included in the compilation of cryolite transitions in Table (1.1). It is noteworthy that \((\text{NH}_4)_3\text{VF}_6\) and \(\text{RbVF}_6\) both appear to possess three phase changes, suggesting similar origins for the transitions in these two compounds.

4.3 **OPTICAL METHODS**

4.3.1 **Introduction**

Lattice mode frequencies can be measured by neutron, infrared and Landau spectroscopy. The need to work with powders rather than crystals (Section 4.1) places restrictions on the type of data that can be obtained. Thus the use of neutron spectroscopy to observe modes with non-zero wave-vectors is precluded, since the method requires large crystals with a volume of the order of 1 cm\(^3\). In the following sections therefore we shall discuss only the infrared and Raman spectroscopy of powders (in fact all the published infrared and Raman data on cryolites is for powders), beginning with a discussion of the characteristics of the spectra observed and the types of information that can be obtained from these, and going on to discuss the properties of the published cryolite spectra in particular.

4.3.2 **Characteristics of Powder Spectra**

Infrared active modes as calculated from group theoretical methods in Chapter II are further split, for ionic materials, into a transverse (TO) and a longitudinal (LO) component\(^\text{86}\). The TO components possess atomic motions at
right angles to the direction of propagation of the incident radiation, while the LO motions are parallel. The LO modes have greater energies than their corresponding TO vibrations.

Naturally we would like to observe both types of mode if we are to set about constructing a lattice dynamical model. However, while it is in principle possible to observe LO frequencies in the infrared for powder reflectance spectra\cite{7}, the technique has not been applied very frequently. Certainly nothing has been published for cryolites. Observation of TO modes is more straightforward. Transmission spectra are taken for a thin film of the sample or for the sample powder dispersed in a suitable matrix material; for each TO mode a single spectral peak is observed just below (but not significantly far from) the true TO frequency. It should be noted that the sample crystallites should not be too small (limit about 30 \( \mu m \) diameter), for if so, for each TO (bulk) mode a crystal surface mode of higher frequency will also be observed. In the limit these surface modes may indeed predominate\cite{99,106}. The difference between corresponding surface and bulk mode frequencies can be particularly large for low frequency, long wavelength modes\cite{80}, a point of especial importance if the soft mode is expected to be infrared-active.

Finally we note that for Raman work background scatter is increased by the use of a powder, and that this effect will be particularly strong in the region near the central peak where any soft mode should appear.
4.3.3 Infrared and Raman Spectra of Cryolites

(1) General Characteristics

The group theoretical decomposition for the ideal cryolite structure (Chapter II) leads us to expect four infrared and four Raman lines. Figure (4.1) shows the transmission infrared powder data for \((\text{NH}_4)_3\text{AlF}_6\) and \((\text{NH}_4)_3\text{FeF}_6\). These spectra are characteristic of cryolites; they can be split into three distinct regions. There is the frequency range of the internal modes of the \(\text{MF}_6\) octahedra (roughly 600 to 270 cm\(^{-1}\) for cryolites), that of the external lattice modes (less than 270 cm\(^{-1}\)) and, where appropriate, the range of the internal modes of the ammonium ion (about 3400 to 1300 cm\(^{-1}\)). We shall consider each of these ranges in turn.

(2) Internal Modes of the \(\text{MF}_6\) Octahedra

The \(\text{MF}_6\) octahedron has six zero wave vector internal modes. Two are infrared active, three Raman active, and the other \((\nu_6)\) is silent. As noted in Section 2.44(2)(c), the relevant frequencies are generally little affected by the surroundings of the \(\text{MF}_6\) complex. Consequently it is usually easy to identify these modes; in the cryolites so far examined they occur in the following regions:

\[
\begin{align*}
\text{A}_{1g} & \quad \nu_1 & 470-550 \text{ cm}^{-1} & \text{Raman active} \\
\text{E}_g & \quad \nu_2 & 350-380 \text{ cm}^{-1} & \text{Raman active} \\
\text{T}_{1u} & \quad \nu_3 & 400-600 \text{ cm}^{-1} & \text{Infrared active} \\
\text{T}_{1u} & \quad \nu_4 & 200-390 \text{ cm}^{-1} & \text{Infrared active} \\
\text{T}_{2g} & \quad \nu_5 & 200-330 \text{ cm}^{-1} & \text{Raman active}.
\end{align*}
\]

There are additional frequency rules:
FIG. 4.1 FORM OF INFRARED TRANSMISSION SPECTRA FOR CRYOLITE POWDERS

After Nyquist and Kagel (1971) (reference 103)
$v_3 > v_4$

$v_1 > v_2 > v_5$

Data for the infrared-active modes are far more extensive than for the Raman. This is to be expected because, apart from the previously mentioned experimental difficulty which work with powders presents, Raman line intensities for metal-fluorine vibrations are generally weak. Attempts were made to obtain Raman spectra from powder samples of $(NH_4)_3AlF_6$ and $(NH_4)_3CrF_6$, using a 1 Watt argon laser, but these were unsuccessful. In fact, there appear to be only two sets of Raman results published to date, one on a range of ammonium cryolites and the other on some potassium cryolites. It is found that the $v_2$ line is generally far weaker than the $v_1$ and $v_5$ lines, and in some cases unobservable.

Below the phase transition temperature the MF$_6$ modes will split as the octahedron is distorted. In some cases this splitting has been observed in the infrared, although the width of the lines makes this difficult. Limited information on the structural nature of some transitions has been obtained in this way.

(3) Lattice Modes

For the external (lattice) modes there is relatively little information available for any temperature. This is to be expected in view of the experimental difficulties; to obtain infrared spectra at the longer wavelengths associated with these modes more complex equipment is needed, while for the Raman spectra there is the previously mentioned strong background scattering in the region of low frequency shifts.
Cryolites with the high temperature cubic structure are expected to have one Raman-active and two infrared-active external modes. These expectations appear to be fulfilled in the infrared for both the spectra in figure (4.1), the lines being at 230 cm\(^{-1}\) and 79 cm\(^{-1}\) for \((\text{NH}_4)_3\text{AlF}_6\) and 230 cm\(^{-1}\) and 90 cm\(^{-1}\) for \((\text{NH}_4)_3\text{FeF}_6\). In both spectra the lines are broad, and the frequency assignments are thus only approximate.

(4) **Ammonium Ion Modes**

(a) **Characteristic Frequencies**

Finally we come to the ammonium ion spectrum. Where this ion is present in a cryolite it may serve as a probe to provide extra information. An undistorted ammonium ion is tetrahedral, with a point group \(T_d\). It possesses four optically active vibrational modes whose frequencies, by convention, are labelled \(\nu_1\) to \(\nu_4\). The \(\nu_1\) and \(\nu_3\) vibrations involve changes in the N-H bond lengths (that is, they are stretching modes) while the \(\nu_2\) and \(\nu_4\) vibrations are bending modes. The free ion properties are as follows:

<table>
<thead>
<tr>
<th>Mode</th>
<th>(\nu_1(A_1))</th>
<th>(\nu_2(E))</th>
<th>(\nu_3(T_2))</th>
<th>(\nu_4(T_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degeneracy</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Approximate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency (cm(^{-1}))</td>
<td>3250</td>
<td>1690</td>
<td>3350</td>
<td>1400</td>
</tr>
<tr>
<td>(Reference 86)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activity</td>
<td>R</td>
<td>R</td>
<td>IR, R*</td>
<td>IR, R</td>
</tr>
</tbody>
</table>

R = Raman active
IR = Infrared active
* weak.
The environment of the ammonium ion will affect these frequencies. In ammonium cryolites with the standard face-centred cubic structure two-thirds of the ammonium ions occupy tetrahedral sites (12 nearest neighbour fluorine ions) and the remainder octahedral sites (six nearest neighbour fluorines). We would thus expect to see two spectral lines for each of the modes $v_1$ to $v_4$.

(b) Hydrogen bonding

The presence of fluorine ions raises the possibilities of hydrogen bonding and consequent ordering of the ammonium ions in the crystal lattice. Such bonding would be expected to decrease the frequencies $v_1$ and $v_3$ and increase $v_2$ and $v_4$, while a restriction on the free motion of the ammonium ion would give rise to a torsional lattice mode, customarily labelled $v_6$. Ordering of the ammonium ions would affect the space group of the cryolite, and it is presumably this fact that Swanson et al.\textsuperscript{132} had in mind when they attributed to $(\text{NH}_4)_3\text{AlF}_6$ and $(\text{NH}_4)_3\text{FeF}_6$ room temperature structures with space group $P\overline{2}3(T^2)$ or $F\overline{4}3m(T_d^2)$. These two configurations differ from the standard $F\overline{m}3m(O_h^5)$ form of figure (1.1) in that only alternate A atom sites (taking the structure formula as $A_2\text{BMF}_6$) are now identical. There does not, however, appear to be any direct experimental evidence in the literature for the occurrence of such structures.

On the other hand there is some data which does suggest that weak hydrogen bonding occurs. It is based on the application of a commonly used diagnostic tool for ammonium ion hydrogen bonding. This test, introduced by Waddington\textsuperscript{144}, is the appearance of a combination ($v_i+v_j$) mode in the
infrared spectrum, typically in the region of 1600 cm\(^{-1}\). A multiplicity of infrared bands around 3000 cm\(^{-1}\) and the splitting of the \(\nu_4\) line are considered corroborative evidence for such hydrogen bonding.

Bukovec et al.\(^{19}\) claimed to have seen \((\nu_2 + \nu_6)\) (~2100 cm\(^{-1}\)), \((\nu_4 + \nu_6)\) (~1960 cm\(^{-1}\)) and \((\nu_2 + \nu_4)\) (~3050 cm\(^{-1}\)) combination lines in the infrared for \((\text{NH}_4)_3\text{AlF}_6\), \((\text{NH}_4)_3\text{GaF}_6\) and \((\text{NH}_4)_3\text{InF}_6\) at room temperature. Some comments on their spectra need to be made, however.

The first is that the lines assigned to \((\nu_2 + \nu_6)\) and \((\nu_4 + \nu_6)\) are very weak. Spectra for the fluoroaluminate and fluorogallate by Nyquist and Kagel\(^{103}\) appear to show these lines also (c.f. their spectra in fig. (4.1)), as did a spectrum for the fluorogallate obtained in the course of work for this thesis (the peaks for the fluoroaluminate were not discerned however). The peaks are very ill-defined and no more prominent than other background features (one can, for example, discern an equally intense "band" near 1850 cm\(^{-1}\) in Nyquist and Kagel's spectra for the aluminate and gallate).

The second comment is that the presence of three lines in the vicinity of 3000 cm\(^{-1}\) has in this case no relevance at all to the question of hydrogen bonding. The highest frequency peak is just the \(\nu_3\) fundamental, while the lowest frequency one, assigned to the first \(\nu_4\) overtone, appears in ammonium salts both with and without hydrogen bonding\(^{144}\). Bukovec et al.\(^{19}\) took the central peak of the set to be the combination band \((\nu_2 + \nu_4)\). This identification would verify the presence of hydrogen bonding, since the peak is prominent and Waddington\(^{144}\) considered that the \((\nu_2 + \nu_4)\) combination was
likely to be intense enough to be visible only when hydrogen bonding was present. The peak labelling, however, is questionable for two reasons:

(i) For all three ammonium salts in Bukovec et alia's data, the value of $v_2$ which can be calculated from their supposed $(v_2+v_6)$ and $(v_4+v_6)$ peaks is of the order of 225 cm$^{-1}$ above that which can be obtained from the line assigned to $(v_2+v_4)$.

(ii) If we recall that there are two types of ammonium ion site, the central peak can be explained as being a second $v_3$ peak ($v'_3$), as labelled in figure (4.1), and also by Mathieu and Poulet. The presence of two ammonium ion environments would also lead us to expect the $v_4$ peak to be split. This is not evident, but the $v_4$ vibration, being a torsional rather than a stretching mode, may have a smaller splitting; this splitting is presumably concealed by the line width.

The observation of the bands assigned to $(v_2+v_6)$ and $(v_4+v_6)$ by more than one set of experimenters in the case's of the fluoroaluminate and fluorogallate gives some assurance that weak hydrogen bonding is present. Measurement of the $v_2$ frequencies by Raman spectroscopy would be of value in checking the assignments, particularly in the case of the supposed $(v_2+v_4)$ peak. Whether or not the hydrogen bonding is strong enough to influence the motion of the ammonium and fluorine ions to a significant extent, in particular to affect the phase changes noticeably and make them atypical of the cryolites as a whole, is another question. Nuclear magnetic resonance could in theory provide data on the motions of these ions which would
clarify the situation, but such results as exist for the ammonium cryolites\textsuperscript{8,56} are suspect (see Section 4.4).

(c) Isotopic Substitution

Assuming that the properties of the ammonium cryolite phase transitions are typical of the cryolites as a whole, the ammonium compounds are convenient objects for study in that their transition temperatures are lower than those of the corresponding alkali metal salts. They also provide the opportunity to apply isotopic replacement studies to help in identifying the optically active modes. Deuteration would give easily measurable frequency shifts; rotational and translatory mode frequencies of the ammonium ion are altered by factors of the order of $1/\sqrt{2}(\approx 0.71)$ and $\sqrt{18/22}(\approx 0.90)$ respectively.

4.3.4 Conclusion

Infrared and Raman spectroscopy are thus seen to be potentially powerful tools for examining the lattice dynamics of cryolites. However, the most desirable data, namely the observation of any Raman active soft modes, will require the production of a suitably large crystal.

4.4 Nuclear Magnetic Resonance

Protons and fluorine ($F^{19}$) nuclei both possess spin $\frac{1}{2}$, and in general it is possible to obtain information on their motion from nuclear magnetic resonance studies. The potentialities of this method are well illustrated in a study of polycrystalline ammonium hexafluorosilicate ($\text{(NH}_4\text{)}_2\text{SiF}_6$) by Blinc and Lahajnar\textsuperscript{13}, in which a complex model of the ammonium ion
motion is derived from a combination of proton and $^{19}$F NMR studies and measurement of deuteron magnetic resonance in $(\text{ND}_4)_2\text{SiF}_6$.

There are two similar but less complete NMR studies on ammonium cryolites in the literature. The first of these is an examination of $(\text{NH}_4)_3\text{AlF}_6$ by Guido and Franconi. They measured the proton and $^{19}$F NMR linewidths in the temperature range between liquid air boiling point and room temperature. By calculations with various models of the atomic motion they claim to have demonstrated that the ammonium ions rotate freely above $-170^\circ$C, at which point the motion changes to rotation about the trigonal axis (this implies a second, previously unreported, phase transition in $(\text{NH}_4)_3\text{AlF}_6$). The implication is that hydrogen bonding is absent. However, there is reason to doubt that Guido and Franconi have used valid models for the atomic motion, since they do not in their text make a distinction between the two types of ammonium ion site in $(\text{NH}_4)_3\text{AlF}_6$.

The second study is an investigation of ammonium hexa-fluorochromate by Belaya et al. Only a single proton NMR line was observed. The resonances from the two types of ammonium ion site must therefore be almost coincident. Analysing and distinguishing between the motions of these two kinds of ammonium ion is therefore impracticable.

This method therefore does not promise any detailed data on the motion of the ammonium ions in cryolites.
4.5 ELECTRON PARAMAGNETIC RESONANCE

4.5.1 Applications of the Method

Some preliminary experimental investigations into the possibility of obtaining information by E.P.R. were carried out. These were motivated by the availability of some small octahedral crystals of \((NH_4)_3AlF_6\) containing nominal dopings of 10% \(Cr^{3+}\) and 2% \(Fe^{3+}\) respectively, and by the initial E.P.R. work on \(Fe^{3+}\) in strontium titanate\(^{95}\) by Müller and Berlinger in which the variation with temperature of the rotation angles of oxygen octahedra of this compound was measured.

In principle the fluorine octahedron distortions and rotations we expect in a cryolite phase transition can be investigated by substituting an ion with a half-filled \(d\) or \(f\) shell at the centre of the octahedron. Examples of such ions are \(Cr^+, Mn^{2+}, Fe^{3+}\) (spin multiplicity \(S = \frac{5}{2}\)) and \(Eu^{2+}, \text{Gd}^{3+}\) and \(Tb^{4+}\) (\(S = \frac{7}{2}\)). Since \(S\) is here greater than \(\frac{3}{2}\) splittings of hexadecapolar or higher form can be observed; in particular the directions of the metal-fluorine bonds (in effect the rotation of the fluorine octahedron) can be determined. These dopant ions have the additional advantages\(^{97}\) that they provide observable spectra over a wide temperature range and are not expected to introduce additional distortions. Examination of the variation of the spin-lattice relaxation rate with temperature, in the first case via line broadening, can provide information on the lattice vibrations and in particular the soft modes.
4.5.2 Experimental Investigations

(1) Method

Observations on the available crystals were carried out in the X-band (~ 9.5 GHz). The crystal temperature was varied by a nitrogen gas stream regulated by a Varian V4540 variable temperature controller.

(2) \((\text{NH}_4)_3\text{AlF}_6:\text{Cr}^{3+}(10\%)\)

The chromium-doped crystal showed a single line only, whose width was constant but whose height began to decrease at about 50°C. The line became invisible around -70°C and did not reappear on further cooling to around -170°C.

We can deduce from this that the lattice dynamical effects associated with the transition become evident well above the transition point. The heavy doping is bound to have a noticeable effect on the transition itself in view of the previously noted phase change for \((\text{NH}_4)_3\text{CrF}_6\) at around -2°C.

(3) \((\text{NH}_4)_3\text{AlF}_6:\text{Fe}^{3+}(2\%)\)

(a) Observations

For the Fe\(^{3+}\)-doped crystal the magnetic field was first rotated in the (001) plane of the crystal at room temperature. Five lines were observed whose separation did not change noticeably with rotation angle. Pronounced line intensity maxima were observed approximately ±30° from the (100) and (010) axes, and less pronounced minima along these axes and midway between them ((110), etc.). The (110) minima were the shallower. A mult
Since the spectrum does not shift as the crystal is rotated we deduce that we are observing the $\frac{3}{2} \leftrightarrow \frac{1}{2}$ transition line only. That it is split into seven lines and that this splitting is still apparent in the multicrystalline sample indicate a superhyperfine interaction with the six fluorine nuclei of the octahedron (each has spin $\frac{1}{2}$). Within experimental limits this interaction must be isotropic. A g-value of 2.003 and a superhyperfine constant of approximately 25 gauss were obtained.

On cooling, both the single and multicrystalline spectra gradually broadened, till at approximately $-70^\circ$C each spectrum had the appearance of a single very broad line. During the cooling the superhyperfine splitting did not change noticeably.

Substantially the same results have since been obtained by Leblé et al. They were also able to resolve the $\frac{3}{2} \leftrightarrow \frac{1}{2}$ lines at room temperature for certain crystal orientations, and in addition observed a complex spectrum below the transition temperature.

(b) Discussion

The above behaviour can be accounted for by the spin Hamiltonian of a $d^5$ ion in a cubic site, viz. at the centre of a fluorine octahedron:

$$
\mathcal{H} = g\beta H \cdot S + \frac{a}{6} \left[ S_x^4 + S_y^4 + S_z^4 - \frac{S(S+1)(3S^2+3S-1)}{5} \right]
+ \sum_{i=1}^{6} \left[ A_S I_{i1} \cdot S + A_p (3I_{z_i} S_z - I_{z_i} S) \right]
$$

(4.2)

Here $\mathcal{H}$ is the magnetic field vector. The labels $x$, $y$ and $z$...
define a right-handed coordinate system with axes along the Fe-F bonds. The vector \( \mathbf{I}_i \equiv (x_i, y_i, z_i) \) \( (i = 1, \ldots, 6) \) represents the nuclear spin of the \( i \)th fluorine atom of the octahedron around the Fe\(^{3+}\) ion, the \( z_i \) direction being parallel to the appropriate Fe-F bond.

Since the superhyperfine interaction is isotropic \( A_p = 0 \). By curve fitting Leblé et al. obtained the following parameters:

\[
\begin{align*}
g & = 2.0029 \\
a & = 35.5 \text{ gauss} \\
A_s & = 23.7 \text{ gauss}
\end{align*}
\]

at room temperature.

Let us write the angle between \( \mathbf{H} \) (in the \( (001) \) plane) and the \( (100) \) axis as \( \theta \). Then the fine structure part of the above hamiltonian gives transition energies to the first order of

\[
\Delta E = g\beta H + \frac{a\mathbf{r}}{\hbar} (3 + 5 \cos 4\theta)
\]

\( r = 0 \) for the \( -\frac{1}{2} \leftrightarrow +\frac{1}{2} \) transition

\[ \mp \frac{5}{2} \] for the \( \pm \frac{1}{2} \leftrightarrow \pm 3\frac{1}{2} \) transitions

\[ \pm 2 \] for the \( \pm 3\frac{1}{2} \leftrightarrow \pm 5\frac{1}{2} \) transitions.

Now the total hyperfine splitting of a single fine-structure line is \( 6A_s = 142.2 \) gauss, whereas the maximum spread of the fine structure is \( 5a = 177.5 \) gauss. There is thus always considerable overlap, and this together with the line width accounts for the difficulty of observing the \( r \neq 0 \) lines. The previously mentioned maximum in peak intensity near \( \theta = \pm 30^\circ \) is explained by noting that for \( \theta = \pm 31^\circ 43' \) the term
Leblé et al.\textsuperscript{75} ascribe the broadening observed near the transition temperature to a slowing down of the reorientation rate of the fluorine octahedra. They postulate that these octahedra possess considerable freedom of motion, and that at higher temperatures this motion averages out the superhyperfine interaction and makes it isotropic. This is to be contrasted with the case of FeF\textsuperscript{3-} in K\textsubscript{2}NaGaF\textsubscript{6} \textsuperscript{59} ($A_s = 24.1$ gauss, $A_p = 7.0$ gauss), where the potassium ion, being larger than the sodium ion which lies on the cubic unit cell edge, will exert a larger restraint on the motion of the FeF\textsuperscript{3-} complex. As the rotational fluctuations slow down, the averaging effect in (NH\textsubscript{4})\textsubscript{3}AlF\textsubscript{6} is expected to be reduced, and the EPR absorption lines consequently to broaden.

The observed broadening is thus in favour of the existence of a soft mode in the (NH\textsubscript{4})\textsubscript{3}AlF\textsubscript{6} transition. Analysis of the effect is complicated through the likely presence of contributions whose action is described by fine structure (as against superhyperfine) terms in the spin Hamiltonian. Both rotations and distortions of the fluorine octahedra can contribute here. There is another effect which makes the situation more complex still. Investigations with strontium titanate\textsuperscript{141,96,98} have shown that in this compound an oxygen octahedron can 'discern', while still above the transition temperature, which of its three four-fold axes it will rotate about at the transition. This effect manifests itself in the average librational amplitude about this particular four-fold axis being larger than those about the other two. If the same effect occurs in cryolites there will be different contributions to the E.P.R. line broadening from librations.
about different four-fold axes of the fluorine octahedron.

Under certain experimental circumstances it is possible to disentangle the various contributions to line broadening. This was achieved for the 110°K strontium titanate transition by von Waldkirch and others\textsuperscript{143,96,98} by E.P.R. observations of Fe\textsuperscript{3+}-oxygen vacancy centres in the salt. However, this case is particularly amenable to investigation because of the high sensitivity of the E.P.R. spectrum to the TiO\textsubscript{6} octahedron rotation, the narrow lines away from the vicinity of the transition temperature, and the ability of the experimenters to obtain a single domain crystal below the transition. Only the last of these advantages might conceivably be attainable for (NH\textsubscript{4})\textsubscript{3}AlF\textsubscript{6} with an Fe\textsuperscript{3+} dopant.

The presence of domains below the phase transition would account at least in part for the complexity of the spectrum observed by Leblé et al. The motion of the fluorine octahedra will also be more restricted, so that there is every likelihood that the superhyperfine interaction will become anisotropic and be responsible for additional complexity. To investigate such spectra large crystals of high quality would be required.

4.5.3 Conclusion

In view of the uncertainty of any success in growing such crystals and the time required for growing from aqueous solution, investigation with Fe\textsuperscript{3+}-doped crystals has been discontinued. It is possible that doping with Gd\textsuperscript{3+} would allow observation of the order parameter via the fine structure, since any covalent bonding of fluorine ions to the
4f\(^7\) configuration is smaller, by a factor of at least 10, than that for the 3d\(^5\) configuration\(^6\) - the ligand hyperfine interaction should consequently be negligible. However, the large radius of the Gd\(^{3+}\) ion (0.938 Å c.f. Fe\(^{3+}\), 0.645 Å and Al\(^{3+}\), 0.530 Å\(^1\)) makes such substitution problematic.

4.6 MöSSBAUER EFFECT

This can be investigated when iron is the trivalent metal in the cryolite, or with suitable iron doping. We do not expect to get overmuch data from this method for temperatures above the transition, since with the iron at the centre of a perfect octahedron no quadrupole splitting is expected, and a pure rotatory mode would be expected to have no effect on the electric field gradient at the nucleus.

The method is discussed here primarily because its results have been used to call into question the accepted structure of ammonium hexafluoroferrate, and this will of course affect the phase change of this compound.

To date the only cryolites investigated by the Mössbauer effect appear to have been K\(_3\)FeF\(_6\)\(^\text{34,26}\) and (NH\(_4\))\(_3\)FeF\(_6\)\(^\text{26,92,93}\). Generally a single broad line is observed at room temperature. On the basis of this broadness Knap et al.\(^6\) suggest that the FeF\(_6\) octahedron in the ammonium salt is distorted. They adduce as evidence the paper by Christoe and Drickamer\(^26\), who performed calculations on data for K\(_3\)FeF\(_6\) and concluded that the line is in fact double, this effect arising from quadrupole splitting caused by a combination of covalency and distorted FeF\(_6\) octahedron effects. At room temperature and atmospheric
pressure the line broadenings of $K_3FeF_6$ and $(NH_4)_3FeF_6$ are of similar magnitude\textsuperscript{26}, and Knap et al. argue that this implies a distortion of the FeF$_6$ octahedron in the ammonium compound also.

However, they do not appear to have considered Mørup and Thrane's work\textsuperscript{92,93}. These researchers observed the Mössbauer spectrum of ammonium hexafluoroferrate at a variety of temperatures in both weak and strong magnetic fields. For strong fields the line widths were reduced considerably, and this was explained by ascribing the line broadening to electronic relaxation, or in other words to the fluctuating magnetic field arising from the surrounding magnetic ions. There is therefore no cause to question the cubic assignment of $(NH_4)_3FeF_6$. In fact a case is thus provided for re-investigating the line broadening in $K_3FeF_6$.

Mørup and Thrane also noted the following data relevant to the transition for $(NH_4)_3FeF_6$:

a) There is a sudden increase in line width on cooling to 263°K, followed by a more gradual increase over a range of about 30°C (at 130 gauss magnetic field). This is presumably due to quadrupole splitting arising from sudden and then progressive distortion of the fluorine octahedron.

b) There is a hysteresis effect in the line width temperature dependence. It occurs over a range of about ½°C at the transition.

The ammonium fluoroferrate phase change is thus first order.
4.7 X-RAY SCATTERING

4.7.1 Use for Phase Transition Investigations

X-ray scattering is a potentially powerful tool for the investigation of structural phase transitions. Given suitable crystals it is possible to carry out structure determinations at different temperatures, to determine the variation of cell constants, and to discern the effects of soft modes either through the presence of large Debye parameters for atoms with large amplitudes of vibration or through peaks in the temperature diffuse scattering originating from the modes themselves. Just below the transition temperature it should be possible, moreover, to obtain direct measurements of the order parameter. This can be seen by taking the standard formula for the amplitude of a scattered X-ray:

\[ A(K) = \sum_{\lambda k} f(\kappa K) \exp\{iK \cdot [\tau(\lambda) + \tau(\kappa)]\} \]  (4.4)

Here \( K = k_s - k_i, k_i \) and \( k_s \) are the wavevectors of the incoming and scattered X-rays respectively, and \( f(\kappa K) \) the scattering factor of the atom \( \kappa \); the rest of the notation is as for Chapters II and III. Then, representing the phase change by a small displacement \( u(\lambda k) \),

\[ u(\lambda k) = \frac{1}{\sqrt{N}} Q(kj) e(\kappa|kj) \exp\{ik \cdot [\tau(\lambda) + \tau(\kappa)]\} \]  (4.5)

associated with the mode \( (kj) \) we get a new amplitude
\[ A'(\vec{K}) = \sum_{\vec{\ell} \vec{\kappa}} f(\vec{\kappa}) \exp\{i \vec{K}.(\vec{\ell} + \vec{\kappa}) + u(\vec{\ell} \vec{\kappa})\} \] (4.6)

We now take a reflection which is absent in the symmetric phase (i.e. \( A(\vec{K}) = 0 \)). Then, expanding equation (4.6) to the first power in the \( u(\vec{\ell} \vec{\kappa}) \)'s and substituting equation (4.5), we find that the intensity \( I(\vec{K}) \) goes as

\[ I(\vec{K}) \sim |A'(\vec{K})|^2 \]

\[ \sim |Q(kj)|^2 \sum_{\vec{B}} \delta(\vec{K} + \vec{k} - 2\pi \vec{B}) \left| \sum_{\vec{\kappa}} f(\vec{\kappa}) \left[ \frac{K.e(\vec{\kappa}|kj)}{\sqrt{M_{\vec{\kappa}}}} \right] \exp\{i(\vec{K} + \vec{k})x(\vec{\kappa})\} \right|^2 \] (4.7)

The summation \( \sum \) indicates a sum over all vectors \( \vec{B} \) of the reciprocal lattice of the symmetric phase, and \( \delta \) as usual refers to the Dirac delta function. It follows from equation (4.7) that in the first order the intensities of X-ray peaks which are seen only in the low temperature phase should be proportional to the square of the order parameter \( Q(kj) \).

There is one proviso, namely that the atomic scattering factors \( f(\vec{\kappa}) \) should not change too quickly near the transition temperature.

4.7.2 Experimental Constraints

At the best, X-ray methods can detect a fractional change of length of the order of \( 10^{-4} \). This resolution is often more than adequate to reveal the changes that occur in crystal lattice parameters at a first order transition. Crystals for X-ray work need not be as large as those required for
spectroscopic investigations, and it should consequently be easier to obtain them. To date, however, only one X-ray investigation on a single crystal of a cryolite \((K_3\text{MoF}_6)\)\(^{141}\) appears to have been carried out.

When powder samples only are available the usefulness of X-ray diffraction is limited. It is still possible to obtain accurate lattice constants since there are methods of correcting for systematic error. However, identifying the space group of the sample material and determining its crystal structure are now more difficult tasks, because less experimental data is available. It may not be possible to obtain a structure with complete certainty; some cases for which this problem has occurred will be discussed later (Section 7.3.3). In addition, with powders the X-ray pattern may on occasion exhibit line broadening. Contributions to this broadening can arise from the actual size of the powder particles (the smaller the size, the broader the lines) and, more importantly, from residual strains present to some extent in the material upon preparation but increased by the grinding process used in making the X-ray sample. Consequences of such broadening are:

a) Weak diffraction lines with high Bragg reflection angles become difficult to detect. Consequently their precise positions are also hard to estimate. It is the high angle lines which normally enable us to obtain accuracy in lattice parameter determination.

b) The transition temperature may be altered and smeared out, as discussed in the section on thermal methods.
4.7.3 Calculations for Cryolites

But it is the powders that are generally available, and there is obviously much information of value to be obtained from X-ray investigation of them. With this in mind a computer program (NUPOWLS) for refining X-ray powder data has been obtained from the University of Canterbury Chemistry Department; it is a modification of a published program, ORFLS. The necessary subroutine for the tetragonal cryolite structure of space group $\text{D}_{4h}^6$ (fig. (2.3)) has been written, and some preliminary calculations using this subroutine carried out. These provide us with further insight into the use of the powder method, and are described below.

Given the $\text{D}_{4h}^6$ structure, formula $\text{A}_2\text{BF}_6$, of fig. (2.3), the structure factor for the reflection with Miller indices $(h_T,k_T,l_T)$ is:

$$F(h_T,k_T,l_T) = \psi(h_T+k_T+l_T)\left[ 4(-1)^{h_T+k_T+l_T}\psi(l_T) f_{A+}(\theta)\exp[-B_A \sin^2 \theta / \lambda^2] \right.$$  

$$+ 2(-1)^{l_T} f_{B+}(\theta)\exp[-B_B \sin^2 \theta / \lambda^2] + 2f_{3+}(\theta)\exp[-B_{3+} \sin^2 \theta / \lambda^2]$$  

$$+ 4f_{-}(\theta)\cos(2\pi l_T z)\exp[-B_\perp \sin^2 \theta / \lambda^2] + 4f_{-}(\theta)\left[ \cos(\varphi (k_T+h_T) \cos \psi) \cos(\varphi (k_T-h_T) \sin \psi) + \right.$$

$$\cos(\varphi (k_T-h_T) \cos \psi) \cos(\varphi (k_T+h_T) \sin \psi) \right]$$  

$$\times \exp\left[ -B_{\perp} \left( \frac{h_T^2+k_T^2}{4a^2} - B_{\perp} \frac{l_T^2}{4c^2} \right) \right] \right)$$

... contd
Here labels of the form $F^{-}_I$ refer to fluorine ions whose M-F bonds lie parallel to the c (long) axis of the crystal, the other fluorines being labelled $F^{-}_I$. The MF$_6$ octahedra have an M-F bond length $z_-$ in the direction of the c axis and $R = \frac{\rho}{\pi \sqrt{2}}$ perpendicular to it (these lengths are expressed as fractions of the unit cell edges c and a respectively).

$$\Psi(I) = 1 \text{ for } I \text{ even}$$
$$= 0 \text{ for } I \text{ odd}$$

The f's represent atomic scattering factors, and the Bragg scattering angle $\theta$ is given by

$$\sin^2 \theta = \frac{x^2}{4} \left\{ \frac{h_T^2 + k_T^2}{a^2} + \frac{l_T^2}{c^2} \right\}$$

Examination of equation (4.8) leads to several points of experimental significance.

First, let $H_T = (h_T + k_T + l_T)$. As $\phi$ tends to zero an X-ray peak remains only if $H_T$ is even. This corresponds to the original face-centred cubic form. The relationships of the tetragonal Miller indices with those of the face-centred cubic cell indexed on a simple cubic unit cell ($h_C, k_C, l_C$) and a primitive unit cell ($h_f, j_f, l_f$) are
\[ h_f = \frac{(k_c + l_c)}{2} = \frac{(h_T + k_T + l_T)}{2} \]

\[ k_f = \frac{(l_c + h_c)}{2} = \frac{(h_T - k_T + l_T)}{2} \quad (4.10) \]

\[ l_f = \frac{(h_c + k_c)}{2} = h_T \]

For \( h_f \) and \( k_f \) to be integral, \( H_T \) must be even.

Second, for \( H_T \) odd, to the first order in \( \phi \)

\[ F(h_T, k_T, l_T) \sim p\phi(h_T\sin(\rho l_T)\cos(\rho h_T) - k_T\cos(\rho k_T)\sin(\rho h_T)), \quad (4.11) \]

in agreement with equation (4.7), and confirming \( \phi \) as the order parameter.

Third, it is evident that if \( \phi \) and the positions of the fluorine atoms are to be obtained with greatest accuracy, the contributions from the metals A, B and M must be as small as possible; that is to say, these atoms must have low atomic numbers. This gives a further reason beyond those already noted (Section 4.3.3(4)(c)) for examining the ammonium cryolites in particular, as the ammonium ions are relatively weak X-ray scatterers.

Calculations of line intensities were carried out on a hypothetical ammonium hexafluoroaluminate compound possessing the \( D_4^h \) structure, with cell dimensions taken to approximate those of the known cubic compound.

For a Debye-Scherrer powder camera the intensity of a line is given by

\[ I(hk) \sim pA(\theta)\left| F \right|^2 \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta} \quad (4.12) \]
The symbol $p$ represents a multiplicity factor giving the number of reflections at Bragg angle $\theta$ with different combinations of Miller indices $(h,k,l)$ but equal structure factors $F$. The coefficient $A(\theta)$ allows for the effect of absorption in the target material. Both $p$ and $A(\theta)$ can be found from data in the International Tables for X-ray Crystallography\textsuperscript{64}. The atomic scattering factors of the metal and fluorine ions were taken from Cromer and Waber's paper\textsuperscript{39}, and that for the ammonium ion was one of two calculated by Davis\textsuperscript{41} from different published wavefunctions (the one used was that for which Davis believed the wavefunction to be the more accurate). Data for anomalous scattering were obtained from the International Tables\textsuperscript{64} and Cromer\textsuperscript{38}, interpolation being necessary since the calculation was done for cobalt radiation for which this information was not readily available. This choice of cobalt was made with a view to extending the calculations to $(\text{NH}_4)_3\text{FeF}_6$, where X-ray fluorescence caused by the presence of iron dictates the use of a cobalt rather than a copper X-ray tube. The B values assigned were those used by Bode and Voce\textsuperscript{14} in their structural refinement from powder data for tetragonal $(\text{NH}_4)_3\text{ScF}_6$, with the aluminium being given the value obtained for scandium.

The calculation was performed for several values of $\phi$. The effect of large oscillations of fluorine ions, as expected near the transition point, was examined by varying the parameter $B_{\text{FII}}$ which depends on the amplitude of these oscillations. The absorption of X-rays in the sample has been taken as being negligible ($A(\theta)$ constant), a condition which can be achieved in practice by mixing the X-ray powder sample with a suitable dilutant.
The intensity dependence on $\phi$ and $B_{F_{II}}^{-}$ (R fixed) for the more prominent X-ray lines is depicted in figure (4.2). Table (4.1) lists these intensities along with the values of the parameters used in their calculation. The intensities have been standardised to a fixed (002) line intensity of 40, since the form of equation (4.8) indicates that all (0,0,2n) line intensities (n an integer) are independent of both $\phi$ and $B_{F_{II}}^{-}$.

Since $H_{T}$-odd line intensities depend only on variables associated with the fluorine ($F_{II}^{-}$) ions, the possibility that these particular lines alone might provide sufficient data to indicate the value of $\phi$ without the need for a full structural refinement is worth investigation (c.f. equation (4.7) and the associated text where the relationship between the order-parameter and intensities of the X-ray peaks is discussed). In this connection only the (212), (210) and (311) lines have sufficient intensity to be useful. We assume that complete structural refinements have been carried out and all crystal parameters determined for the low temperature phase at two temperatures, $T_a$ and $T_b$ say. Then the goal is to obtain values of $\phi$ at temperatures between $T_a$ and $T_b$ from the intensities of the (212), (210) and (311) lines only. This will turn out to be a possibility only if at least one of the parameters $B_{F_{II}}^{-}$ and R is effectively constant in this temperature range. We now consider each of the variables in the expressions for the intensities of these lines in turn:

i) $B_{F_{II}}^{-}$: Since this depends on the $F_{II}^{-}$ ion amplitude of vibration in the X-Y (001) plane, it is expected to increase near the transition temperature. Some indication of its importance may be obtained from Bode and Voce's data for
Table 4.1 X-ray Line Intensities for Theoretical Tetragonal (NH$_4$)$_3$AlF$_6$.

$\lambda_{co} = 1.79021 \, \AA$ (K$_\alpha$)

<table>
<thead>
<tr>
<th>Miller Indices</th>
<th>$\theta$ (degrees)</th>
<th>$\phi$ (degrees)</th>
<th>2.4</th>
<th>4.0</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$ $k$ $l$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 0 1</td>
<td>10.005</td>
<td>97.6</td>
<td>94.6</td>
<td>96.5</td>
<td>101.8</td>
</tr>
<tr>
<td>0 0 2</td>
<td>11.346</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
</tr>
<tr>
<td>1 1 0</td>
<td>11.068</td>
<td>70.0</td>
<td>48.5</td>
<td>72.9</td>
<td>69.9</td>
</tr>
<tr>
<td>1 1 2</td>
<td>16.401</td>
<td>41.4</td>
<td>27.1</td>
<td>43.2</td>
<td>41.2</td>
</tr>
<tr>
<td>2 0 0</td>
<td>16.645</td>
<td>22.8</td>
<td>48.4</td>
<td>22.9</td>
<td>25.7</td>
</tr>
<tr>
<td>2 1 0</td>
<td>18.678</td>
<td>4.9</td>
<td>29.4</td>
<td>0</td>
<td>4.4</td>
</tr>
<tr>
<td>2 0 2</td>
<td>20.344</td>
<td>91.2</td>
<td>53.8</td>
<td>91.0</td>
<td>85.8</td>
</tr>
<tr>
<td>2 1 2</td>
<td>22.076</td>
<td>5.4</td>
<td>32.4</td>
<td>0</td>
<td>4.9</td>
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<tr>
<td>0 0 4</td>
<td>23.176</td>
<td>50.4</td>
<td>50.3</td>
<td>50.4</td>
<td>50.4</td>
</tr>
<tr>
<td>2 2 0</td>
<td>23.896</td>
<td>84.9</td>
<td>48.1</td>
<td>85.9</td>
<td>80.5</td>
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<tr>
<td>3 1 0</td>
<td>26.929</td>
<td>8.6</td>
<td>17.0</td>
<td>7.9</td>
<td>9.0</td>
</tr>
<tr>
<td>3 1 1</td>
<td>27.610</td>
<td>2.1</td>
<td>15.4</td>
<td>0</td>
<td>1.7</td>
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<td>1 0 5</td>
<td>30.813</td>
<td>12.4</td>
<td>13.3</td>
<td>12.3</td>
<td>12.4</td>
</tr>
<tr>
<td>3 2 1</td>
<td>31.713</td>
<td>21.2</td>
<td>14.9</td>
<td>18.9</td>
<td>18.2</td>
</tr>
<tr>
<td>2 2 4</td>
<td>34.382</td>
<td>28.3</td>
<td>14.8</td>
<td>28.7</td>
<td>26.7</td>
</tr>
<tr>
<td>4 0 0</td>
<td>34.950</td>
<td>13.2</td>
<td>7.3</td>
<td>13.3</td>
<td>12.2</td>
</tr>
</tbody>
</table>
FIG. 4.2 VARIATION OF THEORETICAL X-RAY LINE INTENSITY WITH ROTATION ANGLE (\(\phi\)) OF FLUORINE OCTAHEDRA AND FLUORINE DEBYE PARAMETER. TETRAHEDRAL (NH\(_4\))\(_3\)AlF\(_6\), SPACE GROUP D\(_{4h}\)^6. THE BARS INDICATE THE INTENSITY CHANGE AS B\(_{\text{III}}\)\(_{\text{II}}\) OF FLUORINE GOLDS FROM 2.4 TO 6.0 \(\text{Å}^2\).
tetragonal \((\text{NH}_4)_3\text{ScF}_6\). Here \(B_{F^-}\) for \((210)\) and \((212)\) lines

\[
\text{theoretical intensity drop of 9.7\% for the (210) and (212) lines}
\]

(sufficient to reduce an estimate of \(\phi = 17^\circ\) to one of

\(\phi \sim 15^\circ\)) and of 18.5\% for the (311) line. It is possible

therefore that \(B_{F^-}\) varies sufficiently in practice to

require its remeasurement at small temperature intervals, but

evaluation of it at two or more fixed temperatures is

necessary to determine the importance of this variation for

any particular compound.

ii) \(B_{F^-}\) : This can be obtained from the intensity ratio

for the \([(210)\] and \((212)\) lines:

\[
\frac{I(210)}{I(212)} = \frac{\left| f_{F^-}(\theta_{210}) \right|^2 h(\theta_{210})}{2\left| f_{F^-}(\theta_{212}) \right|^2 h(\theta_{212})} \exp\left(2B_{F^-}/c^2\right) \tag{4.13}
\]

where \(\theta_{210}\) and \(\theta_{212}\) are the values of the Bragg angle, \(\theta\), for

the \((210)\) and \((212)\) X-ray lines, and

\[
h(\theta) = \left(1 + \cos^2\theta\right)/\sin^2\theta\cos\theta
\]

iii) \(R\), the \(Al-F^-\) separation: Bode and Voce\(^{14}\) obtained values

of 1.94\(\bar{A}\) and 2.05\(\bar{A}\) for the Sc-\(F^-\) separations in cubic and
tetragonal \((\text{NH}_4)_3\text{ScF}_6\) respectively. This gives a 5% increase

in the Sc-\(F^-\) separation. A change of this size in our

hypothetical tetragonal \((\text{NH}_4)_3\text{AlF}_6\) structure (from 0.31a to

0.315a) increases the intensities of each of the \((212)\), \((210)\)

and \((311)\) lines by a factor of 1.477 (to the accuracy given this

factor is independent of the value of \(\phi\)). Assuming that \(R\)
varies continuously, an intensity change of this size would make it necessary to evaluate this parameter at several temperatures.

In general then, we can expect to have to evaluate \( B_{F^{-}} \), \( \phi \), and \( R \). This is clearly impossible with just the data for the (210), (212) and (311) lines; once \( B_{F^{-}} \) has been obtained (equation (4.13)) we have available only two equations to attempt this task.

4.7.4 Conclusion

It is fortunate that the observed rotation angles of the fluorine octahedra in tetragonal cryolites are relatively large (\( \phi = 17^040' \) for \((\text{NH}_4)_3\text{InF}_6\) and \((\text{NH}_4)_3\text{ScF}_6\)). This fact, combined with the calculated variations of line intensity with \( \phi \) discussed above, indicates that X-ray powder photography should be sufficiently sensitive to order parameter change to give useful data. The emphasis in experimental work has been on this method. A variable temperature attachment has been built to fit a standard Debye-Scherrer powder camera; its construction is described in the following chapter.
CHAPTER V

A VARIABLE TEMPERATURE X-RAY POWDER CAMERA

5.1 INTRODUCTION

In this chapter the design of this camera and the associated equipment will be discussed, beginning with a general description of the complete system, and then covering the details of each component in order. Following this the principle of operation, the circuitry, and the performance of the temperature control system will be considered. A discussion of the methods of temperature measurement and associated problems will conclude the chapter.

Note: Reference labels for component parts in this chapter consist of a lower case letter and/or a number. The letters refer to the labelling of figure (5.1) and the numbers to the (common) labelling of figures (5.2), (5.3) and (5.4).

5.2 GENERAL DESCRIPTION

In the system about to be described a gas stream is used to heat or cool a sample in a Debye-Scherrer X-ray powder camera. There are a number of designs in the literature which employ this general approach. A schematic diagram of the system is shown in figure (5.1), and the layout is depicted in the photograph in figure (5.2).

The camera (n,1) is divided into two concentric chambers. The temperature of the X-ray specimen (n,2) in the inner chamber (o,3) is controlled by a stream of nitrogen entering
FIG. 5.1 SCHEMATIC DIAGRAM OF VARIABLE TEMPERATURE X-RAY CAMERA SYSTEM.

a. Heat exchange gas supply
b. Film chamber gas supply
c. Standard industrial regulator-pressure meter unit
d. Refrigeration expansion valve (Danfoss, type ID)
e. Needle valve
f. Flow meter
g. Gas drying unit
h. Liquid air container
i. Copper cooling coil in liquid air
j. Gas delivery tube (vacuum walled).
k. Gas heating coil
l. Leads to power supply
m. Gas delivery nozzle
n. Basic camera body
o. Sample chamber
p. Film chamber
q. Gas outlet from film chamber
r. Gas vents from sample chamber
s. X-ray specimen.
FIG. 5.1 SCHEMATIC DIAGRAM OF VARIABLE TEMPERATURE X-RAY CAMERA SYSTEM
### Index of Variable Temperature Camera Components

(Refer figures 5.2, 5.3 and 5.4)

<table>
<thead>
<tr>
<th>Number</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Basic Camera Body</td>
</tr>
<tr>
<td>2.</td>
<td>X-ray Sample</td>
</tr>
<tr>
<td>3.</td>
<td>Inner Camera (Sample) Chamber</td>
</tr>
<tr>
<td>4.</td>
<td>Heat Exchange Gas Delivery Nozzle</td>
</tr>
<tr>
<td>5.</td>
<td>Exchange Gas Vents</td>
</tr>
<tr>
<td>6.</td>
<td>Outer Camera (Film) Chamber</td>
</tr>
<tr>
<td>7.</td>
<td>X-ray Film</td>
</tr>
<tr>
<td>8.</td>
<td>Adaptor: Base Plate</td>
</tr>
<tr>
<td>9.</td>
<td>Adaptor: Film Chamber Cover Unit</td>
</tr>
<tr>
<td>10.</td>
<td>Sample Chamber Cover (Tufnol)</td>
</tr>
<tr>
<td>11.</td>
<td>Tufnol Baffle</td>
</tr>
<tr>
<td>12.</td>
<td>Film Guide Ring</td>
</tr>
<tr>
<td>13.</td>
<td>Film Chamber Cover Unit: Lid</td>
</tr>
<tr>
<td>14.</td>
<td>Film Chamber Cover Unit: Brass Alignment Posts</td>
</tr>
<tr>
<td>15.</td>
<td>Film Chamber Cover Unit: Brass Centring Ring</td>
</tr>
<tr>
<td>16.</td>
<td>Polythene Sheet Light Shield</td>
</tr>
<tr>
<td>17.</td>
<td>X-ray Collimator</td>
</tr>
<tr>
<td>18.</td>
<td>X-ray Beam Trap</td>
</tr>
<tr>
<td>19.</td>
<td>Collimator and Beam Trap Ports</td>
</tr>
<tr>
<td>20.</td>
<td>Light Seals</td>
</tr>
<tr>
<td>21.</td>
<td>Film Chamber Gas Inlet Port</td>
</tr>
<tr>
<td>22.</td>
<td>Film Chamber Gas Outlet Port</td>
</tr>
<tr>
<td>23.</td>
<td>Securing Nuts for Sample Chamber Cover</td>
</tr>
<tr>
<td>24.</td>
<td>Copper Guide Tube</td>
</tr>
<tr>
<td>25.</td>
<td>Specimen Mounting Chuck</td>
</tr>
<tr>
<td>26.</td>
<td>Rotating Specimen Table</td>
</tr>
</tbody>
</table>
27. Bond between Tufnol Baffle and Specimen Table (Plasticene)
28. Temperature Gradient Check Thermocouple
29. Control and Monitor
30. Thermocouple Ring
31. Ring Mount Vane
32. PVC Thermocouple Wire Sheathing
33. Gas Delivery Tube-Delivery Nozzle
34. Heat Exchange Gas Delivery Tube
35. Nichrome Gas-Heating Coil
36. Gas Heater Leads
37. Heat Exchange Gas Supply
38. Refrigeration Expansion Valve (Dewar)
39. Needle Valve
40. Rotameter Gas Flow Meter
41. Gas Drying Unit
42. Compressed Air Supply Line
43. Gas Cooling Coil Container
44. Film Chamber Gas Supply
45. Liquid Air Supply Dewar
46. Liquid Air Trans
47. Liquid Air Level Sensors
48. Liquid Air Level Controller
49. Ice Bath for Thermocouple Stand
50. Potentiometer
51. Thermocouple Selection Switch
52. Gas Heater Control Unit
53. Chart Recorder to Monitor
54. Backoff Voltage Supply
FIG. 5.2 VARIABLE TEMPERATURE X-RAY CAMERA SYSTEM
the chamber via a nozzle (m,4) and leaving by gas vents (r,5) in the camera lid.

The nitrogen is stored in cylinders (a,37) under pressure. From these it passes through a system of valves (d,38; e,39), which ensures a constant flow, to a flow meter (f,40) and thence through a drying tube (g,41) to a heat exchange coil (i) immersed in an appropriate coolant liquid (usually liquid air). The cooled nitrogen then goes through a vacuum-walled delivery tube (j,34) where it is warmed to the desired temperature by a heater (k,35) before striking the X-ray sample.

The outer chamber of the camera (p,6) contains the film (7). An independent supply of nitrogen at room temperature (b,44) to this chamber protects the film from large temperature changes in the inner chamber.

5.3 DETAIL OF SYSTEM COMPONENTS

5.3.1 Adaptor Unit

(1) Construction

The purpose of the adaptor to be described is to achieve the delivery of the heat-exchange gas to the X-ray specimen, while at the same time protecting the X-ray film and the moving parts of the camera from the effects of temperature change. It is designed to fit a standard commercially available Debye-Scherrer powder camera (Philips model PW1024). This camera has an internal diameter of 114.83 mm, this size being chosen with the aim that after development the separation on the X-ray film of a pair of diffraction lines of Bragg angle \( \theta \) degrees should be 40 mm. The adaptor design was developed from one for a
A cutaway view of the adaptor assembled and in position in the camera is shown in figure 5.3, and a complementary exploded view appears in the photograph in figure 5.4. It can be seen from these figures that the adaptor, as previously noted in the general description above, divides the camera body into an inner ('sample') chamber (3) and outer ('film') chamber (6). The component parts of the adaptor itself can be considered under four headings:

(a) **The Base Plate (8)**

This is made of brass, and fits closely inside the film guide ring (12) on the inside of the camera base. The close fit ensures that the plate is thus centrally mounted.

(b) **The Film Chamber Cover Unit (9)**

This consists of:

i) the lid proper (13). This is made of brass, is of annular form, and covers the film chamber. The nitrogen gas stream which is used to keep the film near room temperature enters a light trap port (21) in this lid, flows through the film chamber and out a similar light trap port (22) diametrically opposite the first. Polythene adhesive tape is used to secure the outer edge of the lid to the camera body and to seal the film chamber against gas loss.

ii) the centring ring (15). This is also brass. It fits closely over the base plate.

iii) the light shield (16). This is made of black plastic polythene sheet, and is glued along opposite edges to the
FIG. 5.3 CUTAWAY VIEW OF CAMERA WITH ADAPTOR IN PLACE
ORIGINAL CAMERA PARTS ARE SHADED
FIG. 5.4 EXPLODED VIEW OF VARIABLE TEMPERATURE X-RAY CAMERA ADAPTOR UNIT
centring ring and the lid proper respectively to form a cylinder. It thus separates the sample and film chambers, preventing the two gas supplies from mixing and protecting the film from light, while allowing the transmission of X-rays scattered from the specimen.

iv) two brass posts (14). These connect the lid proper to the centring ring. The X-ray collimator (17) and beam trap (18) pass through holes (19) in these posts. Apiezon "Q" sealing compound, a soft black wax-like material, is used to provide light- and gas-tight seals (20) at these holes; this method was found preferable to the use of rubber washer seals which tended to induce mechanical stress and thus misalign the collimator.

(c) The Baffle (11)

This is made of Tufnol, a laminated synthetic resin. It consists of a disc with a central axle. The axle slips over the specimen mounting chuck (25) of the camera, and is secured to the camera's rotating specimen table (26) by a plasticene seal (27). The Lindemann glass tube containing the powdered X-ray specimen (2) is inserted in a hole drilled down the centre of the baffle axle. Plasticene or a similar material holds it in place.

(d) The Sample Chamber Cover (10)

This is also made of Tufnol. It is secured to the lid of the film chamber cover unit by two nuts (23). The screw shafts of these nuts and a copper tube (24) soldered to the base plate serve to align it.

The delivery nozzle for the heat exchange gas (4) passes through the centre of the Tufnol cover, and is glued to it.
This nozzle is made of pyrex and has an evacuated double wall. The gas emerges from the nozzle, passes over the X-ray specimen, is deflected by the Tufnol baffle and leaves the camera through the two vents (5) in the Tufnol cover.

The temperature of the gas stream is monitored and controlled by three thermocouples. The junctions of two of these (29) are Araldited to cotton threads stretched across the end of the delivery nozzle above the X-ray sample tube. To reduce conduction error the leads of these two thermocouples are attached to the inner wall of the nozzle some 2½ centimetres from the end; they then pass back through the end of the nozzle and thence through the Tufnol cover. One of these two thermocouples provides the input to the temperature controller, while the other serves as an independent monitor. The third junction (28) is sited adjacent to the X-ray specimen, but on the opposite side of the X-ray beam from the other two junctions. This way we can get an indication of the temperature gradient in the gas stream. The leads of this thermocouple are stretched across a Tufnol ring (30) in the gas stream. This ring is secured to the Tufnol cover via a vane (31) of the same material. All thermocouple leads are protected in the region outside the camera by PVC sheathing (32) glued to the Tufnol cover.

(2) Loading Procedure

Sample alignment with the Philips Debye-Scherrer camera is usually done before loading the film, but the design of the adaptor necessitates a change of procedure. The film is still loaded first, in the usual way. While still in the darkroom the base plate and film chamber cover unit are put in
place. The Tufnol baffle with the X-ray sample is then inserted, and the collimator and beam trap screwed into position. The film chamber cover unit is then taped to the camera body, and the light sealing compound tamped into place around the collimator and beam trap. The X-ray sample can then be illuminated for aligning by shining a light either into the (still open) sample chamber or down the beam trap (to carry out the latter procedure the end section of the beam trap with its protective lead glass beam stop must be unscrewed. To guard against any possibility of mishap due to forgetfulness one should make it an invariable practice to replace this end section immediately the sample alignment is completed.) Finally, the camera is mounted on its bracket on the X-ray table, and the Tufnol lid to the sample chamber is fixed in place.

5.3.2 Gas Supply Line Components

(1) Gas Supply

The supply to both camera chambers is from bottles of compressed "dry Nitrogen", supplied by New Zealand Industrial Gases Ltd. The manufacturer cites impurity values of less than 0.01 gm m$^{-3}$ for water vapour (equivalent to a dew point of $-60^\circ$C) and less than 5 parts per million of carbon dioxide. Under typical operating conditions (gas flow meter reading 5 litres/minute) two full 165 cubic foot bottles in tandem provided enough gas to supply the camera sample chamber for 26 hours of continuous running. Except for high gas flow (10 litres/minute) and extreme temperatures in the sample chamber a flow rate to the film chamber half that to the sample chamber is adequate, and consequently a single bottle is used to supply this.
Gas Flow Control

Initial flow control for both supply lines is through a standard industrial regulator reducing valve, with pressure gauges on both the high and low pressure sides (c). For the film chamber supply the low pressure side of the regulator is initially adjusted to 40 psi and the flow rate is controlled by a single needle valve between the regulator and the flow meter. Occasional readjustment is required to bring the flow back to its original value. It was considered that this was unimportant since the primary concern was simply to protect the film from any extreme temperatures in the sample chamber rather than to maintain it at a precise temperature. Should thermal expansion of the film or camera prove a problem another valve can be introduced to give a more constant flow.

The need for a constant flow is more evident for the sample chamber supply. To achieve this a Danfoss type 1D automatic refrigeration expansion valve (d,38) is inserted in the flow line. The flow rate is adjusted by a needle valve situated in the line between the expansion valve and the flow meter. In general the low pressure side of the regulator valve has been adjusted to 40 psi. The change in flow meter reading over an experimental run is of the order of 0.1 l/min. The gas temperature change resulting from varying the flow rate when the present control equipment (to be described) is operating has been tested in the region of -60°C (flow 4 to 6 l/min) and of -120°C (flow 9 to 10 l/min). A change of 0.1 l/min in the flow rate, it was found, would result in a temperature change of less than 0.3°C; this will turn out to be less important than other temperature uncertainties.
(3) Gas Flow Measurement

The flow rates in both lines are monitored by rotameter flow meters (f.40) manufactured by the British Oxygen Company. These meters are calibrated for flows of up to 10 litres/minute. They are designed for use with oxygen, and will not therefore give precise nitrogen flow rate values; however approximate reproducibility and ability to detect flow rate changes during a given experimental run are the basic requirements, and these are satisfactorily met.

The flow meter readings were checked on the sample chamber supply line by observing the rate of the pressure drop in the gas supply cylinders and calculating the gas flow required to give this rate (these flows were calculated for a gas at 760 torr and 0°C). These estimated flows are not expected to be particularly accurate as the pressure meter on the industrial regulator reducing valve is a relatively insensitive instrument. Agreement with the flow meter readings within 10% was obtained over several experimental runs, indicating that the flow meter readings are of the correct order of magnitude.

(4) Gas Drying System

When using liquid air to cool the nitrogen stream it was found that snow would gradually block the gas line. To counter this effect a one inch diameter polythene tube containing a kilogram of grade A4 molecular sieve (g.41) was placed in the supply line. The molecular sieve is replaced with regenerated material before each run. Thus far continuous runs of up to twenty hours duration have been carried out with no indication of snow formation.
(5) **Exchange Gas Cooling System**

(a) Principle of Operation: The heat exchange coil (i) is of 3/16 inch i.d. copper tubing. For measurements below room temperature this coil is immersed in liquid air in a thermos flask (h, 43). As the liquid air boils away it is periodically replaced by an automatic filling system, described below.

(b) Automatic Liquid Air Replenishing System: The liquid air is stored under pressure from a compressed air supply (42) in a 25 litre dewar (45). A solenoid valve (46) on the liquid air supply line from the dewar to the thermos controls the filling.

The control circuit (figure 5.5) of the filling system was built to a departmental design. It is based on two liquid air level sensors (47) which are made from standard refrigeration thermostats by replacing the gas originally present in them with oxygen at six atmospheres. The switches connected to the sensors are then closed when the ends of the sensors are immersed in liquid air, but rapidly open when the sensors are withdrawn.

The sensor tips are adjusted to be respectively at the lowest and highest desired levels for the liquid air in the thermos (43). They then control the solenoid valve according to the following cycle (ref. fig. 5.5):

For most of the time during an experimental run no transfer of liquid air from the storage dewar is taking place. The liquid air surface in the thermos is then between the tips of the upper and lower sensors; for the purpose of discussion we take this condition as the starting point of the filling cycle.
Components:
2 modified thermostats, switches open at low temperature
'Speedline' LO5 solenoid valve
'Arrow' 2-pole 230 V a.c. relay coil

FIG. 5.5 LIQUID AIR FILLER CONTROL SYSTEM

FIG. 5.6 TEMPERATURE CONTROLLER PRINCIPLE
The upper sensor switch is closed, all other switches are open, and no current is flowing in the circuit. Eventually the liquid air level falls to the point where the lower sensor tip is uncovered; its associated switch then closes and the relay coil is activated, closing the switches A/1 and A/2. Current then flows through switch A/2 to the solenoid, opening the valve and thus letting liquid air transfer from the storage dewar. The solenoid current continues when the lower sensor tip is covered and the associated switch opens, since current can still reach the relay coil via the line containing the switch A/1. However, when filling of the thermos has proceeded to the point where the upper sensor tip is immersed, the associated switch, in series with switch A/1, opens; the relay coil current is thus cut off, the two relay switches open, and the solenoid valve closes. Since the upper sensor tip is only just below the liquid air surface at this point, evaporation soon uncovers it. The upper sensor switch then opens and we are back to the beginning of the filling cycle.

Under the usual operating conditions, viz. a 5 l/minute nitrogen heat exchange gas flow, the twenty-five litre dewar holds sufficient liquid air for twenty hours of operation, provided that the thermos is filled manually at the start of the experimental run. The separation of the sensor tips can be adjusted so that the time between fillings is of the order of twenty minutes. Thus the supply dewar can be changed, if necessary, without interrupting the experiment.

To obtain economical and reliable operation of this automatic filling system three precautions should be taken:
i) The outlet of the delivery tube from the supply dewar must be clamped parallel to the surface of the liquid in the thermos. This reduces splash loss.

ii) The rate of transfer between dewar and thermos must be kept below a certain value. In effect this means taking care to keep the compressed air supply pressure sufficiently low. A high liquid air flow rate gives splash loss. There will be further loss if the filling of the thermos is so fast that the upper sensor, which possesses some thermal lag, does not have time to turn off the solenoid valve before overflow occurs.

iii) The solenoid valve and delivery tube should be dried between experiments by a stream of warm air. Without this precaution ice was found to eventually form in the valve; this forced it to stay permanently open, and the supply dewar was rapidly emptied.

(6) Gas Delivery Tube and Heater Unit

The gas delivery tube (34) is made of pyrex. It is double-walled, with a vacuum between the walls. One end is joined to the copper heat exchange coil by a glass-metal seal, and the other is connected to the gas delivery nozzle (4) in the sample chamber cover. The junction between the delivery tube and the nozzle is made by a pyrex socket on the delivery tube which seals on to an O-ring (33, figure 5.4) on the nozzle. Nozzle and delivery tube are held together by rubber bands between hooks on the latter and on the sample chamber cover.

The heater for the heat exchange gas (k,35) is a length of nichrome wire with a resistance of 96 ohms. It is wound into a coiled coil about a glass rod, and inserted into the
gas delivery tube. The heater leads pass through the walls of the pyrex socket.

With this system as it at present stands there is considerable transfer of heat from the surroundings to the gas stream before the gas reaches the X-ray sample. The data listed in table (5.1) indicates the size of this effect. This heat transfer sets the lower limit to attainable temperatures.

The means by which heat can be transferred from the surroundings are:

i) conduction through the walls of the socket junction and the heater leads. The socket could be omitted, but the arrangement is convenient for handling and assembling; in particular it has made it possible to repair or alter the heater unit without having to remove the thermocouples in the camera.

ii) Radiation transfer between the two walls of the delivery tube. We can make an estimate of the size of this using a formula given by Saunders for the rate of heat transfer between concentric cylinders. This is

\[ Q = \frac{2\pi r_1 r_2 e_1 e_2 (T_1^4 - T_2^4) L}{r_2 e_2 + r_1 e_1 (1 - e_2)} \tag{5.1} \]

where the inner cylinder has radius \( r_1 \), emissivity \( e_1 \) and temperature \( T_1 \) (K), and \( r_2 \), \( e_2 \) and \( T_2 \) are the corresponding quantities for the outer cylinder. The tube lengths are both \( L \). Let \( \Delta T \) be the temperature rise of the gas. Then

\[ \Delta T = -\frac{Q}{fc} \tag{5.2} \]

where \( f \) is the mass flow rate of the gas and \( c \) its specific heat.
We apply this to the main delivery tube. This does not have the ideal configuration of course - it has a bend in it, the concentric walls are joined at the ends, and the temperatures will not be constant along the walls - so that we can expect only an order of magnitude estimate. To obtain this we take

\[ r_1 = 0.6 \text{ cm} \]
\[ r_2 = 1.0 \text{ cm} \]
\[ L = 39 \text{ cm} \]
\[ T_2 = 290^\circ\text{K (17°C)} \text{ - room temperature} \]
\[ e_1 = e_2 = e \]
\[ c = 0.25 \text{ calories/gm (the specific heat of nitrogen changes little between liquid air and room temperature).} \]

For glass an appropriate value of the emissivity is 0.9, for silvered glass 0.04. Then the values of \( \Delta T \) listed in table (5.2) are obtained. It is apparent from these that radiant transfer of heat between the concentric walls of the delivery tube contributes a substantial proportion of heat from outside sources, and that silvering the tube walls would make this effect negligible. At present no phase transition occurring at less than \(-49^\circ\text{C (} (\text{NH}_4)_3\text{AlF}_6) \) has been observed, so that silvering has not been necessary.

5.4 TEMPERATURE CONTROL SYSTEM

5.4.1 Principle

The X-ray specimen temperature is controlled indirectly by regulating the heat exchange gas temperature. The voltage
Table 5.1. Observed contributions to heating nitrogen exchange gas.

<table>
<thead>
<tr>
<th>Flow Meter Reading (l/min)</th>
<th>Thermocouple Gas Temperature Reading (°C)*</th>
<th>Heat Contribution from Surroundings (W)</th>
<th>Heat Contribution from Heater (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-133</td>
<td>6.7</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>-110</td>
<td>6.6</td>
<td>2.6</td>
</tr>
<tr>
<td>5</td>
<td>-59</td>
<td>5.5</td>
<td>9.3</td>
</tr>
<tr>
<td>5</td>
<td>-35</td>
<td>4.5</td>
<td>12.7</td>
</tr>
<tr>
<td>10</td>
<td>-158</td>
<td>7.8</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>-114</td>
<td>7.4</td>
<td>10.1</td>
</tr>
</tbody>
</table>

* The thermocouple head was at the outlet of the delivery nozzle.

Power from the heater is calculated from a direct current reading; that listed as from the surroundings is the balance required to bring the nitrogen to the observed temperature from an assumed initial -194°C (liquid air temperature).

Table 5.2 Estimated gas temperature rises from radiated heat.

<table>
<thead>
<tr>
<th>Gas Flow Rate (l/min)</th>
<th>e</th>
<th>$T_1$ (°C)</th>
<th>$\Delta T$ (°C) (Calculated)</th>
<th>$\Delta T$ (°C) (observed - refer table 5.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.9</td>
<td>-133</td>
<td>43</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>0.04</td>
<td>-194</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>0.9</td>
<td>-158</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td>10</td>
<td>0.04</td>
<td>-194</td>
<td>0.7</td>
<td>-</td>
</tr>
</tbody>
</table>
output from one of the thermocouples at the gas delivery nozzle outlet (29) is fed to the controller unit where it is electronically subtracted from a predetermined set voltage. This set voltage is equal to that which the thermocouple would supply at the desired control temperature. The difference voltage, after amplification, controls the current to the gas supply heater. Thus, the nearer the thermocouple temperature is to the desired temperature, the smaller the current to the heater. The characteristics of such a control method will be discussed in terms of the idealised system of figure (5.6).

We adopt the following notation:

\(T\): the gas temperature measured by the thermocouple

\(T_f\): the equilibrium value of \(T\), established when the controller is operating

\(E_T\): the thermocouple voltage corresponding to the temperature \(T\)

\(E_{T_s}\): The set voltage supplied by the controller for comparison with \(E_T\)

\(T_s\): the temperature giving a thermocouple voltage of \(E_{T_s}\)

\(T_u\): a potential temperature towards which the gas stream would tend immediately the heater was turned off

\(f\): the exchange gas flow rate (mass per unit time)

\(c\): the exchange gas specific heat

The thermocouple voltage-temperature relationship will be written

\[ E_T = g(T). \] (5.3)

Finally for convenience we define

\[ D = A B R \frac{k}{T_s} \left( \frac{\partial g}{\partial T} \right) / c^k \] (5.4)
where A, B and R are as defined in figure (5.6).

Now the current through the heater is $AB(E_{T_s} - E_T)$. At any instant there is a potential gas temperature rise given by

$$\text{(Power through heater/fc)} = A^2 B^2 R (E_{T_s} - E_T)^2 / fc.$$  

We consider the situation where equilibrium has been nearly attained; then $T$ will be approaching $T_s$, and we can take a Taylor expansion to the first two terms of equation (5.3)

$$E_{T_s} - E_T = \left(\frac{\partial g}{\partial T}\right)_{T_s} (T_s - T)$$  \hspace{1cm} (5.5)$$

The potential temperature rise thus becomes

$$\{A^2 B^2 R (\frac{\partial g}{\partial T})^2 / fc\} (T_s - T)^2 = D^2 (T_s - T)^2 / f,$$

so that at any instant the temperature $T$ will be tending to a potential value given by

$$T \to T_u + \frac{D^2}{f} (T_s - T)^2$$  \hspace{1cm} (5.6)$$

Notice that the value of this potential temperature, $T$, is continually changing; the term $(T_s - T)^2$ varies as $T$ varies, and in general $T_u$ itself will also have a dependence on $T$.

However, when equilibrium is established the relationship (5.6) becomes an equality:

$$T_f = T_u + \frac{D^2}{f} (T_s - T_f)^2$$  \hspace{1cm} (5.7)$$

This equation has one physically acceptable solution for $T_f$: 
\[ T_f = T_s + \left\{ 1 - \left[ 1 + \frac{4D^2(T_s-T_u)}{f} \right]^{\frac{1}{2}} \right\} \frac{2D^2}{f} \]  
\tag{5.8a}

\[ \dot{T}_s = T_s - \frac{f^\frac{1}{2}(T_s-T_u)}{D} \]  
\tag{5.8b}

if \( D \) is large.

It follows from equations (5.8) that the equilibrium temperature \( T_f \) will be lower than the set temperature \( T_s \). Thus

\[ T_u < T_f < T_s. \]  
\tag{5.9}

The quantity \((T_s-T_f)\) will be referred to as the offset, in accordance with normal usage.

5.4.2 Stability Control

The presence of offset presents no difficulty to obtaining any desired value of \( T_f \). The gas temperature can be continuously monitored and the value of \( E_{T_s} \) generated by the controller adjusted until the required temperature is obtained. It is, however, evident from equations (5.4) and (5.8) that various factors can affect the stability of the controlled temperature \( T_f \).

The first of these is the electronic circuitry. Instability here will affect the amplification values \( A \) and \( B \) (hence \( D \)) and the set temperature \( T_s \). This will be discussed further in the next section.

The other factors are changes in the gas flow rate, \( f \), and the ambient temperature. Both of these will affect the temperature \( T_u \). To consider these variations we write the change in \( f \) as \( \delta f \) and that in \( T_u \) as \( \delta T_u \). Then equation (5.8a) gives the change \( \delta T_f \) in \( T_f \) (to the first order) as
\[ \delta T_f = p \delta T_u - Q \frac{\delta f}{f} \]  
(5.10a)

where

\[ p = \frac{(T_s - T_f)}{(T_s + T_f - 2T_u)} \]  
(5.10b)

and

\[ Q = (T_f - T_u)P. \]  
(5.10c)

From the relation (5.9) the quantities \( P \) and \( Q \) are both positive.

Possible steps to improve stability indicated by this equation are as follows:

i) Reduction of the gas flow variation, \( \delta f \), to a minimum. The system of valves on the gas supply line designed to do this was discussed earlier.

ii) Reduction of the variation of \( T_u \). The variation of this potential temperature is complex. It depends on

a) the ambient temperature. Fine control on this is generally impracticable.

b) the rate of heat transfer to or from the surroundings. If this can be reduced a given change in the ambient temperature will have a smaller effect on \( T_u \). The previously suggested silvering of the walls of the gas delivery tube would assist here. The rate of heat transfer also depends on the value of \( T_f \), but this quantity is of course fixed by the requirements of the particular experiment.

c) the gas flow rate. An increase in flow rate means that for a given heat exchange with the surroundings there will be a smaller gas temperature change.
iii) Increase in the amplification factor $D$. Such an increase can be shown to decrease the values of both $P$ and $Q$. Consider a small increase $\Delta D$ in $D$, with corresponding changes $\Delta P$ and $\Delta Q$ in $P$ and $Q$. If the system is to give an unaltered final temperature $T_f$ the value of $T_u$ will remain unchanged, but $T_s$ will have to be altered. Then from equations (5.7), (5.10b) and (5.10c), we have to the first order

$$\Delta P = \frac{-Q}{(T_s+T_f-2T_u)} \frac{\Delta D}{D} \quad (5.11a)$$

and

$$\Delta Q = (T_f-T_u) \Delta P \quad (5.11b)$$

From the relationship (5.9) it follows that if $D$ becomes larger the quantities $P$ and $Q$ are both reduced; thus a large value of $D$ makes the controlled temperature less sensitive to fluctuations in gas flow and ambient conditions.

From expression (5.4) the obvious way to increase $D$ is to increase the amplifications, $A$ and $B$, of the voltage amplifier and the driver. There is a limit to which this can be done however; when a controller of the type discussed has very large amplification the controlled quantity goes into oscillations about a fixed value\(^{46}\).

The offset could in principle be removed completely by use of a combination of proportional, integral and differential control\(^{46}\). The cost of this would be a degree of complication in the controller electronics which cannot be justified in view of the limited accuracy with which the X-ray sample temperature can be measured (see below).
5.4.3 Controller Circuitry

The gas temperature regulator currently in use was obtained from an already existing unit by modifying it along lines suggested by the physics department electronics workshop. The circuit diagram is shown in figure (5.7).

In this unit the control thermocouple voltage is amplified before being compared with a set voltage supplied by the zener diodes. To provide the desired range of temperatures this amplification has been reduced by decreasing the feedback resistance on the initial amplifier as depicted. This will make the stability of the voltage standard more critical, since a given voltage change will now correspond to a larger change in temperature. Using a chart recorder and a high stability voltage signal source (known variation of ±1 mV) as a backoff voltage source the long term stability of the voltage standard near maximum setting was observed over a period of 24 hours. The total variation observed was ±1.1 mV. A typical amplification of the initial amplifier is 160 (the optional feedback resistance in figure (5.7) being 47kΩ). In this case the above voltage variation corresponds to a temperature range of ±0.3°C at -150°C, and to a lesser amount at higher temperatures.

A second modification has been to increase the supply voltage to the 2N3055 power transistor. This was required to give a large enough current to heat the gas. A Heathkit IP-20 regulated d.c. power supply, run typically at 40V, has been used for this purpose.
FIG. 5.7 VARIABLE TEMPERATURE CONTROLLER
The amplified thermocouple voltage can be automatically monitored for stability by means of a chart recorder. A block diagram of the complete system is shown in figure (5.8). Here the backoff voltage is supplied by the same voltage source as was used in checking the zener diode voltage standard, so that stability can be monitored to at least ±0.3°C.

5.4.4 Performance

Abrupt fluctuations occur in the measured temperature of the exchange gas, and it is necessary to average over a period of the order of a minute to obtain the controlled temperature. These fluctuations will be discussed below, but it is here sufficient to note that their origin is not principally in the electronics, since they occur with the heater turned off. Long term stability with the present control system has been checked down to the region of -85°C, variations in the controlled temperature of up to ±0.7°C over periods of 7 hours having been noted. This control is adequate for the accuracy with which it is possible to determine sample temperature (see below).

The short term gas temperature fluctuations detected by the camera thermocouples are of the order of ±0.2°C at and above room temperature, and increase as the controlled temperature is lowered to approximately ±0.6°C at and below -80°C. This again is not large compared with the accuracy of sample temperature measurement, and should, moreover, be somewhat damped out by the thermal inertia of the sample. Part of the cause of these fluctuations may lie in small flow rate variations resulting from condensation of nitrogen in the cooling coil (at a typical liquid air temperature of -194°C a
FIG. 5.8 BLOCK DIAGRAM OF TEMPERATURE CONTROL AND MONITORING ELECTRONICS
pressure of 1.2 atmospheres would give condensation in this part of the gas line); the reduction of the temperature fluctuations with increased gas temperature at the outlet nozzle may then be accounted for by a damping of the flow fluctuations through a corresponding increase in the nitrogen viscosity. If better sample temperature measurement were attained, thus justifying more accurate control, this explanation could be checked by a combination of shortening and lagging the cooling coil so that the nitrogen remained just above its condensation point.

5.5 GAS TEMPERATURE MEASUREMENT

The gas temperature is measured with copper-constantan thermocouples. For work with gases very fine wires must be used. Errors arising from heat conduction along the leads and from radiation from the surroundings are thus minimised. Young found that 0.003 inch (0.0076cm) diameter wires gave satisfactory values for gas temperature, whereas leads of twice that diameter did not. For the present work the thermocouples were constructed from #44BSW (diameter 0.0081cm) copper and #45BSW (diameter 0.0071cm) constantan resin-coated wires (suppliers, Post Radio Supplies, 33 Bourne Gardens, London, E4). The ends of these wires were stripped, twisted together and soft-soldered to form the junction.

Temperature readings are taken against an ice standard. The thermocouples for this are made of the same gauge wires, with their junctions immersed in oil in protective glass tubes.
The thermocouple voltages are measured with a Tinsley potentiometer, type 5592. A Keithley 115 null detector microvoltmeter is used in place of the potentiometer's normal galvanometer. The replacement instrument is easier to read, and its calibrated scale and fast response time make it possible to observe the short period temperature fluctuations.

Temperatures can be obtained from voltage readings using appropriate tables, of which there are several published sets. Allowance must be made for the variation of the voltage-temperature relationship from thermocouple to thermocouple, since the tables can only give this relationship for a representative thermocouple of each type. Accordingly, checks were carried out with three thermocouples at -195.6°C and 58.7°C. These two temperatures were obtained in liquid nitrogen and in a controlled water bath respectively, the calibration being done with a platinum resistance thermometer. In both cases the voltages of the thermocouples were equal to within ±1 μV, equivalent to ±0.07 and ±0.02°C at the lower and higher temperatures respectively. We now define

\[ T_{\text{table}} \]

as the temperature in °C given by a table for a given thermocouple voltage

and

\[ T_{\text{true}} \]

as the corresponding actual temperature.

Then, assuming that the difference \((T_{\text{true}} - T_{\text{table}})\) depends quadratically on \(T_{\text{table}}\), we obtain

\[ T_{\text{true}} = 0.978237T_{\text{table}} + 2.69852 \times 10^{-5}T_{\text{table}}^2 \] (5.12)

for the tables of reference 139. To obtain a more accurate relationship special equipment would be required to obtain other fixed temperatures.
5.6 SAMPLE TEMPERATURE MEASUREMENT

For the camera system as described above there will be an unknown difference between any thermocouple temperature reading and the temperature of the X-ray specimen. This difference will be present even if the thermocouple head is in contact with the sample just out of the X-ray beam, because of the generally low thermal conductivity of a powder sample.

Calculation of this temperature difference is not feasible; there is too complex a gas flow in the region of the sample and specimen table. Calibration with standard substances of known melting points is also impracticable; it would be necessary to match conductivities and absorptivities of sample and standard, as well as to ensure that such parameters as sample tube length, specimen table position, and gas flow were precisely the same for each experimental run. A third alternative is to mix a reference substance of known thermal expansion properties with the specimen. The temperature of the mixture can then be inferred from the lattice constants of the reference as indicated by the combined reference-sample X-ray photograph. The choice of a suitable reference material is discussed below.

A completely satisfactory reference will have the following characteristics:

i) ready availability.

ii) a well-defined lattice giving sharp lines at high diffraction angles so that accurate unit cell dimensions can be obtained.

iii) a large thermal expansion coefficient.
iv) a limited number of lines in the Bragg pattern. This is necessary to minimise the possibility of coincidences with the lines of the substance being examined. A cubic unit cell, preferably of small size, fulfils this requirement.

v) chemical inertness.

vi) low fluorescent background. It follows that the atomic numbers of the constituent atoms of the standard should be as low as possible. In particular, materials containing bromine or rubidium in general give heavy backgrounds no matter what the X-ray radiation employed.

vii) availability of suitable thermal expansion data, namely measurement of unit cell constants at different temperatures by X-ray methods. Measurements by techniques which involve observing bulk-expansion will often give significantly different results owing to the presence of microvoids, cracks, grain boundaries and others flaws in the sample.

A search for suitable materials was made among the elements and the alkali halides. The latter suggest themselves as possible candidates for standards since they generally have a simple structure and possess relatively high linear expansion coefficients (typically of the order of 30 to 40 \( \times 10^{-6} \, ^{\circ}\text{C}^{-1} \) around room temperature).

It turns out that there are very few published sets of results available in the region below room temperature, where most of the phase changes we initially wish to examine occur. Three materials that are found to meet this condition and also satisfy the requirements of cubic structure and a reasonably high thermal expansion coefficient are listed in table (5.3). Data on sodium and potassium chlorides, whose
Table 5.3 X-ray Thermal Expansion Data for Possible Temperature Standards

<table>
<thead>
<tr>
<th>Substance</th>
<th>Lattice Constant (Å)</th>
<th>Reference</th>
<th>Linear Expansion Coefficient* ($a \times 10^{-3}°C^{-1}$)</th>
<th>Temperature Range of Expansion Data (°K)</th>
<th>Purity (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.04954 (25°C)</td>
<td>64</td>
<td>14.4 23.0 24.5</td>
<td>20-125, 298.7 30-180 293-927</td>
<td>99.99 99+</td>
<td>48 128</td>
</tr>
<tr>
<td></td>
<td>4.0010**</td>
<td>48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.04963 (25°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>4.08626 ±0.00004† (25°C)</td>
<td>129</td>
<td>15.5 19.0 19.7</td>
<td>30-180 298-1223</td>
<td>99.7</td>
<td>128 122</td>
</tr>
<tr>
<td>LiF</td>
<td>4.0262 (30°C)</td>
<td>124</td>
<td>14.8 33.2 36.4</td>
<td>4-150 40-180 300-1123 302-750</td>
<td>Unspecified</td>
<td>63 130</td>
</tr>
<tr>
<td></td>
<td>4.02686 (30°C)</td>
<td>130</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.0146 (30°C)</td>
<td>108</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>5.64210 (30°C)</td>
<td>64</td>
<td>28.0 39.7 42.3</td>
<td>273-1038 302-970</td>
<td>Unspecified</td>
<td>107 124</td>
</tr>
<tr>
<td></td>
<td>5.6426 (30°C)</td>
<td>124</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.6305 (30°C)</td>
<td>107</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>6.2930 (30°C)</td>
<td>107</td>
<td>28.2 37.1 39.3</td>
<td>273-1023 293-873 302-940</td>
<td>Unspecified</td>
<td>107 52</td>
</tr>
<tr>
<td></td>
<td>6.2933 (30°C)</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.2936 (30°C)</td>
<td>124</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** This error is the total variation of values obtained by several authors.
† Probable error obtained from results of one experiment only.
higher expansion coefficients favour them for work above room temperature, is also listed. Various of the above conditions exclude most of the alkali halides even in this temperature region; in particular a large proportion are hygroscopic or deliquescent (LiCl, LiBr, LiI, NaBr, KF, KBr, RbI, CsF, CsCl, CsI).

For lithium fluoride and sodium chloride in particular the disagreement between different published results for the lattice constants is considerable (column 2 of table (5.3)). To see what this disagreement means in terms of accuracy of temperature measurement, let us write the difference between maximum and minimum values of unit cell length listed for a given substance at 30°C as Δa. Then we can calculate an equivalent temperature uncertainty ΔT:

$$\Delta T = \frac{\Delta a}{(a \alpha)}$$

where

- a is the unit cell length (mean value),
- $\alpha = \frac{1}{a} \frac{da}{dT}$, the linear expansion coefficient of the material and T is the temperature.

Using the values listed for $\alpha$ at 20°C we obtain the following values of ΔT:

- LiF : 92°C
- NaCl : 51°C
- KCl : 2.6°C.

Clearly the current quality of the lithium fluoride data makes it impossible to use this material as a standard, although its expansion coefficient, small lattice constant and very low X-ray fluorescent background are all in its favour.
The discrepancies in the published data may arise partly through inaccurate sample temperature measurement, but their magnitude suggests that they are largely due to impurities in the materials studied; the purity of the substances used is not even stated in many of the papers (see table (5.3)).

The data for the aluminium and silver is much more satisfactory in this regard. The error of $\pm 4 \times 10^{-5}$°C quoted for silver at 25°C corresponds to a temperature fluctuation of $\pm 0.5$°C; that for aluminium is $\pm 1.1$°C, but it should be noticed that this represents the spread of data for several independent published results, whereas the silver variation is for one experiment only. Unfortunately, both of these materials at present have the disadvantage as standards that the low temperature data is incomplete; in the region 180K to 293K interpolation must be resorted to. In this regard the aluminium data is slightly better in that the one temperature reading in reference 48 (refer table coincide with other high temperature data and indicates that the different samples used to obtain high and low temperature data respectively did have the same expansion properties. The lower atomic number of aluminium also gives it the advantage of a lower X-ray background.

A final problem that should be noted is that it is difficult to prepare pure metals as temperature standards in powder form. Straumanis and Woodard, for example, found that they could not obtain a powder from 99.999% pure aluminium because of its ductility, and were forced to resort to a commercial powder preparation of 99+% pure aluminium.
(Pierce Chemical Company, Rockford, Illinois). However, they obtained agreement with the X-ray data of Figgins et al.\textsuperscript{48} (99.99% pure aluminium wire sample) over the common temperature range of the two experiments (30 to 125K). Thus the 99+% pure material may be a suitable standard, but its expansion at higher temperatures would need to be checked to confirm this.

The potential accuracy of the internal standard method of temperature measurement depends on the sharpness of the diffraction lines. In general, for very sharp well resolved lines unit cell dimensions can be determined to an accuracy of 0.005%\textsuperscript{4,77}. Given a typical linear expansion coefficient, $\alpha = 20 \times 10^{-6} \, ^\circ \text{C}^{-1}$ say, this would give a temperature uncertainty of

$$\pm \left[ \frac{5 \times 10^{-5}}{20 \times 10^{-6}} \right] = \pm 2.5 ^\circ \text{C}$$
CHAPTER VI

X-RAY DATA PROCESSING

6.1 INTRODUCTION

With the camera operating we come to the matter of reading the films and interpreting the data thus obtained. Film reading can be a time-consuming and enervating business, and in view of the number of films that would eventually have to be processed it was considered desirable to automate the proceedings as much as possible. In this chapter the approach adopted to facilitate the film reading will be discussed and the computer processing of the data thus obtained will then be described.

6.2 FILM READING APPARATUS

6.2.1 Design of Apparatus

(1) Introduction: The Initial Microdensitometer

A Joyce-Loebl Mark IIIC double-beam recording microdensitometer was available. In this apparatus a light source is split into two equally intense beams; one beam travels through the film sample being examined and the other through an optical wedge. The wedge sits on a carriage which is moved by a servo-mechanism until the intensity of the beams from the film sample and the wedge are equal. A pen attached to the wedge carriage gives a plot of the film density, from which the positions and areas of X-ray lines can be obtained.
The sample film lies on a carriage capable of taking films up to 25 x 7.5 cm. Plots can be obtained which are 1, 2, 5, 10, 20 or 50 times larger than the original film.

(2) Modifications to Process X-ray Film

As it stands this system has a number of limitations for processing the X-ray powder pattern films. These are:

i) The films are almost 36 cm long. Each one must therefore be mounted on the film carriage and aligned twice to obtain all data.

ii) The graphical output means that further manual processing is required to obtain peak areas and positions.

iii) The plot of film density is produced on sheets of graph paper 25 cm long. A highly magnified plot thus requires a large number of sheets; some seventy were needed for a complete scan of a Debye-Scherrer film at 50:1 magnification (it is convenient to use this magnification when measuring the areas of peak profiles). Not only is this prodigal of graph paper, but it also means that since each sheet must be matched with its neighbours there will be a cumulative error in peak positions.

Modifications have been made to the system in order to overcome these disadvantages. The modified apparatus is shown in figure (6.1). The new equipment has been designed to be easily demountable when the microdensitometer is required for other use.

The new film carriage (3), long enough to hold the complete film (6), is driven via a screw (5) by a Philips stepper motor (1) (type 9904-112-06021). This drive can be
FIG. 6.1 MICRODENSITOMETER MODIFICATIONS

1. Stepper motor
2. Electronics to read data and drive motor
3. Film carriage
4. Demountable bar to guide film carriage
5. Film carriage tracking screw
6. Film
7. Film centring control
8. Microswitch to end tracking
disconnected in order to move the film carriage by hand when focusing and determining the range of film densities to be observed. A film density reading can be taken at the end of each step, determined by the gearing to be approximately $5 \times 10^{-4}$ inches long. This step size is small enough for any likely use, since the very best Debye-Scherrer camera work requires line positions to an accuracy of $0.01 \text{ mm (ca } 4 \times 10^{-4} \text{ inches) }^{136,\text{page179}}$.

Output is obtained from a slide wire potentiometer attached directly to the optical wedge carriage. This potentiometer is part of the original system. A voltage applied across it provides a signal which is fed via an analogue to digital converter to a Digital Equipment Corporation PDP-8 computer. This produces a punched paper tape output. We thus have the potential for fully automating output processing procedures such as peak position and area measurements, and the limitations listed above are all overcome.

Control of the reading procedure is chiefly via a PDP-8 program. This program is designed so that once it is loaded it can be started and stopped from the microdensitometer. This is necessary since the microdensitometer and computer are located in different rooms.

The control program was written by Dr R.E. Basher of the Canterbury University Physics Department and is listed in Appendix E. It operates as follows:

Once the program has been read into the PDP-8 it is started by closing a switch which connects the computer and the driving unit of the stepper motor. The computer tape punch
produces a leader of blank tape ten inches long.

There is provision in the program to change the number of steps the stepper motor takes before a reading is punched out, according to the resolution desired. During the four second interval while the blank tape leader is being produced the program notes the number of times a control switch is closed by the operator. If this is $N$ times, the value $N$ is punched on the tape and thereafter only every $N^{th}$ reading is punched out. The default value of $N$ is that used for the run immediately before, except for when the program has just been loaded, when $N = 1$.

With the leader punched a pulse is now sent from the PDP-8 to the stepper motor, driving the film carriage one step forward. After an appropriate interval to allow the motor to come to rest a return pulse is sent from the motor control to the computer. This causes the PDP-8 to register the potentiometer reading which is punched immediately if appropriate (according to the value of $N$), and the computer then recommences the cycle by instructing the stepper motor to take another step.

The system thus tracks across the film until a lever at the end of the film carriage engages a microswitch (8, fig. (6.1)). This switch breaks the reading cycle by cutting off the return signal from motor control to computer. After a minute without receiving a return pulse the program automatically returns to its starting point. With this arrangement another film can be read without the need to visit the computer room.

Normal scanning time for a complete film is of the order of forty minutes; this is no great inconvenience since, as
just noted, the run is ended automatically and hence no supervision is required.

The paper tape used is eight-track, with one line per reading. This gives a film density scale of 1 to 255, which should be generally adequate for X-ray photographs\textsuperscript{123}. Since the paper tape reader of the computer which will be used to process the data cannot read a blank line, provision is made to punch a value of 1 if the potentiometer voltage reading should be zero.

In the operation of this system one major inconvenience has been encountered. This has arisen from the nature of the drive of the optical wedge carriage. This drive is designed so that when, as with very high film densities, the carriage reaches the end of its track the drive remains turned on but the drive belt slips on its pulley. It is sometimes convenient to operate the microdensitometer in a density range such that this slipping may occur often enough to bring about rapid wear of the drive belt. Steps are being taken to modify the wedge carriage drive so that it turns off when slipping of the drive belt would normally occur.

6.2.2 Optimising Microdensitometer Settings

(1) Practical Limits on Accuracy

Since the microdensitometer observes a finite area of film at any one instant the output obtained will not be an exact reproduction of the film density profile. In the following sections the effect of the instrument settings on the accuracy of the data will be discussed.
The use of X-ray film to register results places an upper limit on the theoretically obtainable accuracy, owing to inhomogeneity of the film emulsion and the grain size. In view of these effects it is not usual to aim at better than 5% accuracy for microdensitometer measurements\textsuperscript{91,150}.

The microdensitometer light beam which passes through the film has a rectangular cross section, with the longer side of the rectangle at right angles to the direction of the film travel. In the following discussion the length of this longer side will be called the beam height; the length of the shorter side will be referred to as the beam width. We define the following variables:

\[ h = \frac{\text{beam height}}{2} \]
\[ a = \text{beam width}. \]

There is a limited freedom to alter the values of \( a \) and \( h \) by adjusting appropriate apertures on the microdensitometer. The larger the cross-sectional area of the beam we choose, the greater the range of film densities that can be observed accurately (this is controlled by the sensitivity of the light detector); on the other hand, smaller dimensions within the limits allowed by film granularity provide more accurate peak traces. For X-ray film the relatively large grain size means that it is not usually worthwhile examining a film area of less than 0.01 square millimetres (Ilford Industrial G film) if reproducibility of readings is to be retained\textsuperscript{150}. With this limitation in mind we shall proceed to consider the respective effects of the beam height and width.
(2) **Effect of Instrument Settings**

(a) **Microdensitometer Beam Height**

The geometry of the Debye-Scherrer camera, with the cone of diffracted X-rays for any given Bragg reflection intersecting a cylindrically shaped film, means that a diffraction line as it appears on the film is curved. It follows that because the microdensitometer light beam which is used to scan the film has a cross-section of finite height (2h) the profile recorded for a diffraction peak represents an average over a finite portion of this curved line. Consequently the centre of gravity of this profile will be shifted in the direction of the centre of curvature of the diffraction line on the X-ray film; the size of this shift will be the greater the more sharply curved the recorded line (i.e. for Bragg diffraction angle $\theta$ in the region of $0^\circ$ or $90^\circ$) and the larger the value of h. Any misalignment of the film on its carriage such that the microdensitometer beam does not track precisely along the central (long) axis of the X-ray pattern will also increase this diffraction peak shift.

Another phenomenon which may shift the recorded diffraction profile is the so-called "umbrella effect". This is discussed in detail by Eastabrook\(^{44}\). It arises as a result of the facts that the X-ray beam is generally divergent and that the length of the X-ray sample irradiated is finite. The total intensity of diffracted X-rays falling at any point on the X-ray film is thus a sum of intensities diffracted from different parts of the X-ray sample with slightly different Bragg diffraction angles. The umbrella effect is particularly noticeable for small values of $\theta$, and shows itself on the X-ray film as a
broadening of the diffraction lines with increasing distance from the central (long) axis of the X-ray pattern. Its effect on the line profiles should therefore be more evident the larger the value of $h$.

A calculation of X-ray peak shifts due to the above effects would require detailed information on the cross-section and divergence of the X-ray beam. This is not readily available, and it is more feasible to obtain these shifts by measurements from a typical X-ray film.

Powder photographs were taken of $(\text{NH}_4)_3\text{GaF}_6$ with the 114.6 mm diameter Debye-Scherrer camera using copper $K_\alpha$ radiation and with the sample contained in a 0.3 mm diameter Lindemann glass tube. Both the narrow and broad X-ray beam collimators (beam diameters 0.5 and 1.0 mm respectively) were used in order to see any trend arising from the umbrella effect. Microdensitometer traces of the (111) line were then recorded. The low Bragg angle ($\theta = 8.5^\circ$) means that any line shifts observed will be the largest seen for this compound.

During these measurements the microdensitometer beam width was fixed ($a = 0.03$ mm) and the results of varying the beam height ($2h$) and the distance ($\Delta$) between the (long) axis of symmetry of the X-ray pattern and the axis along which the beam actually tracked were noted.

For $\Delta$ small and fixed it was found that there was no discernible shift in the peak profile as the microdensitometer beam height, $2h$, was increased from 0.1 mm up to its maximum value of approximately 0.9 mm. However, the profiles obtained for the smaller values of $h$ are very irregular (the result of the film grain). Consequently the zero shift relative to the
maximum h curve has a maximum uncertainty of ±0.04 mm for 2h = 0.01 mm; this drops to ±0.1 mm for 2h = 0.5 mm.

To investigate the results of varying Δ, peak traces were made with the microdensitometer beam height fixed at 0.9 mm. The shifts measured were those of the mid-points of the diffraction profiles measured at half peak maximum. Here the variations due to the film grain presented considerable difficulty to defining accurately both the edges of the peak profile and its actual height, and the results must be regarded as only tentative. Plots of peak shift versus Δ indicated that a peak shift of 0.02 mm (approximately 5% of the f.w.h.m. of the peak for both fine and broad collimators) corresponded to values of Δ of the order of 0.4 mm for the fine collimator and 0.8 mm for the broad one. The initially slower shift of peak centre with increasing Δ for the latter case is evidently the result of the umbrella effect.

As Δ was altered random variations of the order of ±2½% in the f.w.h.m. values of the peaks were observed. These fluctuations were sufficient to obscure any trend which might exist in the peak widths up to Δ = 2 mm. The variations in peak height were of the order of ±2%. No systematic change in peak heights was observed for the fine collimator photograph for Δ in the range of ±2 mm. For the broad collimator, however, there is a reduction in peak height which becomes evident at Δ ~ 0.8 mm and increases to approximately 7% for Δ = 2 mm.

In order to obtain precise measurements with good quality powder patterns it will be necessary to define the variation of peak shift with Δ more accurately, using a fine grained film and possibly a computer program (see section 6.3.3) to fit a
profile to the diffraction curve. The upper limit for accuracy attainable with a 114.6 mm diameter powder camera is discussed by Klug and Alexander. With good quality X-ray photographs (well-defined narrow lines) the line positions must be measured to ±0.02 mm.

Finally, for the purposes of aligning the X-ray film and the microdensitometer it should be noted that the long axis of symmetry of the X-ray pattern will not in general correspond to the centre of the film. This is because the X-ray collimator is not necessarily central in the camera, and X-ray film widths differ slightly from film to film due to tolerance in manufacture.

(b) Microdensitometer Beam Width

There is an error in peak heights called the 'Wooster effect' which arises from the finite width of the microdensitometer beam. Because of this finite width the microdensitometer is measuring an average over the cross-section of the beam. This average, moreover, is not of the film density (which would be preferred, since the exposure-density relationship of X-ray film is fairly linear for low enough exposures) but of the transmitted light.

To discuss this quantitatively we let $I$ be the intensity of transmitted light at a point on the film where the density is $D$. Then

$$D = \log_{10}(I_0/I) \quad (6.2)$$

where $I_0$ is the intensity of the light incident on the film. It follows from this equation that if the light beam is of width $a$, then the average intensity $\bar{I}(\theta)$ observed at a position
on the film will be

\[ \bar{I}(\theta) = \frac{1}{a} \int_{-\frac{a}{2}}^{\theta + \frac{a}{2}} I(\phi) d\phi \]

\[ = \left[ \frac{I_0}{a} \right]^{\theta + \frac{a}{2}}_{\theta - \frac{a}{2}} 10^{-D(\phi)} d\phi \]  \hspace{1cm} (6.3)

This gives a deduced density

\[ \bar{D}(\theta) = \log \left( \frac{I_0}{\bar{I}(\theta)} \right) \]

\[ = \log \left[ \frac{a}{\int_{-\frac{a}{2}}^{\theta + \frac{a}{2}} 10^{-D(\phi)} d\phi} \right] \]  \hspace{1cm} (6.4)

which will usually be lower than the true density \( D(\theta) \).

Wooster\(^{150}\) has discussed the magnitude of this effect for different widths of the microdensitometer beam with triangular and rectangular line profiles of various widths and densities. We can extend the discussion to a general profile by expanding equation (6.4) in a Taylor series in \( a \). The first few terms of the series are:

\[ \bar{D}(\theta, a) = D(\theta) - \frac{a^2}{24} \left( L \left( \frac{dD}{d\theta} \right)^2 - \frac{d^2 D}{d\theta^2} \right) \]

\[ + \frac{a^4}{5760} \left( 2L^3 \left( \frac{dD}{d\theta} \right)^4 + 8L^2 \left( \frac{d^2 D}{d\theta^2} \right) \left( \frac{dD}{d\theta} \right)^2 - 4L \frac{d^2 D}{d\theta^2} \right) \]

\[ - 12L \left( \frac{d^3 D}{d\theta^3} \frac{dD}{d\theta} \right) + 3 \left( \frac{d^4 D}{d\theta^4} \right) \]  \hspace{1cm} (6.5)
where \( L = \ln 10 \).

Now the peak shapes for a Debye-Scherrer camera tend to a Gaussian profile if line broadening is primarily due to internal strain, or to a Cauchy profile if the broadening effect of small particle size predominates \(^{136}, p^{789}\). The respective profiles have the forms

\[
D(\theta) = D_G \exp\left(-\frac{(\theta - \bar{\theta})^2}{2\sigma^2}\right) \quad (6.6)
\]

and

\[
D(\theta) = \frac{D_C}{1 + \kappa^2 (\theta - \bar{\theta})^2} \quad (6.7)
\]

where \( D_G, D_C, \bar{\theta}, \sigma \) and \( \kappa \) are constants. As an example we consider the above Gaussian curve. It can be substituted directly into equation (6.5) to give the modified profile. We are, however, primarily interested in peak areas. Consequently we quote below the ratio of modified to original peak area, obtained by integration on equation (6.5).

\[
\frac{\int_{-\infty}^{\infty} D(\theta, a) d\theta}{\int_{-\infty}^{\infty} D(\theta) d\theta} = 1 - \frac{\sqrt{2}}{96} \frac{L D_G (\frac{a}{\sigma})^2}{1920} + \frac{L^2 D_G^2}{16} (\frac{a}{\sigma})^4
\]

\[
= 1 + D_G \{1.69601 \times 10^{-3} (\frac{a}{\sigma})^4 - 3.39203 \times 10^{-2} (\frac{a}{\sigma})^2 \}
\]

\[+ 3.97398 \times 10^{-4} D_G^3 (\frac{a}{\sigma})^4 \quad (6.8)\]

As is perhaps intuitively evident, the error increases with peak height (density) and decreases with increasing peak width. In using the microdensitometer the aim will be to control peak density (by X-ray exposure time) and microdensitometer beam width so that the error in peak area will be below...
an acceptable limit for all observed peaks. Since, as noted before, the film properties make it practicable to go for no better than 5% accuracy, a 1% error due to the Wooster effect is acceptable.

To see what this entailed in practice a trace of one of the narrower peaks was taken from the best quality cryolite film thus far obtained (a beam width narrow enough for the narrowest peak will be adequate for wider ones). For a narrow beam \( a = 0.02 \text{ mm} \) the peak was found to have a \( D_G \) value of approximately 0.7, and to be closely Gaussian (rather than a Cauchy profile) with \( \sigma = 0.151 \text{ mm} \) (equivalent to 0.0756 degrees).

Taking this value of \( \sigma \) and using equation (6.8), we obtain the following set of percentage errors in peak area for different densities:

<table>
<thead>
<tr>
<th>Slit width, ( a )(mm)</th>
<th>0.02</th>
<th>0.04</th>
<th>0.05</th>
<th>0.06</th>
<th>0.08</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{a}{\sigma} )</td>
<td>0.1325</td>
<td>0.2649</td>
<td>0.3311</td>
<td>0.3974</td>
<td>0.5298</td>
</tr>
<tr>
<td>( D_G )</td>
<td>0.03</td>
<td>0.12</td>
<td>0.18</td>
<td>0.27</td>
<td>0.47</td>
</tr>
<tr>
<td>0.5</td>
<td>0.06</td>
<td>0.24</td>
<td>0.37</td>
<td>0.53</td>
<td>0.94</td>
</tr>
<tr>
<td>1.0</td>
<td>0.09</td>
<td>0.36</td>
<td>0.55</td>
<td>0.79</td>
<td>1.4</td>
</tr>
<tr>
<td>1.5</td>
<td>0.12</td>
<td>0.47</td>
<td>0.74</td>
<td>1.1</td>
<td>1.9</td>
</tr>
<tr>
<td>2.0</td>
<td>0.15</td>
<td>0.59</td>
<td>0.92</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1 Variation of peak area error with microdensitometer beam width.

Morimoto and Uyeda have investigated the density versus exposure curves for various brands of X-ray film. Their data indicates that departure from a linear exposure-density relation-
ship makes it difficult to carry out measurements on lines where the density becomes greater than 2 (Morimoto and Uyeda standardised densities by defining appropriate developing conditions for each brand of film. These conditions are listed in their paper). With this restriction, table (6.1) indicates that a beam width of up to 0.06 mm will generally be satisfactory. This, incidentally, gives a total beam area of \((0.8 \times 0.06) = 0.048\) square millimeters, which is well above the 0.01 square millimetres needed to obtain reproducible results with Ilford Industrial G film. It follows therefore that such high speed films with their attendant large granularity will have sufficient resolution for our purposes.

(3) **Calibration of Instrument Settings**

The microdensitometer has a micrometer control for setting the beam width via an adjustable slit, but there is no means of indicating the beam height. Moreover, the micrometer has been found to have a zero which shifts when the slit is completely closed, and it is therefore more straightforward to use a microscope stage micrometer placed in the plane of the film sample to fix both the height and width of the beam. This stage micrometer possesses a transparent scale with divisions of 0.01 mm. There is a screen in the microdensitometer on which a magnified image of the beam cross-section and scale are projected, and the latter can be easily read on this by using a jeweller's coupe.
6.3 PROCESSING OF FILM DATA

6.3.1 Introduction

A deal of processing is required before the paper tape output data can be used to calculate unit cell parameters and perform a structural analysis. The non-linearity of the film density versus exposure curve must be allowed for, the peaks identified, and their positions and areas calculated. In the following section the approaches adopted and the appropriate programming will be discussed. A program to obtain unit cell parameters from the resultant data will then be described. Structural analysis itself has been discussed already in Section 4.7.3.

6.3.2 Film Linearity

Morimoto and Uyeda\textsuperscript{91} have obtained exposure (E) versus density (D) data up to D = 2.0 for a number of commercially available X-ray films (the densities are for defined developing conditions listed for each film type by the authors). The dependence of E on D can only be taken as linear for lower density values. In particular for the commonly used Ilford Industrial G and Kodak No-Screen films a parabolic relationship of the form

\[ E = aD + bD^2 \]  

is necessary to describe the data up to D = 2.0 to within 1% accuracy\textsuperscript{87} (i.e. the accuracy within which Morimoto and Uyeda quote their observed densities); the constants a and b depend on the particular film. Thus we may choose to measure the X-ray peak areas only for D in the linear region (typically below D = 1.0) or, alternatively, seek to measure the constants...
a and b. The simplest approach to the latter method would be to provide a calibration strip on the film.\textsuperscript{136,p277} The present camera provides an unexposed strip down one side of the X-ray film onto which a calibrated strip could be photographed.

As we are restricted in the maximum density it is possible to observe on a film, it now becomes difficult to observe the weaker X-ray peaks. This difficulty can be overcome by mounting several films concentrically in the Debye-Scherrer camera. The exposure time is then made long enough to observe the fainter peaks on the innermost film. The inner films act as absorbers of the scattered X-rays so that on the outer films the more intense peaks are of acceptable density. Data for film speeds and X-ray absorption properties\textsuperscript{2,91,137} can be used to obtain a suitable combination of films to cover the desired range of X-ray intensities. The Philips 114.6 mm diameter camera as it stood proved capable of taking up to five concentric films at once. Of course the inner films need to be cut slightly shorter than the outer ones and the scattering angle to length scales will differ.

6.3.3 Peak Identification and Measurement

As far as is possible we want the necessary procedures to be carried out by computer. The principal difficulty here is the automatic location of the peaks. For low density peaks in particular, criteria need to be established to identify them above the background noise. Once the peaks are found their areas and centres of density can then be calculated directly or, alternatively, by integration of the equation of a fitted profile curve. The latter approach is preferable since it
enables us to distinguish overlapping peaks such as are especially likely to be encountered just below a phase transition when the unit cell distortion may be relatively small. There are a number of papers in the literature giving various approaches to this problem of estimating true background and peak areas and positions\textsuperscript{24,79,82,138}.

As an initial approach a program was written to read the data and to estimate the average value of each consecutive set of, typically, ten points (the number of points averaged over could be varied). These averages were then printed out as a compressed plot of film density versus position. From this graph peaks could then be located manually and their approximate positions read into the computer as starting points for further refinement. The amount of manual labour involved was still considerable however, and constituted a significant bottleneck in data processing.

It has therefore been decided to adapt the program used by Sonneveld and Visser\textsuperscript{123} for Guinier powder photographs. Their program calculates a curve for the background and also produces an estimate of the noise. This noise level can be used as a criterion for accepting or rejecting possible X-ray peaks. These peaks are then fixed to a Gaussian (or other) profile, and the corresponding calculated areas and line positions printed out. For Debye-Scherrer films the necessary presence of pairs of lines will provide an extra check on the line identification procedure.

Sonneveld and Visser's programme also has provision for comparing films, as for example, those of the same substance but with different exposure times. This could be of value for the multiple film procedure described in the previous section.
6.3.4 Refining Unit Cell Parameters

The actual assignment of a space group from an X-ray powder pattern is a complex matter for lower symmetry structures, requiring a variety of approaches not susceptible to computer analysis. The methods are covered in Azároff and Buerger's book. Once the space group and approximate cell parameters have been established, however, they can be used to predict the positions of Bragg reflections and so refine the parameters by a suitable program. Such accurate parameters are required for phase change investigations; the smaller the change in parameter with temperature we can measure the better.

The peak positions predicted by the Bragg relationship and those actually observed with a Debye-Scherrer camera differ in a systematic way. A discussion of the sources of this systematic error is given by Taylor et al. It turns out that if the sample is centred carefully, the error, \( \Delta d = d - d_0 \), in the true lattice spacing \( d_0 \) is given closely by

\[
\frac{\Delta d}{d_0} = -\frac{k}{2} \cos^2 \theta \left( \frac{1}{\sin \theta} + \frac{1}{\theta} \right)
\]  

(6.10)

over a wide range of observed Bragg diffraction angles \( \theta \) (\( \theta \) in radians).

The parameter \( d \) is given by the usual Bragg relationship

\[
d = \frac{\lambda}{2 \sin \theta}
\]  

(6.11)

with \( \lambda \) the X-ray wavelength. The constant \( k \) depends on the sample used, on its thickness and density, and on the X-ray radiation.
For a cubic compound equation (6.10) provides a straightforward method of obtaining an accurate lattice constant. Using equation (6.11) and the Miller indices appropriate to each line an apparent lattice constant, a, is calculated from each observed value of $\theta$. A plot of $a$ against the function
$$
\frac{\cos^2 \theta}{2} \left( \frac{1}{\sin \theta} + \frac{1}{\theta} \right)
$$
should then give a straight line which cuts the $a$ axis (where $\theta = 90^\circ$) at the true value of the lattice constant.

However, we are primarily interested in non-cubic structures such as occur below the cryolite phase transition temperatures. Here the use of equation (6.10) is more complex. Various approaches have been developed for numerical calculation of lattice parameters by fitting to approximations of this equation$^{32,60}$. Normally these will not give the best fit. The commonly used Cohen procedure$^{32}$, for example, tends to overestimate cell dimensions slightly$^{72}$ and has the additional disadvantage that it is impossible to make provision, by weighting, for the higher accuracy of line positions often obtained for high values of $\theta$.

With computing facilities generally available, however, there is no need to use these approximate methods, and a computer program is being modified to make full use of equation (6.10). The starting point was the program POWDER, obtained from the University of Canterbury Chemistry Department (the original source is unknown). This program in its original form refines diffractometer data, assuming no systematic error. It is applicable to any space group. The best estimates of lattice parameters and their standard deviations are printed out, together with the predicted and observed X-ray line positions.
The refinement method this program uses is standard, as described by Deming. Refinement is initially carried out on low angle lines only. As more accurate parameters are obtained the calculation is repeated using progressively more of the higher angle lines.

The method requires initial test values of the unit cell parameters to be entered. During the first cycle of POWDER these are used to obtain theoretical observed values of the Bragg diffraction angle $\theta$; in each later cycle the refined parameters obtained from the previous cycle are used for this calculation. In order to modify the program to allow for the systematic error of the Debye-Scherrer method these calculated Bragg diffraction angles must be altered by an amount determined by equation (6.10). This modification has been introduced into the program as follows:

For given test values of the lattice parameters and given Miller indices a true interplanar spacing $d_0$ is calculated. An "ideal" Bragg diffraction angle $\theta_0$ is then defined via Bragg's law as

$$\sin \theta_0 = \frac{\lambda}{2d_0} \quad \text{(6.12)}$$

whereas the expected observed angle $\theta$ is given by

$$\sin \theta = \frac{\lambda}{2d}. \quad \text{(6.13)}$$

Here the notation is that of equations (6.10) and (6.11). Introducing equations (6.12) and (6.13) into equation (6.10) gives

$$\sin \theta_0 = \sin \theta \left[ 1 - \frac{k}{2} \cos^2 \theta \left( \frac{1}{\sin \theta} + \frac{1}{\theta} \right) \right]. \quad \text{(6.14)}$$
Given a value for \( k \), this equation can now be solved for \( \theta \), since \( \theta_0 \) depends only on the unit cell parameters and Miller indices. The solution is achieved by iteration, starting from a trial value \( \theta' \) given by

\[
\sin \theta' = \sin \theta_0 \left[ 1 - \frac{k}{2} \cos^2 \theta_0 \left( \frac{1}{\sin \theta_0} + \frac{1}{\theta_0} \right) \right]
\]  \hspace{1cm} (6.15)

The value of \( k \) effectively adopts the function in the program of an additional lattice parameter; a trial value is read along with the other trial parameters at the start of the program, and all are refined together.

The refinement method of POWDER allows the contributions of different lines to be weighted according to their accuracy. In this regard it is worthwhile noting that an approach to calculating the actual standard deviations in such line positions for the purpose of weighting has been given by Langford and Wilson\(^\text{73} \). Their method takes into account the error arising from non-uniform shrinkage of the film during development.
CHAPTER VII

PRELIMINARY X-RAY RESULTS AND SUGGESTIONS FOR FURTHER WORK

7.1 INTRODUCTION

As noted in Chapter IV the ammonium cryolites promise to be good subjects for X-ray powder investigation, and preliminary photographs have been taken of some of their low temperature phases. The results of these are summarised below. Following this, we discuss the ammonium cryolites in general, using the data obtained and published data to assess the best direction for further investigations.

7.2 PRELIMINARY X-RAY DATA

7.2.1 Ammonium Hexafluoroaluminate, \((\text{NH}_4)_3\text{AlF}_6\)

The low X-ray background obtained in photographing this material makes it a good subject for X-ray powder photography. Furthermore, a good sample with well defined lines at high Bragg angles has been obtained. These high angle lines are broadened by the grinding which usually accompanies preparation of a Debye-Scherrer sample. Thus to obtain maximum information photographs of both unground and ground samples are required, the first for accurate determination of unit cell dimensions and the second to obtain accurate intensity readings for structural refinement.

A photograph of a mixture of \((\text{NH}_4)_3\text{AlF}_6\) and lithium fluoride was taken. While the fluoride turned out to be of no help in obtaining the sample temperature, the average of the
camera thermocouple readings gives an approximate value of
\(-85^\circ\text{C}\) (the phase transition point for \((\text{NH}_4)_3\text{AlF}_6\) being
approximately \(-49^\circ\text{C}\) \(^{117}\)).

The diffraction angles and lattice plane separations
obtained are listed in table (7.1). There were some regions
of increased density on the film which could have been due to
a number of overlapping lines, but only lines which it was
considered were certainly present are listed. A few of the
most intense lines could be doubled, but a shorter exposure at
the same temperature would be required to see if this were so.

Steward and Rooksby\(^{127}\) did not list their X-ray data for
this compound, and went no further than describing the low
temperature symmetry as 'lower than tetragonal'. In the
present work attempts were made using Bjurström charts\(^4\) to
match the data of table (7.1) to tetragonal and hexagonal
systems, and a match to the orthorhombic system by the standard
method of searching for systematics in the differences of the
\(\sin^2\theta\) values (\(\theta\) being the Bragg angle) for different pairs of
lines was also tried. All were unsuccessful.

There are numerical procedures for matching powder
diffraction data to still less symmetric systems\(^4\). The com-
plexities of these are such that it would first be desirable
to obtain further photographs, preferably without the lithium
fluoride standard present in case it has obscured any lines,
before proceeding. A low temperature attachment for a Buerger
precession camera has become available in the university
chemistry department, and since we have small crystals of
\((\text{NH}_4)_3\text{AlF}_6\) this could provide complementary information.
Table 7.1. Low Temperature X-ray Pattern for (NH₄)₃AlF₆

Radiation: Copper Kα, Nickel filter.

<table>
<thead>
<tr>
<th>Bragg Angle, θ (degrees)</th>
<th>Lattice Spacing, d (Å)</th>
<th>Bragg Angle, θ (degrees)</th>
<th>Lattice Spacing, d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.62</td>
<td>5.145</td>
<td>29.07</td>
<td>1.587</td>
</tr>
<tr>
<td>9.94</td>
<td>4.466</td>
<td>29.26</td>
<td>1.575</td>
</tr>
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<td>13.07</td>
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<td>29.38</td>
<td>1.571</td>
</tr>
<tr>
<td>14.15</td>
<td>3.153</td>
<td>29.71</td>
<td>1.554</td>
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<td>1.523</td>
</tr>
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<td>14.97</td>
<td>2.985</td>
<td>30.77</td>
<td>1.507</td>
</tr>
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<td>2.706</td>
<td>31.06</td>
<td>1.494</td>
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<td>17.39</td>
<td>2.579</td>
<td>32.58</td>
<td>1.432</td>
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<td>18.05</td>
<td>2.489</td>
<td>33.30</td>
<td>1.404</td>
</tr>
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<td>19.94</td>
<td>2.261</td>
<td>33.50</td>
<td>1.397</td>
</tr>
<tr>
<td>20.37</td>
<td>2.215</td>
<td>34.45</td>
<td>1.363</td>
</tr>
<tr>
<td>22.16</td>
<td>2.044</td>
<td>35.41</td>
<td>1.331</td>
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<td>22.99</td>
<td>1.974</td>
<td>36.73</td>
<td>1.289</td>
</tr>
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<td>1.934</td>
<td>37.87</td>
<td>1.256</td>
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<tr>
<td>24.72</td>
<td>1.843</td>
<td>38.57</td>
<td>1.236</td>
</tr>
<tr>
<td>25.10</td>
<td>1.818</td>
<td>40.24</td>
<td>1.193</td>
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<tr>
<td>25.43</td>
<td>1.795</td>
<td>41.34</td>
<td>1.167</td>
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<td>26.30</td>
<td>1.740</td>
<td>48.59</td>
<td>1.028</td>
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<td>26.84</td>
<td>1.707</td>
<td>50.22</td>
<td>1.003</td>
</tr>
<tr>
<td>27.61</td>
<td>1.663</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.2.2 Ammonium Hexafluorochromate, (NH$_4$)$_3$CrF$_6$

Photographs of both phases were taken with copper K$_\alpha$ radiation. The background due to fluorescence of the chromium was found to be relatively intense, and for this reason it is doubtful that acceptable diffraction line intensities can be obtained without going well into the non-linear response region of the X-ray film. The diffraction lines themselves were not sufficiently sharp for there to be any back reflections visible for the low temperature phase; however, the shadow on the film of the low temperature camera fittings enabled the 90° Bragg angle position to be determined.

The room temperature structure is the standard face-centred cubic one (figure (1.1)). The low temperature pattern was obtained at approximately -105°C, and the positions of the lines are listed in table (7.2). A microdensitometer trace of the pattern up to a Bragg angle of approximately 37° is shown in figure (7.1); from this it can be seen that line profiles frequently overlap, and the need for a program to unfold these profiles, as described earlier, is evident.

Attempts were made using Bjurstrøm charts to match the observed pattern to tetragonal and hexagonal systems. Neither attempt met with success, but the tetragonal case is sufficiently interesting to merit further discussion.

A tentative fit to the tetragonal system was made by calculating unit cell parameters from the observed lines at Bragg angles of 19.62 and 20.04 degrees; these lines are clearly defined in the photograph. The predicted lines for the tetragonal system are listed alongside the observed ones in table (7.2), and are also portrayed superimposed over the microdensitometer trace in fig. (7.1). Lattice constants
Notes:

1) This is a very approximate position which had to be estimated from the microdensitometer trace rather than by direct measurement.

2) This line may be obscured by adjacent lines.

3) Any discrepancy here between observed and predicted lines could be attributed to the closeness of this line to the next one, making estimation of the centre difficult.

4) The identification of the theoretical and observed line with one another is questionable, in view of the disagreement in diffraction angles. This is the closest fit, however.

5) The dimensions of the tetragonal lattice were assigned to fit these two lines exactly.

6) The microdensitometer profile (see fig. (7.1)) shows a broad band in this region. This band could be an unresolved combination of these lines.

7) This line is possibly present but obscured by the profiles at the lines on each side of it (see microdensitometer profile).

8) Appears as a single broad line.

9) The microdensitometer trace indicates a broad band in the region of these lines and the ones between them, which could be interpreted as a superposition of all of them.
Table 7.2 Low Temperature X-ray Pattern for \((\text{NH}_4)_3\text{CrF}_6\) 
Radiation: Copper K\(\alpha\), Nickel filter

<table>
<thead>
<tr>
<th>Bragg Angle (\theta) (degrees)</th>
<th>Lattice Spacing (d(\AA))</th>
<th>Predicted Lines for tetragonal lattice (a=6.436\AA, c=9.065\AA)</th>
<th>Tetragonal Miller indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.45</td>
<td>5.25</td>
<td>(8.48) (5.230) (1) (0) (1)</td>
<td></td>
</tr>
<tr>
<td>9.79</td>
<td>4.53</td>
<td>(9.67) (4.591) (0) (0) (2)</td>
<td></td>
</tr>
<tr>
<td>10.38</td>
<td>4.28</td>
<td>(9.87) (4.500) (1) (1) (0)</td>
<td></td>
</tr>
<tr>
<td>13.98</td>
<td>3.191</td>
<td>(13.88) (3.214) (1) (1) (2)</td>
<td></td>
</tr>
<tr>
<td>14.50</td>
<td>3.080</td>
<td>(14.02) (3.182) (2) (0) (0)</td>
<td></td>
</tr>
<tr>
<td>16.20</td>
<td>2.764</td>
<td>(15.72) (2.846) (2) (1) (0)</td>
<td></td>
</tr>
<tr>
<td>16.47</td>
<td>2.720</td>
<td>(16.23) (2.758) (1) (0) (3)</td>
<td></td>
</tr>
<tr>
<td>16.88</td>
<td>2.385</td>
<td>(16.48) (2.718) (2) (1) (1)</td>
<td></td>
</tr>
<tr>
<td>17.17</td>
<td>2.611</td>
<td>(17.15) (2.615) (2) (0) (2)</td>
<td></td>
</tr>
<tr>
<td>18.04</td>
<td>2.250</td>
<td>(18.59) (2.419) (2) (1) (2)</td>
<td></td>
</tr>
<tr>
<td>19.62</td>
<td>2.206</td>
<td>(19.62) (2.296) (0) (0) (4)</td>
<td></td>
</tr>
<tr>
<td>20.04</td>
<td>2.250</td>
<td>(20.04) (2.250) (2) (2) (0)</td>
<td></td>
</tr>
<tr>
<td>21.72</td>
<td>2.083</td>
<td>(21.71) (2.084) (2) (1) (3)</td>
<td></td>
</tr>
<tr>
<td>22.48</td>
<td>2.017</td>
<td>(22.32) (2.045) (1) (1) (4)</td>
<td></td>
</tr>
<tr>
<td>24.47</td>
<td>1.861</td>
<td>(24.46) (1.862) (2) (0) (4)</td>
<td></td>
</tr>
<tr>
<td>24.91</td>
<td>1.837</td>
<td>(24.73) (1.843) (3) (1) (2)</td>
<td></td>
</tr>
<tr>
<td>25.93</td>
<td>1.763</td>
<td>(25.55) (1.788) (2) (1) (4)</td>
<td></td>
</tr>
<tr>
<td>26.39</td>
<td>1.735</td>
<td>(26.41) (1.733) (3) (2) (1)</td>
<td></td>
</tr>
<tr>
<td>28.79</td>
<td>1.601</td>
<td>(28.67) (1.607) (2) (2) (4)</td>
<td></td>
</tr>
<tr>
<td>30.18</td>
<td>1.533</td>
<td>(28.99) (1.591) (4) (0) (0)</td>
<td></td>
</tr>
<tr>
<td>32.75</td>
<td>1.425</td>
<td>(32.73) (1.426) (3) (3) (2)</td>
<td></td>
</tr>
<tr>
<td>33.95</td>
<td>1.381</td>
<td>(32.80) (1.423) (4) (2) (0)</td>
<td></td>
</tr>
<tr>
<td>36.13</td>
<td>1.307</td>
<td>(33.73) (1.388) (3) (0) (5)</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 7.1 MICRODENSITOMETER TRACE OF X-RAY POWDER PATTERN OF (NH₄)₃CrF₆ (LOW TEMPERATURE PHASE) COMPARED TO TETRAGONAL UNIT CELL PATTERN. ARROWS INDICATE UNEXPLAINED PEAKS.
a = 6.436Å
and
c = 9.065Å
were obtained; these would be consistent with the room
temperature cubic unit cell, which has a published lattice
constant of 9.01Å \(^14\), and with the hypothesis that the
transition is the cubic to tetragonal type \((O_\text{h}^5 \text{ to } D_{4h}^6)\)
discussed in Chapter III.

A detailed comparison of the calculated tetragonal
pattern with the observed lines is made in the notes accompany­
ing table (7.1). The four experimental lines that appear to
have no tetragonal equivalent are all faint, and because of the
noise level associated with the high background from the
fluorescent radiation their positions are hard to measure
accurately.

In view of the generally good fit to a tetragonal pattern
for the stronger lines various checks were carried out to see
if these unexplained lines could be attributed to other sources.
As mentioned in the notes for table (7.1) it is conceivable,
though unlikely, that one of the lines corresponds to the (212)
line of the tetragonal system, with the relatively high back­
ground noise level perhaps accounting for the discrepancy in
position. Calculations using wavelengths associated with
absorption edges, with copper K\(\beta\) radiation, and with tungsten L
radiation (which X-ray tubes can generate as they age) offered
no possible alternative explanation for any of the lines.
Impurities in the sample are an unlikely source, since none of
the four diffraction lines was discerned in a room temperature
photograph. A check was also made on the possibility that a
proportion of the sample was still cubic, but this was also fruitless.

Taking these four lines as genuine then, we can still hypothesise that the low temperature structure is basically tetragonal, but with a slight distortion of as yet uncertain form. Photographs at other temperatures are needed at this point to see how line intensities and positions vary.

7.2.3 Ammonium Hexafluoroferrate, (NH₄)₃FeF₆

The presence of iron in this compound makes it necessary to use cobalt $K_α$ radiation to avoid an unacceptably high background. The cobalt tube has a lower power rating than the copper (280 versus 800W) and cobalt radiation is more readily absorbed. Considerably longer exposure times are therefore necessary.

A photograph of the low temperature phase was taken at a temperature of approximately -65°C. The positions of the lines are listed in table (7.3). For comparison the pattern for a tetragonal compound with unit cell dimensions

\[
a = 6.392 \ \AA \\
c = 9.286 \ \AA
\]

is also listed; the lattice constants were chosen to give an exact match at the (220) and (004) lines.

The appearance of the photograph is substantially the same as that Steward and Rooksby\textsuperscript{127} obtained at liquid air temperature (they give $a = 6.39 \ \AA$ and $c = 9.30 \ \AA$), with the exception of the two lines at 9.42 and 22.21 degrees. The cause of these two lines is uncertain, but as they were also present superimposed on the standard cubic pattern at room temperature
Table 7.3 Low Temperature X-ray Pattern for $\text{NH}_4_3\text{FeF}_6$

Radiation: Cobalt $K_{\alpha}$, Iron filter.

<table>
<thead>
<tr>
<th>Bragg Angle $\theta$ (degrees)</th>
<th>Lattice Spacing $d(\AA)$</th>
<th>Predicted Lines for tetragonal lattice $a=6.392\AA, c=9.286\AA$</th>
<th>Tetragonal Miller indices $h k l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) 9.42</td>
<td>5.47</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9.88</td>
<td>5.24</td>
<td>9.79 5.27</td>
<td>1 0 1</td>
</tr>
<tr>
<td>11.18</td>
<td>4.616</td>
<td>11.12 4.643</td>
<td>0 0 2</td>
</tr>
<tr>
<td>16.05</td>
<td>3.237</td>
<td>16.04 3.239</td>
<td>1 1 2</td>
</tr>
<tr>
<td>2) 16.42</td>
<td>3.167</td>
<td>16.27 3.196</td>
<td>2 0 0</td>
</tr>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>18.74</td>
<td>2.786</td>
<td>18.74 2.786</td>
<td>1 0 3</td>
</tr>
<tr>
<td>19.31</td>
<td>2.707</td>
<td>19.13 2.732</td>
<td>2 1 1</td>
</tr>
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<td>19.93</td>
<td>2.626</td>
<td>19.89 2.633</td>
<td>2 0 2</td>
</tr>
<tr>
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<td>2 1 2</td>
</tr>
<tr>
<td>1) 22.21</td>
<td>2.368</td>
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<td>-</td>
</tr>
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</tr>
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<td>2.260</td>
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<td>2 2 0</td>
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<td>-</td>
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<td>2 1 3</td>
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</tr>
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<td>3) 25.83</td>
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<td>{25.69 2.065 }</td>
<td>1 1 4</td>
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<td>26.14</td>
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<td>26.95 1.975</td>
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<td>28.61</td>
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<tr>
<td>-</td>
<td>-</td>
<td>31.93 1.692</td>
<td>3 1 3</td>
</tr>
</tbody>
</table>

Notes:
1) These two lines do not fit the tetragonal pattern (see text).
2) Occurs as a shoulder on the outside of the adjacent peak; hence difficult to measure position accurately.
3) Very faint and hard to measure.
they do not affect the tetragonal fit. The 9.42 degree line is possibly due to strong absorption of X-rays in the sample; this can lead to splitting of the true diffraction lines at low diffraction angles. Dilution of the sample material would test this explanation.

7.3 Survey of the Ammonium Cryolites

7.3.1 Introduction

A review of the information presently available on the structures and phase transitions of ammonium cryolites will give us a basis for discussing the direction future research should take. The reasons for choosing this particular set of all the cryolites which have transitions were discussed in Chapter IV. In short they are

a) the conveniently attainable transition temperatures (less than 100°C)

b) the relative ease of preparation

c) the greater amenability to X-ray investigation of the fluorine atom motions because of the low scattering factors of the ammonium ions.

For convenience of discussion we shall consider these materials under three headings, according to whether the trivalent metal in the cryolite belongs to the group IIIA elements, the group IIIB elements, or the first row transition metal series.
7.3.2 Group IIIA - Sc, Yt, La, Ac

The only compound in this class reported in the literature thus far is the fluoroscandate, $(\text{NH}_4)_3\text{ScF}_6$\textsuperscript{14,20}. Bode andVoice\textsuperscript{14} assign to it the standard face-centred cubic structure at high temperatures. The transition occurs at $47^\circ\text{C}$\textsuperscript{20}, and below this the structure is reported to be the tetragonal ($D_{4h}^6$) type as depicted in fig. (2.3), with the fluorine octahedra rotated about their fourfold axes by $17^\circ40'$ at room temperature. The low atomic number of scandium (21) and the particularly convenient transition temperature make this a good compound for X-ray investigation. However, the expense of scandium salts does not encourage experimentation in crystal growing.

7.3.3 Group IIIB - Al, Ga, In, Tl

The fluoroaluminate, -gallate and -indate have been reported\textsuperscript{14}. The published structures and phase transitions are listed in table (7.4).

Two things stand out immediately from this table:

1. There is a deal of ambiguity about the actual structures of almost all phases. All X-ray structural analyses to date have been carried out on data obtained from polycrystalline samples, and this fact is largely responsible for the uncertainty.

2. Assuming that the data, insofar as it does restrict possible structures, is reliable, there is no evident systematic progression of any property other than the transition temperature.
Table 7.4 Group IIIB Ammonium Cryolites

<table>
<thead>
<tr>
<th>Compound</th>
<th>Low Temperature Structure</th>
<th>Transition Temperature(°C)</th>
<th>High Temperature Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{NH}_4)_3\text{AlF}_6)</td>
<td>Unknown; lower than tetragonal(^{(127)})</td>
<td>-49(^{(117)})</td>
<td>Standard face-centred cubic, (\text{O}^5_h)</td>
</tr>
</tbody>
</table>
| \((\text{NH}_4)_3\text{GaF}_6\) | Unreported                  | -25\(^{(117)}\) | Either \(^{(118)}\)  
  a) microtwinned \(\text{T}^6_h\) structure, or  
  b) \(\text{O}^5_h\,"\text{K}_3\text{FeF}_6\)-type" structure. |
| \((\text{NH}_4)_3\text{InF}_6\) | Either  
  a) \(\text{D}^6_{4h}\) structure\(^{(14)}\) or  
  b) \(\text{C}^5_{\text{h}}\)\(^{(117)}\) | +82\(^{(117)}\) | Either \(^{(117)}\)  
  a) space group \(\text{O}^5_{\text{h}}\), type undefined, or  
  b) \(\text{T}^6_{\text{h}}\) |

Notes:

a) Numbers in brackets indicate the data sources.

b) The so-called "\(\text{K}_3\text{FeF}_6\)-type" structure has a similar unit cell to the standard face-centred cubic structure (figure (1.1)), except that the fluoride ions lie slightly off the cubic unit cell edges in the \(\ell\) sites (International Tables notation \(6^4\)). These sites have 192-fold symmetry; hence the fluorine ions are randomly distributed to fill one-eighth of the available sites in the unit cell. \(\text{K}_3\text{FeF}_6\) itself, incidentally, probably does not possess this structure, but is more likely tetragonal\(^{110,111,142}\).
7.3.4 The First Row Transition Metals - Ti, V, Cr, Mn, Fe, Co, Ni, Cu

Ammonium fluorometallates have been reported with trivalent titanium<sup>101</sup>, vanadium, chromium and ferric ions<sup>14</sup>.

1. Titanium

Trivalent titanium is expected to exhibit the Jahn Teller effect. Thus, all $[\text{TiF}_6^{3-}]$ octahedra observed to date are distorted, possessing four long coplanar Ti-F bonds, and two short ones<sup>21,100</sup>. Bukovec and Siftar<sup>20</sup> carried out differential thermal analysis of $(\text{NH}_4)_3\text{TiF}_6$ above room temperature, and found phase transitions at $35^\circ\text{C}$ and $100^\circ\text{C}$. To date no X-ray data has been published for any of the three known phases of this compound; the fluorotitanate ion distortions have been inferred from optical and infrared data.

2. Vanadium

In the work carried out for this thesis three transitions were discovered at approximately $-9$, $-21$ and $-34^\circ\text{C}$. The room temperature powder photograph is consistent with the standard $\text{O}_5^5\text{h}$ cryolite structure; no data on the other three phases is yet available.

3. Chromium

There is a transition at about $-2^\circ\text{C}$ from the standard cubic form to one which is probably distorted tetragonal.

4. Iron

This compound has the standard high-temperature cubic cryolite structure at room temperature. At approximately $-10^\circ\text{C}$ there is a transition to a tetragonal structure. The exact positions of the fluorine ions in this structure have not yet been ascertained. The transition is known from Mössbauer work<sup>92</sup> to be first order with a hysteresis of approximately $0.5^\circ\text{C}$. 
7.4 SUGGESTIONS FOR FURTHER WORK

7.4.1 Summary of Experimental Methods

(1) Introduction

In this thesis we have been establishing the groundwork for the theoretical and experimental investigation of structural phase transitions in cryolites. Now, in this final section, we come to summarise the present status of the work and to consider a suitable path for future research.

The eventual goal of such a study as described in this thesis is to provide an individual explanation for each transition in terms of the lattice dynamics of the compound. The information required to set up a suitable model can be classified under two main headings: structural (we must know how the mean positions of the atoms change with temperature) and spectroscopic (we need data on the interatomic forces involved). It is convenient to review what we know under these two headings.

(2) Structural Investigations

In the review of the ammonium cryolites above little indication of any systematic variation of properties from compound to compound was found. Thus, little light on the transitions is to be expected from examining a group of compounds using only one or two experimental methods. Each transition must be considered separately, with all suitable experimental techniques being brought to bear on it.

The general lack of unambiguous structural information on ammonium cryolites stands out in the above review. This is also the situation for the cryolites taken as a whole. Such
information as is available is almost exclusively derived from X-ray powder diffraction data which, while it may be suitable for refinement if the basic structure of the phase is known, does not always provide enough information to determine that structure with certainty in the first place. X-ray diffraction studies with crystals will have to be done to determine these structures unambiguously for at least one temperature in the domain of each phase; powder photographs may then be adequate to track the variation of the positional parameters of the different atoms over the temperature domain of that phase.

A Buerger precession camera, suitable for X-ray crystal studies and possessing a commercial low temperature attachment has become available in the Chemistry Department of this university. The only immediately available crystallites of suitable size are of ammonium hexafluoroaluminate, \((\text{NH}_4)_3\text{AlF}_6\). It should be possible to obtain at least small crystals of many of the other ammonium cryolites by evaporation from appropriate solutions; the vanadium (III) and ferric salts are probable exceptions because, respectively, of instability in aqueous solution and a tendency to incorporate water molecules into the crystal lattice (see Appendix D).

For the study of powders the Debye-Scherrer system described in Chapter V provides adequate temperature stability, but the measurement of the actual temperature at the sample is not as accurate as desired. A few compounds may be particularly difficult to work with. Ammonium hexafluorochromate is such a case; with copper radiation, as noted before, there is an unacceptably large background from fluorescent radiation. The commonly available X-ray tubes with iron and cobalt targets
would only make the fluorescence stronger, and chromium radiation would demand long exposures because of absorption at the relatively long wavelength. The relative weakness of the cobalt tube radiation presents a similar problem for ammonium hexafluoroferrate; this is particularly unfortunate as this compound appears to have one of the simpler low temperature structures.

Within the cryolites we are generally restricted to X-ray methods for obtaining structural data. EPR studies with Fe$^{3+}$ as a dopant, which have given such precise structural information for the perovskites, are impracticable because of the effect of the superhyperfine interaction of the ferric ion and the fluorine nuclei (Chapter IV).

(3) Spectroscopic Methods

We have noted in Chapter IV that neutron spectroscopy is impracticable because large enough crystals cannot be made. The measurement of infrared spectra is straightforward, and should present no insurmountable difficulties. Raman spectra are another matter. We must have them if we are to gain enough data to attempt any model building. More fundamentally, they are needed to show whether or not a soft mode does in fact exist, and if it does to measure how its frequency varies with temperature.

The Raman lines are expected to be weak for cryolites (Chapter IV). This means that single crystal rather than powder samples are needed, and of course crystals have the extra advantage of allowing polarisation studies. A variable temperature dewar suitable for Raman studies is available and a new laser producing a 2 mm diameter beam with a power output
of approximately seven watts (5145 Å line) - roughly seven times as powerful as that previously available at this University - has recently been acquired.

The chief problem that faces us, then, is to grow crystals large enough for Raman measurements. In this regard there is little published data on cryolite crystal growth (Appendix D). Crystals of K₃CrF₆ and K₃AlF₆ with volumes of the order of 3 mm³ have been obtained from fluxes⁵⁰. An (NH₄)₃AlF₆ crystal with dimensions 3 x 2 x 2 mm, of more convenient size for Raman spectroscopy, has been grown by slow evaporation of a concentrated hydrofluoric acid solution⁸³. Ammonium hexafluoroaluminate has the added advantage for Raman work that its crystals are not coloured.

7.4.2 Conclusion

We have noted above that the most promising path for future research is to concentrate on one particular material at a time. In general the limited temperature range over which the equipment currently available allows us to take measurements restricts us to examining the phase changes of the ammonium cryolites (Tl₃ScF₆ and Tl₃VF₆ with transitions at 95 and 115°C respectively (table 1.1) are possible exceptions).

The first priority should be to attempt to grow crystals of a number of ammonium cryolites large enough for Raman investigations. Once this has been done for any given compound and the Raman spectrum observed it is worthwhile attempting to obtain the other data required for model building from infrared and X-ray structural investigations of that material; the latter two methods are almost certain to produce satisfactory results. Ammonium hexafluoroaluminate is the most
immediately appealing substance for investigation in view of the reported growth of a crystal large enough for Raman work and the immediate availability of small crystallites suitable for X-ray crystallography. The ammonium hexafluorogallate and hexafluorindate are more soluble in water, and it may thus be possible to obtain even bigger crystals of these materials.
REFERENCES


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118. Schwarzmann, S.  Z. Kristallogr. 120, 286 (1964).


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APPENDIX A

Character Tables of Multiplier Representations

A.1 Notation

For the particular representations listed it turns out that the irreducible multiplier representations are identical to the ordinary irreducible representations of the point group of the associated wave vector. This follows because the multipliers of the representations, as given by equation (2.20), are all unity, either as a result of the space group's being symmorphic ($O_h^5$) or, for the $\Gamma$ point representations of $D_{4h}^6$, because the wave vector is zero. The ordinary representation labels (A, B, E and T) for the point groups are listed immediately to the right of Kovalev's $^{68}$ irreducible multiplier representation labels which are used in the text. Subscripts g ('gerade') and u ('ungerade') indicate representations even and odd under inversion respectively. The third set of representation labels is one in common use; see, for example, references 25 and 67.

Of the operation labels, $C_n$ represents a rotation through an angle $(2\pi/n)$, $E$ is the identity, $I$ the inversion, $\sigma$ a reflection, and $S_n$ a rotation of $(2\pi/n)$ followed by reflection in the plane perpendicular to the rotation axis. A number immediately before one of these labels indicates the number of different operations of that type with equal character occurring in the group.
### A.2 $\Gamma$ Point Characters for $O_4^{5h}$

<table>
<thead>
<tr>
<th>Representation</th>
<th>Operation</th>
<th>$E$</th>
<th>$3C_2$</th>
<th>$6C_2'$</th>
<th>$6C_2$</th>
<th>$I$</th>
<th>$3\sigma_h$</th>
<th>$6\sigma_d$</th>
<th>$6S_4$</th>
</tr>
</thead>
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<td>$\tau_1 A_{1g}$</td>
<td>$\Gamma^{1+}$</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
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<td>1</td>
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<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
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<td>-1</td>
<td>-1</td>
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<td>2</td>
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<td>-1</td>
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<td>0</td>
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<td>-2</td>
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<td>-2</td>
</tr>
<tr>
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<td>0</td>
<td>-1</td>
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<td>0</td>
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</tbody>
</table>

### A.3 X Point Characters for $O_4^{5h}$; $\Gamma$ Point Characters for $D_4^{6h}$

<table>
<thead>
<tr>
<th>Representation</th>
<th>Operation</th>
<th>$C_2$</th>
<th>$2C_4$</th>
<th>$2C_2'$</th>
<th>$2C_2$</th>
<th>$I$</th>
<th>$\sigma_h$</th>
<th>$2S_4$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
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<tr>
<td>$\tau_1 A_{1g}$</td>
<td>$X^{1+}$</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\tau_2 A_{1u}$</td>
<td>$X^{1-}$</td>
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<td>1</td>
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<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\tau_3 A_{2g}$</td>
<td>$X^{2+}$</td>
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<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
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<td>-1</td>
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<td>-1</td>
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<td>-1</td>
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<td>1</td>
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<tr>
<td>$\tau_5 B_{1g}$</td>
<td>$X^{3+}$</td>
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<tr>
<td>$\tau_7 B_{2g}$</td>
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<td>1</td>
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<td>$\tau_8 B_{2u}$</td>
<td>$X^{4-}$</td>
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<td>1</td>
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<td>1</td>
<td>-1</td>
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<tr>
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</tr>
</tbody>
</table>

The $\Gamma$ point group of $D_4^{6h}$ is isomorphic to the point group of $X$ of $O_4^{5h}$, hence the character tables are identical.
A.4 L Point Characters for $O_h^5$

<table>
<thead>
<tr>
<th>Representation</th>
<th>Operation</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C'_2$</th>
<th>$I$</th>
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The point group of the $L$ vector is $D_{3d}$.

A.5 W Point Characters for $O_h^5$

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<th>Representation</th>
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<td>$\Gamma_5$</td>
<td>$E$</td>
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</table>

The point group of the $W$ vector is $D_{2d}$.
APPENDIX B

Normal Modes and Dynamical Matrices for the Cryolite Structure

B.1 Normal Modes

B.1.1 Notation

The orthogonal displacement vectors $f(k_\sigma \mu \delta)$ produced by the program ACMI are listed below. Here coefficients $(\sigma, \mu, \delta)$ are defined as for equation (2.24), with $\sigma$ the representation label, $\mu$ the multiplicity index, and $\delta$ the degeneracy index.

From equation (2.11) we can see that the essential part of a mode corresponding to eigenvector $e(k|j)$ is contained in the $3r$ components $e_\alpha(k|j)$ of $e(k,j)$; the vectors $e(k,j)$ can be written as sums on the $f$-vectors:

$$e(k,\sigma,\nu,\delta) = \sum_{\mu=1}^{C_\sigma} \eta(\sigma,\mu,\nu) f(k,\sigma,\mu,\delta) \quad (B.1)$$

(cf. equation (2.27)). The coefficients $\eta(\sigma,\mu,\nu)$ cannot be obtained from group theory but depend on the dynamics of the system.

The majority of components $f_\alpha(k|k_\sigma \mu \delta)$ in a given vector $f$ are zero; only non-zero ones are listed to save space. The notation is best indicated by an example. Consider the displacement vector

$$\{ZF3 \rightarrow 2YF5 + (\exp[i\pi])(ZF4 \rightarrow 2YF6)\}.$$

Its components are then
\[ f_3(F3|\tilde{z}j) = 1 \]

\[ f_3(F4|\tilde{z}j) = \exp(i\phi) \]

\[ f_2(F5|\tilde{z}j) = -2 = 2 \exp(-\frac{i\pi}{2}) \]

\[ f_2(F6|\tilde{z}j) = -2 \exp(i\phi) = 2 \exp[i(\phi - \frac{\pi}{2})] \]

All other components \( f_\alpha(\kappa|\tilde{z}j) = 0 \).

Here the label \( j \) represents the set of labels \((\sigma\mu\delta)\). The atoms labelled by \( F3 \) and \( F4 \) both move along the \( Z \) axis direction, while atoms \( F5 \) and \( F6 \) move along the \( Y \) direction with amplitudes twice those of \( F3 \) and \( F4 \). All other atoms in the primitive unit cell of the crystal are stationary. The significance of the arguments of the exponentials is evident when we consider the complete expression for the mode (equation (2.11)). Thus

\[ u_3(\ell,F3) = \exp(ik.l) \exp[-i\omega(k,j)t] \]

\[ u_3(\ell,F4) = \exp(ik.l) \exp[i(\phi-\omega(k,j)t)] \]

so that the motion of atom \( F4 \) lags behind that of \( F3 \) by phase angle \( \phi \).

In the listings that follow atom labels are as in figures (2.2) and (2.3). Modes are labelled \((\sigma,\mu,\delta)\) where these three symbols have the same significance as above.

The following abbreviations are adopted:

\[ p = \exp(2\pi i/3), \quad p^* = \exp(-2\pi i/3), \quad i = \sqrt{-1} = \exp \left( \frac{\pi i}{2} \right), \]

\[ i^* = \exp(-\frac{\pi i}{2}) \]
B.1.2 Listings

(1) $O_n^5 \text{I}$

\[ T(k_i = 0) = \tau_1 + \tau_5 + 2\tau_7 + \tau_8 + \tau_9 + 5\tau_{10} \]

\[ (111) = \frac{XF_1 - XF_2 + YF_3 - YF_4 + ZF_5 - ZF_6}{\sqrt{6}} \]

\[ (511) = \frac{XF_1 - XF_2 + p(YF_3 - YF_4) + p^*(ZF_5 - ZF_6)}{\sqrt{6}} \]

\[ (512) = (511)^* \]

\[ (711) = \frac{ZF_3 - ZF_4 + YF_5 - YF_6}{\sqrt{4}} \]

\[ (712) = \frac{ZF_1 - ZF_2 + XF_5 - XF_6}{\sqrt{4}} \]

\[ (713) = \frac{YF_1 - YF_2 + XF_3 - XF_4}{\sqrt{4}} \]

\[ (721) = \frac{XA_1 - XA_2}{\sqrt{2}} \]

\[ (722) = \frac{YA_1 - YA_2}{\sqrt{2}} \]

\[ (723) = \frac{ZA_1 - ZA_2}{\sqrt{2}} \]

\[ (811) = \frac{XF_3 + XF_4 - XF_5 - XF_6}{\sqrt{4}} \]

\[ (812) = \frac{YF_1 + YF_2 - YF_5 - YF_6}{\sqrt{4}} \]

\[ (813) = \frac{ZF_1 + ZF_2 - ZF_3 - ZF_4}{\sqrt{4}} \]

\[ (911) = \frac{ZF_3 - ZF_4 - YF_5 + YF_6}{\sqrt{4}} \]

\[ (912) = \frac{ZF_1 - ZF_2 - XF_5 + XF_6}{\sqrt{4}} \]

\[ (913) = \frac{YF_1 - YF_2 - XF_3 + XF_4}{\sqrt{4}} \]

\[ (10,11) = \frac{XF_1 + XF_2}{\sqrt{2}} \]

\[ (10,12) = \frac{YF_1 + YF_2 + YF_5 + YF_6}{\sqrt{4}} \]
(10,13) = \frac{(ZF1 + ZF2 + ZF3 + ZF4)}{\sqrt{4}}

(10,21) = \frac{(XF3 + XF4 + XF5 + XF6)}{\sqrt{4}}

(10,22) = \frac{(YF3 + YF4)}{\sqrt{2}}

(10,23) = \frac{(ZF5 + ZF6)}{\sqrt{2}}

(10,3\alpha) = \frac{(X \alpha A1 + X \alpha A2)}{\sqrt{2}}

(10,4\alpha) = \frac{X M}{\alpha}

(10,5\alpha) = \frac{X B}{\alpha}

where \(X_{\alpha} = X, Y \) or \(Z\) according as \(\alpha = 1, 2 \) or \(3\).

(2) \(\frac{\hbar}{5} X_{Z}\)

Because of the form of Kovalev's tables of irreducible representations the \(X\)-vector has been taken along the \(Z\)-axis.

For the decomposition we have

\[
\mathcal{T}(k_{\alpha} X_{Z}) = \frac{1}{(0,0,1)} = 3\tau_1 + \tau_3 + 4\tau_4 + \tau_5 + \tau_6 + \tau_7 + \tau_8 + 3\tau_9 + 6\tau_{10}
\]

(111) = \frac{(XF1 - XF2 + YF3 - YF4)}{\sqrt{4}}

(121) = \frac{(ZF5 - ZF6)}{\sqrt{2}}

(131) = \frac{(ZA1 - ZA2)}{\sqrt{2}}

(311) = \frac{(YF1 - YF2 - XF3 + XF4)}{\sqrt{4}}

(411) = \frac{(ZF1 + ZF2 + ZF3 + ZF4)}{\sqrt{4}}

(421) = \frac{(ZF5 + ZF6)}{\sqrt{2}}

(431) = ZM
(441) = ZB

(511) = (XF1 - XF2 - YF3 + YF4)/\sqrt{4}

(611) = (ZA1 + ZA2)/\sqrt{2}

(711) = (YF1 - YF2 + XF3 - XF4)/\sqrt{4}

(811) = (ZF1 + ZF2 - ZF3 - ZF4)/\sqrt{4}

(911) = (ZF1 - ZF2 + i(ZF3 - ZF4))/\sqrt{4}

(921) = (XF5 - XF6 + i(YF5 - YF6))/\sqrt{4}

(931) = (XA1 - XA2 + i(YA1 - YA2))/\sqrt{4}

(9h2) = (9h1), h = 1, 2, 3

(10,11) = (XF1 + XF2 + i(YF3 + YF4))/\sqrt{4}

(10,21) = (YF1 + YF2 + i(XF3 + XF4))/\sqrt{4}

(10,31) = (XF5 + XF6 + i(YF5 + YF6))/\sqrt{4}

(10,41) = (XA1 + XA2 + i(YA1 + YA2))/\sqrt{4}

(10,51) = (XM + iYM)/\sqrt{2}

(10,61) = (XB + iYB)/\sqrt{2}

(10,h2) = (10,h,1), h = 1, ... , 6

These vectors have components \( f_{\alpha}(\kappa|\kappa_X^j) \). If

\[
f_{\alpha}(\kappa|\kappa_X^j) = |f_{\alpha}(\kappa|\kappa_X^j)|\exp[i\phi(\alpha,\kappa,\kappa_X^j)]
\]

the corresponding displacement is
\( u_\alpha (\kappa z) = \left[ f_\alpha (\kappa \mid k_x z \rangle \mid / M_\kappa^2 \right] \exp \left[ i (2\pi \frac{\kappa z}{a} + \phi (\alpha, \kappa, k_x z \rangle - \omega \langle k_x z \rangle t) \right] \)

with a period of \( a \) in the Z-direction only. Here

\( \kappa = (k_x, k_y, k_z) \).

\[(3) \quad \frac{O_L^5}{n} \]

\[ T_{\kappa L} = \frac{1}{a} \left[ \kappa_x, \kappa_y, \kappa_z \right] = 4\tau_1 + \tau_2 + \tau_3 + 4\tau_4 + 5\tau_5 + 5\tau_6 \]

\[(111) = (X_{F1} - X_{F2} + Y_{F3} - Y_{F4} + Z_{F5} - Z_{F6})/\sqrt{6} \]

\[(121) = ((Y_{F1} + Z_{F1})/\sqrt{2} - (Y_{F2} + Z_{F2})/\sqrt{2} + (X_{F3} + Z_{F3})/\sqrt{2} \]

\[-(Z_{F4} + X_{F4})/\sqrt{2} + (X_{F5} + Y_{F5})/\sqrt{2} \]

\[-(X_{F6} + Y_{F6})/\sqrt{2})/\sqrt{6} \]

\[(131) = ((X_{A1} + Y_{A1} + Z_{A1})/\sqrt{3} + (X_{A2} + Y_{A2} + Z_{A2})/\sqrt{3})/\sqrt{2} \]

\[(141) = (X_{B} + Y_{B} + Z_{B})/\sqrt{3} \]

\[(211) = ((Y_{F1} - Z_{F1})/\sqrt{2} + (Y_{F2} - Z_{F2})/\sqrt{2} + (Z_{F3} - X_{F3})/\sqrt{2} \]

\[+ (Z_{F4} - X_{F4})/\sqrt{2} + (X_{F5} - Y_{F5})/\sqrt{2} \]

\[+ (X_{F6} - Y_{F6})/\sqrt{2})/\sqrt{6} \]

\[(311) = ((Y_{F1} - Z_{F1})/\sqrt{2} - (Y_{F2} - Z_{F2})/\sqrt{2} + (Z_{F3} - X_{F3})/\sqrt{2} \]

\[-(Z_{F4} - X_{F4})/\sqrt{2} + (X_{F5} - Y_{F5})/\sqrt{2} \]

\[-(X_{F6} - Y_{F6})/\sqrt{2})/\sqrt{6} \]

\[(411) = (X_{F1} + X_{F2} + Y_{F3} + Y_{F4} + Z_{F5} + Z_{F6})/\sqrt{6} \]
\[(421) = \frac{(YF1 + ZF1)}{\sqrt{2}} + \frac{(YF2 + ZF2)}{\sqrt{2}} + \frac{(ZF3 + XF3)}{\sqrt{2}} + \frac{(ZF4 + XF4)}{\sqrt{2}} + \frac{(XF5 + YF5)}{\sqrt{2}} + \frac{(ZF6 + XF6)}{\sqrt{2}}\]

\[(431) = \frac{(XA1 + YA1 + ZA1)}{\sqrt{3}} - \frac{(XA2 + YA2 + ZA2)}{\sqrt{3}}\]

\[(441) = \frac{(XM + YM + ZM)}{\sqrt{3}}\]

\[(511) = \frac{(XF1 - XF2 + p(YF3 - YF4) + p*(ZF5 - ZF6))}{\sqrt{6}}\]

\[(521) = \frac{(YF1 - YF2 + p(ZF3 - ZF4) + p*(XF5 - XF6))}{\sqrt{6}}\]

\[(531) = \frac{(ZF1 - ZF2 + p(XF3 - XF4) + p*(YF5 - YF6))}{\sqrt{6}}\]

\[(541) = \frac{((XA1 + pYA1 + p*ZA1)}{\sqrt{3}} + \frac{(XA2 + pYA2 + p*ZA2)}{\sqrt{3}}\]

\[(551) = \frac{(XB + pYB + p*ZB)}{\sqrt{3}}\]

\[(5h2) = (5h1)^* \text{ for } h = 1, \ldots, 5\]

\[(611) = \frac{(XF1 + XF2 + p(YF3 + YF4) + p*(ZF5 + ZF6))}{\sqrt{6}}\]

\[(621) = \frac{(YF1 + YF2 + p(ZF3 + ZF4) + p*(XF5 + XF6))}{\sqrt{6}}\]

\[(631) = \frac{(ZF1 + ZF2 + p(XF3 + XF4) + p*(YF5 + YF6))}{\sqrt{6}}\]

\[(641) = \frac{((XA1 + pYA1 + p*ZA1)}{\sqrt{3}} - \frac{(XA2 + pYA2 + p*ZA2)}{\sqrt{3}}\]

\[(651) = \frac{(XM + pYM + p*ZM)}{\sqrt{3}}\]

\[(6h2) = (6h1)^* \text{ for } h = 1, \ldots, 5.\]
These are the components $f_{\alpha}(\kappa | \mathbf{k}_{L}^{j})$. Writing

$$f_{\alpha}(\kappa | \mathbf{k}_{L}^{j}) = |f_{\alpha}(\kappa | \mathbf{k}_{L}^{j})| \exp \{i \phi(\alpha, \kappa, \mathbf{k}_{L}^{j}) \}$$

we obtain a corresponding displacement

$$u_{\alpha}(\kappa) = \left[ |f_{\alpha}(\kappa | \mathbf{k}_{L}^{j})| \mathbf{M}_{k} \right] \exp \left[ i \left( 2\pi \frac{\kappa_{x} + \kappa_{y} + \kappa_{z}}{2a} \right) \right]$$

with a period of $2a$ in each of the $X$, $Y$ and $Z$ directions.

(4) $\mathcal{O}_{5}^{W}$

$$\mathcal{T}(\mathbf{k}_{W} = \frac{1}{a}(1,0,1)) = 5\tau_{1} + 2\tau_{2} + 5\tau_{3} + 2\tau_{4} + 8\tau_{5}$$

(111) $= (XF1 - XF2 + YF3 - YF4)/\sqrt{4}$

(121) $= (ZF1 + ZF2 - ZF3 - ZF4)/\sqrt{4}$

(131) $= (ZF5 - ZF6)/\sqrt{2}$

(141) $= ((XA1 - iYA1)/\sqrt{2} + (YA2 - iXA2)/\sqrt{2})/\sqrt{2}$

(151) $= ZB$

(211) $= (YF1 - YF2 - XF3 + XF4)/\sqrt{4}$

(221) $= ((XA1 - iYA1)/\sqrt{2} + (-YA2 + iXA2)/\sqrt{2})/\sqrt{2}$

(311) $= (XF1 - XF2 - YF3 + YF4)/\sqrt{4}$

(321) $= (ZF1 + ZF2 + ZF3 + ZF4)/\sqrt{4}$

(331) $= (ZF5 + ZF6)/\sqrt{2}$

(341) $= ((XA1 + iYA1)/\sqrt{2} - (YA2 + iXA2)/\sqrt{2})/\sqrt{2}$

(351) $= ZM$
\begin{align*}
(411) &= (YF1 - YF2 + XF3 - XF4)/\sqrt{4} \\
(421) &= ((XA1 + iYA1)/\sqrt{2} + (YA2 + iXA2)/\sqrt{2})/\sqrt{2} \\
(511) &= (XF1 + XF2 + i(YF3 + YF4))/\sqrt{4} \\
(521) &= (YF1 + YF2 - i(XF3 + XF4))/\sqrt{4} \\
(531) &= (ZF1 - ZF2 + i(-ZF3 + ZF4))/\sqrt{4} \\
(541) &= (XF5 + iYF6)/\sqrt{2} \\
(551) &= (YF5 - iXF6)/\sqrt{2} \\
(561) &= ZA2 \\
(562) &= ZA1 \\
(571) &= (XM + iYM)/\sqrt{2} \\
(581) &= (XB - iYB)/\sqrt{2} \\
(5h2) &= (5h1)^* \quad h = 1, \ldots, 5, 7, 8
\end{align*}

These are the components $f_\alpha(\kappa | k_wj)$. Writing

$$f_\alpha(\kappa | k_wj) = |f_\alpha(\kappa | k_wj)| \exp\{i\phi(\alpha, \kappa, k_wj)\}$$

we obtain a corresponding displacement

$$u_\alpha(k_wj) = \left[|f_\alpha(\kappa | k_wj)|/M_k^2\right]\exp\left[i\left(2\pi\left(\frac{k_x}{a} + \frac{k_z}{2a}\right)ight) + \phi(\alpha, \kappa, k_wj) - \omega(k_wj)t \right]$$
$$\mathcal{T}(k_{\Gamma} = 0) = 3\tau_1 + 4\tau_2 + 4\tau_3 + 5\tau_4 + 3\tau_5 + 2\tau_6 + 2\tau_7$$
$$+ \tau_8 + 6\tau_9 + 12\tau_{10}$$

Cartesian coordinates are in the tetragonal coordinate system (see fig. (2.3)).

$$(111) = (XF_{11} - XF_{21} + YF_{31} - YF_{41} - YF_{12} + YF_{22}$$
$$+ XF_{31} - XF_{41})/\sqrt{8}$$

$$(121) = (YF_{11} - YF_{21} - XF_{31} + XF_{41} + XF_{12} + XF_{22}$$
$$- YF_{32} + YF_{42})/\sqrt{8}$$

$$(131) = (ZF_{51} - ZF_{61} + ZF_{52} - ZF_{62})/\sqrt{4}$$

$$(211) = (ZM_{1} - ZM_{2})/\sqrt{2}$$

$$(221) = (ZB_{1} - ZB_{2})/\sqrt{2}$$

$$(231) = (ZF_{11} + ZF_{21} + ZF_{31} + ZF_{41} - ZF_{12} - ZF_{22}$$
$$- ZF_{32} - ZF_{42})/\sqrt{8}$$

$$(241) = (ZF_{51} + ZF_{61} - ZF_{52} - ZF_{62})/\sqrt{4}$$

$$(311) = (ZA_{11} + ZA_{21} - ZA_{12} - ZA_{22})/\sqrt{4}$$

$$(321) = (XF_{11} - XF_{21} + YF_{31} - YF_{41} + YF_{12} - YF_{22}$$
$$- XF_{32} + XF_{42})/\sqrt{8}$$

$$(331) = (YF_{11} - YF_{21} - XF_{31} + XF_{41} + XF_{12} - XF_{22}$$
$$+ YF_{32} - YF_{42})/\sqrt{8}$$
(341) = \(\frac{ZF51 - ZF61 - ZF52 + ZF62}{\sqrt{4}}\)

(411) = \(\frac{ZM1 + ZM2}{\sqrt{2}}\)

(421) = \(\frac{ZB1 + ZB2}{\sqrt{2}}\)

(431) = \(\frac{ZA11 + ZA21 + ZA12 + ZA22}{\sqrt{4}}\)

(441) = \(\frac{ZF11 + ZF21 + ZF31 + ZF41 + ZF12 + ZF22 + ZF32 + ZF42}{\sqrt{8}}\)

(451) = \(\frac{ZF51 + ZF61 + ZF52 + ZF62}{\sqrt{4}}\)

(511) = \(\frac{-ZA11 + ZA21 - ZA12 + ZA22}{\sqrt{4}}\)

(521) = \(\frac{XF11 - XF21 - YF31 + YF41 + YF12 - YF22 + XF32 - XF42}{\sqrt{8}}\)

(531) = \(\frac{YF11 - YF21 + XF31 - XF41 + XF12 - XF22 - YF32 + YF42}{\sqrt{8}}\)

(611) = \(\frac{-ZA11 + ZA21 + ZA12 - ZA22}{\sqrt{4}}\)

(621) = \(\frac{ZF11 + ZF21 - ZF31 - ZF41 + ZF12 + ZF22 - ZF32 - ZF42}{\sqrt{8}}\)

(711) = \(\frac{XF11 - XF21 - YF31 + YF41 - YF12 + YF22 - XF32 + XF42}{\sqrt{8}}\)

(721) = \(\frac{YF11 - YF21 + XF31 - XF41 - XF12 + XF22 + YF32 - YF42}{\sqrt{8}}\)
\begin{align}
(811) &= (ZF_{11} + ZF_{21} - ZF_{31} - ZF_{41} - ZF_{12} - ZF_{22} \\
& \quad + ZF_{32} + ZF_{42})/\sqrt{8} \\
(911) &= (-XA_{12} + XA_{21} + i(-YA_{11} + YA_{22}))/\sqrt{4} \\
(921) &= (-YA_{12} + YA_{21} + i(XA_{11} - XA_{22}))/\sqrt{4} \\
(931) &= (ZF_{11} - ZF_{21} + i(-ZF_{31} + ZF_{41}))/\sqrt{4} \\
(941) &= (XF_{51} - XF_{61} + i(-YF_{51} + YF_{61}))/\sqrt{4} \\
(951) &= (ZF_{32} - ZF_{42} + i(ZF_{12} - ZF_{22}))/\sqrt{4} \\
(961) &= (XF_{52} - XF_{62} + i(-YF_{52} + YF_{62}))/\sqrt{4} \\
(9j2) &= (9j1)^*, \quad j = 1, \ldots, 6 \\
(10,j1) &= (XJ - iYJ)/\sqrt{2} \\
J &= M_1, M_2, B_1, B_2 \text{ for } j = 1, 2, 3, 4 \text{ respectively.} \\
(10,51) &= (XA_{12} + XA_{21} + i(-YA_{11} - YA_{22}))/\sqrt{4} \\
(10,61) &= (YA_{12} + YA_{21} + i(XA_{11} + XA_{22}))/\sqrt{4} \\
(10,71) &= (XF_{11} + XF_{21} + i(-YF_{31} - YF_{41}))/\sqrt{4} \\
(10,81) &= (YF_{11} + YF_{21} + i(XF_{31} + XF_{41}))/\sqrt{4} \\
(10,91) &= (XF_{51} + XF_{61} + i(-YF_{51} - YF_{61}))/\sqrt{4} \\
(10,10,1) &= (XF_{32} + XF_{42} + i(-YF_{12} - YF_{22}))/\sqrt{4} \\
(10,11,1) &= (YF_{32} + YF_{42} + i(XF_{12} + XF_{22}))/\sqrt{4} \\
(10,12,1) &= (XF_{52} + XF_{62} + i(-YF_{52} - YF_{62}))/\sqrt{4} \\
(10,k2) &= (10,k1)^* \text{ for } k = 1, \ldots, 12.
\end{align}
B.2 Dynamical Matrices for $O_h^5$

B.2.1 Introduction

The Fourier transformed dynamical matrix has elements

$$D_{\alpha,\kappa;\beta,\kappa'}(k) = D_{\alpha\beta}(\kappa\kappa'|k)$$

$$= \frac{1}{(M M')^{\frac{1}{2}}} \sum_{\lambda,\lambda'} \phi_{\alpha\beta}(\lambda\kappa,\lambda'\kappa') \exp(-ik_{\lambda}\lambda' - i\kappa_{\lambda'})$$

(see equation (2.13)).

As discussed in Chapter 2, the symmetry of the crystal is evinced in the commuting of matrices $D(\kappa)$ and $T(\kappa,R)$. This enforces certain mathematical relationships between different elements $D_{\alpha\beta}(\kappa\kappa'|k)$. These relationships are listed in the following four tables for the perfect (face-centred cubic) cryolite structure for the $\Gamma$, $X$, $L$ and $W$ wave vectors.

In the matrices listed zero elements are indicated by dots. The amplitudes of the other elements are represented by capital letters. Equal amplitudes are thus indicated by the same letter or combination of two letters. When the matrix elements are complex, the phase is indicated by a lower case letter (see table B.4)). In the row and column labels $(\alpha,\kappa)$, $X$, $Y$ and $Z$ indicate that $\alpha$ is equal to 1, 2 and 3 respectively, while the atom labels $\kappa$ are those of figure (2.2).

All the elements for the $\Gamma$, $L$ and $X$ wave vectors are real. This result follows from equation (2.17), since the wave vectors in these cases are equivalent to one-half of an inverse lattice vector.

B.2.2 Form of the Fourier Transformed Dynamical Matrices
### Table (B.1)

Form of Dynamical Matrix for Null Wave Vector (Γ), Face-Centred Cubic Cryolite Structure.

<table>
<thead>
<tr>
<th>Row Label</th>
<th>XF2</th>
<th>XF3</th>
<th>XF4</th>
<th>XF5</th>
<th>XF6</th>
<th>YA1</th>
<th>ZA1</th>
<th>YA2</th>
<th>ZA2</th>
<th>XM</th>
<th>ZM</th>
<th>XB</th>
<th>ZB</th>
</tr>
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<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
<td>L</td>
<td>M</td>
<td>N</td>
<td>F</td>
<td>G</td>
<td>0</td>
<td>-G</td>
<td>-O</td>
</tr>
<tr>
<td>ZF1</td>
<td>H</td>
<td>I</td>
<td>J</td>
<td>K</td>
<td>J</td>
<td>L</td>
<td>M</td>
<td>H</td>
<td>F</td>
<td>G</td>
<td>0</td>
<td>-G</td>
<td>-O</td>
</tr>
<tr>
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<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
<td>L</td>
<td>M</td>
<td>N</td>
<td>F</td>
<td>G</td>
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<td>-G</td>
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<tr>
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<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
<td>L</td>
<td>M</td>
<td>N</td>
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<td>G</td>
<td>0</td>
<td>-G</td>
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<td>D</td>
<td>K</td>
<td>M</td>
<td>L</td>
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<td>N</td>
<td>F</td>
<td>G</td>
<td>0</td>
<td>-G</td>
<td>-O</td>
</tr>
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<td>C</td>
<td>I</td>
<td>B</td>
<td>M</td>
<td>M</td>
<td>N</td>
<td>F</td>
<td>G</td>
<td>0</td>
<td>-G</td>
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<td>C</td>
<td>K</td>
<td>I</td>
<td>H</td>
<td>M</td>
<td>N</td>
<td>F</td>
<td>G</td>
<td>0</td>
<td>-G</td>
<td>-O</td>
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<td>D</td>
<td>I</td>
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<td>-O</td>
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<td>F</td>
<td>G</td>
<td>0</td>
<td>-G</td>
<td>-O</td>
</tr>
<tr>
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<td>D</td>
<td>K</td>
<td>J</td>
<td>C</td>
<td>I</td>
<td>H</td>
<td>M</td>
<td>N</td>
<td>F</td>
<td>G</td>
<td>0</td>
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</tr>
<tr>
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<td>L</td>
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<td>L</td>
<td>E</td>
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<tr>
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<tr>
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<td>L</td>
<td>E</td>
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<td>L</td>
<td>M</td>
<td>N</td>
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<td>M</td>
<td>L</td>
<td>E</td>
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<td>F</td>
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<td>-O</td>
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<td>F</td>
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<td>N</td>
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<td>R</td>
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<td>O</td>
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<td>O</td>
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<td>O</td>
<td>G</td>
<td>G</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
</tbody>
</table>

*Notes: Form of Dynamical Matrix for Face-Centred Cubic Cryolite Structure.*
| YF1 | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * |
| ZF1 | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * |
| XG1 | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * |
| YG1 | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * |
| ZG1 | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * |
| XH1 | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * |
| YH1 | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * |
| ZH1 | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * | * * * * |

**Table (B.2) Form of Dynamical Matrix for Wave Vector \( \mathbf{k} \) (along (0,0,1) axis), Face-Centred Cubic Cryolite Structure**
TABLE (B.3) FORM OF DYNAMICAL MATRIX FOR WAVE VECTOR \( \mathbf{L} \) \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\), FACE-CENTRED CUBIC CRYOLITE STRUCTURE.
<table>
<thead>
<tr>
<th>Row</th>
<th>Label</th>
<th>( X_1F_1 )</th>
<th>( X_2F_1 )</th>
<th>( X_3F_1 )</th>
<th>( X_4F_1 )</th>
<th>( X_5F_1 )</th>
<th>( X_6F_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_1F_1 )</td>
<td>( \pm \alpha )</td>
<td>( \pm \alpha )</td>
<td>( \pm \alpha )</td>
<td>( \pm \alpha )</td>
<td>( \pm \alpha )</td>
<td>( \pm \alpha )</td>
<td>( \pm \alpha )</td>
</tr>
<tr>
<td>( X_2F_1 )</td>
<td>( \pm \beta )</td>
<td>( \pm \beta )</td>
<td>( \pm \beta )</td>
<td>( \pm \beta )</td>
<td>( \pm \beta )</td>
<td>( \pm \beta )</td>
<td>( \pm \beta )</td>
</tr>
<tr>
<td>( X_3F_1 )</td>
<td>( \pm \gamma )</td>
<td>( \pm \gamma )</td>
<td>( \pm \gamma )</td>
<td>( \pm \gamma )</td>
<td>( \pm \gamma )</td>
<td>( \pm \gamma )</td>
<td>( \pm \gamma )</td>
</tr>
</tbody>
</table>

**TABLE (B.4)** FORM OF DYNAMICAL MATRIX FOR WAVE VECTOR \( \mathbf{W} (1,0,0) \), FACE-CENTRED CUBIC CRYOLITE STRUCTURE.

Notation: \( \alpha, r, e, s, t, u, v, w, x, y \) and \( z \) are arbitrary complex numbers with unit amplitude. A bar over a lower case letter indicates complex conjugation.
B.2.3 Block Diagonalised Form of Dynamical Matrices for Cubic $O_h^5$ Structure

(1) Introduction

The block diagonalised forms, $D(k)_{BD}$, of the preceding matrices are listed below. These represent the greatest simplification possible without solving the eigenvalue equations explicitly. Block diagonalisation is achieved by a unitary transformation $U$ on $D(k)$. The columns of $U$ are the set of $3r \times 1$ vectors described by the normal modes $(\sigma, \mu, \delta)$ possessing elements $f_{\alpha}(K!kapo)$ as listed in section B.1.2. In the matrix $U$ the ordering of these columns from left to right is such that index $\mu$ varies faster than $\delta$ which varies faster than $\sigma$.

The matrix $D(k)_{BD}$ is written in the form

$$D(k)_{BD} = \eta_{\alpha} \alpha + \eta_{\beta} \beta + \ldots$$

$\alpha$ being a matrix and $\eta_{\alpha}$ the number of times it occurs on the diagonal of $D(k)_{BD}$. Matrices $\alpha, \beta, \ldots$ etc. are Hermitian.

(2) Wavevector $\Gamma(000)$

$$D(k_{\Gamma})_{BD} = \alpha + 2\beta + 3\gamma + 3\delta + 3\epsilon + 3\zeta$$
Matrix Definitions

\[ \alpha = A - B - 4D \]

\[ \beta = A - B + 2D \]

\[ \gamma = (H - I - 2J) \begin{bmatrix} 2\sqrt{2} M \\ (-P-Q) \end{bmatrix} \]

\[ \delta = H + I - 2K \]

\[ \epsilon = H - I + 2J \]

\[ \zeta = \begin{bmatrix} A + B & -2\sqrt{2} C & 2E & \sqrt{2} F & -\sqrt{2} G \\ (H+I+2K) & -2\sqrt{2} L & 2N & -2 O \\ -P+Q & \sqrt{2} R & \sqrt{2} S \\ -T & -U \\ -V \end{bmatrix} \]
(3) Wavevector $x_z (001)$

$$D(k_x)_{BD} = \alpha + \beta + \gamma + \delta + \epsilon + \zeta + \eta + 2\theta + 2\kappa$$

Matrix Definitions

$$\alpha = \begin{pmatrix}
(AA - AB - 2AD) & -2\sqrt{2}AF & 2\sqrt{2}AH \\
(BF - BG) & -2BH & -BO - BP
\end{pmatrix}$$

$$\beta = -AK - AL + 2AM$$

$$\gamma = \begin{pmatrix}
(AR - AS - 2AT) & 2\sqrt{2}AV & 2AX & 2AY \\
(BF + BG) & \sqrt{2}BI & \sqrt{2}BJ & -BS & -BT & BV
\end{pmatrix}$$

$$\delta = AA - AB + 2AD$$

$$\epsilon = -BO + BP$$

$$\zeta = -AK - AL - 2AM$$

$$\eta = AR - AS + 2AT$$

$$\theta = \begin{pmatrix}
(AR + AS) & -2AU & -2AW \\
(-AZ - BA) & -2BB & (BK + BL)
\end{pmatrix}$$

$$\kappa = \begin{pmatrix}
(AA + AB) & -2iAC & -2AE & 2iAG & -\sqrt{2}AI & -\sqrt{2}AJ \\
(-AK + AL) & -2iAN & 2AO & -\sqrt{2}AP & i\sqrt{2}AQ \\
(-AZ + BA) & 2iBC & -\sqrt{2}BD & i\sqrt{2}BE & (BK - BL) & i\sqrt{2}BM & i\sqrt{2}BN & -BQ & -BR & -BU
\end{pmatrix}$$

Associated Irreducible Representation

$$\tau_1, \tau_3, \tau_4, \tau_5, \tau_6, \tau_7, \tau_8, \tau_9, \tau_{10}$$
Matrix Definitions

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{(AA-AC+2AF)}{-2AI} \sqrt{2} )</td>
<td>( \frac{(AS+AT-AU-AV + AW+2AX-AY + 2AZ+BA-BA)}{2} )</td>
<td>( \frac{(AS+AT-AU-AV + AW+2AX-AY + 2AZ+BA-BA)}{2} )</td>
<td>( \frac{(AA+AC+2AF)}{+2AI} \sqrt{2} )</td>
</tr>
<tr>
<td>( +AG-AH-AJ )</td>
<td>( +AW+2AX+AY )</td>
<td>( +AW+2AX+AY )</td>
<td>( +AG+AH+AJ )</td>
</tr>
<tr>
<td>( -AM-2AN )</td>
<td>( +BE-BF )</td>
<td>( +BE+BF+BG )</td>
<td>( +AM+2AN )</td>
</tr>
</tbody>
</table>

Associated Irreducible Representation

<table>
<thead>
<tr>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>( \tau_3 )</th>
<th>( \tau_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{(AS+AT-AU-AV + AW+2AX-AY + 2AZ+BA-BA)}{2} )</td>
<td>( \frac{(BO+2BP+2BR)}{2} )</td>
<td>( \frac{(BO+2BP+2BR)}{2} )</td>
<td>( \frac{(BO+2BP+2BR)}{2} )</td>
</tr>
<tr>
<td>( \sqrt{2} )</td>
<td>( \sqrt{2} )</td>
<td>( \sqrt{2} )</td>
<td>( \sqrt{2} )</td>
</tr>
<tr>
<td>( (-BC+BD-2BL+BM-BN) )</td>
<td>( (-BC+BD-2BL+BM-BN) )</td>
<td>( (-BC+BD-2BL+BM-BN) )</td>
<td>( (-BC+BD-2BL+BM-BN) )</td>
</tr>
<tr>
<td>( (2AM+2AN) )</td>
<td>( (2AM+2AN) )</td>
<td>( (2AM+2AN) )</td>
<td>( (2AM+2AN) )</td>
</tr>
</tbody>
</table>

Notation: \( p = \exp(2\pi i/3) \), \( p^* = \exp(-2\pi i/3) \), \( i = \sqrt{-1} \)
(5) Wave Vector W(1 0 ½)

\[ D_{WBD}^{(k)} = \alpha + \beta + \gamma + \delta + 2\varepsilon \]

Notation is as for table (B.4), except that complex conjugation is now indicated by an asterisk.

Matrix Definitions

\[
\begin{align*}
\alpha &= (AA-AC-2AF) i(AB-AD+2AG) \sqrt{2(s+s*)AI} 2n*(-AJ+AK) -2iAP \\
&\quad -2n*(AJ+AK) + 2n(BF-BG) -2BL \\
&\quad n*[(l+i*)z -(1+i*)z*]BT \\
&\quad \frac{(-BR+BS)}{2n*CB} + \frac{(BW-BX+BY+BZ)}{2n*CA} -CH \\
\beta &= (-AQ-AR+2AS) 2n(-AV+AW) \\
&\quad \frac{(BW-BX+BY+BZ)}{2n*CB} \\
\gamma &= (AA-AC+2AF) i(AB-AD-2AG) -\sqrt{2(s-s*)AI} 2n*(AJ+AK) 2iAN \\
&\quad 2n*(AJ+AK) + 2n(BF+BG) -2BJ \\
&\quad \frac{(-BR+BS)}{2n*CB} + \frac{(BW+BX+BY+BZ)}{2n*CA} -CH \\
\delta &= (-AQ-AR-2AS) -2n(AV+AW) \\
&\quad \frac{(BW+BX+BY+BZ)}{2n*CB} \\
\end{align*}
\]

Associated Irreducible Representation

\[ \tau_1 \]

\[ \tau_2 \]

\[ \tau_3 \]

\[ \tau_4 \]
$$\varepsilon = (AA+AC) \quad 2iAE \quad i(AB+AD) \quad \sqrt{2}r^*r_{AH} \quad \sqrt{2}i^*r_{AH} \quad -2n^*AL \quad -\sqrt{2}AM \quad -\sqrt{2}AO$$

$$(-AQ+AR) \quad -2AT \quad \sqrt{2}i^*AU \quad \sqrt{2}tAU \quad -2nAX \quad i\sqrt{2}AY \quad i\sqrt{2}AZ$$

$$(BA+BB) \quad \sqrt{2}q^*BD \quad i\sqrt{2}qBD \quad -2nBH \quad -i\sqrt{2}BI \quad -i\sqrt{2}BK$$

$$-BM \quad i*v_{BN} \quad -\sqrt{2}wBD \quad xBP \quad yBQ$$

$$-BM \quad -\sqrt{2}w^*BO \quad ix*BP \quad iy*BQ$$

$$-CC \quad \sqrt{2}nCD \quad -\sqrt{2}nCE$$

$$-CF \quad CG$$

$$-CI$$
Degeneracy for Time-Reversal-Invariance

The program ACMI which has been used for group theoretical analysis of the cryolite structure is unable to apply time-reversal-invariance restrictions in deriving orthogonal lattice modes. It is therefore necessary to demonstrate that time-reversal-invariance has no effect on the results.

Maradudin and Vosco give formulae for testing for time-reversal-degeneracy. The possibility of such degeneracy arises for space group representations with wavevector $\mathbf{k}$ only if the point group, $G_0$, of the crystal contains an element, $S_-$, such that

$$S_-\mathbf{k} = -\mathbf{k} + 2\pi \mathbf{g}$$

(C.1)

where $\mathbf{g}$ is an inverse lattice vector for the crystal space group. The criterion ($P$) for degeneracy then assumes one of two forms:

a) when $S_-$ belongs to $G_0(\mathbf{k})$, the point group of $\mathbf{k}$, the criterion is written

$$P = \sum_{\mathbf{R}} \exp[-i\pi (\mathbf{b} + R^{-1} \mathbf{b}) \cdot \mathbf{v}(\mathbf{R})] \chi^{(S)}(\pi \mathbf{b}; R^2)$$

(C.2)

where $\mathbf{b} = \mathbf{k}/\pi$ (the vector $\mathbf{b}$ thus defined is an inverse lattice vector).
The summation is over all elements $\tilde{R}$ of $G_0(\tilde{k})$. The vector $\tilde{v}(R)$ is the fractional translation that belongs to the element $\{\tilde{R}\tilde{v}(R)\}$ of the crystal space group, while $\chi^{(S)}(\pi\tilde{b}; \tilde{R}^2)$ is the character, for the irreducible multiplier representation $\tau^{(S)}$ being tested, of the rotational element $\tilde{R}^2 = \tilde{R}\tilde{R}$.

b) when $\tilde{S}$ does not belong to $G_0(\tilde{k})$ the degeneracy criterion becomes

$$P = \sum_{\tilde{R}} \exp[-i(k+R^{-1}\tilde{A}_0^{-1}\tilde{k}) \cdot \tilde{v}(A_0 \tilde{R})] \chi^{(S)}(\tilde{k}; \tilde{A}_0^{-1}\tilde{R}_0 \tilde{R})$$

(C.3)

where $A_0$ is a rotational element belonging to the coset $\tilde{S}G_0(\tilde{k})$ and the other notation is as before.

In both cases $P$ can assume one of three values:

(i) $P = h$, where $h$ is the order of $G_0(\tilde{k})$. In this instance time-reversal-invariance does not lead to any new degeneracy.

(ii) $P = 0$.

(iii) $P = -h$. For these last two values of $P$ new degeneracy arises. The modes degenerate with those of representation $\tau^{(S)}$ belong to a representation $\bar{\tau}^{(S)}$ whose matrices are given by

$$\bar{\tau}^{(S)}(\pi\tilde{b}, R) = \exp[2\pi i\tilde{b} \cdot \tilde{v}(R)] \bar{\tau}^{(S)}(\pi\tilde{b}, \tilde{R})$$

(C.4)

when $\tilde{S}$ belongs to $G_0(\tilde{k})$, and

$$\bar{\tau}^{(S)}(\tilde{k}, R) = \exp[i((k+\tilde{A}_0^{-1}\tilde{k}) \cdot \tilde{v}(A_0^{-1} \tilde{R} \tilde{A}_0)$$

$$+ (k-R^{-1}\tilde{k}) \cdot \tilde{v}(A_0))] \bar{\tau}^{(S)}(\tilde{k}, \tilde{A}_0^{-1} \tilde{R}_0 \tilde{A}_0)$$

(C.5)

otherwise. The asterisks, as usual, indicate complex conjugation.
The representation \( \tilde{T}(S) \) is equivalent to \( T(S) \) when \( P = -h \) and inequivalent when \( P = 0 \).

We are interested in representations for the \( \Gamma, X, L \) and \( W \) vectors of space group \( O_\text{h}^5 \) and the \( \Gamma \) wavevector of \( D_{4h}^6 \). The point groups of all but the \( W \) wavevector contain the inversion element, and the relevant criterion, equation (C.2), becomes

\[
P = \sum \chi^{(S)}(\pi b; R^2) \quad (C.6)
\]

The exponential terms have vanished either because \( b = 0 \) (for the two \( \Gamma \) wavevectors) or because the vectors \( v(R) \) are null (\( O_\text{h}^5 \) being a symmorphic space group).

For the \( W \) wavevector of space group \( O_\text{h}^5 \) we can take \( A_0 = S_+ = \tilde{I} \), where \( \tilde{I} \) is the inversion element. Again, all vectors \( v(R) \) are null and equation (C.3) becomes

\[
P = \sum \chi^{(S)}(\pi \tilde{w}; \tilde{R} \tilde{R} \tilde{R} \tilde{R}) \quad (C.7)
\]

When these criteria were evaluated for the \( \Gamma, X, L \) and \( W \) wavevectors of \( O_\text{h}^5 \) and the \( \Gamma \) point of \( D_{4h}^6 \) it was found that in every case time-reversal-invariance did not give any extra degeneracy.
APPENDIX D

Preparation of Materials

D.1 General Preparative Methods

A comprehensive coverage of preparative methods is to be found in the series of books "Halides of the Transition Elements"\(^1\),\(^2\),\(^3\). Common methods are:

a) the interaction in the melt of a mixture of a trivalent metal salt with an alkali metal hydrogen difluoride or fluoride. The proportions of the components of the mixture may need to be carefully controlled to obtain the desired compound. The reactions are carried out either in a vacuum or in an atmosphere of hydrogen fluoride or an inert gas.

b) the action of fluorine, generally at a raised temperature, on an appropriate mixture of a trivalent metal salt and an alkali metal chloride.

The ammonium compounds are liable to decompose before melting, and hence preparation from solution must usually be resorted to. The following modification of published methods\(^4\) has been found to be a convenient and generally applicable method of preparation for this class of materials:

1. Prepare a hot (70-90°C) concentrated solution of ammonium fluoride in water in a plastic beaker.
2. Dissolve an appropriate quantity of a soluble salt of the trivalent metal in a minimum amount of water.
3. To this solution add sufficient aqueous ammonia solution to precipitate out the hydroxide. This usually appears as a gelatinous mass. Sufficient ammonia will give a persistent ammonia smell.
4. Boil in a fume cupboard till the ammonia odour disappears.

5. Remove from the heat and allow the suspension to settle. Decant part of the liquid and test the decanted portion with universal indicator. It is usually about pH6. If it is still alkaline continue the boiling and repeat the test.

6. Add the precipitate a small amount at a time to the hot ammonium fluoride solution, stirring the solution continually during this process. The ammonium hexa-fluorometallate normally appears in a finely suspended form which is easily distinguishable in appearance from the gelatinous hydroxide.

7. Filter the hot solution into another plastic beaker using a plastic funnel.

8. Open out the filter paper and leave the precipitate to dry.

N.B. Heating may cause decomposition.

Comments:

1. Ammonium fluoride attacks glass; hence the use of plastic equipment.

2. The amount of ammonium fluoride required to ensure a pure product can be determined from tables in the cases of ammonium fluoroaluminate\textsuperscript{119}, gallate\textsuperscript{133} and indate\textsuperscript{42}. For other compounds one must make a guess and add a large excess for safety.

3. There is conflicting evidence in the literature as to whether or not it is possible to obtain (NH\textsubscript{4})\textsubscript{3}FeF\textsubscript{6} from aqueous solution. Cox and Sharpe\textsuperscript{36} maintained that water of crystallisation invariably replaces the fluorine ions in part, so that compounds of the form (NH\textsubscript{4})\textsubscript{3-x}FeF\textsubscript{6-x}xH\textsubscript{2}O...
are obtained. The best they could achieve was $x=0.4$. Consequently Haendler et al.\cite{57} have devised a method of synthesising ammonium fluorometallates from methanol solution. Nevertheless, the latest X-ray data for $(\text{NH}_4)_3\text{FeF}_6$\cite{132}, quoted in the ASTM Powder Diffraction Files, are for a compound prepared from ammonium fluoride, aqueous ferric chloride and hydrofluoric acid. For the present work this compound has been obtained ready made from K & K Laboratories Inc., Plainview, New York, and checked not only against its X-ray pattern but also against its infrared spectrum. The latter would be expected to show anomalies, particularly in the M-F stretching region, if significant amounts of water were present.

4. It is recommended that for $(\text{NH}_4)_3\text{VF}_6$ steps be taken to dry the material promptly, as reduction of the $V^{3+}$ ion (green) to $V^{2+}$ (blue) took place if the material was left long in solution before filtering. There is an alternative method available of preparing $(\text{NH}_4)_3\text{VF}_6$ from a melt of ammonium hydrogen fluoride, $\text{NH}_4\text{HF}_2$, and vanadium oxide, $\text{V}_2\text{O}_3$.

D.2 Crystal Growth

There are only a few cases in the literature of cryolite crystal growth from the melt. Garton and Wanklyn\cite{50} have obtained crystals of $\text{K}_3\text{CrF}_6$ and $\text{K}_3\text{AlF}_6$ with volumes of the order of $3 \text{ mm}^3$ by flux growth. The $\text{K}_3\text{MoF}_6$ crystals of Toth et al.\cite{141} appear to have been only large enough for X-ray investigation. Bucher et al.\cite{18} have been able to grow crystals with the elpasolite structure by a zone refining technique. The cubic cryolites and the elpasolites differ
only in the way in which the tetrahedral and octahedral sites for positive monovalent ions are filled; for the cryolites both types of site are filled by the same kind of ion, while for the elpasolite each site type has a different ion species (thus elpasolite itself is $K_2NaAlF_6$, c.f. the cryolites $K_3AlF_6$ and $Na_3AlF_6$). This similarity of structure suggests that the zone refining technique may be suitable for growing cryolite crystals also.

The ammonium cryolite crystals will generally have to be grown from solution. Two difficulties confront us:

1) Ammonium cryolites are relatively insoluble in water.
2) An excess of ammonium fluoride is required in solution to ensure that the correct compounds crystallise. This is evident from the solubility data of references 42, 119 and 133. Such an excess must render the ammonium cryolite less soluble and make crystal growth the more difficult.

Some small octahedral ammonium fluoroaluminate crystals obtained by evaporation of a warm solution were available, but these were not large enough to be used for infrared and Raman spectroscopy. No success was obtained from attempting to grow larger crystals from these by slow evaporation. A paper by Manoharan and Rogers later discovered discusses a method by which a $3 \times 2 \times 2$ mm crystal of $(NH_4)_3AlF_6$ containing approximately 0.5% $(NH_4)_3VOF_5$ was obtained. The means was slow evaporation from concentrated hydrofluoric acid solution (48% HF).
APPENDIX E

Microdensitometer Control Program

/ CONTROLS DATA ACQUISITION.
/ OUTPUTS DATA CONTINUALLY.
/ OPERATES ON TIMESHARE ONLY.
/ IS CALLED BY COMMAND IDP.
/ AFTER STARTING IT COUNTS THE NO. OF MOTOR STEPS IN
/ FIRST 4 SECS, USING THIS AS THE FREQUENCY RATE. THE RATE
/ AT WHICH DATA IS OUTPUTED.
/ IF NO DATA IS RECEIVED FOR SIXTY SECS, THE PREVIOUS DATA
/ RECORD IS ENDED WITH TEN INCHES OF LEADER/TRAILER TAPE.
/ READY FOR THE NEXT RECORD.

/ TIMESHARE DEFINITIONS.
LOTCH=23
LCRLF=20
LCMND=3
.ONE SEC CLOCK.*

0034 0000 CLOCX, 0
/ COMMAND TABLE *
 0776 0420 0420 / !DP
0777 6000 DENSITY
/ CONTROL AND OUTPUT: *
 5000

6000 0000 DENSITY, 0
6001 7200 CLA
6002 1364 TAD M72
6003 3373 DCA END
6004 3368 DCA COUNT
6005 6354 6354 /STEP AND WAIT FOR MOTOR
6006 4277 JMS WAITING
6007 3034 DCA CLOCK
6010 6354 RATING, 6354 /COUNT NO OF STEPS IN 1ST 4 SECS
6011 2360 1SZ COUNT
6012 4277 JMS WAITING
6013 1034 TAD CLOCK
6014 1361 TAD M4
6015 7710 SPA CLA
6016 5218 JMP RATING
6017 1360 TAD COUNT /IF STEPPING AT FULL SPEED (COUNT
6020 1362 TAD M14 /15 > 14) LEAVE RATE UNALTERED.
6021 7780 SNA CLA
6022 5225 JMP .+3
6023 1360 TAD COUNT
6024 3366 DCA RATE
6025 1365 TAD M100 /PUNCH UP TEN INCHES BLNK TAPE
6026 3367 DCA CHEC
6027 4463 JMS 1 LOTCH
6030 2367 1SZ CHEC
6031 5227 JMP .-2
6032 1366 TAD RATE /1ST DATUM IS RATE
6033 3370 DCA DATA
6034 7048 CMA
6035 3367 DCA CHEC
6036 6354 CONTROL, 6354
6037 3034 DCA CLOCK
6040 1378 TAD DATA /IF DATA = 0, REPLACE WITH 1.
6041 7450 SNA
6042 7291 CLA IAC
6043 2367 1SZ CHEC /PUNCH DATA AT END OF 'RATE' STEPS
6044 5256 JMP WAIT
6045 4463 JMS 1 LOTCH
6046 2373 1SZ END /AFTER 72 CHARACTERS DO CANVAGE
6047 5233 JMP .+4
6050 4400 JMS 1 LCRLF
6051 1364 TAD M72
6052 3373 DCA END
6053 1366 TAD RATE
6054 7041 CIA
6855  3267  DCA CHEC
6856  4277  WAIT, JMS WAITING
6857  1834  TAD CLOCK /IF NO STEPS IN LAST 60 SECS,
6858  1363  TAD M60 /BEGIN NEW RECORD,
6859  7700  SMA CLA
6860  5201  JMP DENS TY+1 /TURN OFF INTERRUPT FACILITY
6861  6062  TDF /AND PREPARE AND READ A/D CONV TR.
6864  6532  6532
6865  6531  6531
6866  5265  JMP -1
6867  5334  6334
6868  6061  10N
6871  7912  RTR /ADJUST AND SCALE DATA
6872  7012  RTR
6873  1371  TAD FIDDLE
6874  7041  CIA
6875  3379  DCA DATA
6876  5236  JMP CTRO L
6877  0000  WAITING, 0
6100  4403  JMS I LC MND /SAFETY EXIT
6101  6351  6351 /HAS MOTOR FINISHED STEPPING?
6102  5300  JMP -2 /YES, WAIT UNTIL ABOUT 36 MS IS
6103  1372  TAD DELAY /UP BEFORE TRYING TO TURN FLAG OFF
6104  7001  IAC
6105  7510  SPA
6106  5304  JMP -2
6107  6352  6352
6110  5677  JMP I WAITING /VARIABLES.
6111  *6160
6116  0000  COUNT, 0
6117  7774  MA, -4
6118  7762  M14, -16
6119  7704  M60, -74
6120  7670  M72, -119
6121  7634  M100, -144
6122  0001  RATE, 1
6123  0000  CHEC, 0
6124  0000  DATA, 0
6125  0000  FIDDLE, 200
6126  4002  DELAY, 4000
6127  0000  END, 0

CHEC  6167
CLOCK  0034
CTRO L  6036
COUNT  6160
DATA  6170
DELAY  6172
DENS TY  6000
END  6173
FIDDLE  6171
LC MND  0003
LC HL F  0020
LOTCH  0023
M100  6165
M14  6162
M4  6161
M60  6163
M72  6164
RATE  6166
RATING  6010
WAIT  6056
WAITING  6077