THE ZEEMAN-RAMAN AND -INFRARED
SPECTRA OF TRANSITION-METAL IONS
IN SINGLE CRYSTALS

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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1977
To

My parents
ABSTRACT

The results of Raman and infrared investigations of the spectra of Co$^{2+}$ ions in CsCdCl$_3$ and CsMgCl$_3$ are reported. These ions substitute for the divalent cations in these double chlorides and experience a trigonal crystal field which splits the four spin-orbit levels of the $^4T_{1g}$($^4F$) ground manifold into six Kramers doublets with energies lying within 0 - 1400 cm$^{-1}$. Electronic transitions within this ground term have been observed and are satisfactorily fitted using the complete 3d$^7$ configuration crystal field matrices. Zeeman-Raman and -infrared experiments on CsCdCl$_3$:Co and CsMgCl$_3$:Co have been performed and yield g values for the excited electronic states. These excited state g values are also calculated using crystal field theory and are in good agreement with those obtained experimentally. Selection rules governing the occurrence of the electronic Zeeman transitions are derived for the appropriate cobalt ion site symmetries and are in agreement with the results. The Raman and infrared spectra of Co$^{2+}$ ions in CsCoCl$_3$ and KCdCl$_3$ are measured and are presented, together with the results of optical studies of Co$^{2+}$ ions in CsCdCl$_3$. A preliminary investigation of the electronic transitions of Fe$^{2+}$ ions in CdCl$_2$-type crystals has been carried out using Raman and infrared spectroscopy. The spectral data, together with a tentative analysis, are presented.
ACKNOWLEDGMENTS

Many fellow postgraduate colleagues and members of the academic and technical staff of the Physics Department have assisted in the preparation and presentation of this thesis. I am indebted to all of them, but more especially to the following people.

I wish to express my gratitude to Professors A.G. McLellan, B.G. Wybourne and W.L. Jones for accepting me as a postgraduate student and the tax-payers of New Zealand for providing me with a Teaching Fellowship.

I greatly appreciate the help of my amiable supervisor, Dr. Glynn D. Jones. His unflagging optimism, enthusiasm and morale-boosting confidence have carried me through this research project. Thanks are due to Dr. Rod W. Syme for helpful discussions, useful suggestions and his supervision during Dr. Jones' absence. Sincere thanks go to my old mate Chris Tomblin for experimental assistance and his companionship.

My acknowledgment is extended to the following:

Messrs. Bob Tyree and Terry Rowe for technical assistance and advice;
Tom Walker for his prompt supply of cryogenic refrigerants;
Ross Ritchie for growing some of the crystals;
Laurie Hunter for his high quality photographic work;
Ms Philippa MacLean for tracing the diagrams; and
Mrs. Mary Boswell for the neat typing of this thesis.

My parents are a constant inspiration to me. I am deeply indebted to them for this, their understanding, moral and financial support.

Last, but not least, I am grateful to Bill and Jean Orchard for providing me with a home from home.

Meng Hau Kuok

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The principal part of this research work involves the investigation of the electronic spectra of the cobaltous ions present as impurities in single crystals of CsCdCl$_3$ and CsMgCl$_3$. The divalent cobalt ions substitute for the divalent cations in these double chlorides and experience a crystalline field of predominantly cubic symmetry with a slight trigonal distortion.

The electronic transitions of interest are between the spin-orbit and trigonal crystal field states of the $^4T_{1g}$ cubic field ground term. They are readily observed by Raman scattering and infrared absorption spectroscopy. Analyses of the spectra recorded were made using crystal field theory. The energy levels of the cobalt ion were calculated using all 120 energy states of the 3d$^7$ configuration.

The CsMgCl$_3$:Co and CsCdCl$_3$:Co systems differ in several respects. For the centrosymmetric CsMgCl$_3$:Co, electric dipole transitions within the d$^7$ configuration are strictly forbidden by Laporte's rule. Electronic transitions in CsMgCl$_3$:Co however were found to occur through the magnetic dipole mechanism. For CsCdCl$_3$, the majority of cobalt ions substitute for the C$_{3v}$ cadmium ion sites. These sites lack inversion symmetry so the electronic transitions observed are electric dipole allowed and are thus more intense than those of CsMgCl$_3$:Co.

The goal of this work was to measure the Zeeman effect on the cobalt spectra. There are several reasons for this. Firstly only a magnetic field can lift the Kramer's degeneracy of the cobalt ion energy levels. Secondly Zeeman studies could test the adequacy or otherwise of the crystal field theory for interpreting the spectra obtained. Finally such studies could help identify the many vibronic absorptions encountered in the infrared spectra. The lines of the spectra of cobalt ions in CsMgCl$_3$ and CsCdCl$_3$ are sufficiently intense and narrow for
Zeeman-Raman and -infrared investigations to be feasible. No such investigation on any transition-metal ion has been reported in the literature.

An outline of the structure of this thesis is as follows.

Chapter II contains a description of the structures of the crystals examined. An account of the theory of single cobaltous ion spectra is given for the CsMgCl$_3$ and CsCdCl$_3$ systems. This includes the Hamiltonian interactions appropriate for the cobaltous ion and their associated parameters.

The experimental techniques and instruments employed for the infrared- and optical-absorption and Raman scattering experiments are documented in Chapter III. A section on the growth, orientation and preparation of the crystals is also included.

Chapters IV to VII deal with the zero-field and Zeeman-Raman and infrared investigations on the CsMgCl$_3$:Co and CsCdCl$_3$:Co systems and constitute the major portion of this thesis. The recorded spectra are presented, discussed and analysed using the complete 3d$^7$ crystal field analysis of Chapter II. Magnetic splitting factors for the low-lying energy levels of the cobalt ion are determined from the Zeeman spectra.

A preliminary examination of CsCoCl$_3$ and cobalt-doped KCdCl$_3$ using Raman scattering and infrared absorption spectroscopy was performed. The spectral data are presented in Chapter VIII. Also included in this chapter are experimental results of optical absorption studies on CsCdCl$_3$:Co.

Preliminary Raman and infrared studies on the electronic spectra of the ferrous ion have initiated a new field of research in the department. CdBr$_2$ and CdCl$_2$ crystals are found to be suitable hosts for this ion. Intraconfigurational electronic transitions are expected to be only magnetic dipole allowed for the centrosymmetric CdCl$_2$-type system. However electric dipole electronic transitions were observed
for the ferrous-doped CdBr₂ in the infrared region thus inferring the manifestation of a Jahn-Teller distortion. Chapter IX is concerned with the Raman and infrared spectra of the ferrous ion.

Finally Chapter X contains an overall summary and conclusion of this thesis work undertaken, together with suggestions for further research.
2.1 CRYSTAL STRUCTURE

2.1.1 CsCdCl₃

CsCdCl₃ (1) crystallizes in the hexagonal space group \( \mathcal{D}_{6h}^4 \). There are two crystallographically distinct types of cadmium ions occupying sites of \( \mathcal{D}_{3d} \) and \( \mathcal{C}_{3v} \) symmetries and these are labelled \( \text{Cd}(1) \) and \( \text{Cd}(2) \) respectively. The unit cell shown in Fig.2-1 has six molecules which include two \( \text{Cd}(1) \) and four \( \text{Cd}(2) \) ions. In both sites the cadmium ions are surrounded by distorted octahedra of chloride ions. The chloride ions \( \text{Cl}(2) \) surrounding the \( \text{Cd}(1) \) ions form nearly perfect octahedra whereas the octahedra of chloride ions, \( \text{Cl}(1) \) and \( \text{Cl}(2) \), surrounding the \( \text{Cd}(2) \) ions are more distorted. The angle subtended at the \( \text{Cd}(2) \) ion by the \( \text{Cl}(2) \) ion and the threefold axis is \( 56.45^\circ \) while the corresponding angle for the \( \text{Cl}(1) \) ion is \( 50.86^\circ \). As these angles are not too different and as the \( \text{Cd}(2) \)–\( \text{Cl}(2) \) distance (2.588Å) is about equal to the \( \text{Cd}(2) \)–\( \text{Cl}(1) \) distance (2.639Å), the \( \mathcal{C}_{3v} \) symmetry of the \( \text{Cd}(2) \) ion site is approximately \( \mathcal{D}_{3d} \).

Two octahedra containing \( \text{Cd}(2) \) ions share a face forming a \( [\text{Cd}_2\text{Cl}_9]^\text{5-} \) unit which then shares corners with six different octahedra containing \( \text{Cd}(1) \) ions.

2.1.2 CsMgCl₃ and CsCoCl₃

Both CsMgCl₃ (2) and CsCoCl₃ (3) are isostructural with the hexagonal CsNiCl₃ which belongs to the space group \( \mathcal{D}_{6h}^4 \) with two formula units per unit cell. The divalent cations occupy trigonal \( \mathcal{D}_{3d} \) sites, the coordination spheres about them being octahedra of chloride ions. These octahedra share faces to form infinite parallel linear chains directed along the crystallographic \( c \) axis. Within a chain, pairs of divalent cations are bridged by three chloride ions. Fig.2-2 shows a perspective view of the unit cell content of these two compounds.
Fig. 2-1: Unit cell structure of the CsCdCl₃ crystal.
Fig. 2-2: CsMgCl$_3$-type structure
2.1.3 KCdCl₃

KCdCl₃ is isomorphous with NH₄CdCl₃ which is orthorhombic with the space group D₁₆²h. Each cadmium ion is located at a monoclinic Cs site and is surrounded by a distorted octahedron of chloride ions. This site symmetry can be approximately described by the C₂ḥ point group. The unit cell comprises four KCdCl₃ molecules.

2.1.4 CdCl₂ and CdBr₂

CdBr₂ has the CdCl₂-type structure which has the D₃d space group with one molecule unit per unit cell. The cadmium ion in CdCl₂ is located in the centre of a distorted octahedron of chloride ions and has a trigonal D₃d site symmetry. The CdCl₂ crystal comprises layers of chloride ions which are nearly cubic close packed, with cadmium ions sandwiched between alternative chloride-ion layers which are perpendicular to the crystal c axis.

2.2 THE THEORY OF SINGLE COBALTIOUS ION SPECTRA

2.2.1 Introduction

In this work the double chlorides CsMgCl₃, CsCdCl₃, CsCoCl₃ and KCdCl₃ were examined. With the exception of KCdCl₃, the divalent cations of these crystals occupy sites of trigonal symmetry. The cobalt impurity ions substitute for the divalent cations in CsMgCl₃ and CsCdCl₃. Each Co²⁺ ion is surrounded by six chloride ligands forming a distorted octahedron with the degree of distortion varying from crystal to crystal. The Co²⁺ ion has a lowest-energy electronic configuration [Ar]3d⁷ which possesses 120 states.

In a crystalline environment the appropriate Hamiltonian for a Co²⁺ ion is

\[ \mathcal{H} = - \sum_i \left( \frac{\hbar^2}{2m} \nabla_i^2 + \frac{Ze^2}{r_i} \right) + \frac{1}{2} \sum_{i \neq j} \frac{\mathbf{e}_i^2}{r_{ij}} + \sum_i \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i + V \]  

(2.1)

where the summations are over all the electrons. The first term
represents the central field potential; the second term, the
interelectronic repulsion and the third term, the spin-orbit coupling.
The final term V represents the potential provided by the ion's ligands
and may be written as

$$V = V_c + V_T \tag{2.2}$$

where $V_c$ and $V_T$ are the cubic and lower-symmetry crystal field
potentials.

Application of an external magnetic field $H$ adds an extra interaction
term to the Hamiltonian (the Zeeman term) given by

$$\mathcal{H}_z = \beta \sum_i (S_i + 2S_i) \cdot \mathbf{H} = \beta (L+2S) \cdot \mathbf{H} \tag{2.3}$$

where $\beta = \frac{\epsilon h}{2mc}$ is the Bohr magneton.

The coulombic interaction among the seven d electrons gives rise
to eight free-ion L-S multiplets $^4F, ^4P, ^2G, ^2P, 2^2D, ^2H$ and $^2P$ of
which the lowest energy one is $^4F$. This $^4F$ multiplet has sevenfold
orbital and fourfold spin degeneracy. For the ion in a crystal field
the degeneracy of all the multiplets are partially lifted to give terms
which may be labelled by the irreducible representations (irreps) of the
crystal field symmetry group. In a field of cubic symmetry, the Co$^{2+}$
free-ion terms are split as follows:

$$^4F + ^4T_{1g} + ^4T_{2g} + ^4A_{2g}$$

$$^4P + ^4T_{1g}$$

$$^2G + ^2A_{1g} + ^2E_g + ^2T_{1g} + ^2T_{2g} \tag{2.4}$$

$$^2D + ^2E_g + ^2T_{2g}$$

$$^2H + ^2E_g + 2^2T_{1g} + 2^2T_{2g}$$

For the 3$d^7$ configuration all these terms are even under inversion
symmetry and this is signified by the subscript $g$.

The ground term $^4T_{1g}(^4F)$ of the cubic field is split by the spin-orbit
interaction into levels labelled by the irreps of the cubic double group. They are derived from the direct product of $T_{1g}$ and the irrep $\Gamma_8$ of the spin $3/2$ function associated with the $^4T_{1g}$ term. The direct product yields $\Gamma_6^+, \Gamma_8^+, \Gamma_9^+$ and $\Gamma_7^+$ states listed in order of increasing energy.

For crystals having $D_{3d}$ or $C_{3v}$ trigonal symmetry these states are further split by the trigonal crystal field into levels $\gamma_4^+$ and $\gamma_5^+ + \gamma_6^+$ described by the irreps of the trigonal double group. In the case of the $C_{3v}$ symmetry, which lacks inversion symmetry, these levels have no parity. The $\gamma_5^+$ and $\gamma_6^+$ irreps are complex conjugates and degenerate in the absence of a magnetic field and are henceforth referred to as $\gamma_{5,6}^+$. Each $\Gamma_8^+$ quartet gives rise to the $\gamma_4^+$ and $\gamma_{5,6}^+$ states while the $\Gamma_6^+$ and $\Gamma_7^+$ each becomes a $\gamma_4^+$ state.

All these trigonal crystal field states are Kramers doublets and the application of a magnetic field will remove this degeneracy. Zeeman investigation on cobalt ions in the $D_{3d}$ sites of CsMgCl$_3$ and the $C_{3v}$ sites of CsCdCl$_3$ (Sec.4.4) has been carried out in this work. The magnetic field reduces these $D_{3d}$ and $C_{3v}$ symmetries with the resulting symmetries being dependent on its orientation with respect to the crystal axes. A field directed along the $c$ axis will lower these symmetries to $C_{3i}$ and $C_3$ respectively. In the case of a field applied perpendicular to the $c$ axis, different symmetries result depending whether or not it is directed along a twofold axis. (The Co(2) ion site symmetry in CsCdCl$_3$ is approximately $D_{3d}$ (Sec.2.1) and a pseudo twofold axis is implied for the case of this ion.) For the field along such an axis the $D_{3d}$ and $C_{3v}$ site symmetries of the cobalt ions reduce to $C_{2h}$ and $C_2'$ and for arbitrary orientations the respective symmetries are $C_1$ and $C_1$.

The Zeeman levels can be labelled by the irreps of the appropriate point groups and can be derived by use of Koster's compatibility tables (8). Fig. 2-3 shows the energy level scheme of the cobalt ion for the successive application of the various interactions of equations (2.1) and (2.3). The assignment for the Zeeman levels shown in the figure is purely schematic.
The states labelled by symmetry groups without inversion symmetry have no parity labels.

**Fig. 2-3:** Schematic energy-level diagram of the Co\(^{2+}\) ion.
Transitions between these levels can occur in several ways, e.g., by infrared absorption and Raman scattering. The $x,y$ and $z$ components of the electric dipole and magnetic dipole operators for absorption of infrared radiation transform like the displacement vector $\mathbf{r}_i = x_i, y_i, z_i$ and the rotation operator respectively. The symmetric Raman polarizability tensor $\alpha_{ij}^\text{R}(i,j = x,y,z)$ transforms like the $\mathbf{r}_i \cdot \mathbf{r}_j (r_i, r_j = xy, xz, yz, x^2, y^2, z^2)$ operator. These operators transform as particular irreps of the appropriate cobalt ion site symmetry. Infrared absorption corresponding to a transition between an initial state $i$ and a final state $f$ is allowed if the direct product $\Gamma_i \times \Gamma_f$ contains $\Gamma_f$. Here $\Gamma_i$, $\Gamma_f$ and $\Gamma_o$ are respectively the irreps of the initial and final states and either the electric dipole or magnetic dipole operator in the appropriate symmetries.

A transition from the state $i$ to the state $f$ can give rise to a Raman line in the $(ij)$ polarization spectrum (Sec.4.1) if $\Gamma_f$ occurs in the reduction of $\Gamma_o \times \Gamma_i$ where $\Gamma_o$ is the irrep of $\alpha_{ij}^\text{R}$.

2.2.2. The Hamiltonian interaction terms and their associated parameters.

For an analysis of the Raman and infrared data, the strong-field energy matrices calculated by Johnstone (9) for the case of Co$^{2+}$ ions in CdCl$_2$-type crystals were used. In this coupling scheme, the cubic field which is first considered, splits the d orbitals into $e_g$ and $t_{2g}$ orbitals. The seven d electrons are placed into these orbitals to give rise to configurations $t_{2g}^p e_g^q$ where $p + q = 7$. The energy levels for a 3$d^7$ configuration are complementary to those for a 3$d^3$ configuration because of the equivalence of three electrons with three holes in a d$^n$ configuration. In these two configurations, the crystal field and spin-orbit interactions have opposite signs.

The interelectronic repulsion term of equation (2.1) will split the 3$d^3$(3$d^7$) configuration into a number of terms labelled by the cubic field irreps $\chi_r$. Such terms, designated by $2s+1\chi_r$ arise from the four
possible configurations $t_m^m e_{eg}^n (m + n = 3)$ for the $3d^3$ configuration.

The effects of spin-orbit coupling and the trigonal crystal field are then calculated for these terms. The final wavefunctions maybe written as

$$|t_m^m e_{eg}^n, \alpha, 2s + 1 \Gamma_1 \rangle, \lambda\rangle$$

where $\lambda$ identifies the basis functions of the trigonal double group and $\alpha$ is an additional label to distinguish wavefunctions when there is more than one with the same group theoretical labels in any configuration.

Here $\alpha$ is taken as the irrep of states of the parent $t_m^m e_{eg}^{n-1}$ configuration.

All the matrix elements of the cubic field potential for these strong-field wavefunctions are necessarily diagonal and can be expressed in terms of the single parameter $Dq$ as follows

$$<t_m^m e_{eg}^n | V | t_m^m e_{eg}^n > = n 10 Dq$$  \hspace{1cm} (2.5)

The energy matrices of the electrostatic and spin-orbit interactions have been calculated in the strong-field scheme for the $3d^3$ configuration by Sugano (10) and Schroeder (11) respectively. The electrostatic interaction has non-zero matrix elements only between levels belonging to the same $2s + 1 \chi_r$ terms and can be expressed in terms of two Racah parameters $B$ and $C$. The spin-orbit interaction $V(1T_1)$ is characterized by two parameters $\zeta$ and $\zeta'$ defined in terms of the one-electron reduced matrix elements of $V(1T_1)$ as follows:

$$3i\zeta = <t_2 || V(1T_1) || t_2 >$$

$$-3\sqrt{2}i\zeta' = <t_2 || V(1T_1) || e >$$  \hspace{1cm} (2.6)

The trigonal field matrices have been calculated by Johnstone and Zdansky (9) using the strong-field approach. With the trigonal (z) axis directed along the [111] direction of the crystal the potential due to a field of $D_{3d}$ symmetry can be expressed by (12)
\[ v_T = A_2 \{ xy + yz + xz \} + A_4 \{ yz(r^2 - 7x^2) + xz(r^2 - 7y^2) \]  
\[ + xy(r^2 - 7z^2) \} . \]  
(2.7)

The above crystal field transforms as the cubic representation \( T_2 \) and has one-electron matrix elements which are nonvanishing only between two \( t_{2g} \) and between the \( t_{2g} \) and \( e_g \) orbitals. The trigonal field can be expressed in terms of the one-electron reduced matrix elements as follows:

\[ v = \sqrt{2} < t_2 \| v(T_2) \| t_2 > \]  
(2.8)

\[ v' = \frac{1}{\sqrt{6}} < t_2 \| v(T_2) \| e > \]  

The effect of a magnetic field on the cobalt ion levels can be evaluated from the matrix elements of the Zeeman operator \( kL + 2S \) between the strong-field wavefunctions, where \( k \) is an orbital reduction factor. This operator transforms as the cubic \( T_1 \) representation of the octahedral group and its matrix elements are characterized by two orbital reduction parameters \( K \) and \( K' \) defined as

\[ \sqrt{6} i K = < t_2 \| H_z^{(T_1)} \| t_2 > \]  
(2.9)

\[ -2\sqrt{3} i K' = < t_2 \| H_z^{(T_1)} \| e > \]  

where \( < t_2 \| H_z^{(T_1)} \| t_2 > \) and \( < t_2 \| H_z^{(T_1)} \| e > \) are the one-electron reduced matrix elements of the Zeeman interaction \( H_z^{(T_1)} \). These parameters are related to the spin-orbit parameters \( \zeta \) and \( \zeta' \) by

\[ K = \zeta / \zeta_o \quad \text{and} \quad K' = \zeta' / \zeta_o \]  
(2.10)

where \( \zeta_o \) is the free-ion spin-orbit coupling parameter.
CHAPTER III
EXPERIMENTAL TECHNIQUES

3.1 THE CRYSTALS

3.1.1 Crystal Growth

All crystals examined were prepared from high-quality anhydrous powders. These powders were dehydrated in a vacuum oven, maintained at 100°C, over a period of several days.

Single crystals were grown from the melt using the well established technique described by Rollerson. In this the starting material, placed in a quartz tube, is purified by gradual heating of the charge to 50°C above its melting point under a stream of dry hydrogen-chloride or -bromide gas as appropriate. This removes traces of hydroxides and moisture. An ampoule is then lowered through a Bridgman tubular furnace with a temperature gradient of 50°C per cm. The lowering rate for most cases is 1mm per hour except for CsCoCl₃ where it is 0.5mm per hour.

Not all of the crystals were refined using commercially available hydrogen chloride gas from cylinders. K CdCl₃ grew better from powders purified by hydrogen chloride gas generated by the action of concentrated sulphuric acid on concentrated hydrochloric acid. Phosgene gas was used to purify CsCoCl₃ and some of the CsCdCl₃ starting materials as suggested by Trutia and Lebl. Any poisonous phosgene gas in excess of the safety level could be detected by a change in colour from yellow to deep orange of the phosgene indicator papers used. These were prepared by soaking filter papers in an alcoholic solution containing 10% mixture of equal parts of p-dimethyl aminobenzaldehyde and diphenylamine and then dried.

Crystal boules of CsCdCl₃, CsMgCl₃ and K CdCl₃ obtained in this
manner are optically clear while CsCoCl$_3$ has a green blue colour. Cobalt-doped crystals grown are blue and transparent. The CsCdCl$_3$:Co crystals show an appreciable concentration gradient with the portions of the crystals nearest the tapered tip having the least cobalt ion concentration. Attempts to determine the cobalt concentration of these crystals by spectrophotometric means were thwarted by their insolubility in pure and acidified water. The KCdCl$_3$:Co crystals suffer from cracks. The Fe$^{2+}$ doped CdCl$_2$ and CdBr$_2$ crystals appear brownish.

3.1.2 Orientation and polishing of crystal specimens.

Except for CsCdCl$_3$ all the crystals examined were hygroscopic and were stored and handled in a glove-box maintained at 15% humidity. CsCdCl$_3$ exhibits no cleavage and the direction of its crystallographic axis was determined with the aid of a polarizing microscope. The microscope's objective lens of magnification 40X was used in conjunction with an ocular of magnification 10X. Orientation of CsCdCl$_3$ was done as follows. A chunk of crystal, placed on the microscope stage, was rotated until an isogyre cross appeared within the field of view. The final alignment was achieved when the centre of the isogyre cross did not shift from the centre of the cross hairs during rotation of the stage. The crystal axis was then parallel to the axis of the microscope. The specimen was then ground to required size and thickness with silicon carbide powder. A final polish using a tin oxide-methanol paste on a rotating baize-covered lap gave a high-lustre finish.

The $c$ axes of CsMgCl$_3$ and CsCoCl$_3$ lie in their [1120] cleavage planes. This greatly facilitates polarization infrared experiments. However for axial infrared and Zeeman-Raman ($H\parallel c$) experiments, the direction of the $c$ axis had to be located. The required direction
is parallel to the intersection of any two cleavage planes. This fact however cannot be utilized for small crystals. Alternatively
the Beckman spectrophotometer (Sec. 3.3.1) can be employed in locating the crystal axis. This was done by rotating a polarizer until the π or σ spectrum of a cleaved sample was obtained and then noting the corresponding orientations of both the polarizer and the sample. For the π and σ spectra the c axis is respectively parallel and perpendicular to the polarizer's axis.

\[ \text{CdBr}_2 \text{ and CdCl}_2 \text{ cleave along planes perpendicular to their } c \text{ axes. These crystals together with CsMgCl}_3 \text{ and CsCoCl}_3 \text{ were polished in the glove-box using emery paper. The procedure which involved mounting of the crystals onto a polishing-jig is described in detail by Johnstone}^{(9)}. \]

Of all the crystals studied, K\text{CdCl}_3 proved to be the most difficult to orientate as it is hygroscopic and has no obvious cleavage planes. Determination of its c axis with a polarizing microscope was not feasible as the microscope could not fit into the glove-box. Hence no polarization studies of this crystal was attempted.

3.2 RAMAN MEASUREMENTS

3.2.1 Conventional Raman

A Spectra-Physics model 171 15-watt argon-ion laser served as the excitation source in the Raman scattering experiments. The laser has its light stabilized to an intensity fluctuation of less than 0.5%. Apart from the laser, the Raman system used is that set up by Lockwood \( ^{(17)} \) and Christie \( ^{(18)} \). A Jarrell-Ash model 25-103 one-metre double monochromator is used to disperse the scattered light and the spectrometer output is detected by an EMI 6255 SA photomultiplier which is thermoelectrically cooled to \(-25^\circ\text{C}\). Photon counting techniques
are used and the output pulses from the photomultiplier are amplified and height-discriminated by a pulse rate detector. A ratemeter then time-averages the resultant pulses to give a d.c. voltage proportional to the pulse rate received which is then displayed on a chart recorder.

The principal laser lines used were the 4765, 4880 and 5145 Å lines, the maximum power outputs of which are 3, 7 and 6W respectively. However power outputs of up to only 3W were required. Narrow band-interference filters were placed in the incident beam path to remove spurious plasma lines which are listed by Loader (19).

For polarization studies, a Spectra-Physics model 310 polarization rotator was attached to the front of the laser. The rotator can alter the plane of polarization of the incident beam to any desired angle. The scattered radiation was analysed using either a polaroid sheet or a Nicol prism. The latter has slightly better polarizing qualities while the former does not defocus the beam as much.

Spectra were recorded using the conventional right-angled scattering geometry in which the laser light is incident on the bottom face of the crystal and scattered light at 90° to this is collected from a vertical surface by the spectrometer optics. This arrangement however proved to be unsuitable for highly absorbing crystals such as CsCoCl₃. For these crystals the surface scattering technique provided an alternative method. In this method the laser light is incident on one face of the crystal at grazing angle while the scattered radiation off the same face is still observed at 90° to the incident beam.

Raman measurements at cryogenic temperatures were carried out with an Andonian optical dewar. The dewar body comprises an inner liquid helium reservoir, an outer liquid nitrogen jacket and a heat exchange space. Depending on the temperature required, the inner reservoir could either be filled with liquid-nitrogen or -helium. When the latter was used, the outer jacket was filled with liquid
nitrogen. The exchange space was then pressurized with nitrogen or helium gas as appropriate. At one atmospheric pressure these gases condensed to liquid at the bottom of the exchange space. Crystals were mounted onto a copper block attached to the bottom of this exchange space and were cooled by the condensed gas through thermal contact. A copper-constantan thermocouple attached to the copper block recorded a temperature of $15^\circ K$ when liquid helium was used. Owing to heating by the laser beam the crystal temperature was as high as $25^\circ K$.

Two different sample holders were made for the two scattering arrangements. For the conventional $90^\circ$ geometry, the sample holder used had a vertical face against which the crystals are clamped. Crystals used in this arrangement are required to have one horizontal and two parallel vertical faces. The sample was mounted with the bottom horizontal face receiving the laser beam, and one of the vertical faces facing the spectrometer's collection optics. These faces were either cleaved or polished as appropriate for the crystals studied.

A sample holder with a face inclined at $30^\circ$ was used in the surface scattering technique. Specimens attached onto this face were examined with the laser beam incident from below on a crystal surface and the light scattered horizontally off the same surface was analysed.

3.2.2 Zeeman-Raman

Zeeman-Raman measurements were obtained using a British Oxygen Company (B.O.C.) 6-tesla split-solenoid superconducting magnet. The field homogeneity is better than $1\%$ over a 15mm diameter spherical volume. The solenoid is mounted with its bore horizontal and four slots in its equatorial plane gave both vertical and horizontal access to its centre. These slots permitted the use of the $90^\circ$ scattering
geometry. The magnet was used in conjunction with a B.O.C. cryostat which has a liquid air vessel surrounding its inner helium reservoir (Fig.3-1). This cryostat together with the rest of the Raman system is pictorially depicted in Fig.3-2. The reservoir has sapphire windows and the outer vessel quartz windows. The solenoid, held by three support rods, was positioned so that its ports faced one pair of windows while its vertical slots faced a second pair set at right angles to that of the first.

A stainless steel rod with several recesses cut along its lower portion served as the sample holder. Several specimens were each glued onto a recess using GE 7031 varnish. The sample rod passed through the solenoid's horizontal slots and the specimen of interest was positioned at the centre of the solenoid.

Overnight cooling of the magnet assembly and cryostat was necessary to ensure efficient use of liquid helium. It was found that gradual cooling of CsMgCl₃ and CsCdCl₃ crystals was essential to prevent them from cracking. So these were also cooled overnight. This was done by closing the container and pressurizing it with pure helium gas which served a twofold purpose. It acted as a heat conducting medium as well as preventing the hygroscopic crystals from moisture contamination.

Thirty litres of liquid helium were expended for a typical Zeeman experiment giving a spectral run of about five hours. Problems with bubbling of the liquid helium causing fluctuating light intensity were resolved by pumping the liquid helium to its superfluid state (\(-2^0\)K). Once this was attained the magnet was energised using a B.O.C. model DPS 60/72A power supply.

A periscope-like arrangement of two prisms was needed to raise the horizontal laser beam to meet the specimen positioned at the centre of the magnet. The scattered radiation, which passed down the
Fig. 3-1: Cross-section of the B.O.C. cryostat exposing the superconducting 6-tesla magnet.
Fig. 3-2: The Zeeman-Raman experimental arrangement.
solenoid's bore, was focussed onto the spectrometer slit by a suitable lens system.

Whereas the slit is vertical, the brightest portion of the specimen's image is horizontal due to the horizontal illumination. Owing to this and the small size of the solenoid's windows and the need for the radiation to pass through a total of four windows and two prisms, the signal-to-noise ratio achieved in this Zeeman arrangement was a factor of 15 inferior to the conventional arrangement.

3.3 INFRARED MEASUREMENTS

3.3.1 Conventional Infrared

Infrared studies were performed using a Beckman IR12 spectrophotometer with a frequency range of 200 - 4000 cm$^{-1}$. A Nernst glower acts as the infrared source and the detector is an evacuated thermocouple. The instrument has a maximum resolution of 0.25 cm$^{-1}$ at 923 cm$^{-1}$. It was continuously purged with dry air to minimise absorption bands due to atmospheric water vapour. As the sizes of the crystals studied were much smaller than the optical beam's cross-sectional dimensions, a Beckman 46286 beam condenser was employed. By reducing the cross-sectional size of the beam incident on the specimen to 1 x 5mm, a high intensity of light transmission could be obtained. Polarization studies were performed with a Beckman 24473 silver chloride polarizer.

Crystals were mounted onto a copper sample holder attached to the tip of the inner can of a conventional cold-finger dewar. For low temperature studies, the inner can was filled with the required refrigerant. Good thermal contact was achieved by having an indium foil sandwiched between the sample and its holder. The lowest temperature attained was estimated at 15°K. Transmission down to 300 cm$^{-1}$ was ensured by the use of cesium bromide windows.
3.3.2 Zeeman-Infrared

The field for the Zeeman-infrared experiments was generated by a 4-tesla Oxford Instrument solenoidal superconducting magnet. Fig. 3-3 shows the magnet assembly which is housed in a stainless steel dewar constructed in the department. The actual magnet itself is situated near the bottom of the helium reservoir which has a capacity of five litres. An 8-litre liquid air jacket surrounds the upper half of the helium can. The lower portion of the can is surrounded by a copper radiation shield which is in contact with the liquid air jacket. Along the bore of the magnet is a tight-fitting stainless steel tube whose ends are soldered onto the walls of the helium can. A copper ring, brazed onto the central portion of the inside of this tube, acts as a sample-holder mount.

Preparation for a Zeeman experiment was done in the following manner. The specimen was clamped onto a detachable copper sample-holder which was then screwed into the copper ring using a tubular key. The cylindrical tail-piece, equipped with two cesium bromide windows, was then screwed onto the bottom flange of the dewar. After evacuating the dewar to below 30\mu Hg, the outer jacket was filled with liquid air. Liquid helium was transferred from a storage can to the reservoir via a transfer tube. Cooling of the crystal was by thermal contact through the stainless steel tube and the sample-holder. Three Allen Bradley resistors each located at the top, centre and bottom of a stainless steel tube, inserted in the reservoir, acted as liquid helium level indicators. The bottom of this tube rested on top of the magnet. A B.O.C. PS 60/72 A power supply was employed to energise the magnet which was operated in the persistent current mode. The field was homogeneous to 1% over a 1cm diameter spherical volume.

Owing to the size of the magnet the dewar's tail-piece occupied most of the sample compartment of the Beckman instrument. This meant
Fig. 3-3: Zeeman-infrared superconducting magnet dewar.

- Evacuated space
- Liquid-nitrogen can surrounded by super insulation
- Nylon support ring
- Radiation shield
- Tube containing Allen Bradley resistors
- Cesium bromide window
- Crystal specimen
- Solenoid
that the Beckman beam condenser could not be used for the Zeeman-
infrared scans. Omission of the beam condenser resulted in an intensity
loss of 50%. To compensate for this, wider slit widths and higher signal
gains were needed.

Unlike the 6-tesla Raman magnet, the 4-tesla one is not of the
split-solenoid type. Because of this limitation, Zeeman-infrared
measurements could only be done with the field directed along the
radiation beam.

3.4 OPTICAL MEASUREMENTS

Optical absorption spectra were recorded with a model 1700, 75cm
focal length f6.8 Czerny Turner spectrometer manufactured by Spex
Industries Inc. The spectrometer is capable of a 0.1Å resolution.
Crystals were mounted in the same Andonian dewar as that used in the
Raman experiments. Light from a 100 W quartz-iodine lamp was
focussed on the sample, the transmitted radiation in turn being focussed
on the slit of the spectrometer. The resulting output from an E.M.I.
type 9558 QB photomultiplier tube was amplified and displayed by a
chart recorder.
CHAPTER IV
RAMAN SCATTERING STUDIES

4.1 INTRODUCTION

Since its discovery the Raman effect has been a useful technique for studying vibrational and rotational transitions in molecules and solids. However thirty-five years were to elapse before the first electronic Raman effect in solids was reported\(^{(20)}\). Like ordinary lattice Raman scattering, electronic Raman scattering is a weak process and hence requires a powerful exciting source. Research in this field is greatly facilitated by the laser which had its advent in 1960.

Raman scattering is a two-photon process and is therefore weaker than optical absorption which involves only one photon. Despite this, Raman scattering has several advantages. First the Raman operator has even parity whereas the electric dipole operator for optical absorption is odd. Intraconfigurational transitions connect states of the same parity and as such are allowed by Raman scattering while forbidden in electric dipole processes. This allows direct observation of electronic transitions by Raman scattering, while in electric dipole absorptions, the spectra are plagued by electric dipole allowed vibronic sidebands.

A second advantage is that Raman scattering involves optical wavelengths while optical absorptions due to low-lying electronic levels are in the infrared where vibrational absorptions of the host crystal frequently obscure electronic absorptions. Thirdly the laser radiation is monochromatic, collimated and polarized. This allows ready determination of the polarization properties of Raman transitions.

The notation shown on the Raman spectra such as \( a(ij)b \) is that adopted by Damen et.al.\(^{(21)}\), where \( a \) and \( b \) indicate the directions of incident and scattered photons and \( i \) and \( j \) are their respective directions of electric vectors. \((a,b,i,j = X,Y,Z \) and the convention
that the \(c\) axis be chosen as the cartesian \(Z\) axis is followed). Right-angled scattering of uniaxial crystals gives rise to nine possible polarization configurations viz., \((XX),(XY),(XZ),(YX),(YY),(YZ),(ZX),(ZY)\) and \((ZZ)\).

The Raman work done in this thesis comprises two parts, the first of which involves conventional Raman spectroscopy and served as a preliminary to the Zeeman-Raman work. The zero-field and Zeeman investigations are described in Chapters IV and V respectively.

In this work the Raman scattering from single crystals of \(\text{CsCoCl}_3\) and cobalt-doped crystals of \(\text{CsMgCl}_3\), \(\text{CsCdCl}_3\) and \(\text{KCl}_3\) were investigated. The experimental results of scattering by both phonons and \(\text{Co}^{2+}\) ions in these crystals are presented. The electronic transitions of interest are between the levels of the \(4\ T_{1g}(^{4}F)\) cubic field ground term of the \(\text{Co}^{2+}\) ion.

Sec. 4.2 gives a general description of the recorded spectra while spectra for each crystal are singly discussed in Sec. 4.3. The principal part of this work is centred on the \(\text{CsMgCl}_3\) and \(\text{CsCdCl}_3\) systems.

Kardontchik et al. \(22\) have reported the polarized Raman spectra of \(\text{Co}^{2+}\) ion impurities in \(\text{CsMgCl}_3\). They observed three of the five transitions between the low-lying electronic levels. Their observations are confirmed and extended to include the detection of the two remaining electronic transitions.

Raman scattering results on \(\text{CsCdCl}_3:\text{Co}, \text{KCl}_3:\text{Co}\) and \(\text{CsCoCl}_3\) are original and are presented for the first time. An in-depth study of the scattering from \(\text{CsCdCl}_3:\text{Co}\) was done. As described in Sec. 2.1, the \(\text{Co}^{2+}\) ions in \(\text{CsCdCl}_3\) occupy two non-equivalent cation sites. One would therefore expect two sets of electronic lines. However as will be shown the spectra observed are principally due to \(\text{Co}^{2+}\) ions in the \(C_{3v}\) sites thus simplifying the interpretation of these spectra. Only three transitions to the highest levels were observed for the \(\text{Co}^{2+}\) ions.
in these \( C_{3v} \) sites. Polarization studies were carried out to establish the group symmetry of these electronic lines.

Once the observed transitions had been assigned the Raman work was extended to cover the effects of an external magnetic field on these transitions. Both the \( \text{CsMgCl}_3:\text{Co} \) and \( \text{CsCdCl}_3:\text{Co} \) systems were investigated by Zeeman-Raman studies which are described in the following chapter.

### 4.2 GENERAL

An argon-ion laser provides an ideal excitation source for the blue cobalt-doped double chloride crystals studied in this work. The 4765 and 4880Å radiation give optimum electronic Raman scattering for these crystals while the 5145Å radiation was found to be less satisfactory. This is because these crystals absorbed the latter line much more and its frequency is well removed from any electronic level of \( \text{Co}^{2+} \) ion that could give resonant enhancement. Moreover the scattering efficiency is proportional to the fourth power of the excitation frequency. Raman spectra were recorded at liquid-nitrogen and helium temperatures from the excitation frequency up to a Stokes shift of 1500 cm\(^{-1}\).

Intense sharp lines are a characteristic feature of the spectra in the region from 0 to 300 cm\(^{-1}\). These are due to the first-order scattering by phonons of the crystals. Second-order phonon scattering lines were observed for the Raman scattering of \( \text{CsCdCl}_3 \). They are weaker than the first-order scattering and for the case of \( \text{CsCdCl}_3 \) have energies above 300 cm\(^{-1}\). For \( \text{Co}^{2+} \) doped crystals, the high energy portions of their spectra beyond 800 cm\(^{-1}\), exhibit lines that are weaker and broader than the first-order phonon scattering and with intensities linearly dependent on the cobalt ion concentrations. Scattering from corresponding crystals doped with \( \text{FeCl}_2 \) do not reproduce these lines.
These lines are attributed to the highest three electronic transitions of the \( \text{Co}^{2+} \) ion within the \( ^4T_{1g} \) (4F) cubic field manifold.

Raman lines due to the lowest two electronic transitions occur among those of the first- and second-order phonon scattering. As these lines are relatively weak they can be masked by the more intense phonon lines as was found for the case of \( \text{CdCl}_2:\text{Co} \) by Christie et al.\(^{(29)} \). The electronic lines can be differentiated from the phonon lines by a comparison with spectra of corresponding \( \text{Fe}^{2+} \) doped crystals. The transition to the \( \gamma_4^+(\Gamma_8^+) \) state of \( \text{CsMgCl}_3:\text{Co} \) was identified in this manner.

Fluorescence lines were encountered only in the scattering from \( \text{CsMgCl}_3:\text{Co} \). Unlike Raman lines, fluorescence lines have the same absolute frequencies irrespective of the excitation frequency.

For \( \text{CsMgCl}_3:\text{Co} \) and \( \text{CsCdCl}_3:\text{Co} \), the strongest two electronic lines are those due to transitions from the \( \gamma_4^+(\Gamma_6^+) \) ground state to the \( \gamma_4^+(\Gamma_8^+) \) and \( \gamma_{5,6}^+(\Gamma_8^+) \) upper levels. As shown by Christie\(^{(18)} \) the scattering efficiency of the \( \gamma_4^+ \rightarrow \gamma_5^+ \) transition is zero in the (ZZ) polarization. This has been verified for the case of \( \text{CsMgCl}_3:\text{Co} \) by Kardotchk et al.\(^{(22)} \). Kiel and Porto\(^{(23)} \) have shown that the polarization selection rules are identical for the \( D_{3d} \) and \( C_{3v} \) symmetries. Hence the \( \gamma_4^+ \rightarrow \gamma_{5,6}^+ \) transition of the \( \text{Co}^{2+} \) ions in the \( C_{3v} \) sites of \( \text{CsCdCl}_3 \) should also be absent in the (ZZ) polarization. In Sec.4.3 a comparison of the (ZZ) and (ZY) spectral intensities was made to distinguish the \( \gamma_4^+(\Gamma_8^+) \) and \( \gamma_{5,6}^+(\Gamma_8^+) \) lines of these \( \text{Co}^{2+} \) ions. The identification of the observed electronic lines by polarization was borne out by the electronic Zeeman-Raman studies described in the following chapter.
4.3 RESULTS

4.3.1 CsCdCl$_3$:Co

Raman studies of pure and Co$^{2+}$ doped CsCdCl$_3$ crystals were made at liquid nitrogen and liquid helium temperatures. The nominal CsCoCl$_3$ impurity content ranged from 5 to 10 mole %.

Pure CsCdCl$_3$ crystals cooled to 80 and 15$^\circ$K were investigated by Raman scattering using the 4765, 4880 and 5145Å radiation. These proved to be equally efficient for the colourless crystals. A set of the 15$^\circ$K spectra of six independent polarization configurations of a CsCdCl$_3$ crystal is displayed in Fig. 4-1. Table 4-1 lists the frequencies and line widths of the lines detected. Transitions were observed within the 40-250 and 300-650 cm$^{-1}$ regions. The former region contains ten lines of varying intensities, the strongest of which is at 248.7 cm$^{-1}$. Some of the weaker lines are absent in certain polarization configurations. The relative intensities of the 115.2 and 127.7 cm$^{-1}$ lines in (ZZ) contrasts sharply with that of the other polarizations in that the former line is stronger than the latter only in (ZZ). This fact was utilized as a check on the crystal orientation for the many (ZZ) polarized spectral runs done.

Bands lying in the next region are generally weaker and broader than the lower-energy lines. A total of six of these bands were recorded, with the band shifted by 602 cm$^{-1}$ and having a line width of 35 cm$^{-1}$ being the broadest. For a comparison of intensities, they are shown together with the lower-energy lines in the randomly polarized spectrum of Fig. 4-2.

In the spectra of cobalt-doped crystals, four additional lines, whose frequencies are listed in Table 4-2, were observed. Figs. 4-3 and 4-4 show the four independent polarized components of the 15$^\circ$K CsCdCl$_3$:Co 5 mole % spectrum exhibiting these four lines which peak at 873, 897, 947 and 1070 cm$^{-1}$. The 873 and 947 cm$^{-1}$ lines are the
Fig. 4-1: First-order Raman spectra of undoped CsCdCl₃ recorded at 15°K.
Fig. 4-2: Raman spectrum of undoped CsCdCl$_3$ recorded at $15^\circ$K.
TABLE 4-1: Frequencies and linewidths of first and second order phonon scattering lines of CsCdCl₃ and CsMgCl₃ at 15°K. All measurements are in cm⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>CsCdCl₃</th>
<th></th>
<th>CsMgCl₃</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First order spectrum</td>
<td>Second order spectrum</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Freq.</td>
<td>Width</td>
<td>Freq.</td>
<td>Width</td>
</tr>
<tr>
<td>CsCdCl₃</td>
<td></td>
<td></td>
<td>CsMgCl₃</td>
<td></td>
</tr>
<tr>
<td>First order spectrum</td>
<td></td>
<td></td>
<td>First order spectrum</td>
<td></td>
</tr>
<tr>
<td>Freq.</td>
<td>Width</td>
<td>Freq.</td>
<td>Width</td>
<td></td>
</tr>
<tr>
<td>46 ± 2</td>
<td>-</td>
<td>351 ± 2</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>52 ± 1</td>
<td>-</td>
<td>418 ± 2</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>71 ± 1</td>
<td>3</td>
<td>447 ± 3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>85 ± 1</td>
<td>4</td>
<td>479 ± 2</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>115.2 ± 0.5</td>
<td>3.7</td>
<td>510 ± 3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>127.7 ± 0.5</td>
<td>3.8</td>
<td>602 ± 4</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>156 ± 2</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170 ± 1</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>208 ± 1</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>248 ± 0.5</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second order spectrum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freq.</td>
<td>Width</td>
<td>Freq.</td>
<td>Width</td>
<td></td>
</tr>
<tr>
<td>55.5 ± 0.5</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>129.0 ± 0.5</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>190.0 ± 0.5</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>257.0 ± 0.5</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 4-2: Experimental and computed\(^a\) frequencies and assignments of the zero-field electronic levels of the \(^{4}T_{1g}(^{4}F)\) ground term of the Co\(^{2+}\) ion. All measurements (in cm\(^{-1}\)) were taken at 15\(^{0}\)K.

<table>
<thead>
<tr>
<th>Assignment(^b)</th>
<th>(\text{CsMgCl}_3:Co)</th>
<th>(\text{CsCdCl}_3:Co(2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma_{4}^{+}(\Gamma_{7}^{+}))</td>
<td>1378.1</td>
<td>1380±2</td>
</tr>
<tr>
<td>(\gamma_{5,6}^{+}(\Gamma_{8}^{+}))</td>
<td>1263.7</td>
<td>1264±1</td>
</tr>
<tr>
<td>(\gamma_{4}^{+}(\Gamma_{8}^{+}))</td>
<td>823.1</td>
<td>823±1</td>
</tr>
<tr>
<td>(\gamma_{5,6}^{+}(\Gamma_{8}^{+}))</td>
<td>466.6</td>
<td>472±4</td>
</tr>
<tr>
<td>(\gamma_{4}^{+}(\Gamma_{8}^{+}))</td>
<td>231.9</td>
<td>234±2</td>
</tr>
<tr>
<td>(\Gamma_{8}^{+}) of Co(1) in (\text{CsCdCl}_3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cobalt cluster line of (\text{CsMgCl}_3)</td>
<td>-</td>
<td>848±2</td>
</tr>
</tbody>
</table>

\(^a\): The frequencies were computed using the following parameters (in cm\(^{-1}\))

<table>
<thead>
<tr>
<th>(\text{Dq})</th>
<th>(B)</th>
<th>(C)</th>
<th>(\zeta)</th>
<th>(V)</th>
<th>(V')</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CsMgCl}_3:Co)</td>
<td>-678.0</td>
<td>790.0</td>
<td>3320.0</td>
<td>-498.8</td>
<td>130.6</td>
</tr>
<tr>
<td>(\text{CsCdCl}_3:Co(2))</td>
<td>-674.0</td>
<td>790.0</td>
<td>3320.0</td>
<td>-522.5</td>
<td>327.4</td>
</tr>
</tbody>
</table>

\(^b\): The assignments for the Co(2) ion for \(\text{CsCdCl}_3\) have no parity labels.
Fig. 4-3: 15°K polarized Raman spectra of CsCdCl₃:Co 5 mole %
Fig. 4-4: 15°K polarized Raman spectra of CsCdCl₃:Co 5 mole %

\[ Y(XZ)X \]
Gain x 1.1

\[ Y(XY)Z \]
strongest and it is only in the (XY) configuration that they have roughly equal intensities. The intensity of the 897 \,\text{cm}^{-1} \text{ line shows little variation in all the four polarization configurations of the spectrum.}

In contrast the 1070 \,\text{cm}^{-1} \text{ line is more sensitive to polarization and is absent in the (ZY) configuration.}

Apart from an intensity increase, increasing the Co\,^{2+} ion concentration to 10\% does not alter the features of the spectrum. The frequencies of the transitions obtained by scattering from the pure host crystals are inappreciably affected by the introduction of Co\,^{2+} ion impurities.

### 4.3.2 CsMgCl\(_3\) :Co

CsMgCl\(_3\) crystals containing 3 and 5 weight \% of CoCl\(_2\) were investigated by Raman scattering using the 4727, 4765 and 4880 \,\text{Å} \text{ radiation.}

Figs. 4-5 and 4-6 display the arbitrarily polarized 15\(^\circ\)K spectra of CsMgCl\(_3\) :Co 5 wt. \% while Tables 4-1 and 4-2 summarize the results obtained.

Lines shifted by 55.5, 129.0, 190.0, 234 and 257.0 \,\text{cm}^{-1} \text{ can be seen in the liquid helium spectrum. Except for the 234 \,\text{cm}^{-1} \text{ line they are intense and sharp with line widths ranging from 3 to 5 \,\text{cm}^{-1}.}

The 129.0 \,\text{cm}^{-1} \text{ line has an asymmetric profile due to a side band located on its high energy side. At liquid nitrogen temperatures, the weak 234 \,\text{cm}^{-1} \text{ line is obscured by the wings of the intense 257.0 \,\text{cm}^{-1} \text{ line.}}

Fig. 4-6 shows five lines of widely varying intensities in the middle and high energy portions of the spectrum. These lines occur at 472, 823, 848, 1264 and 1380 \,\text{cm}^{-1} \text{ with the 823 and 1264 \,\text{cm}^{-1} \text{ ones being the strongest. Among these the narrowest is the 823 \,\text{cm}^{-1} \text{ line while the broadest is the 472 \,\text{cm}^{-1} \text{ band with respective widths of 5 and 16 \,\text{cm}^{-1}. All these five lines together with the one at 234 \,\text{cm}^{-1} \text{ have intensities that increased with increasing Co\,^{2+} ion}}
Fig. 4-5: Raman spectrum of CsMgCl$_3$:Co 5 wt. % measured at 15°K
Fig. 4-6: Raman spectrum of CsMgCl$_3$:Co 5 wt. % measured at 15°C.

- Gain $\times 3$
- Frequency (cm$^{-1}$)

- Intensity

Frequency range: 425 to 1430 cm$^{-1}$
concentration. Spectra obtained by scattering from \( \text{Fe}^{2+} \) doped crystals do not contain them. However the lines shifted by 55.5, 129.0, 190.0 and 257.0 cm\(^{-1}\) remained in these spectra.

One fluorescence line was encountered at the absolute frequency of 19,798 ± 2 cm\(^{-1}\) using the 4880Å excitation radiation. This line was not reproduced by scattering from \( \text{Fe}^{2+} \) doped crystals.

4.4 ANALYSIS OF THE RAMAN SPECTRA

Raman lines produced by scattering from pure host crystals are due to the phonon modes of the crystals themselves. The lines, whose frequencies are listed in Table 4-1, appear in the scattering spectra of pure \( \text{CsCdCl}_3 \) and \( \text{CsMgCl}_3 \) and are therefore ascribed to vibrational modes.

\( \text{CsMgCl}_3 \) has two formula molecules per unit cell and so possesses 27 optical phonon modes. Five Raman-active and five infrared-active modes are predicted from a factor-group analysis based on the \( \text{CsMgCl}_3 \) structure. Of the Raman-active modes, which are given by the representation

\[
\Gamma = A_{1g} + E_{1g} + 3E_{2g},
\]

four are internal modes of vibration associated with chains of \([\text{MgCl}_6]^{4-}\) octahedra while one \((E_{2g})\) is a translatory lattice mode. The infrared-active modes, given by the representation

\[
\Gamma = 2A_{2u} + 3E_{1u},
\]

consist of three internal modes and two translatory lattice modes \( (A_{2u} + E_{1u}) \). Chadwick et.al.\(^{(24)} \) have detected lines at 54, 133, 183 and 264 cm\(^{-1}\) in the polarized Raman spectrum of \( \text{CsCoCl}_3 \) and identified them as \( E_{2g}, E_{1g}, E_{2g} \) and \( A_{1g} \) modes respectively.
CsMgCl$_3$ is isomorphous with CsCoCl$_3$ and the frequencies of its Raman lines are close to those of CsCoCl$_3$. On the basis of this, the 55.5, 129.0, 190.0 and 257.0 cm$^{-1}$ Raman lines are tentatively assigned as the $E_{2g}$, $E_{1g}$, $E_{2g}$ and $A_{lg}$ modes of CsMgCl$_3$. Polarization studies are needed to confirm the species assignment of these lines.

As CsCdCl$_3$ has six formula molecules per unit cell, the number of optical phonon modes permitted is 87. Owing to the large number of possible modes and the complicated ion arrangement of this crystal, no attempt was made to determine the symmetry species of the observed phonon lines of CsCdCl$_3$.

The Raman lines whose frequencies appear in Table 4-2 are attributed to electronic transitions of the Co$^{2+}$ ion for the following reasons. Firstly they are not present in the Raman scattering spectra of corresponding Fe$^{2+}$ doped crystals and secondly their intensities correlate with the Co$^{2+}$ concentration. Their electronic nature is confirmed by their Zeeman shifts observed in the Zeeman-Raman experiments (Chapter V). Analyses of the electronic Raman results are considered separately for the two double chlorides below.

4.4.1 CsCdCl$_3$ :Co

As stated in Sec.2.1, the Cd$^{2+}$ ions in CsCdCl$_3$ occupy two distinct types of sites having $D_{3d}$ and $C_{3v}$ symmetries with the ratio of Cd(1) to Cd(2) sites being 1:2. However several workers studying the E.P.R. spectra of transition metal ions in these crystals have found that these impurity ions do not occupy the two possible cadmium sites in this ratio. Chang et.al.\(^{(1)}\), discovered that V$^{2+}$ and Ni$^{2+}$ ions substitute almost exclusively in one of the two cadmium sites. While they could not positively identify this site they did suggest it to be the smaller $D_{3d}$ site. McPherson and Chang\(^{(25)}\) found that the Mn$^{2+}$ ions show little
discrimination in the occupation of either site and that the ratio of the
two kinds of Mn$^{2+}$ sites is 3:7. On the other hand Graham and White\(^{(26)}\)
found that Cu$^{2+}$ ions have a preference for the larger $C_{3v}$ sites.

Cobalt ions have been examined by EPR by Edgar\(^{(27)}\) using
concentrations of 0.1%. He found that these ions occurred in sites in
the ratio 1:10 and suggested that the $C_{3v}$ sites have the higher occupancy.
In the CsCdCl$_3$ crystals studied in this thesis, Co$^{2+}$ ion concentrations
of up to 10 mole % were used. So although the relative Co$^{2+}$ ion
occupancy of the two sites can be different from Edgar's EPR ratio it is
expected that the Co$^{2+}$ ions substitute into both sites.

Four electronic lines shifted by 873, 897, 947 and 1070 cm$^{-1}$ were
observed for CsCdCl$_3$:Co. They are transitions due to both Co(1) and
Co(2) ions. Reference to the infrared absorption results of Chapter VI
was made in order to sort out the two different types of cobalt
transitions. As the $C_{3v}$ site lacks inversion symmetry, electric dipole
transitions of cobalt ions in these sites are not forbidden. The
infrared absorption data reveal that the 873 and 947 cm$^{-1}$ lines are
electric dipole in nature and are therefore attributed to cobalt ions
in the $C_{3v}$ sites.

As the 897 cm$^{-1}$ line does not appear in the infrared spectra, it
was ascribed to cobalt ions in the $D_{3d}$ sites. These sites possess
inversion symmetry and pure electronic transitions would only be
magnetic dipole allowed and hence weak. The 897 cm$^{-1}$ line also has a
weak scattering in comparison with the 893 and 947 cm$^{-1}$ lines, consistent
with the 1:10 ratio of the Co(1) and Co(2) sites found by Edgar\(^{(27)}\).
Furthermore the 897 cm$^{-1}$ line was found to be rather insensitive to
polarization, consistent with the nearly perfect octahedral $D_{3d}$ site
(Sec. 2.1).

The polarized spectrum of Fig. 4-3 shows that the (ZZ) spectral
intensities of the 947 and 873 cm$^{-1}$ lines are reduced by 60% and 35%
respectively. The $\gamma_{5,6}$ line has, in principle, a zero scattering in the (ZZ) polarization (Sec. 4.2). The 947 and 873 cm$^{-1}$ lines are therefore assigned as transitions from the $\gamma_4(\Gamma_8')$ ground state to the $\gamma_{5,6}(\Gamma_8')$ and $\gamma_4(\Gamma_8')$ excited states respectively of the Co(2) ion. The former line does not have a zero intensity in the (ZZ) polarization due to insufficient crystal quality such as the possible wandering of the $c$ axis within the crystal$^{(28)}$. Any slight misalignment of the crystal would also contribute to the observed depolarization. CsCdCl$_3$ grown from purification by phosgene gas instead of the usual hydrogen chloride gas were no better in quality and similar polarization results were obtained. No improvement to the polarization results was found using the back scattering technique.

The highest energy line at 1070 cm$^{-1}$ is assigned to the $\gamma_4(\Gamma_7)$ level of the Co(2) ion. Transitions to the lowest two levels $\gamma_{5,6}(\Gamma_8')$ and $\gamma_4(\Gamma_8')$ predicted to lie at 395.5 and 291.1 cm$^{-1}$ were not detected because of their weak intensities and also because they occurred among the host lattice phonon lines.

4.4.2 CsMgCl$_3$:Co

The complete set of five transitions within the $4T_{1g}$ ground term of cobalt ions in CsMgCl$_3$ as well as an additional line at 848 cm$^{-1}$ were observed. Three of these lines at 234, 823 and 1264 cm$^{-1}$ are in agreement with those reported by Kardontchik et.al.$^{(22)}$, who assigned them as the $\gamma_4^+(\Gamma_8^+)$, $\gamma_4^+(\Gamma_8')$ and $\gamma_{5,6}^+(\Gamma_8')$ states respectively. The infrared absorption measurements described in Sec. 6.4 confirm the symmetry assignments of the 823 and 1264 cm$^{-1}$ lines.

The other two lines, first reported here, at 472 and 1380 cm$^{-1}$ are assigned to the remaining transitions within the $4T_{1g}$ ground term.
Although polarization Raman studies were not possible on these weak lines the Zeeman-infrared results reported in Chapter VII show that the 1380 cm\(^{-1}\) line is due to the \(\gamma_4^+(\Gamma_6^+) + \gamma_4^+(\Gamma_7^+)\) transition. The remaining line at 472 cm\(^{-1}\) is assigned as a \(\gamma_4^+(\Gamma_6^+) \rightarrow \gamma_5^+,(\Gamma_8^+)\) transition.

The additional line at 848 cm\(^{-1}\) is absent from the infrared absorption spectra and is unassigned. It could arise from clusters of at least two cobalt ions.

4.5 CRYSTAL FIELD FITTING OF EXPERIMENTAL DATA

All the single ion electronic transitions observed are between the six spin-orbit and trigonal crystal field levels of the \(\frac{4}{2} T_g(\frac{4}{2} F)\) cubic field ground manifold. These levels can be determined by the crystal field theory in terms of the spin-orbit parameters \(\zeta\) and \(\zeta'\) and the trigonal field parameters \(v\) and \(v'\) and are also indirectly dependent on the values of the cubic field parameter \(D_q\) and the electrostatic parameters \(B\) and \(C\). Since \(\zeta\) and \(\zeta'\) are frequently closely equal as was found for CdCl\(_2\)-type crystals\(^{(29)}\), for the analysis \(\zeta\) was set equal to \(\zeta'\) and the energy fit was thus made using only three independent parameters \(v,v'\) and \(\zeta\). With three parameters only, systems for which more than two electronic transitions are known can be analysed.

The Co(I) system of CsCdCl\(_3\) for which only one transition was detected could not therefore be analysed.

A preliminary fitting was performed for both the cobalt ions in the \(C_{3v}\) sites of CsCdCl\(_3\) and in the \(D_{3d}\) sites of CsMgCl\(_3\) using the crystal field parameters obtained by Edgar\(^{(27)}\) using a superposition crystal field model developed by Newman\(^{(30)}\). In this the crystal field is described in terms of the \(B^k_q\) crystal field parameters and the tensor operators \(C^k_q\) as
where the first and second parts are the trigonal and cubic components of the crystal field. The summation is over three holes in the 3d shell.

In the superposition model, the $B^k_q$ parameters are expressed in terms of the intrinsic parameters $B^k$ and the angular positions $(\theta_j, \phi_j)$ of the j ligands relative to the central ion by

$$B^k_q = \sum_j B^k c^k_q(\theta_j, \phi_j) \quad (4.4)$$

where the relevant coordination factors $c^k_q$ are

$$c^2_o = (3 \cos^2 \theta - 1)/2$$
$$c^4_o = (35 \cos^4 \theta - 30 \cos^2 \theta + 3)/8 \quad (4.5)$$
$$c^4_3 = 35 \cos \theta \sin^3 \theta \cos 3\phi$$
$$c^4_{-3} = 35 \cos \theta \sin^3 \theta \sin 3\phi$$

The angular positions of the ligands for the Cd(2) and Mg cation sites of CsCdCl$_3$ and CsMgCl$_3$ are given by Edgar (27). Using these angular positions and the intrinsic parameters $B^2_o$ and $B^4_o$ values of CdCl$_2$ he calculated the parameters $B^2_o$, $B^4_o$ and $B^4_3$ for the crystal fields due to the ligands for the above double chlorides. The crystal fields due to the more distant ions were estimated on a point charge model and the crystal field parameters for the total crystal field experienced by the Co$^{2+}$ ion in the two systems are given below in units of cm$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>$B^2_o$</th>
<th>$B^4_o$</th>
<th>$B^4_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsCdCl$_3$:Co(2)</td>
<td>90</td>
<td>9781</td>
<td>-11135</td>
</tr>
<tr>
<td>CsMgCl$_3$:Co</td>
<td>-716</td>
<td>10678</td>
<td>-10839</td>
</tr>
</tbody>
</table>

These $B^k_q$ parameters are related to the strong field parameters $D_q$, $v$ and $v'$ by
These are corrected relations from those of Edgar who gave $B_0^2 = v - \sqrt{2} v'$ instead of $B_0^2 = v - 2\sqrt{2} v'$. Substitution of Edgar's parameter values into the above yielded respective $Dq$ values of -678 and -674 cm$^{-1}$ for CsMgCl$_3$:Co and CsCdCl$_3$:Co(2). For both systems the parameters $B$ and $C$ were set at the respective values of 790 and 3320 cm$^{-1}$ determined for CdCl$_2$:Co by Robson (31).

The total crystal field is a sum of superposition model contributions from the nearest-neighbour ligands and the point charge model contributions from the more distant ions. The $B_0^2$ values for these are comparable and are of opposite sign for both CsMgCl$_3$:Co and CsCdCl$_3$:Co(2). Hence for the initial crystal fitting the only parameters varied are the second-order axial parameter $B_0^2$ and the spin-orbit parameter $\zeta(=\zeta')$. A fit to within 2 cm$^{-1}$ was obtained. A least-squares routine then varied all three parameters $\zeta$, $v$ and $v'$ until agreement to within experimental accuracy was obtained. Their final values are listed in Table 4-2 together with the energy level fits. Both CsMgCl$_3$:Co and CsCdCl$_3$:Co(2) have the $I^+_8$ doublet levels inverted with respect to the case of CdCl$_2$:Co for which $v = 57$, $v' = -345$, $\zeta = -512$ and $\zeta' = -513$ cm$^{-1}$ (Ref. 29).

The coordination sphere of the cobalt ion is elongated along the [111] cubic axis for the double chlorides while for the case of CdCl$_2$ it is compressed in the [111] cubic axis. This gives quite different ratios of the $v$ and $v'$ parameter values in all three crystals which is sufficient to give an altered energy level scheme for CdCl$_2$ as compared to the double chlorides.
The final values of $B^2_0$ and $B^4_0$ obtained from the least-squares fit are 529 and 9671 cm$^{-1}$ for CsCdCl$_3$:Co(2) and -1412 and 11,208 cm$^{-1}$ for CsMgCl$_3$:Co. While the $B^4_0$ values are in good agreement with those estimated by Edgar, the $B^2_0$ values differ rather significantly from his values of 90 and -716 cm$^{-1}$ for CsCdCl$_3$:Co(2) and CsMgCl$_3$:Co respectively. Substitution of these final $B^2_0$ and $B^4_0$ values into equation 4.4 yield intrinsic parameters $\overline{B}^2$ and $\overline{B}^4$ values of -799 and -4014 cm$^{-1}$ for CsCdCl$_3$:Co(2) and -12559 and -4271 cm$^{-1}$ for CsMgCl$_3$:Co. In his calculation of the crystal fields for cobalt ions in the two double chlorides, Edgar assumed their values of the intrinsic parameters $\overline{B}^2$ and $\overline{B}^4$ to be the same as those of CdCl$_2$:Co which are -11000 and -4060 cm$^{-1}$. While this assumption is reasonable for the case of CsMgCl$_3$:Co, it is shown by the data here to be not justifiable for the case of CsCdCl$_3$:Co(2).

The final values of the crystal field parameters, which are listed in Table 4-2, were used to evaluate the energies of the electronic states of the cobalt ion and their associated $g$ values in both 0 and 40 kG fields using two computer programs Oscstrengths/120 and Oscstrengths/3942 listed in the appendix. The former program incorporates the entire 120-dimension energy matrix and is used for $H_{\parallel C}$. In the other program used for $H_{\parallel C}$, the 120-dimension energy matrix is factorized into two 39-dimension $\gamma^+_{4}(-\frac{1}{2})$ and $\gamma^+_{4}(-\frac{1}{2})$ block matrices and a 42-dimension $\gamma^+_{5,6}$ matrix. This factorization was done because the $Z$ component of the Zeeman operator, appropriate for $H_{\parallel C}$, only connects states labelled by the same irreps. The computed frequencies and $g$ values of the low-lying electronic levels of cobalt ions in CsCdCl$_3$ and CsMgCl$_3$ are listed in Tables 4-2 and 4-3 respectively.
TABLE 4-3: Computed $g$ values of the Co$^{2+}$ ion in CsMgCl$_3$ and CsCdCl$_3$ at 0 and 40 kG fields.

| State          | $g_{||}$ | $g_{\perp}$ | $g_{||}$ | $g_{\perp}$ | $g_{||}$ | $g_{\perp}$ |
|----------------|---------|-------------|---------|-------------|---------|-------------|
|                | 0 kg    | 40 kG       |         |             |         |             |
| $\gamma^+_4 (\Gamma^+_7)$ | 2.02 | 3.12 | 2.02 | 3.12 | 2.02 | 3.12 |
| $\gamma^+_5,6 (\Gamma^+_8)$ | 5.21 | 0.0 | 6.06 | 0.0 | 6.05 | 0.0 |
| $\gamma^+_4 (\Gamma^+_8)$ | 3.13 | 0.10 | 3.13 | 0.10 | 3.13 | 0.10 |
| $\gamma^+_5,6 (\Gamma^+_8)$ | 0.18 | 0.0 | 0.52 | 0.0 | 0.49 | 0.0 |
| $\gamma^+_4 (\Gamma^+_8)$ | 3.56 | 1.34 | 3.56 | 1.34 | 3.56 | 1.34 |
| $\gamma^+_4 (\Gamma^+_6)$ | 7.81 | 2.17 | 7.80 | 2.17 | 7.81 | 2.17 |

| State          | $g_{||}$ | $g_{\perp}$ | $g_{||}$ | $g_{\perp}$ | $g_{||}$ | $g_{\perp}$ |
|----------------|---------|-------------|---------|-------------|---------|-------------|
|                |         |             |         |             |         |             |
| $\gamma^+_4 (\Gamma^+_7)$ | 1.19 | 2.05 | 1.19 | 2.05 |         |             |
| $\gamma^+_5,6 (\Gamma^+_8)$ | 3.65 | 0.0 | 3.89 | 0.0 |         |             |
| $\gamma^+_4 (\Gamma^+_8)$ | 2.93 | 0.48 | 2.93 | 0.48 |         |             |
| $\gamma^+_5,6 (\Gamma^+_8)$ | 2.31 | 0.0 | 2.42 | 0.0 |         |             |
| $\gamma^+_4 (\Gamma^+_8)$ | 0.64 | 2.48 | 0.64 | 2.48 |         |             |
| $\gamma^+_4 (\Gamma^+_6)$ | 5.36 | 3.97 | 5.36 | 3.97 |         |             |
5.1 **INTRODUCTION**

As stated in Sec. 2.2 the electronic states of the cobalt ion are split in the presence of a magnetic field. The magnetic splitting factors of these states can be obtained by a Raman study of the transitions between the split electronic components of these states. An electronic Zeeman-Raman investigation of cobalt ions in CsMgCl$_3$ and CsCdCl$_3$ was made as a sequel to the Raman work described in the preceding chapter. The two strongest lines due to the $\gamma_4^+ (\Gamma_6^+)$ and $\gamma_4^+ (\Gamma_7^+)$ transitions are sufficiently intense and narrow for Zeeman-Raman measurements to be feasible. They are also well isolated from neighbouring lines which might interfere with any resulting Zeeman splittings or shifts.

The static magnetic field was generated by a 60 kG superconducting magnet which, together with the specimens, was immersed in pumped liquid helium at 20K. Spectral scans were done at two crystal orientations viz., with the c axis directed along and at right angles to the magnetic field. These orientations will be referred to as $H \parallel c$ and $H \perp c$ respectively. Because of the restricted optical access of the Zeeman-Raman system, the detection system was operated at its maximum sensitivity.

None of the electronic Raman lines examined exhibited any detectable splitting. In case the split components of a given electronic line could have been partially superimposed on each other, a polarizer was inserted in the scattered beam in an attempt to separate them. However no effect on the frequencies of the electronic Zeeman-Raman lines was found when the polarizer was present.

An account of the Zeeman-Raman spectra of cobalt ions in CsCdCl$_3$
and CsMgCl$_3$ is presented in Sec. 5.2. The analysis of the experimental data is given in Sec. 5.3.

5.2 DESCRIPTION OF THE ZEEMAN-RAMAN SPECTRA

5.2.1 CsCdCl$_3$:Co

The 4765 and 4880Å laser lines were used to excite CsCdCl$_3$ crystals containing a nominal molar doping of 5% CsCoCl$_3$. Laser output of up to 2.5W was used with the spectral slit widths ranging from 1.5 to 2.5 cm$^{-1}$. Spectra were recorded at magnetic field strengths of 20, 40 and 60 KG and typical spectra are displayed in Fig. 5-1. None of the electronic lines examined showed any splittings nor signs of broadening. The variations in the line widths detected for any one electronic level at different field strengths are of the order of the experimental uncertainties. Nevertheless the peaks of the electronic lines moved up to higher frequencies when the magnetic field was applied. The shifts were found to be proportional to the magnitude of the applied field.

The Zeeman data for the $\gamma_4 (\Gamma'_8)$ and $\gamma_5, 6 (\Gamma'_8)$ lines of the Co(2) ions together with the $\Gamma'_8$ doublet of Co(1) ions for both $H||c$ and $H\perp c$ are summarized in Table 5-1. The notation $\Delta \lambda_n$ which appears in the table denotes the displacements observed, in cm$^{-1}$, of the electronic Raman lines from their zero-field positions.

At maximum field the $\gamma_4 (\Gamma'_8)$ and $\gamma_5, 6 (\Gamma'_8)$ lines shifted by 4.7 and 5.2 cm$^{-1}$ for $H\perp c$ while for the $H||c$ orientation the respective shifts were 3.2 and 2.4 cm$^{-1}$. For a 60 KG field directed perpendicular to the $c$ axis, a shift of 2.8 cm$^{-1}$ was recorded for the $\Gamma'_8$ doublet of the Co(1) ion.
Fig. 5-1: Electronic Zeeman-Raman spectra of Co$^{2+}$ ions in CsMgCl$_3$ and CsCdCl$_3$ recorded at 2$^0$K.
TABLE 5-1: Zeeman-Raman data on CsCdCl₃:Co(2) and CsMgCl₃:Co at 2⁰K. The symbols $\Delta E_n$ and $w$ denote the shifts of the Raman lines from the zero field positions and the corresponding linewidths in cm⁻¹ respectively. Each value of $\Delta E_n$ and $w$ has an experimental uncertainty of ±0.4 cm⁻¹.

<table>
<thead>
<tr>
<th>H(kG)</th>
<th>CsCdCl₃</th>
<th></th>
<th>CsMgCl₃</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>40</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>$\gamma_{5,6}^+ (\Gamma_8^+)$</td>
<td>$w$</td>
<td>$\Delta E_n$</td>
<td>$w$</td>
<td>$\Delta E_n$</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>1.5</td>
<td>6.3</td>
<td>3.4</td>
</tr>
<tr>
<td>$\gamma_4^+ (\Gamma_8^+)$</td>
<td>4.0</td>
<td>1.4</td>
<td>4.0</td>
<td>3.1</td>
</tr>
<tr>
<td>$\Gamma_8^+$</td>
<td>4.3</td>
<td>0.5</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$\gamma_{5,6}^+ (\Gamma_8^+)$</td>
<td>4.7</td>
<td>0.8</td>
<td>4.4</td>
<td>1.5</td>
</tr>
<tr>
<td>$\gamma_4^+ (\Gamma_8^+)$</td>
<td>3.4</td>
<td>0.8</td>
<td>3.3</td>
<td>1.9</td>
</tr>
<tr>
<td>$\gamma_4^+ (\Gamma_8^+)$</td>
<td>3.4</td>
<td>0.8</td>
<td>3.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

$a$: $\Gamma_8^+$ state of Co(1) in CsCdCl₃.
5.2.2 CsMgCl$_3$:Co

Electronic Zeeman-Raman spectra of CsMgCl$_3$ crystals containing 2.5 and 5.0% by weight of CoCl$_2$ were obtained using the 4765Å laser line and the same spectrometer settings as for CsCdCl$_3$:Co. The behaviour of the $\gamma^+_4 (\Gamma^+_8)$ and $\gamma^+_5,6 (\Gamma^+_8)$ electronic lines were studied at various magnetic field strengths. Portions of the spectra are shown in Fig.5-1 while Table 5-1 lists the experimental results.

As for CsCdCl$_3$:Co, no splittings or broadening of the electronic lines were detected. Again the only effect of the magnetic field was the shifting of the lines to higher frequencies. On application of a 60 kG field, the $\gamma^+_4 (\Gamma^+_8)$ and $\gamma^+_5,6 (\Gamma^+_8)$ lines were seen to shift by 3.1 and 3.5 cm$^{-1}$ for $H || c$ while corresponding shifts of 6.0 and 2.3 cm$^{-1}$ were recorded for $H || c$.

5.3 ANALYSIS OF THE ZEEMAN-RAMAN SPECTRA

Although no visual splitting of the electronic Raman levels occurred the magnetic splitting factors of these levels ($g$) can still be extracted from the Zeeman data as will be shown below. When the magnetic field is applied all the electronic Raman lines shifted to higher frequencies. These shifts are proportional to the magnitude of the applied field indicating that magnetic field interaction between adjacent electronic states is negligible.

In an external magnetic field both the initial and final electronic states of a given transition are split into two components. For the ground state the upper component is depopulated at 20K and hence all the Zeeman-Raman transitions originate from the lower component. In general there should be one transition to each of the two components of the split excited state. However only one of these was observed for
The $g_\perp$ values for the $\gamma_4^+ (I_8^+)$ state of CsMgCl$_3$:Co and CsCdCl$_3$:Co are less than 0.5 and its Zeeman components could not be resolved. The $g_\perp$ value of the $\gamma_5,6^+ (I_8^+)$ state is zero. Hence only one transition to each of these states was observed for Hlc. This contrasts with the case of MgCl$_2$:Co where a splitting of 5 cm$^{-1}$ was recorded at 60kG for the $\gamma_4^+ (I_8^+)$ state consistent with its relatively large predicted $g_\perp$ value of 1.86$^{32}$. Despite their large $g_{||}$ values (Table 4-3), no splittings of the $\gamma_4^+ (I_8^+)$ and $\gamma_5,6^+ (I_8^+)$ lines were detected in the Hlc spectra. This is ascribed to the weak intensities of their absent Zeeman components.

The frequencies of all possible electronic transitions can be calculated in the following manner. The shifts of the ground and excited states from their zero-field positions are first evaluated from the EPR$^{27,33}$ and computed $g$ values respectively (Table 4-3). By adding or subtracting these shifts from the experimental zero-field transition frequencies, the Zeeman transition frequencies can thus be obtained.

Zeeman-infrared studies of CsMgCl$_3$:Co and CsCdCl$_3$:Co yielded more complete results and hence the Zeeman levels were assigned using these Zeeman-infrared results (Chapter VII). Using the Zeeman-infrared energy level schemes, the observed electronic Zeeman-Raman transitions were matched to appropriate energy level separations. Figs. 5-2 and 5-3 which summarize the experimental and calculated frequencies of the electronic Zeeman-Raman transitions together with their assignments, show that the two sets of transition frequencies are in good agreement.

In general the observed shift $\Delta E_n$ of a Zeeman line from its zero-field frequency is the difference in the shift $\Delta E_o$ of the ground state up or down in energy and the shift $\Delta E$ of the excited state up or down in energy. This is mathematically expressed as

$$\Delta E_n = \Delta E_o \pm \Delta E. \quad (5.1)$$
Fig. 5-2: Zeeman energy-level diagram illustrating Raman transitions observed for CsCdCl$_3$:Co(2) 5 mole % at 2°K. Figures in parentheses denote the observed frequencies in cm$^{-1}$.

\[ \gamma_6(-) \quad \gamma_6(+) \quad \gamma_5,8(\Gamma_8) \quad \gamma_4(\Gamma_8) \quad \gamma_4(\Gamma_6) \quad \gamma_5 \quad \gamma_4 \]

\[
\begin{align*}
Y_6(-) & \quad \rightarrow \quad \gamma_5,8(\Gamma_8) \quad \rightarrow \quad \gamma_4(\Gamma_8) \quad \rightarrow \quad \gamma_4(\Gamma_6) \quad \rightarrow \quad \gamma_5 \quad \rightarrow \quad \gamma_4 \\
953.09 & \quad (953.0) \\
950.09 & \quad (950.2) \\
876.64 & \quad (876.2) \\
873.0 & \\
877.81 & \quad (877.7) \\
5.29^3 & \\
7.74^2 & \\
4.10^1 & \\
5.45^1 & \\
0.48^1 & \\
\end{align*}
\]

\[ C_3 \quad 60 \text{ kG} \quad 0 \text{ kG} \quad C_{3v} \quad 60 \text{ kG} \quad C_2 \quad \text{or} \quad C_1 \]

\[ \begin{align*}
(H \parallel c) & \\
(H \perp c) & \\
\end{align*} \]

\[ \begin{align*}
a & = \gamma_3(C_2) \quad \text{or} \quad \gamma_4(+)(C_1) \\
b & = \gamma_4(C_2) \quad \text{or} \quad \gamma_2(-)(C_1) \\
\end{align*} \]

1: Shifts calculated from computed $g$ values of Table 4-3.

2, 3: Shifts calculated from EPR $g$ values of 5.53 and 3.78 respectively.
Fig. 5-3: Zeeman energy-level diagram illustrating Raman transitions observed for CsMgCl₃:Co 2.5 and 5.0 wt. % at 2°C. Figures in parentheses denote the observed frequencies in cm⁻¹.

1: Shifts calculated from computed g values of Table 4-3.
2, 3: Shifts calculated from EPR g values of 7.37 and 2.51 respectively.
4: An unambiguous assignment cannot be made as the observed transition might have also terminated on the upper component a.
TABLE 5-2: Comparison of Zeeman-Raman experimental and computed 
g values of Co\(^{2+}\) at 60 kG.

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>Expt. (g_{\parallel})</th>
<th>Compt.</th>
<th>Expt. (g_{\perp})</th>
<th>Compt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsMgCl(_3):Co</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\gamma_{5,6}^{+}(\Gamma_{8}^{+}))</td>
<td>5.73±0.28</td>
<td>6.06</td>
<td>0.01±0.28</td>
<td>0.00</td>
</tr>
<tr>
<td>(\gamma_{4}^{+}(\Gamma_{8}^{+}))</td>
<td>3.08±0.28</td>
<td>3.13</td>
<td>0.30±0.28</td>
<td>0.10</td>
</tr>
<tr>
<td>(\gamma_{4}^{+}(\Gamma_{6}^{+}))</td>
<td>7.37(^{a})</td>
<td>7.80</td>
<td>2.51(^{a})</td>
<td>2.17</td>
</tr>
<tr>
<td>CsCdCl(_3):Co(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\gamma_{5,6}^{+}(\Gamma_{8}^{+}))</td>
<td>3.82±0.28</td>
<td>3.89</td>
<td>0.07±0.28</td>
<td>0.00</td>
</tr>
<tr>
<td>(\gamma_{4}(\Gamma_{8}^{+}))</td>
<td>3.24±0.28</td>
<td>2.93</td>
<td>0.42±0.28</td>
<td>0.48</td>
</tr>
<tr>
<td>(\gamma_{4}(\Gamma_{6}^{+}))</td>
<td>5.53(^{b})</td>
<td>5.36</td>
<td>3.78(^{b})</td>
<td>3.97</td>
</tr>
</tbody>
</table>

\(^{a}\): EPR values of Rinneberg and Hartmann\(^{(33)}\)

\(^{b}\): EPR values of Edgar\(^{(27)}\)

Now the energy shift \(\Delta E_{i}\) in cm\(^{-1}\) of an electronic state \(i\) is related to its magnetic splitting factor \(g_{\parallel}\) by

\[
\Delta E_{i} = \frac{\beta}{2} g_{\parallel} H
\]

(5.2)

where \(\beta(=0.04668\) cm\(^{-1}\)/kG) is the Bohr magneton and \(H\) is the applied magnetic field in kG. The excited state magnetic splitting factor is thus given by

\[
g = \pm \left( g_{0} - \frac{2}{\beta H} \Delta E \right)
\]

(5.3)

Reference to Figs. 5-2 and 5-3 shows that the electronic Zeeman-Raman transitions terminate on the lower split components of the excited states and hence the positive sign of equation (5.3) applies for this case.

Thus the \(g\) values for the excited states can be evaluated from the
ground state $g$ values, known from EPR measurements, and the net shifts of the electronic Zeeman-Raman lines. The resulting $g$ values are listed in Table 5-2 and are in good agreement with those computed from the crystal field model.
6.1 INTRODUCTION

In this chapter the axial and polarized infrared spectra of cobaltous ions doped in the double chlorides CsMgCl$_3$ and CsCdCl$_3$ are presented and discussed. The electronic transitions observed are between the spin-orbit and trigonal crystal field levels of the $^4T_{1g}(^4F)$ cubic field ground manifold of the cobaltous ion (Sec. 2.2).

An analysis of the experimental results of Raman scattering from the two systems has been given in the previous chapter. The absorption spectra recorded comprise both pure electronic and vibronic bands, whereas the Raman spectra due to cobalt ions consist only of electronic transitions.

In both the double chlorides the cobalt ions are located in sites of trigonal symmetry. While these sites are centrosymmetric (D$_{3d}$) in CsMgCl$_3$, the majority of cobalt ions in CsCdCl$_3$ are in an environment lacking inversion symmetry (C$_{3v}$) - Sec. 4.4. Owing to this difference in site symmetry the single cobalt ion electronic transitions occur through different mechanisms for the two crystals. In CsMgCl$_3$:Co, electric dipole electronic transitions within the $^4T_{1g}$ cubic field term are strictly forbidden while magnetic dipole electronic transitions are allowed. The electronic lines of CsMgCl$_3$:Co are usually weaker than those of CsCdCl$_3$:Co(2) where the electronic transitions are principally electric dipole in character.

Both sharp and broad electric dipole polarized vibronic bands form part of the features of the spectra. Lattice phonon frequencies of the host crystals were obtained from analyses of these vibronic bands. The pure electronic and vibronic transitions are individually discussed below for each crystal.
6.2 GENERAL DESCRIPTION OF THE SPECTRA

The axial and polarized spectra of CsMgCl$_3$ and CsCdCl$_3$ containing cobalt ions were measured from 400-1700 cm$^{-1}$. Within this energy region the pure host crystals are transparent down to their reststrahlen absorption band edges which occur at 600 and 450 cm$^{-1}$ for CsMgCl$_3$ and CsCdCl$_3$ respectively. Extra bands and lines occur in the spectra of cobalt-doped crystals. These bands and lines have intensities that are dependent on the cobalt ion concentration and are absent in spectra of Fe$^{2+}$-doped crystals. They are attributed to either no-phonon electronic transitions of the cobalt ions or vibronic transitions associated with these electronic transitions. The electronic infrared lines were identified by the coincidence of their frequencies, to within ± 2 cm$^{-1}$, with those of electronic transitions of cobalt ions observed in the Raman spectra of the same crystals. For the case of CsMgCl$_3$:Co, polarization studies can distinguish the electronic from the vibronic transitions as the former are magnetic dipole allowed while the latter are electric dipole in nature.

Sets of vibronic bands occur at definite energy separations from each of their parent electronic lines. These energy separations, or vibronic intervals, give the frequencies of peaks in the phonon density of states for the host crystals. Some of these frequencies match those of the $\kappa = 0$ optical phonons found by Raman scattering.

The spectra of CsMgCl$_3$:Co are characterized by strong vibronic bands relative to the electronic lines, while those of CsCdCl$_3$:Co have the electronic lines as their dominant feature. The spectra recorded for these two systems are described in the following section.
6.3 RESULTS

6.3.1 CsMgCl$_3$:Co

Infrared spectra of CsMgCl$_3$ doped with 0 to 2.5% by weight of CoCl$_2$ were recorded at liquid nitrogen and liquid helium temperatures. Figs. 6-1, 6-2 and 6-3 depict the main spectral features of these crystals while the associated spectral data are listed in Tables 6-1 and 6-2.

Axial Spectra

These have the $c$ axis of the crystal along the direction of propagation of the incident radiation.

With the exception of a broad band centred at 1415 cm$^{-1}$, strong narrow lines are the main characteristics of the 80°K axial spectrum in the 700-1700 cm$^{-1}$ region. The six most intense lines have peaks at 943.0, 1042.0, 1051.5, 1264.0, 1476.0 and 1592.0 cm$^{-1}$ with the 1264.0 cm$^{-1}$ line being the strongest. As with all the spectra recorded, the spectrum in Fig. 6-1 shows in addition, water vapour absorption lines in the 1300-1700 cm$^{-1}$ region. These can be distinguished from the absorption lines due to the crystals by their known frequencies and by their independence of the crystals' temperature.

As can be seen from Figs. 6-2 and 6-3 the lines became sharper and shifted to lower frequencies when the crystals were cooled to 15°K. At this temperature, the 1262 cm$^{-1}$ assumed an asymmetrical shape due to a side-band at 1256 cm$^{-1}$. The 1148 cm$^{-1}$ line present in the 80°K spectrum vanished. Several weak lines at 80°K became more pronounced, among them are the 822.0, 843.0 and 1379.0 cm$^{-1}$ lines.

Polarized Spectra

These are of two types. The $\pi$ polarization spectra have the $E$ vector of the incident radiation along the crystal $c$ axis and the
Fig. 6-1: Axial and polarized infrared spectra of CsMgCl$_3$:Co 2.5 wt. % measured at 80°K
Fig. 6-2: Axial and polarized infrared spectra of CsMgCl$_3$:Co 2.5 wt. % measured at 150K.
Fig. 6-3: Polarized infrared spectra of CsMgCl₃:Co 1.0 wt. % measured at 15^°K
TABLE 6-1: Infrared data of CsMgCl$_3$:Co 2.0wt.% measured at 80$^\circ$K. All measurements are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Width</th>
<th>Frequency</th>
<th>Width</th>
<th>Frequency</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>773 ±2</td>
<td>-</td>
<td>788 ±1</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>826 ±1</td>
<td>7</td>
<td>826 ±1</td>
<td>8</td>
<td></td>
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</tr>
<tr>
<td>846 ±1</td>
<td>-</td>
<td>846 ±1</td>
<td>-</td>
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<tr>
<td>943.0±0.8</td>
<td>10</td>
<td>956 ±2</td>
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<tr>
<td>1042.0±0.7</td>
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<td>1051.5±0.7</td>
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</tr>
<tr>
<td>1148 ±1</td>
<td>-</td>
<td>1184 ±1</td>
<td>-</td>
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<tr>
<td>1264.0±0.5</td>
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<td>1264 ±1</td>
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</tr>
<tr>
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<td>1415 ±6</td>
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<td></td>
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<tr>
<td>1415 ±8</td>
<td>66</td>
<td>1476.0±0.7</td>
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<tr>
<td>1476.0±0.7</td>
<td>9</td>
<td>1591.5±0.7</td>
<td>8</td>
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</tr>
<tr>
<td>Axial</td>
<td>Freq (cm(^{-1}))</td>
<td>Width (cm(^{-1}))</td>
<td>Int (cm(^{-2}))</td>
<td>Freq (cm(^{-1}))</td>
<td>Width (cm(^{-1}))</td>
</tr>
<tr>
<td>-------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td></td>
<td>822.0±0.7</td>
<td>4</td>
<td>0.2</td>
<td>822.0±0.7</td>
<td>6</td>
</tr>
<tr>
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<td>843.0±0.7</td>
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<tr>
<td></td>
<td>941.0±0.5</td>
<td>6.5</td>
<td>3.1</td>
<td>941.0±0.5</td>
<td>7</td>
</tr>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1000.0±1</td>
<td>1000.0±1</td>
<td>1000.0±1</td>
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<td>1074 ±2</td>
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<td>1048.2±0.7</td>
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<tr>
<td></td>
<td>1118 ±1</td>
<td>1123 ±3</td>
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<td>1118 ±1</td>
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<tr>
<td></td>
<td>1130 ±2</td>
<td>-</td>
<td></td>
<td>1130 ±2</td>
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<tr>
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<td>1143 ±2</td>
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</tr>
<tr>
<td></td>
<td>1155 ±1</td>
<td>1155 ±1</td>
<td>8</td>
<td>1179 ±1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1200 ±1</td>
<td>9</td>
<td>0.5</td>
<td>1200 ±1</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1241 ±1</td>
<td>1241 ±1</td>
<td></td>
<td>1241 ±1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1256 ±1</td>
<td>-</td>
<td></td>
<td>1256 ±1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1262.5±0.5</td>
<td>2.9(^{a})</td>
<td>8.3(^{a})</td>
<td>1263 ±1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1379.0±0.7</td>
<td>3</td>
<td>0.5</td>
<td>1379.0±0.5</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>1390 ±5</td>
<td>68</td>
<td>1390 ±5</td>
<td>1415 ±8</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>1420 ±5</td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1474.6±0.5</td>
<td>4.2(^{a})</td>
<td>5.6(^{a})</td>
<td>1474.6±0.5</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>1591.0±0.5</td>
<td>4.8</td>
<td>2.5</td>
<td>1591.0±0.5</td>
<td>5.8</td>
</tr>
</tbody>
</table>

\(^{a}\): Data obtained from CsMgCl\(_3\):1.0wt.\%Co.
σ polarization spectra have the _E_ vector of the incident radiation normal to the crystal c axis.

In general, the 80°K spectrum (Fig. 6-1) resembles that of the axial. The differences in the intensities of the 1380 and 1264 cm⁻¹ lines are the main dissimilarity of the two spectra. In the σ spectrum, the former line has a greater intensity while the latter line is weaker. In Fig. 6-1 there are absorption lines in the π spectrum which are not present in the other two. These include the two pairs of lines at (773;788) and (863;878) cm⁻¹ which are located symmetrically on the opposite sides of the 826 cm⁻¹ line with their separations from it being 37 and 52 cm⁻¹. Among the lines which are only present in the π spectrum are the strong, narrow line at 1034.5 cm⁻¹, the broader lines at 956 and 980 cm⁻¹ and a weak line at 1184 cm⁻¹. The 1591.5 cm⁻¹ line gains in intensity in going from the axial to the π spectrum while the reverse is the case for the 1476 cm⁻¹ line.

On cooling to 15°K, the lines narrowed and shifted to lower frequencies. Several additional weak structures not observed at 80°K now appeared. These include the 1123, 1155, 1192 cm⁻¹ lines in the σ spectrum and the 1118, 1130, 1143, 1179 and 1200 cm⁻¹ lines in the π spectrum. In contrast the 1148, 1184 and the (773;788) cm⁻¹ lines of the 80°K spectra have now disappeared. The 1262.5 cm⁻¹ line in the π spectrum has an asymmetric profile due to a weak shoulder at 1256 cm⁻¹. A weak side-band appeared on the 1039.0 cm⁻¹ line of the σ spectrum.

Reference to Figs. 6-2 and 6-3 shows that it is in fact the remnant of the intense π-polarized 1032.3 cm⁻¹ line. The intensity of this line gives an indication of the degree of misalignment of the crystal c axis with the infrared radiation.

The 848 cm⁻¹ line, observed by Raman scattering, does not appear in any of the infrared spectra.
6.3.2 CsCdCl$_3$:Co

An investigation of CsCdCl$_3$ crystals containing nominal concentrations of 0 to 10 molar % of CsCoCl$_3$ was carried out at liquid nitrogen and liquid helium temperatures. The spectra obtained were found to be similar for the different cobalt ion concentrations.

Axial Spectra

Low temperature axial spectra are shown in Figs. 6-4 and 6-5 while Tables 6-3 and 6-4 list the frequencies and intensities of the absorption bands observed.

Two intense, sharp lines of frequencies 876.0 and 950.5 cm$^{-1}$ are the dominant features of the 80°K spectrum. The other bands observed are much weaker and only one weak band was seen between the two major lines. Except for the 670 cm$^{-1}$ line due to atmospheric carbon dioxide, no absorption was observed in the region below the 876.0 cm$^{-1}$ line down to the absorption edge of the host lattice at 450 cm$^{-1}$. In the high energy portion of the spectrum lie two broad bands centered at 1070 and 1165 cm$^{-1}$ and two narrower bands at 1030 and 1110 cm$^{-1}$.

When the crystals were cooled to 15°K, the bands revealed some fine structure while the lines became sharper and shifted to lower frequencies. The two main lines have peaks at new frequencies of 871.2 and 946.1 cm$^{-1}$. The 1030 cm$^{-1}$ band was resolved into two narrower lines of frequencies 1024.6 and 1030.0 cm$^{-1}$ while the 1110 cm$^{-1}$ band sharpened and shifted to 1105.5 cm$^{-1}$. The broad band has fine structure with peaks at 1054, 1060, 1066 and 1075 cm$^{-1}$. Additional new absorptions were also observed. Among them are bands centred at 1134 and 1225 cm$^{-1}$ and a sharp but weak satellite line at 878.5 cm$^{-1}$.

Polarized Spectra

The results of infrared polarization studies are presented in
Fig. 6-4: 80°K axial infrared spectrum of CsCoCl$_3$:Co 5 mole %
Fig. 6-5: 15°K axial and polarized infrared spectra of CsCdCl₃:Co 5 mole %
TABLE 6-3: 80°K infrared data on CsCdCl₃ crystals containing nominal concentrations of 5mole% of CsCoCl₃.

<table>
<thead>
<tr>
<th>Axial</th>
<th>σ</th>
<th>π</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freq. (cm⁻¹)</td>
<td>Width (cm⁻¹)</td>
<td>Int. (cm⁻²)</td>
</tr>
<tr>
<td>876.2±0.5</td>
<td>4.0</td>
<td>7.5</td>
</tr>
<tr>
<td>932 ±3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>950.5±0.5</td>
<td>8.3</td>
<td>5.6</td>
</tr>
<tr>
<td>1031 ±3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1075 ±5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1111 ±2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1165 ±7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a: The frequencies are for both the Axial and σ spectra.
b: Int = Width(cm⁻¹) x Peak Absorbance for 1 cm thickness.
<table>
<thead>
<tr>
<th>Axial</th>
<th>( w )</th>
<th>( \Lambda )</th>
<th>( \Theta )</th>
<th>( \pi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>871.2±0.4</td>
<td>1.5</td>
<td>6.0</td>
<td>2.1</td>
<td>5.2</td>
</tr>
<tr>
<td>878.3±0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>905 ±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>916 ±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>928.0±0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>946.1±0.4</td>
<td>3.1</td>
<td>5.4</td>
<td>2.7</td>
<td>7.1</td>
</tr>
<tr>
<td>958 ±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>964 ±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>978 ±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>999 ±2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1024.6±0.5</td>
<td>3.5</td>
<td>0.6</td>
<td>3.5</td>
<td>0.6</td>
</tr>
<tr>
<td>1030 ±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1054 ±0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1060 ±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1066 ±1</td>
<td>32</td>
<td>33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1075 ±1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1105.5±0.5</td>
<td>4.0</td>
<td>0.8</td>
<td>4.8</td>
<td>0.9</td>
</tr>
<tr>
<td>1133 ±3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1150 ±3</td>
<td>36</td>
<td>36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1168 ±3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1225 ±2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1255 ±3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 6-5 with Tables 6-3 and 6-4 containing the experimental data. The figure shows that the $\sigma$ spectrum is similar to the axial one, whereas the $\pi$ spectrum differs from the axial spectrum. The two strongest lines that appear in both the axial and $\sigma$ spectra are noticeably reduced in intensity in the $\pi$ spectrum. The 1029.5 and 1105.5 cm$^{-1}$ lines increase in intensity in going from the axial to the $\pi$ spectrum. Additional lines at 922, 970, 980, 1006, 1052, 1082 cm$^{-1}$ and a broad band centred at 1255 cm$^{-1}$ also appear in the $\pi$ spectrum.

6.4 ANALYSIS OF THE INFRARED SPECTRA

6.4.1 CsMgCl$_3$:Co

Electronic Transitions

In Sec. 4.4 the complete set of five electronic transitions of single cobalt ions detected by Raman scattering was given. Of these only the highest three electronic lines were observed by infrared absorption. The remaining two transitions are obscured by the intense reststrahlen absorption band of the CsMgCl$_3$ crystal. The coincidence of the axial and $\pi$ spectra of the three electronic lines observed shows their magnetic dipole character.$^{34}$

Selection rules for the magnetic dipole transitions of a cobalt ion in the $D_{3d}$ site of CsMgCl$_3$ can be derived as follows. All the electronic transitions of interest originate from a $\gamma_4^+$ ($\Gamma_6^+$) ground state and terminate on excited states of either $\gamma_4^+$ ($\Gamma_7^+$ or $\Gamma_8^+$) or $\gamma_5^+6$ ($\Gamma_8^+$) symmetry (Sec. 2.2). The $z$ and $(x,y)$ components of the magnetic dipole operator transform as the $\gamma_2^+$ and $\gamma_3^+$ irreps, respectively, of the $D_{3d}$ double group. From the following direct products

$$\gamma_4^+ \times \gamma_2^+ = \gamma_4^+$$

$$\gamma_4^+ \times \gamma_3^+ = \gamma_4^+ + (\gamma_5^+ + \gamma_6^+)$$

(6.1)
it is evident that electronic transitions to the $\gamma_{5,6}^+$ states are absent in the $\sigma$ spectrum (Sec. 2.2). Because the 1262.5 cm\(^{-1}\) line has only a remnant absorption in the $\sigma$ spectrum, it is identified as the transition to the $\gamma_{5,6}^+(T_{8}^+)$ state. The 822.0 and 1379.0 cm\(^{-1}\) lines appear in both the $\sigma$ and $\pi$ spectra and are therefore assigned as transitions to the $\gamma_{4}^+(T_{3}^+)$ and $\gamma_{4}^+(T_{7}^+)$ levels respectively.

The crystal field theory, described in Chapter II, can be used to calculate the intensities of these electronic transitions as follows.

The oscillator strength, $f$, of a magnetic dipole transition between two electronic states $|g\rangle$ and $|e\rangle$ is given by\(^{(35)}\)

$$f = 1.21 \times 10^{-10} \, n \nu |g| L_i + 2S_i |e\rangle|^2$$  \hspace{1cm} (6.2)

where $n$ is the refractive index of the crystal at transition frequency $\nu$ (cm\(^{-1}\)) and $L_i$ and $S_i$ are the components of the orbital and spin angular momenta respectively. The matrix elements of $(L_z + 2S_z)$ and $(L_x + 2S_x)$ may be obtained by evaluating these operators between the six levels of the $^4T_{1g}$ cubic field ground term. These levels are characterized by the eigenvectors of the twelve lowest levels of the full 120 dimension free-ion and crystal field matrices of the $3d^3$ configuration.

Experimentally the oscillator strength $f$, of a Gaussian line can be evaluated by using the following relation\(^{(36)}\)

$$f = \frac{0.87 \times 10^{17}}{N} \left( \frac{n}{n^2 + 2} \right)^2 \mu_{ab} V_{ab} \nu_{ab}$$  \hspace{1cm} (6.3)

where $N$ is the number of absorbing ions/cm\(^3\), $n$ is the refractive index of the crystal, $\mu_{ab}$ is the peak absorbance of the line in cm\(^{-1}\) and $V_{ab}$ is the width of the line in eV. A Lorentzian line of the same peak absorbance and width has an oscillator strength a factor of approximately 1.5 greater. In order to calculate $N$, the actual concentration of cobalt ions in the crystals used has to be known. A
check on the nominal doping was done by comparing the peak absorbance of the $^4_{1g} (^4P)$ bands for a solution containing a known weight of the doped crystals with that for a CsCoCl$_3$ solution of known concentration. In general the nominal dopings were close to that measured in this way. The value of the refractive index, $n$, for CsMgCl$_3$ was taken to be 1.7 as for MgCl$_2$.\(^{(32)}\)

Table 6-5 gives a comparison of the experimental and computed oscillator strengths of the three electronic transitions observed. The reasonable agreement between the two sets of values confirms the assignment of these transitions and their magnetic dipole origin.

Besides the single cobalt ion lines observed, absorption due to cobalt ion pairs and clusters also appear in the spectra. The intensities of the lines due to cobalt ion pairs have a quadratic dependence on the cobalt ion concentration, while that due to more complex clusters have a more rapidly varying dependence. The intensities of the lines at 843 and 1256 cm$^{-1}$ show a greater than linear dependence on the cobalt ion concentration. They are therefore attributed to clusters of at least two cobalt ions. These two lines seen at concentrations of 1.5% and above are not present in the spectra of CsMgCl$_3$:Co 1 wt. % shown in Fig. 6-3.

**Vibrionic Transitions**

The vibrionic bands have a wide range of widths and intensities. Their frequencies are listed in Table 6-6 together with those of their electronic parent lines and the corresponding vibronic intervals.

In CsMgCl$_3$:Co, odd vibrations can couple to the even electronic wavefunctions giving rise to electric dipole polarized vibronic transitions. This is substantiated by the coincidence of the axial and $\sigma$ polarised traces of the vibronic bands observed. Some of these bands such as those at 860 and 1032.3 cm$^{-1}$ appear only in the $\pi$ spectrum.
TABLE 6-5: Computed and experimental oscillator strengths for assigned IR transitions in CsMgCl$_3$:Co $2^+$ at 15°K

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Experimental Frequency (cm$^{-1}$)</th>
<th>Oscillator Strength ($10^{-10}$)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\sigma$ Expt.</td>
<td>Compt.</td>
<td>$\pi$ Expt.</td>
</tr>
<tr>
<td>$\gamma_4^+(\Gamma_{7^+})$</td>
<td>1379.0</td>
<td>155</td>
<td>892</td>
<td>20</td>
</tr>
<tr>
<td>$\gamma_5^+(\Gamma_{8^+})$</td>
<td>1262.5</td>
<td>21</td>
<td>0</td>
<td>868</td>
</tr>
<tr>
<td>$\gamma_4^+(\Gamma_{8^+})$</td>
<td>822.0</td>
<td>20.9</td>
<td>30.7</td>
<td>6.9</td>
</tr>
<tr>
<td>$\gamma_5^+(\Gamma_{8^+})$</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma_4^+(\Gamma_{8^+})$</td>
<td>-</td>
<td>-</td>
<td>2927</td>
<td>3301</td>
</tr>
</tbody>
</table>
TABLE 6-6: Analysis of vibronic bands of CsMgCl$_3$Co 2.0wt.% to give frequencies (cm$^{-1}$) of peaks in the phonon density of states.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Electronic Parent</th>
<th>Vibronic Parent</th>
<th>Vibronic Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>80°K</td>
<td>826 ±1</td>
<td>788 ±1</td>
<td>-38 ±2</td>
</tr>
<tr>
<td></td>
<td>863 ±1</td>
<td>873 ±2</td>
<td>37 ±2</td>
</tr>
<tr>
<td></td>
<td>878 ±1</td>
<td>773 ±2</td>
<td>-53 ±3$^a$</td>
</tr>
<tr>
<td></td>
<td>1264.0±0.5</td>
<td>1148 ±1</td>
<td>52 ±2$^a$</td>
</tr>
<tr>
<td></td>
<td>1380.5±0.7</td>
<td></td>
<td>-116 ±2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>116.5±1.2</td>
</tr>
<tr>
<td>15°K</td>
<td>822.0±0.7</td>
<td>860.0±0.7</td>
<td>38.0±1.4</td>
</tr>
<tr>
<td></td>
<td>873 ±1</td>
<td>941.0±0.5</td>
<td>51 ±2$^a$</td>
</tr>
<tr>
<td></td>
<td>953 ±1</td>
<td>977 ±2</td>
<td>119.0±1.2</td>
</tr>
<tr>
<td></td>
<td>1032.3±0.5</td>
<td>1039.1±0.5</td>
<td>131 ±2$^a$</td>
</tr>
<tr>
<td></td>
<td>1048.2±0.7</td>
<td>1032.3±0.5</td>
<td>155 ±3</td>
</tr>
<tr>
<td></td>
<td>1262.5±0.5</td>
<td>1379.0±0.5</td>
<td>210.3±1.2</td>
</tr>
<tr>
<td></td>
<td>1390 ±5</td>
<td>1420 ±5</td>
<td>217.1±1.2</td>
</tr>
<tr>
<td></td>
<td>1474.6±0.5</td>
<td>1474.6±0.5</td>
<td>226.2±1.4</td>
</tr>
<tr>
<td>1379.0±0.5</td>
<td></td>
<td>1591.0±0.5</td>
<td>116.4±1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1390 ±5</td>
<td>128 ±6$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1420 ±5</td>
<td>158 ±6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1474.6±0.5</td>
<td>212.1±1.0</td>
</tr>
</tbody>
</table>

$^a$: cf. Raman phonon lines of Table 4-1.
Of particular interest are the two pairs of lines (773;788) cm$^{-1}$ and (863;878) cm$^{-1}$ located symmetrically about the $\gamma_4^+(\Gamma_{8}^+)$ electronic line of the 80$^\circ$K spectrum of Fig. 6-1. The former two lines are difference lines while the latter two lines are the summation lines. Vibronic difference lines are temperature dependent and have vanishing intensities at low temperatures due to depopulation of the vibronic levels above the ground state. They are known as hot bands for this reason. The (773;788) cm$^{-1}$ pair and the 1148 cm$^{-1}$ lines are examples of hot bands as they disappear at liquid helium temperatures. The corresponding summation line for the 1148 cm$^{-1}$ line happens to coincide with the $\gamma_4^+(\Gamma_{7}^+)$ electronic line at 1379.0 cm$^{-1}$ which is principally magnetic dipole polarized.

Reference to Table 6-6 shows that only one complete set of three vibronic lines, corresponding to a vibronic interval of 211 cm$^{-1}$, was identified for the three electronic transitions observed. The intensities of the vibronic bands in any one set, associated with the $\gamma_4^+(\Gamma_{8}^+)$, $\gamma_5,6^+(\Gamma_{8}^+)$ and $\gamma_4^+(\Gamma_{7}^+)$ levels have decreasing magnitudes in the order listed. The number of the identified vibronic bands associated with the $\gamma_5,6^+(\Gamma_{8}^+)$ and $\gamma_4^+(\Gamma_{7}^+)$ electronic parents is in each case less than that associated with the $\gamma_4^+(\Gamma_{8}^+)$ level. The non-observation of the missing vibronic bands could be due to their weak intensity or their masking by water vapour absorption lines.

The vibronic intervals are attributed to peaks in the phonon density of states for CsMgCl$_3$. Of the seven vibronic intervals identified only two have frequencies corresponding to the $k = 0$ Raman phonons.

A check on the assignment of the vibronic bands to particular electronic parent lines can be made by studying their behaviour under an applied magnetic field. Such studies will be described in the following chapter.
Electronic Transitions

An assignment of the single cobalt ion transitions due to the Raman scattering of CsCdCl$_3$:Co was made earlier in Sec. 4.4. Of the total of four electronic Raman lines observed, three were attributed to Co(2) ions while the remaining line at 897 cm$^{-1}$ was identified as the unresolved $\Gamma_8'$ doublet of the Co(1) ion.

The infrared lines at 871.2 and 946.1 cm$^{-1}$ match the frequencies of the 873 and 947 cm$^{-1}$ Raman lines and are therefore assigned as the trigonal crystal field split components of the $\Gamma_8'$ doublet of the Co(2) ions. These ions are in C$_{3v}$ sites and hence electric dipole transitions between levels of the $4T_{1g}(4F)$ cubic field term are allowed. This assignment is consistent with the coincidence of the axial and $\sigma$ spectra of these electronic lines$^{(34)}$.

States in the 3d$^6$4p configuration are admixed with those of the same symmetry representations in the 3d$^7$ configuration by the odd terms of the trigonal C$_{3v}$ crystal field. Some odd character is thus gained by the $\gamma_4$ and $\gamma_{5,6}$ states, of interest, of the Co(2) ions. The $\gamma_2$ and $(\gamma_x,\gamma_y)$ components of the electric dipole transition operator transform as the respective $\gamma_2$ and $\gamma_3$ irreps of the C$_{3v}$ double group. The direct product representations

$$\gamma_4 \times \gamma_2 = \gamma_4$$

$$\gamma_4 \times \gamma_3 = \gamma_4 + (\gamma_5 + \gamma_6)$$

show that (Sec. 2-2) the absorption intensity for the $\gamma_4 \rightarrow \gamma_{5,6}$ transitions is zero in the $\pi$ spectrum as $\gamma_4 \times \gamma_2$ does not contain $\gamma_{5,6}$.

This selection rule can be utilized to identify the trigonal crystal field component $\gamma_4$ and $\gamma_{5,6}$ states of the $\Gamma_8'$ doublet. Reference to the $\pi$ spectrum of Fig. 6-5 however reveals that the intensities of both
these electronic lines are greatly reduced and an unambiguous identification cannot be made. Zeeman-infrared studies carried out on these lines (Chapter VII) substantiated their labelling determined earlier from the results of the polarization Raman scattering experiments (Chapter IV). Due to a lack of information on the $3d^64p$ configuration of the cobalt ion, the electric dipole intensities of the electronic transitions of the $Co(2)$ ion could not be calculated.

None of the other three electronic transitions of the $Co(2)$ ion were observed. The lowest two electronic lines have predicted frequencies of 291 and 396 cm$^{-1}$ and would lie under the intense reststrahlen band of the $CsCdCl_3$ host. In analogy to the case of $CdCl_2:Co$, it is likely that the $\gamma_4 (I_7)$ state of $Co(2)$ was not observed because of its weak intensity.$^{(37)}$

None of the electronic transitions of the $Co(1)$ ion was detected. One of them has been found by Raman scattering to have a frequency of 897 cm$^{-1}$. It was attributed as the transition to the unsplit $I_8^+$ doublet. The existence of this level can be inferred from the positions of its vibronic bands in the infrared spectra. Non-observation of any of the electronic lines of the $Co(1)$ ions can be partially ascribed to their relatively low concentrations (Sec. 4.4) and partially to the necessarily weak magnetic dipole absorptions for these ions which are in $D_{3d}$ sites.

**Vibronic Transitions**

The most striking feature in the axial and $\sigma$ spectra is the two electronic lines. It is only in the $\pi$ spectrum that the vibronic bands have intensities comparable to those of the electronic transitions. The electric dipole nature of the vibrationally induced bands is shown by the matching of the axial with the $\sigma$ spectrum. Some of these bands can only be accounted for by the existence of the electronic transition...
TABLE 6-7: Analysis of vibronic bands in CsCdCl₃:Co 5 mole % to give frequencies (cm⁻¹) of peaks in the phonon density of states at 15°K.

<table>
<thead>
<tr>
<th>Electronic parent</th>
<th>Vibronic</th>
<th>Vibronic Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>871.2±0.4</td>
<td>905 ±1</td>
<td>34 ±1</td>
</tr>
<tr>
<td></td>
<td>980 ±1ᵃ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>999 ±1</td>
<td>109 ±1</td>
</tr>
<tr>
<td></td>
<td>1029.5±0.5</td>
<td>128 ±1ᶜ</td>
</tr>
<tr>
<td></td>
<td>1150 ±3</td>
<td>279 ±3</td>
</tr>
<tr>
<td>946.2±0.4</td>
<td>978 ±1</td>
<td>32 ±1</td>
</tr>
<tr>
<td></td>
<td>1052.0±0.6ᵇ</td>
<td>105.8±1.0</td>
</tr>
<tr>
<td></td>
<td>1075 ±1</td>
<td>129 ±1ᶜ</td>
</tr>
<tr>
<td></td>
<td>1105.5±0.5</td>
<td>159.4±0.9ᶜ</td>
</tr>
<tr>
<td></td>
<td>1225 ±2</td>
<td>279 ±2</td>
</tr>
<tr>
<td>Co(1)</td>
<td>928 ±0.5</td>
<td>31 ±3</td>
</tr>
<tr>
<td>897 ±2ᵇ</td>
<td>1006.0±0.7ᵃ</td>
<td>109 ±3</td>
</tr>
<tr>
<td></td>
<td>1024.6±0.5</td>
<td>128 ±3ᶜ</td>
</tr>
<tr>
<td></td>
<td>1054.0±0.5</td>
<td>157 ±3ᶜ</td>
</tr>
<tr>
<td></td>
<td>1168 ±3</td>
<td>271 ±5</td>
</tr>
</tbody>
</table>

ᵃ: Appear only in π spectrum.
ᵇ: Raman data (Table 4-2); not seen in the infrared spectra.
c: cf. Raman phonon lines of Table 4-1.
to the $\Gamma_8^+$ doublet of the Co(I) ion. Sets of three vibronic bands associated with the three electronic parent levels were found and are indicated by arrows in Fig. 6-5. In any one set the vibronic band associated with the $\gamma_4 (\Gamma_8')$ level of the Co(2) ion is the weakest while the other two bands have comparable intensities. The strongest set corresponds to an energy separation of 158 cm$^{-1}$.

The results are presented in Table 6-7. Two of the vibronic intervals coincide with two of the $k = 0$ Raman phonons listed in Table 4-1.
CHAPTER VII
ZEEMAN-INFRARED STUDIES.

7.1 INTRODUCTION

Although Zeeman-optical results of cobalt ions have been reported\(^{(38)}\), no such studies in the infrared region have appeared in the literature. In the preceding chapter, the electronic and vibronic lines of CsMgCl\(_3\):Co and CsCdCl\(_3\):Co were often found to be sharp and well isolated from each other. An obvious extension of the earlier infrared work is an investigation of these crystals under an applied magnetic field. Axial and polarized spectra of these crystals were recorded at magnetic field strengths of up to 40 kG. A discussion and analysis of the spectra obtained for CsMgCl\(_3\):Co and CsCdCl\(_3\):Co are individually presented in Sec. 7.3 and 7.4 respectively.

While only shifts were detected in the Zeeman-Raman spectra, the Zeeman-infrared experiments yielded both shifts and splittings of the electronic and vibronic lines. The Zeeman-infrared experimental arrangement has several advantages over that of the Zeeman-Raman. First, because the crystals examined are at a higher temperature in the former, the upper component of the zero-field ground state is not completely depopulated. Hence electronic Zeeman-infrared transitions that originate from this component are observable. Second, the Beckman IR12 spectrophotometer has a higher signal-to-noise ratio than the Raman system.

7.2 GENERAL

Crystals used in the Zeeman-infrared work were doped with less than 3 weight % of CoCl\(_2\). This ensured that transitions due to clusters of cobalt ions and the inhomogeneous line broadening caused by neighbouring cobalt ions were both kept to a minimum. Specimens used had a mean thickness of 4.5 mm. As the field was generated by a superconducting
magnet, spectral runs were performed only at liquid helium temperatures
with the crystal temperature estimated at 15°K (Sec. 3.3). All
measurements were made at a slow scanning speed of 1.6 cm⁻¹/min., and
an 8-second time constant. Owing to the simple solenoid magnet used,
the applied field was always directed along the infrared radiation beam.
This meant that only axial spectra could be measured when the field is
directed along the crystal c axis (H∥c) while only σ and π polarization
spectra could be recorded when the field is normal to the crystal c
axis (H⊥c).

Zeeman-infrared measurements on the γ₄⁺(I₈⁺), γ₅,₆⁺(I₈⁺) and γ₄⁺(I₇⁺)
levels of CsMgCl₃:Co and the γ₄⁺(I₈⁺) and γ₅,₆⁺(I₈⁺) levels of CsCdCl₃:Co(2),
together with their stronger vibronic bands were made. All the
electronic lines examined split in the maximum field of 40 kG and these
splittings are apparent in at least one of the spectra obtained. The
biggest splitting observed was 17.2 cm⁻¹ measured for the transition to
the γ₅,₆⁺(I₈⁺) level of CsCdCl₃:Co(2) for H∥c. In contrast the transition
to the γ₅,₆⁺(I₈⁺) level of CsMgCl₃:Co only showed signs of an incipient
splitting for H∥c even at full field. The maximum number of resolved
components detected for any one electronic line was three, and only
occurred for the transition to the γ₅,₆⁺(I₈⁺) level of CsCdCl₃:Co(2).
Upon subjecting the crystals to a 20 kG field, only two of the five
electronic lines exhibited any apparent splittings. These are the
transitions to the γ₄⁺(I₈⁺) and γ₄⁺(I₇⁺) states of CsMgCl₃:Co. Marginal
or zero shifts were recorded for the other electronic levels.

Experimental data from Zeeman-infrared studies can provide the g
values of the excited electronic states. These studies can also help
assign vibronic bands, as these have the same Zeeman pattern as their
electronic parents. Impurity absorptions due to atmospheric water vapour
and localized oxygen phonons, which plagued some of the spectra recorded,
are unaffected by the magnetic field and so can readily be identified as
such.
7.3 RESULTS

7.3.1 CsMgCl₃:Co

Zeeman measurements were made on CsMgCl₃ crystals doped with 1 to 2 weight % of CoCl₂. Portions of the axial and polarized spectra obtained are displayed in Figs. 7-1 to 7-7 while spectral data are listed in Tables 7-1 and 7-2. Fig. 6-2 shows that the electronic lines of CsMgCl₃:Co have greatly different strengths. While no difficulties were encountered in obtaining a strong line for the γ⁵⁺₆(Γ₈⁺) level for a 1% cobalt ion doping, the γ⁴⁺₈(Γ₈⁺) absorption proved to be too weak for a Zeeman study at this concentration even for the maximum crystal thickness of 5.5 cm. Hence the Zeeman effect on the γ⁴⁺₈(Γ₈⁺) level was measured using 2% cobalt ion concentrations, for which a sufficiently strong line due to this level was obtained.

Axial (H∥c) Spectra

At 20 kG, two of the zero-field electronic lines each split into two components. The γ⁴⁺₈(Γ₈⁺) line was marginally resolved into lines at 820 and 824 cm⁻¹ as shown in Fig. 7-1. The γ⁴⁺₇(Γ⁺) line split into two components of equal strength separated by 8.0 cm⁻¹ (Fig. 7-6) while the γ⁵⁺₆(Γ₈⁺) line did not even shift (Fig. 7-4).

When the field was increased to its maximum strength of 40 kG, the γ⁴⁺₈(Γ₈⁺) line broadened and shifted up to 826 cm⁻¹. The 20 kG-resolved components of the γ⁴⁺₇(Γ⁺) state were further pushed apart to 16.0 cm⁻¹ at 40 kG, with the higher-energy component being twice as intense as the other. While no splitting or shift was observed for the γ⁵⁺₆(Γ₈⁺) state, it nevertheless broadened at 40 kG.

The 941.0, 1039.1, 1048.2, 1474.6 and 1591.0 cm⁻¹ vibronic lines were selected for Zeeman studies because of their stronger and narrower profiles. The first three are associated with the γ⁴⁺₈(Γ₈⁺) electronic
Fig. 7-1: 15°K Zeeman-infrared spectra of CsMgCl₃:Co showing the $\gamma^+_4 (^P^+_8)$ electronic line and its associated vibronic bands.
Fig. 7-2: Zeeman-infrared pattern of the $\gamma_4^+(T'_{8}^+)$ electronic state of CsMgCl$_3$:Co measured at 150K.
Fig. 7-3: 15°K Zeeman-infrared spectra of the vibronic bands associated with the $\gamma^+_4(\Gamma'^+_8)$ electronic level of CsMgCl$_3$:Co.
Fig. 7-4: 15°C axial (H⊥c) Zeeman-infrared spectra of the \( \gamma_{5,6}^+ (\gamma_6^+) \) electronic state of \( \text{CsMgCl}_3:\text{Co} \) and its associated vibronic band.
Fig. 7-5: 15°K polarized (H||c) Zeeman-infrared spectra of the $\gamma_{5,6}^+(\Gamma_{8}^+)$ electronic state of CsMgCl$_3$:Co and its associated vibronic band
Fig. 7-6: 15°K axial (H||C) Zeeman-infrared spectra of the $\gamma_4^+(\Gamma_7^+)$ electronic state of CsMgCl$_3$:Co and its associated vibronic band.
Fig. 7-7: $15^\circ K$ polarized (Hlc) Zeeman-infrared spectra of the $\gamma_4^+ (\Gamma_7^+)$ electronic state of CsMgCl$_3$:Co and its associated vibronic band.
### TABLE 7-1: Zeeman-infrared axial (H||c) data on CsMgCl$_3$:Co 2.0 wt.% at 15°K.

The shifts are measured from the zero-field positions.

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Width (cm$^{-1}$)</th>
<th>Shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>939.5±0.8a</td>
<td>9</td>
<td>-1.5</td>
</tr>
<tr>
<td>943.0±0.8a</td>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>1037 ±1a</td>
<td>11</td>
<td>-2.1</td>
</tr>
<tr>
<td>1040.7±0.5a</td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td>1049.1±0.8a</td>
<td>8</td>
<td>0.9</td>
</tr>
<tr>
<td>1262.4±0.5*</td>
<td>3.7</td>
<td>-0.1</td>
</tr>
<tr>
<td>1375.5±0.5</td>
<td>2.5</td>
<td>-3.5</td>
</tr>
<tr>
<td>1383.5±0.8</td>
<td>3.8</td>
<td>4.5</td>
</tr>
<tr>
<td>1474.6±0.5b,*</td>
<td>4.4</td>
<td>0.0</td>
</tr>
<tr>
<td>1587.1±0.8c</td>
<td>5</td>
<td>-3.9</td>
</tr>
<tr>
<td>1594.9±0.5c</td>
<td>5</td>
<td>3.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Width (cm$^{-1}$)</th>
<th>Shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>826 ±1</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>938 ±1a</td>
<td>4.8</td>
<td>-3.0</td>
</tr>
<tr>
<td>945.0±0.5a</td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>1029 ±1a</td>
<td></td>
<td>-3.3</td>
</tr>
<tr>
<td>1035.6±0.5a</td>
<td>4.4</td>
<td>-3.5</td>
</tr>
<tr>
<td>1043.1±0.5a</td>
<td>6.2</td>
<td>4.0</td>
</tr>
<tr>
<td>1052.0±0.8a</td>
<td>8</td>
<td>3.8</td>
</tr>
<tr>
<td>1263.0±0.8*</td>
<td>6.9</td>
<td>0.5</td>
</tr>
<tr>
<td>1371.5±0.5</td>
<td>3.5</td>
<td>-7.5</td>
</tr>
<tr>
<td>1387.5±0.8</td>
<td>4.5</td>
<td>8.5</td>
</tr>
<tr>
<td>1475.5±0.5b,*</td>
<td>5.7</td>
<td>0.9</td>
</tr>
<tr>
<td>1583.5±0.8c</td>
<td>6</td>
<td>-7.5</td>
</tr>
<tr>
<td>1599.0±0.5c</td>
<td>6.2</td>
<td>8.0</td>
</tr>
</tbody>
</table>

* : Data obtained from CsMgCl$_3$:Co 1.0 wt.%

a,b,c: Vibronic absorptions associated with the $\gamma_4^+(\Gamma_8^+)$, $\gamma_{5,6}^+(\Gamma_8^+)$ and $\gamma_4^+(\Gamma_7^+)$ electronic parent levels respectively.

Each curly bracket indicates the split components of a zero-field line.
TABLE 7-2: Zeeman-infrared polarization (H\textsubscript{LC}) data on CsMgCl\textsubscript{3}:Co 1.5wt.% at 15\textdegree K.

The shifts are measured from the zero-field positions.

<table>
<thead>
<tr>
<th>Σ Frequency (cm\textsuperscript{-1})</th>
<th>Width (cm\textsuperscript{-1})</th>
<th>Shift (cm\textsuperscript{-1})</th>
<th>Π Frequency (cm\textsuperscript{-1})</th>
<th>Width (cm\textsuperscript{-1})</th>
<th>Shift (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 kG {819.5±0.5\textsuperscript{*}</td>
<td>4</td>
<td>-2.5</td>
<td>819 ±1</td>
<td>-</td>
<td>-3.0</td>
</tr>
<tr>
<td>824.5±0.5\textsuperscript{*}</td>
<td>5</td>
<td>2.5</td>
<td>824 ±1</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>939 ±1\textsuperscript{a}</td>
<td>11</td>
<td>-2.0</td>
<td>1030 ±1\textsuperscript{a}</td>
<td>8.2</td>
<td>2.3</td>
</tr>
<tr>
<td>943.5±0.8\textsuperscript{a}</td>
<td>2.5</td>
<td></td>
<td>1034.6±0.5\textsuperscript{a}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1036.6±0.8\textsuperscript{a}</td>
<td>14</td>
<td>-2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1041.4±0.5\textsuperscript{a}</td>
<td>2.3</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1050.0±0.8\textsuperscript{a}</td>
<td>6</td>
<td>1.8</td>
<td>1244 ±1</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>1263 ±2</td>
<td>13</td>
<td>0.5</td>
<td>1261 ±1</td>
<td>8.3</td>
<td>-1.5</td>
</tr>
<tr>
<td>1264.6±0.5</td>
<td></td>
<td></td>
<td>1264.6±0.5</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>[1374.4±0.5</td>
<td>5.2</td>
<td>-4.6</td>
<td>[1374 ±1</td>
<td>3</td>
<td>-5.0</td>
</tr>
<tr>
<td>1384.2±0.5</td>
<td>4.1</td>
<td>5.2</td>
<td>1384 ±1</td>
<td>3.5</td>
<td>5.0</td>
</tr>
<tr>
<td>[1473 ±1\textsuperscript{b}</td>
<td>10.3</td>
<td>-1.6</td>
<td>[1472 ±1\textsuperscript{b}</td>
<td>11.0</td>
<td>-2.6</td>
</tr>
<tr>
<td>1476.5±0.5\textsuperscript{b}</td>
<td>1.9</td>
<td></td>
<td>1476.5±0.5\textsuperscript{b}</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>1591.0±0.7\textsuperscript{c}</td>
<td>9</td>
<td>0.0</td>
<td>1591.0±0.5\textsuperscript{c}</td>
<td>8.2</td>
<td>0.0</td>
</tr>
<tr>
<td>20 kG {1039.4±0.5\textsuperscript{a}</td>
<td>7</td>
<td>0.3</td>
<td>*Data obtained from CsMgCl\textsubscript{3}:Co 2.0wt.%. The footnote of Table 7-1 applies.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1048.3±0.8\textsuperscript{a}</td>
<td>8</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[1376.5±0.5</td>
<td>4</td>
<td>-2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1381.3±0.5</td>
<td>5</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1591.0±0.7\textsuperscript{c}</td>
<td>7.1</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
level and the remaining two with the $\gamma_{5,6}^+(I^\prime_8)$ and $\gamma_{4}^+(I^\prime_7)$ electronic levels respectively.

Figs. 7-4 and 7-6 show that the Zeeman behaviour of the 1474.6 and 1591.0 cm$^{-1}$ vibronic lines is analogous to that of their electronic parent levels.

The Zeeman effects of the 941.0, 1039.1 and 1048.2 cm$^{-1}$ vibronic lines belonging to the $\gamma_{4}^+(I^\prime_8)$ electronic level are as follows. The 941.0 cm$^{-1}$ line split into two components separated by 7 cm$^{-1}$ at 40 kG (Fig. 7-1). The 0, 20 and 40 kG traces of the 1039.1 and 1048.2 cm$^{-1}$ vibronic lines are shown in Fig. 7-3. Due to a slight misorientation of the crystal, the $\pi$-polarized 1032.3 cm$^{-1}$ line has a remnant visible in the 0 kG spectrum. In a 20 kG field, both the vibronic lines broadened and moved further apart and peaked at 1040.7 and 1049.1 cm$^{-1}$ with a weak shoulder appearing on the former line. At 40 kG the 1040.7 cm$^{-1}$ line was resolved into two well-defined components at 1035.6 and 1043.1 cm$^{-1}$, while the 1049.1 cm$^{-1}$ line shifted up to 1052.0 cm$^{-1}$.

**Polarized (H\textsubscript{lc}) Spectra**

When the crystals were exposed to a 40 kG field, each of the three electronic lines split into two components. Fig. 7-2 shows that in both the $\sigma$ and $\pi$ spectra, the components of the $\gamma_{4}^+(I^\prime_8)$ state are of equal intensity and are 5 cm$^{-1}$ apart.

At 20 and 40 kG, the components of the $\gamma_{4}^+(I^\prime_7)$ state are separated by 4.8 and 9.8 cm$^{-1}$ respectively in the $\sigma$ spectrum of Fig. 7-7. In the $\pi$ spectrum recorded at 40 kG, the components appear as weaker absorptions with frequencies identical to their $\sigma$-polarized counterparts.

Fig. 7-5 of the $\pi$ spectrum shows that at 40 kG the $\gamma_{5,6}^+(I^\prime_8)$ line experienced an incipient splitting, while only a broadening of its remnant absorption occurred in the $\sigma$ spectrum.
Zeeman effects for the main polarized vibronic transitions observed are described below starting with the π spectrum measured at 40 kG. The π-polarized 1032.3 cm\(^{-1}\) vibronic line split into a main component which peaked at 1034.6 cm\(^{-1}\) and its side band at approximately 1030 cm\(^{-1}\) (Fig. 7-3). Their separation agrees well with that of 5 cm\(^{-1}\) measured for their \(\gamma_4^+ (\Gamma_8^+)\) electronic parent level. The 1474.6 cm\(^{-1}\) vibronic line associated with the \(\gamma_5^+ (\Gamma_8^+)\) state was resolved into a 1476.5 cm\(^{-1}\) line and a weak shoulder at 1472 cm\(^{-1}\). Unlike its \(\gamma_4^+ (\Gamma_7^+)\) electronic parent line which split at 40 kG, the 1591.0 cm\(^{-1}\) vibronic line only broadened in the same field as is shown in Fig. 7-7.

The σ spectrum is as follows. Three vibronic absorptions, of the \(\gamma_4^+ (\Gamma_8^+)\) electronic state, at 941.0, 1039.1 and 1048.2 cm\(^{-1}\) were chosen for study. At 40 kG a mean splitting of 4.6 cm\(^{-1}\), consistent with that of the electronic parent state, was recorded for both the first two lines while only a shift was observed for the third line (Figs. 7-1 and 7-3). In a 40 kG field the 1474.6 cm\(^{-1}\) vibronic line, associated with the \(\gamma_5^+ (\Gamma_8^+)\) electronic state, experienced an incipient splitting (Fig. 7-5), while the 1591.0 cm\(^{-1}\) vibronic line associated with the \(\gamma_4^+ (\Gamma_7^+)\) electronic state just broadened (Fig. 7-7).

### 7.3.2 CsCdCl\(_3\) :Co(2)

Crystals used for this Zeeman work contained nominal doping of 1.0, 2.0 and 5.0 mole % of CsCoCl\(_3\). Portions of typical axial and polarized spectra recorded are presented in Figs. 7-8 to 7-10, while the numerical results are summarized in Tables 7-3 and 7-4. The vibronic absorptions of CsCdCl\(_3\) :Co although sharp, are however in most cases too weak for Zeeman studies. The main set of vibronic lines examined is the one corresponding to a vibronic interval of 158 cm\(^{-1}\). Only one of them visibly split under a magnetic field. The magnetic behaviour of
Fig. 7-8: 15°K axial (H//c) Zeeman-infrared spectra of CsCdCl₃:Co(2) 5 mole % illustrating the $\gamma_4(\Gamma'_8)$ electronic line and its associated vibronic band.
Fig. 7-9: 150 K axial (H||c) Zeeman-infrared spectra of CsCdCl₃:Co(2) 5 mole % illustrating the \( \gamma_{5,6}(I''') \) electronic line and its associated vibronic band.
Fig. 7-10: Zeeman-infrared pattern of the \( \gamma_4 (1^e) \) and \( \gamma_{5,6} (1^e) \) electronic levels of CsCdCl\(_3\):Co(2) 5 mole \%, and their associated vibronic bands, recorded at 150 K.
TABLE 7-3: Zeeman-infrared axial data on CsCdCl$_3$:Co 2 mole % at 15$^\circ$K for (H||c)

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Shift (cm$^{-1}$)$^a$</th>
<th>Width (cm$^{-1}$)</th>
<th>Int. (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$869.0 \pm 0.5$</td>
<td>-2.2</td>
<td>3</td>
<td>0.52</td>
</tr>
<tr>
<td>$873.5 \pm 0.5$</td>
<td>2.3</td>
<td>4.3</td>
<td>1.54</td>
</tr>
<tr>
<td>880 ±1</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>930.0 ±0.7$^b$</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>937.5 ±0.7$^b$</td>
<td>-8.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>947.2 ±0.5</td>
<td>1.1</td>
<td>6.3</td>
<td>2.33</td>
</tr>
<tr>
<td>954.7 ±0.5$^b$</td>
<td>8.6</td>
<td>6</td>
<td>0.81</td>
</tr>
<tr>
<td>1027.0 ±0.5$^b$</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1032 ±1$^c$</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1106.6 ±0.5$^d$</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>20 kg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>871.0 ±0.5</td>
<td>-0.2</td>
<td>4.3</td>
<td>2.85</td>
</tr>
<tr>
<td>879 ±1</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>928.5 ±0.7$^b$</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>946.1 ±0.5</td>
<td>0.0</td>
<td>4.1</td>
<td>3.29</td>
</tr>
<tr>
<td>1025.0 ±0.6$^b$</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1030.5 ±0.6$^c$</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1105.5 ±0.5$^d$</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$: Shifts from zero-field positions.

$^b,c,d$: Designate the vibronic lines associated with the $\Gamma_8'$ doublet of Co(2), $\gamma_4'(\Gamma_8')$ and $\gamma_5,6'(\Gamma_8')$ electronic parent levels respectively.

Each curly bracket indicates the set of split components of a zero-field line.
TABLE 7-4: Zeeman-infrared polarization data on CsCdCl₃:Co 5 mole %
at 15°K for a 40 kG field (Hlc)

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Shift (cm⁻¹)ᵃ</th>
<th>Width (cm⁻¹)</th>
<th>Int. (cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>868.6±0.5</td>
<td>-2.6</td>
<td>3</td>
<td>0.97</td>
</tr>
<tr>
<td>874.4±0.5</td>
<td>3.2</td>
<td>3.3</td>
<td>4.45</td>
</tr>
<tr>
<td>931.0±0.8ᵇ</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>943 ±1</td>
<td>-3.1</td>
<td>4</td>
<td>0.39</td>
</tr>
<tr>
<td>949.8±0.5</td>
<td>3.7</td>
<td>4.8</td>
<td>3.98</td>
</tr>
<tr>
<td>959 ±2</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1027.6±0.6ᵇ</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1033.2±0.8ᶜ</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1057.0±0.7ᵇ</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1070 ±3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1109.0±0.7ᵈ</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

σ spectrum

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Shift (cm⁻¹)ᵃ</th>
<th>Width (cm⁻¹)</th>
<th>Int. (cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>868.6±0.5</td>
<td>-2.6</td>
<td>7</td>
<td>0.55</td>
</tr>
<tr>
<td>875.0±0.5</td>
<td>3.2</td>
<td>6.0</td>
<td>1.09</td>
</tr>
<tr>
<td>943 ±1</td>
<td>-3.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>950.0±0.5</td>
<td>3.9</td>
<td>6.0</td>
<td>0.97</td>
</tr>
<tr>
<td>1027 ±1ᶜ</td>
<td>-2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1033.0±0.6ᶜ</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1056 ±1ᵈ</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1070 ±1</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1085 ±3</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1109.0±0.7ᵈ</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

π spectrum

The footnote of Table 7-3 applies.
the two electronic $\gamma_4 (\Gamma_8')$ and $\gamma_5,6 (\Gamma_8')$ lines proved to be more interesting as their profiles were significantly altered by the field.

Axial (H||c) Spectra

When the crystals were subjected to a 40 kG field, the following changes to the features of the zero-field axial spectra were noted. The $\gamma_4 (\Gamma_8')$ electronic line resolved into two components 4.5 cm$^{-1}$ apart, with the higher energy component being three times as intense as the other (Fig. 7-8). The 878.3 cm$^{-1}$ satellite line, which is distinct and sharp in the absence of a field, now appeared as a weak, broad side band. Three components constitute the 40 kG trace of the split $\gamma_5,6 (\Gamma_8')$ electronic level shown in Fig. 7-9, the weakest of which is the 937.5 cm$^{-1}$ line. The central line at 947.7 cm$^{-1}$ is three times stronger than the remaining component at 954.7 cm$^{-1}$. This is contrary to the usual structure of split electronic lines which have the weaker components on the lower energy side. Both the electronic lines remained unresolved and unshifted at 20 kG. However they each assumed an asymmetric line shape.

Polarized (H\perp c) Spectra

These spectra described below were recorded with the crystals exposed to the maximum field of 40 kG. They are depicted in Fig. 7-10.

$\sigma$-polarized Spectrum

Under this field, the $\gamma_4 (\Gamma_8')$ electronic line was transformed into two components at 868.6 and 874.4 cm$^{-1}$, with the former being the weaker. The 878.3 cm$^{-1}$ zero-field satellite line is no longer apparent having being masked by the strong 874.4 cm$^{-1}$ line. The $\gamma_5,6 (\Gamma_8')$ electronic line partially split into two components at 943.5 and 949.8 cm$^{-1}$, with the lower energy component being the weaker. A side band at around 959 cm$^{-1}$ appeared on the 949.8 cm$^{-1}$ line.
A comparison of Fig. 7-10 with Fig. 6-5 shows that the fine structure, appearing on the broad band centred at 1070 cm\(^{-1}\) of the latter figure, has been smeared out by the field. A line at 1057 cm\(^{-1}\) is the only remaining structure. All the vibronic bands examined shifted to higher frequencies.

\[\pi\]-polarized Spectrum

The Zeeman effects on the two electronic \(\gamma_4(T^\prime_8)\) and \(\gamma_{5,6}(T^\prime_8)\) lines in the \(\pi\) spectrum were identical to that of the \(\sigma\) spectrum. Under the influence of the field the vibronic bands became broader, which resulted in the weaker ones being less pronounced. Only the sharp intense 1029.5 cm\(^{-1}\) vibronic line, associated with the \(\gamma_4(T^\prime_8)\) electronic state, was seen to split into two components. The other vibronic bands examined followed the general trend of being shifted to higher frequencies.

7.4 ANALYSIS OF ZEEMAN-INFRARED SPECTRA

The Kramer's degenerate levels of the cobaltous ions are each split by a magnetic field into two components. The frequencies of the electronic Zeeman transitions, between the split components of the ground state and those of the excited states of these ions in CsMgCl\(_3\) and CsCdCl\(_3\) in a 40 kG field were computed using the Oscstrengths/H3942 and Oscstrengths/H120 programs listed in the appendix. The computed frequencies are listed in Tables 7-5 and 7-6 for CsMgCl\(_3\):Co and Table 7-7 for CsCdCl\(_3\):Co(2).

The experimental electronic Zeeman-infrared transition frequencies could be matched to the computed transition frequencies to within 2 cm\(^{-1}\) shown in the above tables. However Table 5-2 reveals that the \(g\) values for the \(\gamma_4^+(T^+_6)\) ground state computed from the crystal field model differ by as much as 0.4 from the EPR values. A better agreement between the experimental and computed transition frequencies can be
TABLE 7-5: Computed and experimental frequencies and oscillator strengths for assigned electronic transitions in CsMgCl$_3$:Co 2.0 wt. % at 15°K for 40 kG (H||c)

<table>
<thead>
<tr>
<th>Electronic-Zeeman transition</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Osc. Strength (10$^{-10}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_4^+(\Gamma_6^+) \to \gamma_5^+(\Gamma_7^+)$</td>
<td>1387.5</td>
<td>1387.28</td>
</tr>
<tr>
<td>$\gamma_5^+(\Gamma_6^+) \to \gamma_4^+(\Gamma_7^+)$</td>
<td>1371</td>
<td>1368.93</td>
</tr>
<tr>
<td>$\gamma_4^+(\Gamma_6^+) \to \gamma_6^+(\Gamma_8^+)$</td>
<td>1263</td>
<td>1265.33</td>
</tr>
<tr>
<td>$\gamma_5^+(\Gamma_6^+) \to \gamma_6^+(-)(\Gamma_8^+)$</td>
<td>1262.07</td>
<td>604</td>
</tr>
<tr>
<td>$\gamma_5^+(\Gamma_6^+) \to \gamma_5^+(\Gamma_8^+)$</td>
<td>-</td>
<td>1276.65</td>
</tr>
<tr>
<td>$\gamma_5^+(\Gamma_6^+) \to \gamma_4^+(\Gamma_8^+)$</td>
<td>-</td>
<td>1250.75</td>
</tr>
<tr>
<td>$\gamma_4^+(\Gamma_6^+) \to \gamma_5^+(\Gamma_8^+)$</td>
<td>826</td>
<td>827.55</td>
</tr>
<tr>
<td>$\gamma_5^+(\Gamma_6^+) \to \gamma_4^+(\Gamma_8^+)$</td>
<td>-</td>
<td>818.83</td>
</tr>
</tbody>
</table>

obtained by using the EPR g values for the ground states, together with the computed g values for the excited states. The splittings evaluated using these g values were added or subtracted, as appropriate, from the zero-field transition frequencies to yield the energy level schemes of Figs. 7-11 and 7-12. Agreement between the transition frequencies thus calculated and the observed frequencies is now within 0.5 cm$^{-1}$.

Fig. 2-3 displays the Zeeman levels of the cobalt ion labelled by the irreps of the various symmetry groups appropriate for the cobalt ion site in a magnetic field. Selection rules governing the electronic Zeeman-infrared transitions can be derived from the direct products of these irreps with the irreps of the appropriate transition operators (Sec.2.2).

For CsMgCl$_3$:Co the transition operator is magnetic dipole while for CsCdCl$_3$:Co(2) it is electric dipole in character. The magnetic dipole and electric dipole transition operators transform similarly except that,
Table 7-6: Computed and experimental Zeeman frequencies and oscillator strengths for assigned electronic transitions in CsMgCl₃:Co 1.5 wt. % at 15°K for 40 kg (Hic).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a + b</td>
<td>1383.12</td>
<td>1384.2±0.5</td>
<td>63.8</td>
<td>254.6</td>
<td>1384 ±1</td>
<td>7.1</td>
<td>18.2</td>
<td></td>
<td>19.3</td>
<td>16.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b + a</td>
<td>1373.25</td>
<td>1374.4±0.5</td>
<td>43.7</td>
<td>185.3</td>
<td>1374 ±1</td>
<td>5.5</td>
<td>18.1</td>
<td></td>
<td>19.3</td>
<td>16.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a + a</td>
<td>1377.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>19.3</td>
<td>16.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b + b</td>
<td>1379.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>19.3</td>
<td>16.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a + a,b</td>
<td>1265.69</td>
<td>1264.6±0.5</td>
<td>0.1</td>
<td>1264</td>
<td>1261 ±2</td>
<td>36</td>
<td>1761</td>
<td>1761</td>
<td>1149</td>
<td>1149</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b + a,b</td>
<td>1261.65</td>
<td>1261 ±1</td>
<td>0.1</td>
<td>1261 ±2</td>
<td>1261 ±1</td>
<td>36</td>
<td>1761</td>
<td>1761</td>
<td>1149</td>
<td>1149</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a + b</td>
<td>825.37</td>
<td>824.5±0.5</td>
<td>10.7</td>
<td>8.6</td>
<td>824 ±1</td>
<td>-</td>
<td>1.1</td>
<td>-</td>
<td>1.2</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b + a</td>
<td>821.13</td>
<td>819.5±0.5</td>
<td>6.0</td>
<td>6.5</td>
<td>819 ±1</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>1.2</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a + a</td>
<td>825.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b + b</td>
<td>821.32</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a = γ₃⁺(C₂h) or γ₂⁺⁺(C₁)  
b = γ₄⁺⁺(C₂h) or γ₂⁺⁻⁻(C₁)

* Not observed experimentally.
for groups having inversion symmetry, the former has even parity while the latter odd parity. The irreps of the $x,y$ and $z$ components of these two transition operators are given below for the different reduced symmetries.

<table>
<thead>
<tr>
<th>Operator</th>
<th>$C_{3i}(C_{3})$</th>
<th>$C_{2h}(C_{2})$</th>
<th>$C_{1}(C_{1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$z$ component</td>
<td>$\gamma_{1}^{+}$</td>
<td>$\gamma_{2}^{+}$</td>
<td>$\gamma_{1}^{+}$</td>
</tr>
<tr>
<td>dipole</td>
<td>$\gamma_{2}^{+}$</td>
<td>$\gamma_{3}^{+}$</td>
<td>$\gamma_{1}^{+}$</td>
</tr>
<tr>
<td>electric</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$z$ component</td>
<td>$\gamma_{1}^{-}$</td>
<td>$\gamma_{2}^{-}$</td>
<td>$\gamma_{1}^{-}$</td>
</tr>
<tr>
<td>dipole</td>
<td>$\gamma_{2}^{-}$</td>
<td>$\gamma_{3}^{-}$</td>
<td>$\gamma_{1}^{-}$</td>
</tr>
</tbody>
</table>

Here $C_{3i}$, $C_{2h}$ and $C_{1}$ are the effective site symmetries of the $D_{3d}$ cobalt ion in CsMgCl$_3$. For the $C_{3}$, $C_{2}$ and $C_{1}$ symmetries, appropriate to the $C_{3v}$ cobalt ion in CsCdCl$_3$, the same irreps occur but with no parity.
labels. The electronic Zeeman states of the cobalt ions in both systems are also characterized by the same group irreps, except that those of CsMgCl$_3$:Co have even parity while those of CsCdCl$_3$:Co(2) have no parity labels (Sec. 2.2). Hence the following direct product representations, although written specifically for CsMgCl$_3$:Co, are also applicable for the case of CsCdCl$_3$:Co(2).

Transitions due to a given component of the electric dipole transition operator occur in opposite polarization to the same component of the magnetic dipole transition operator because of the orthogonality of the \( \mathbf{E} \) and \( \mathbf{B} \) vectors of the infrared radiation. Thus in the \( \sigma \) spectrum, where the \( \mathbf{E} \) vector is perpendicular to the crystal \( \mathbf{c} \) axis, infrared absorption occurs through the \( x, y \) components of the electric dipole transition operator or the \( z \) component of the magnetic dipole transition operator. On the other hand in the \( \pi \) spectrum, where the \( \mathbf{E} \) vector is parallel to the crystal \( \mathbf{c} \) axis, the infrared absorption is caused by the \( z \) component of the electric dipole transition operator or the \( x, y \) component of the magnetic dipole transition operator.

The selection rules for the electronic Zeeman transitions of the cobalt ions in the two double chlorides are derived as follows.

For \( H \parallel \mathbf{c} \), the appropriate symmetry is \( C_{3i}(C_3) \) and the zero-field \( \gamma_4^+ (\Gamma_6^+) \) ground state is split into the \( \gamma_4^+ \) and \( \gamma_5^+ \) states, while the upper Zeeman states are labelled by the \( \gamma_4^+, \gamma_5^+ \) and \( \gamma_6^+ \) irreps as shown in Fig. 2-3. From the product representations

\[
\gamma_4^+ \times (\gamma_2^+ + \gamma_3^+) = \gamma_5^+ + \gamma_6^+
\]

\[
\gamma_5^+ \times (\gamma_2^+ + \gamma_3^+) = \gamma_4^+ + \gamma_6^+
\]

it follows that the \( \gamma_4^+ \rightarrow \gamma_4^+ \) and \( \gamma_5^+ \rightarrow \gamma_5^+ \) electronic transitions are both magnetic- and electric-dipole forbidden in the axial (\( H \parallel \mathbf{c} \)) spectra of CsMgCl$_3$:Co and CsCdCl$_3$:Co(2).
For $\text{HgCo}$, the $D_{3d}(C_{3v})$ site symmetry of the cobalt ion is lowered to either $C_{2h}(C')$ if the magnetic field is directed along a twofold crystal axis or $C_1(C_1)$ otherwise. Even for a 40 kG field, the Zeeman interaction is small compared with the trigonal crystal field experienced by the cobalt ions. Hence the cobalt ion site symmetry is very nearly $D_{3d}(C_{3v})$, and the electronic lines still largely retain their zero-field polarizations in the polarized ($\text{HgCo}$) Zeeman-infrared spectra. For this reason the Zeeman ($\text{HgCo}$) spectra are labelled as either the $\sigma(\text{HgCo})$ or $\pi(\text{HgCo})$ spectra. In the former, the $B$ vector of the infrared radiation is parallel to the crystal's threefold axis while in the latter the $B$ vector is perpendicular to the crystal's threefold axis.

In the $C_{2h}(C')$ symmetry, the split components of both the electronic ground- and excited-states transform as either the $\gamma_3$ and $\gamma_4$ irreps. The $z$ component of the magnetic dipole transition operator transforms as the $\gamma_2^+$ irrep of $D_{3d}(C_{3v})$, which becomes the $\gamma_2^+$ irrep of $C_{2h}(C')$. The $x,y$ component of this transition operator transforms as the $\gamma_3^+$ irrep of $D_{3d}$ which decomposes to $\gamma_1^+ + \gamma_2^+$ in $C_{2h}$. The $C_{2h}$ group has its $z$ axis along the magnetic field direction and the $\gamma_1^+$ component of the $x,y$ component of the magnetic dipole transition operator is along this $z$ axis. Since the infrared radiation is also directed along this $z$ axis, this $\gamma_1^+$ component is not operative. Hence for the $\pi(\text{HgCo})$ spectra recorded, only the $\gamma_2^+$ component of the magnetic dipole transition operator need be considered. From the product representations

$$\gamma_3^+ \times \gamma_2^+ = \gamma_4^+$$

$$\gamma_4^+ \times \gamma_2^+ = \gamma_3^+$$

(7.2)

it follows that, for $\text{CsMgCl}_3:Co$, the $\gamma_3^+ + \gamma_3^+$ and $\gamma_4^+ + \gamma_4^+$ magnetic dipole electronic transitions are absent in both the $\sigma(\text{HgCo})$ and $\pi(\text{HgCo})$ spectra. These results also apply for the electric dipole electronic transitions of $\text{CsCdCl}_3:Co(2)$. 
In the $C_1(C_1)$ symmetry, all the six lowest Kramer's doublets are split into levels labelled by the $\gamma_2^+$ irreps, while the $x,y$ and $z$ components of the electric- and magnetic-dipole transition operators transform as the $\gamma_1^+$ irrep. Hence all the electronic transitions are allowed in both polarizations for the two systems examined.

Polarized Zeeman-infrared spectra were recorded with the magnetic field applied in an arbitrary direction in a plane normal to the crystal $c$ axis, and the effective cobalt ion site symmetry is $C_1(C_1)$. However not all the electronic transitions were observed, indicating the operation of selection rules appropriate for a symmetry higher than $C_1(C_1)$. Such a symmetry can, in CsMgCl$_3$:Co, occur for the case of the magnetic field directed along a twofold crystal axis and this would be the approximate symmetry if the field is not too far removed from this axis. For the $C_{2h}$ symmetry, only two electronic transitions are expected for each polarization in qualitative agreement with observation. In the case of CsCdCl$_3$:Co(2) there is no twofold crystal axis. However, as mentioned in Sec. 2.2, an approximate $C_2$ symmetry exists for the magnetic field applied along a pseudo twofold crystal axis and this symmetry gives results similar to that of the $C_{2h}$ symmetry of CsMgCl$_3$:Co.

By utilizing the selection rules derived above for the $C_{3i}(C_3)$ and $C_{2h}(C_2)$ groups, the observed electronic Zeeman-infrared transitions can be assigned as is shown in Figs. 7-11 and 7-12. For the $H_{||c}$ case the zero-field electronic ground state components are labelled by the $\gamma_4^+$ and $\gamma_5^+$ irreps of the $C_{3i}(C_3)$ group, and for $H_{\perp c}$ by either the $\gamma_3^+$ and $\gamma_4^+$ irreps of the $C_{2h}(C_2)$ group or the $\gamma_2^+$ irrep of the $C_1(C_1)$ group. They may alternatively be characterized by effective spin values of $+\frac{1}{2}$ and $-\frac{1}{2}$, with the $+\frac{1}{2}$ irrep having the lower energy. The lowest Zeeman levels are therefore assigned as the $+\frac{1}{2}$ irrep namely $\gamma_4^+$, $\gamma_3^+$ and $\gamma_2^+ (+\frac{1}{2})$ for the respective $C_{3i}(C_3)$, $C_{2h}(C_2)$ and $C_1(C_1)$ symmetries.
Fig. 7-11: Zeeman energy-level diagram illustrating IR transition observed for CsMgCl$_3$:Cq 1.0 to 2.0 wt. % at 15°K. Figures in parentheses denote experimental frequencies (cm$^{-1}$).

$\gamma_5^+$(C$_2h$) or $\gamma_2^+(-)(C_1)$  
$\gamma_4^+$(C$_2h$) or $\gamma_2^+(-)(C_1)$

1: Shifts calculated from computed g values of Table 4.3.
2,3: Shifts calculated from EPR g values of 7.37 and 2.51 respectively.
Fig. 7-12: Zeeman energy-level diagram illustrating IR transitions observed for CsCdCl₃:Co(2) 1,2 and 5 mole % at 15°K. Figures in parentheses denote experimental frequencies in cm⁻¹.

\[ \gamma_6(-) \]
\[ \gamma_6(+) \]
\[ \gamma_4 \]
\[ \gamma_5 \]
\[ \gamma_4 \]

\[ 947.85 \ (947.2) \]
\[ 937.53 \ (937.5) \]
\[ 873.62 \ (873.5) \]
\[ 871.2 \]
\[ 868.78 \ (869.0) \]
\[ 944.1 \]
\[ 954.67 \ (954.7) \]
\[ 949.63 \ (948.8) \]
\[ 942.57 \ (943) \]

\[ a \]
\[ b \]
\[ a, b \]

\[ 40 \text{ kG} (H \| c) \]
\[ 0 \text{ kG} \]
\[ 40 \text{ kG} (H \perp c) \]

\[ a = \gamma_3(C_2) \text{ or } \gamma_2(+)(C_1) \]
\[ b = \gamma_4(C_2) \text{ or } \gamma_2(-)(C_1) \]

1: Shifts calculated from computed g values of Table 4-3.
2,3: Shifts calculated from EPR g values of 5.53 and 3.78 respectively.
TABLE 7-8: Comparison of infrared experimental and computed $g$ values of $\text{Co}^{2+}$.

<table>
<thead>
<tr>
<th>Electronic State</th>
<th>$g_{\parallel}$ Expt.</th>
<th>$g_{\parallel}$ Compt.</th>
<th>$g_{\perp}$ Expt.</th>
<th>$g_{\perp}$ Compt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CsMgCl}_3:\text{Co}$ $\gamma_4^+ (^2F_7^+)$</td>
<td>1.74$\pm$0.21</td>
<td>2.02</td>
<td>3.06$\pm$0.21</td>
<td>3.12</td>
</tr>
<tr>
<td>$\gamma_5^+ (^3F_8^+)$</td>
<td>6.84$\pm$0.21</td>
<td>6.06</td>
<td>0.26$\pm$0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>$\gamma_4^+ (^2F_8^+)$</td>
<td>3.09$\pm$0.32</td>
<td>3.13</td>
<td>0.17$\pm$0.21</td>
<td>0.10</td>
</tr>
<tr>
<td>$\text{CsCdCl}_3:\text{Co}(2)$ $\gamma_5,6^+ (^2F_8')$</td>
<td>4.02$\pm$0.11$^a$</td>
<td>3.89</td>
<td>0.46$\pm$0.21</td>
<td>0.00</td>
</tr>
<tr>
<td>$\gamma_4^+ (^2F_7')$</td>
<td>3.07$\pm$0.21</td>
<td>2.93</td>
<td>0.35$\pm$0.21</td>
<td>0.48</td>
</tr>
</tbody>
</table>

$a$: Only this experimental $g$ value was not evaluated using equation (5.3).

The observed Zeeman-infrared transitions, for each of the zero-field electronic state, originated from either the upper or lower component of the zero-field electronic ground state. Hence their magnetic splitting factors were evaluated using equation (5.3) which incorporates the EPR ground state $g$ values. In the case of the electronic $\gamma_5,6^+ (^2F_8')$ state of $\text{CsCdCl}_3:\text{Co}(2)$, its $g_{\parallel}$ value was evaluated from the difference of the frequencies of the observed transitions that originated from the lower component of the zero-field $\gamma_4^+ (^2F_7')$ ground state. The excited state predicted $g$ values were computed from the crystal field model as discussed in Sec. 4.5. They are in good agreement with those obtained from the Zeeman-infrared experiments. Table 7-8 lists these two sets of $g$ values.

The predicted oscillator strengths for the magnetic dipole electronic
The transitions of CsMgCl$_3$:Co at 40 kG were calculated using equation (6.2). The matrix elements of the components of the magnetic dipole transition operator ($L_z + 2S_z$) and ($L_x + 2S_x$), which appear in the equation, were evaluated between the lowest twelve electronic Zeeman states for both $\mathbb{H}_c$ and $\mathbb{H}_{lc}$ using the computer programs Oscstrengths/H3942 and Oscstrengths/H120 respectively (Appendix ). The predicted oscillator strengths were multiplied by the appropriate Boltzmann factors $[1 + \exp(-\frac{E}{kT})]^{-1}$ and $\exp(-\frac{E}{kT})[1 + \exp(-\frac{E}{kT})]$ for the lower and upper components of the zero-field ground state $E$ cm$^{-1}$ apart. Here $k$ is the Boltzmann constant and the crystal temperature $T$ was assumed to be 15°K. The experimental oscillator strengths of the observed electronic Zeeman-infrared transitions for CsMgCl$_3$:Co were also calculated using the procedure outlined in Sec. 6.4. Tables 7-5 and 7-6 list the experimental and predicted oscillator strengths and show reasonable agreement between these two sets of values. The notations $\pi(k\parallel H)$ and $\pi(k\perp H)$, that appear in Table 7-6, designate the two different $\pi$ spectra. In the former the direction $k$ of the infrared radiation is parallel to the magnetic field, while in the latter it is normal to the magnetic field. Of these two spectra, only the $\pi(k\parallel H)$ spectrum can be measured with the existing Zeeman-infrared arrangement in which the direction of the radiation is restricted along the solenoidal magnet's axis. The oscillator strengths of the $\gamma_3^+ \rightarrow \gamma_3^+$ and $\gamma_4^+ \rightarrow \gamma_4^+$ electronic transitions which are only permitted in the $\pi(k\parallel H)$ spectrum, and are therefore not observed with the optical arrangement employed, are listed for completeness.

The behaviour of the vibronic bands under a magnetic field was found to parallel that of their electronic parent states. The only exception was found for the case of the 1591.0 cm$^{-1}$ vibronic line in the polarized Zeeman spectra of CsMgCl$_3$:Co shown in Fig. 7-7. While a splitting of 10 cm$^{-1}$ was recorded at 40 kG for its $\gamma_4^+(T_7^+)$ electronic parent state, the 1591.0 cm$^{-1}$ vibronic line did not even shift under the same field.
Such a difference in behaviour is not easily explained. For the case of large electron-phonon interaction vibronic splittings, Satten et al.\textsuperscript{(39)} have shown that vibronic levels can have $g$ values which are smaller than those of their electronic parent levels. However it is not evident that the $\text{CsMgCl}_3:\text{Co}$ system satisfies the criterion of large electron-phonon interaction splittings, compared to the Zeeman splittings, for such effects to occur. Water absorption lines occur in the region of the 1591 cm$^{-1}$ vibronic line and could complicate the Zeeman spectra sufficiently, resulting in an appreciable anomalous effect.
CHAPTER VIII

THE RAMAN AND INFRARED SPECTRA OF CsCoCl₃

AND KCdCl₃:Co AND THE OPTICAL SPECTRA OF CsCdCl₃:Co.

8.1 KCdCl₃:Co AND CsCoCl₃

8.1.1 Introduction

The electronic transitions of Co²⁺ ions in KCdCl₃:Co and CsCoCl₃ crystals were investigated using Raman and infrared spectroscopy. On substituting for the Cd²⁺ ions in KCdCl₃, the Co²⁺ ions are located in sites of C₃ᵥ (=C₃h) symmetry. Owing to the difficulty in locating the crystal axis, no polarization studies of KCdCl₃:Co were attempted. The Co²⁺ ions in CsCoCl₃ are in sites of D₃d symmetry. Polarized infrared spectra of CsCoCl₃ have been measured. Melamud et al. (40) have found that CsCoCl₃ undergoes a transition to antiferromagnetism at 21.5°K.

An account of the spectra obtained is given below.

8.1.2 KCdCl₃:Co

The Raman experiments were performed at liquid nitrogen temperatures and the infrared experiments at both liquid-nitrogen and -helium temperatures. Table 8-1 summarizes the numerical results. All crystals examined contained a nominal doping of 2 mole % of KCoCl₃.

In the low-energy portion of the randomly polarized Raman spectrum of Fig. 8-1, lie 12 lines of varying intensities with frequencies ranging from 35-265 cm⁻¹. Barr and Goldstein (41) have reported the vibrational Raman spectrum of pure KCdCl₃ and, except for two lines at 70 and 124 cm⁻¹, their results are in agreement with those found in this work. Lines shifted by 465, 542, 913, 1103 and 1188 cm⁻¹ also appear in the spectrum.
Fig. 8-1: $80^\circ$K Raman spectrum of a randomly orientated KCdCl$_3$ crystal containing 2 mole % of KCoCl$_3$. 

Gain $\times 35$
Fig. 8-2: Infrared spectra of a randomly orientated KCdCl$_3$ crystal containing 2 mole % of KCoCl$_3$.
TABLE 8-1:  Spectral data on randomly orientated crystals of KCdCl₃:Co₂ mole %. All measurements are in cm⁻¹.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Width</th>
<th>Frequency</th>
<th>Width</th>
</tr>
</thead>
<tbody>
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<td>35±2</td>
<td>-</td>
<td>465±4</td>
<td>15</td>
</tr>
<tr>
<td>55±2</td>
<td>-</td>
<td>542±4</td>
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</tr>
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<td>86±2</td>
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</tr>
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</tr>
<tr>
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<tr>
<td>200±2</td>
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</tr>
<tr>
<td>225±1</td>
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</tr>
<tr>
<td>252±1</td>
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<td></td>
</tr>
<tr>
<td>265±3</td>
<td>-</td>
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</tr>
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</table>

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Width</th>
<th>Frequency</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>717.0±0.8</td>
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<td>717.0±0.8</td>
<td>5</td>
</tr>
<tr>
<td>910.0±0.8</td>
<td>6</td>
<td>906.0±0.5</td>
<td>3</td>
</tr>
<tr>
<td>1101.5±0.8</td>
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<td>1099.5±0.5</td>
<td>11</td>
</tr>
<tr>
<td>1186.0±0.8</td>
<td>10</td>
<td>1181.5±0.5</td>
<td>7</td>
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</table>
As seen in Fig. 8-2, the $80^\circ K$ infrared spectrum of a randomly orientated KCdCl$_3$:Co crystal exhibits four sharp lines only. Unlike the other spectra of CsCdCl$_3$:Co and CsMgCl$_3$:Co, it is devoid of any broad bands. Of these four lines, only the one at 717 cm$^{-1}$ does not appear in the Raman spectra. The remaining three lines are attributed to electronic transitions of the Co$^{2+}$ ion. On cooling to liquid helium temperatures, only the 717 cm$^{-1}$ line remained unshifted while a weak band appeared at 1173 cm$^{-1}$. The 717 cm$^{-1}$ line is assigned as an oxygen-induced absorption, analogous to the 700 cm$^{-1}$ line observed in the infrared spectra of oxygen-ion doped CdCl$_2$ by Johnstone$^9$.

8.1.3 CsCoCl$_3$

The Raman and infrared spectral data on CsCoCl$_3$ obtained at liquid-nitrogen and -helium temperatures are presented in Table 8-2. The randomly polarized Raman spectrum (Fig. 8-3), recorded at liquid helium temperatures, shows four lines shifted by 137, 188, 266 and 296 cm$^{-1}$ in its low-energy region. The first three lines match three of the Raman lines reported by Chadwick et al.$^{24}$ at 133, 183, and 264 cm$^{-1}$. In the higher-energy region of the spectrum are a sharp line at 851 cm$^{-1}$ and two weak broad bands at 990 and 1084 cm$^{-1}$.

Infrared polarization studies were done using cleaved samples with faces containing the crystal $c$-axis. Representative spectra measured at liquid-nitrogen and -helium temperatures are shown in Fig. 8-4, while the spectral data are summarized in Table 8-2. As the 1085 cm$^{-1}$ band was very sensitive to polarization, its variation in intensity was used as a guide to set the orientation of the polarizer. The spectrum in which this band appears most intense is designated 'polarizer 90°', while that in which it is least intense, 'polarizer 0°'. It is not possible to determine which of these spectra is $\sigma$ and which is $\pi$ because
Fig. 8-3: Randomly polarized Raman spectrum of CsCoCl$_3$ recorded at liquid helium temperatures.
Fig. 8-4: Polarized infrared spectra of CsCoCl$_3$. 

Transmittance vs. Frequency ($10^3$cm$^{-1}$) for different polarizer angles.
TABLE 8-2: Spectral data on CsCoCl$_3$. All measurements are in cm$^{-1}$.

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<thead>
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<th>Raman</th>
<th></th>
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</tr>
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<td>L.He</td>
<td>L.N$_2$</td>
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<tr>
<td>Frequency</td>
<td>Width</td>
<td>Frequency</td>
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</tr>
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<td>187±2</td>
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<td>137±3</td>
<td>7</td>
<td></td>
</tr>
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<td>266±2</td>
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<td>8</td>
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</tr>
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<td>854±2</td>
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<td>266±2</td>
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</tr>
<tr>
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<table>
<thead>
<tr>
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<td></td>
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<td>Polarizer - 0°</td>
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<td></td>
</tr>
<tr>
<td>Frequency</td>
<td>Frequency</td>
<td>Frequency</td>
<td>Frequency</td>
<td>Frequency</td>
</tr>
<tr>
<td>457±2</td>
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<td>450±5</td>
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<td></td>
</tr>
<tr>
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<td>750±3</td>
<td>967±2</td>
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</tr>
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<td>810±2</td>
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<td>851±2</td>
<td>1003±1</td>
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<td>972±2</td>
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<td>910±2</td>
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<td>1123±2</td>
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<td>1192±2</td>
<td>1220±2</td>
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<tr>
<td>1265±5</td>
<td>1263±2</td>
<td></td>
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</tr>
</tbody>
</table>
No axial samples of CsCoCl$_3$ could be prepared. These samples would need to be less than 1 mm thick because of the high molar extinction coefficient of CsCoCl$_3$ (14), and their preparation would entail polishing in a direction normal to the cleavage planes. This is not feasible as these crystals are fragile.

Both the Raman and infrared spectra, recorded at liquid helium temperatures, exhibit no definite antiferromagnetic ordering effects. This is ascribed to insufficient cooling of the specimens to below the Neel temperature of 21.5°K.

8.2 CsCdCl$_3$:Co

8.2.1 Results

Earlier optical absorption studies on CsCdCl$_3$:Co have been undertaken by Gilmore (42) and Shaha et al. (43). In this work higher resolution axial and polarized spectra of this crystal were measured in the 18250 to 18700 cm$^{-1}$ energy range at liquid-nitrogen and -helium temperatures. The crystals used contained nominal concentrations of 1 and 2.5 mole % of CsCoCl$_3$. Fig. 8-5 depicts the typical spectra recorded while the associated spectral data are listed in Table 8-3.

Fig. 8-5 reveals that the $\sigma$ spectrum resembles that of the axial indicating that the transitions observed are electric dipole allowed. A similar result was found for the absorptions of the same crystal in the infrared region as reported in Sec. 6.3. The main feature of these two optical spectra is an intense broad band centred at around 18549 cm$^{-1}$. Several peaks appear on this band, the most prominent of which are the two sharp lines which peak at 18513 and 18501 cm$^{-1}$. In the low-energy region of these spectra are three weak bands at 18423, 18302 and 18286 cm$^{-1}$. In contrast the $\pi$ spectrum is relatively featureless and only contains the remnants of the 18501 and 18286 cm$^{-1}$ lines.
Fig. 8-5: Optical absorption spectra of CsCdCl$_3$:Co 2.5 mole % recorded at 15°K.
**TABLE 8-3:** Observed band frequencies (cm\(^{-1}\)) for the optical absorption spectra of CsCdCl\(_3\):Co 2.5 mole % at 15\(^\circ\)K.

<table>
<thead>
<tr>
<th>Axial/(\sigma)</th>
<th>(\pi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18286±3</td>
<td>18286±3</td>
</tr>
<tr>
<td>18302±7</td>
<td>-</td>
</tr>
<tr>
<td>18423±7</td>
<td>-</td>
</tr>
<tr>
<td>18471±7</td>
<td>-</td>
</tr>
<tr>
<td>18501±2</td>
<td>18501±2</td>
</tr>
<tr>
<td>18513±2</td>
<td>-</td>
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<td>18520±3</td>
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<td>-</td>
</tr>
<tr>
<td>18678±14</td>
<td>-</td>
</tr>
</tbody>
</table>

**TABLE 8-4:** A tentative identification of the electronic lines and their associated vibronic bands of CsCdCl\(_3\):Co.

<table>
<thead>
<tr>
<th>Electronic parent</th>
<th>Vibronic parent</th>
<th>Vibronic interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>18286±3</td>
<td>18501±2</td>
<td>215±5</td>
</tr>
<tr>
<td></td>
<td>18549±3</td>
<td>263±6</td>
</tr>
<tr>
<td></td>
<td>18605±7</td>
<td>319±10</td>
</tr>
<tr>
<td>18302±7</td>
<td>18513±2</td>
<td>211±9</td>
</tr>
<tr>
<td></td>
<td>18567±7</td>
<td>265±14</td>
</tr>
<tr>
<td></td>
<td>18622±7</td>
<td>320±14</td>
</tr>
</tbody>
</table>
8.2.2 Analysis

Gilmore (42) observed bands at 18505 and 18550 cm\(^{-1}\) in his 5\(^{0}\)K spectra of randomly orientated CsCdCl\(_3\):Co crystals. He assumed the cobalt ions to be in sites of predominantly cubic symmetry and attributed most of the structure of the band at 18550 cm\(^{-1}\) to the \(4T_1(4F) + 2T_1(2P)\) electronic transition of the cobalt ions (Sec. 2.2).

Shaha et. al. (43) have reported a sharp band at 18550 cm\(^{-1}\) in the 20\(^{0}\)K polarized spectra of CsCdCl\(_3\):Co. They assigned it as the spin forbidden transition to the doublet \(2T_1(2G)\) state instead of the \(2T_1(2P)\) state as assigned as Gilmore.

Zeeman-optical investigations of CdCl\(_2\) crystals doped with cobalt ions have been carried out by Johnstone (44). He obtained 1.3\(^{0}\)K spectra, each of which exhibits an intense broad band with several peaks on it, the strongest of which is at 19002 cm\(^{-1}\). Weaker lines occur at lower energies. Among these are the 18823 and 18812 cm\(^{-1}\) lines which he ascribed to electronic transitions to the \(\gamma_4^+(\Gamma_8^+)+\gamma_5,6^+(\Gamma_8^+)\) states arising from a \(2T_{1g}\) cubic field term. The peaks on the broad band were identified as vibronic lines associated with these electronic levels.

The CsCdCl\(_3\):Co spectrum of Fig. 8-5 is similar to that of CdCl\(_2\):Co even though it is expected that the former will comprise strong electric dipole electronic transitions, while the latter is known to have relatively weak magnetic dipole electronic transitions. By analogy, the two lines at 18302 and 18286 cm\(^{-1}\) are tentatively assigned as the electronic transitions to the trigonal crystal field split components of the \(\Gamma_8(2T_1)\) state arising from either the \(2P\) or \(2G\) or \(2H\) cubic field multiplet. Their electric dipole character indicates that they are due to the Co\(^{2+}\) ions in the C\(_{3v}\) sites, consistent with the preponderance of these over those in the D\(_{3d}\) sites as established in Sec. 4.4.

Vibronic transitions associated with these two electronic levels could then be invoked to explain the stronger peaks appearing on the
intense broad band. These vibronic intervals are analysed to give frequencies of the peaks in the phonon density of states in the CsCdCl₃ host. However none of these vibronic intervals, listed in Table 8-4, match those obtained from an analysis of the infrared spectra of CsCdCl₃:Co. Hence the assignment of the lines at 18286 and 18302 cm⁻¹ as being electronic in origin needs to be reconsidered. A Zeeman investigation is needed to verify this assignment.
CHAPTER IX
THE RAMAN AND INFRARED SPECTRA OF FERROUS IONS IN
CdCl₂-TYPE CRYSTALS.

9.1 INTRODUCTION
A preliminary investigation of the Raman and infrared spectra of ferrous ions in CdCl₂ and CdBr₂ crystals was undertaken as a conclusion to this research project. There are several reasons for doing this. Firstly, the transitions of single cobalt ions are now well understood and it is appropriate to extend the investigation to the other ions of the transition-metal ion series. Secondly, the ferrous ion possesses an orbital triplet T₂g ground term which, just as for the Co²⁺ ion, can be split by the first order spin-orbit coupling. The ferrous ions are reasonably stable against oxidation and are quite readily accepted as impurities by CdBr₂ and CdCl₂.

In this chapter the results of this investigation are presented together with a tentative interpretation of the spectra obtained.

9.2 RESULTS OF CdBr₂:Fe

9.2.1 Raman Spectra
Raman scattering studies of CdBr₂ crystals containing nominal concentrations of 5 and 10 wt. % of FeBr₂ were done using the 4579, 4765, 4880 and 5145Å laser lines. Fig. 9-1 displays typical polarized Raman spectra recorded at 80⁰K.

Besides the 81 and 151 cm⁻¹ phonon lines four other lines at 285, 497, 553 and 589 cm⁻¹ appeared in the Raman spectra obtained. These four lines are weak, with the 285 cm⁻¹ line being the weakest. Of these four lines, only the 285 cm⁻¹ line appears in the Raman spectrum of Zn²⁺-doped CdBr₂ and is therefore assigned as an impurity activated
Fig. 9-1: 80°K Raman spectra of four independent polarization configurations of a CdBr$_2$:Fe 5 wt. % crystal.
second-order phonon scattering line. The remaining lines at 497, 553 and 589 cm\(^{-1}\) are attributed to electronic transitions of the ferrous ions.

Since the 80\(^0\)K Raman measurements were done, Tomblin\(^{(45)}\) has carried out measurements at 15\(^0\)K and obtained Raman lines at 491\(\pm\)1, 539\(\pm\)2, 550\(\pm\)1, 586\(\pm\)3 and 602\(\pm\)3 cm\(^{-1}\). He also observed Raman lines at 492\(\pm\)1, 551\(\pm\)1, 591\(\pm\)3 and 603\(\pm\)5 cm\(^{-1}\) in the 40 kG (H\(\parallel\)c) Zeeman-Raman spectrum of CdBr\(_2\):Fe recorded at 2\(^0\)K.

### 9.2.2 Infrared Spectra

Infrared measurements of CdBr\(_2\) crystals doped with nominal concentrations of 2.5, 5 and 10 wt. % of FeBr\(_2\) were recorded at liquid-nitrogen and helium temperatures. The spectra of all these crystals exhibit similar features and representative axial and polarization spectra, obtained at 80\(^0\)K, are shown in Fig. 9-2. The liquid helium spectra of CdBr\(_2\):Fe 5 wt. % exposed to 0, 20 and 40 kG fields are depicted in Fig. 9-3. Table 9-1 and 9-2 list the spectral data.

The spectra were measured over the 300 - 1500 cm\(^{-1}\) energy range within which CdBr\(_2\) is transparent down to 320 cm\(^{-1}\). Each of the 80\(^0\)K spectra exhibits an intense wide band with structure on it. On the lower energy side of this band are lines at 493 and 551 cm\(^{-1}\) which appear only in the axial and \(\sigma\) spectra. These absorptions do not appear in the spectra of cobalt-doped CdBr\(_2\) and are therefore attributed to iron. The 493 and 551 cm\(^{-1}\) lines match two of the Raman lines to within 2 cm\(^{-1}\) and are therefore identified as electronic lines. The similarity of the axial and \(\sigma\) spectra indicates that all the absorption features of the spectra are electric dipole in nature.

On cooling to 15\(^0\)K, the peaks of the two electronic lines shifted to 491.0 and 547.5 cm\(^{-1}\). Additional lines appeared at 605, 621 and 640 cm\(^{-1}\) and the broad band now has a weak shoulder at 790 cm\(^{-1}\). The
Fig. 9-2: Infrared spectra of CdBr$_2$:Fe 5 wt. % measured at 80°K.
Fig. 9-3: Zeeman axial (H||c) infrared spectra of CdBr$_2$:Fe 5 wt. % measured at 15°K
TABLE 9-1: Infrared axial and polarisation 80°K data on CdBr₂ containing a nominal doping of 10 wt.% of FeBr₂. All measurements are in cm⁻¹.

<table>
<thead>
<tr>
<th>Axial</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Freq.</td>
<td>Width</td>
<td>Freq.</td>
<td>Width</td>
</tr>
<tr>
<td>493±1</td>
<td>25</td>
<td>493±1</td>
<td>23</td>
</tr>
<tr>
<td>551±1</td>
<td>22</td>
<td>551±1</td>
<td>23</td>
</tr>
<tr>
<td>683±2</td>
<td>684±2</td>
<td>645±3</td>
<td></td>
</tr>
<tr>
<td>736±3</td>
<td>160</td>
<td>735±3</td>
<td>165</td>
</tr>
<tr>
<td>770±5</td>
<td></td>
<td>770±5</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 9-2: Zeeman-infrared axial (H||c) data on CdBr₂ containing a nominal doping of 5.0 wt.% of FeBr₂. All measurements were made at 15°K and are in units of cm⁻¹.

<table>
<thead>
<tr>
<th>0 kg</th>
<th>40 kg</th>
<th>20 kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freq.</td>
<td>Width</td>
<td>Freq.</td>
</tr>
<tr>
<td>491.0±0.7</td>
<td>16</td>
<td>493.5±0.7</td>
</tr>
<tr>
<td>547.5±0.7</td>
<td>12</td>
<td>550.0±0.7</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>573.5±0.7</td>
</tr>
<tr>
<td>605±1</td>
<td>607±1</td>
<td></td>
</tr>
<tr>
<td>621±2</td>
<td>622±2</td>
<td></td>
</tr>
<tr>
<td>640±2</td>
<td>180</td>
<td>639±2</td>
</tr>
<tr>
<td>676±2</td>
<td>677±2</td>
<td></td>
</tr>
<tr>
<td>732±2</td>
<td>733±2</td>
<td></td>
</tr>
<tr>
<td>769±2</td>
<td>775±2</td>
<td></td>
</tr>
<tr>
<td>790±5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
605 cm\(^{-1}\) line also appears in the 15\(^0\)K Raman spectrum measured by Tomblin and so is ascribed to an electronic transition of iron.

The 676, 732 and 790 cm\(^{-1}\) bands are each separated by 185 cm\(^{-1}\) from the 491.0, 547.5 and 605 cm\(^{-1}\) electronic lines respectively, and are therefore assigned as vibronic bands of these respective electronic lines. The 769 cm\(^{-1}\) band is separated by 182±5 cm\(^{-1}\) from the electronic transition at 586 cm\(^{-1}\) detected by Raman scattering, so it is identified as a vibronic band. The vibronic interval of 185 cm\(^{-1}\) is in good agreement with the value of 183.3±1.5 cm\(^{-1}\) obtained from a vibronic analysis of CdBr\(_2\):Co by Johnstone and Jones (37).

Fig. 9-3 of the Zeeman spectra shows that the absorptions shifted to higher frequencies under a 40 kG field thus confirming their electronic and vibronic nature. Of particular interest is the 573.5 cm\(^{-1}\) line that only appeared in the presence of a magnetic field. Because its frequency and separation from the electronic line at 550 cm\(^{-1}\) remained unchanged at 20 kG, it is unlikely that these two lines are Zeeman split components of a single electronic state. These two lines did not change in intensity as the magnetic-field was altered from 20 to 40 kG.

The zero-field energy separation of 184 cm\(^{-1}\) is maintained at 40 kG between the 677 and 732 cm\(^{-1}\) vibronic bands and their respective electronic parent lines at 493.5 and 550.0 cm\(^{-1}\). An additional weak absorption appeared at 759 cm\(^{-1}\) and is 186±4 cm\(^{-1}\) from the 573.5 cm\(^{-1}\) line, which suggests that the latter is an electronic line. From the shift estimated from its 769 cm\(^{-1}\) vibronic band, the 586 cm\(^{-1}\) electronic Raman line was predicted to peak at 592 cm\(^{-1}\) at 40 kG. This was verified by Tomblin who observed an electronic Zeeman-Raman line at 591±3 cm\(^{-1}\) at 40 kG.
9.3 RESULTS OF CdCl$_2$:Fe

A cursory investigation of FeCl$_2$-doped CdCl$_2$ crystals was performed. The 80°K Raman spectrum features two broad bands centred at 459 and 570 cm$^{-1}$ which are attributed to electronic transitions of the ferrous ion as they are absent in the spectra of CoCl$_2$-doped CdCl$_2$. The 80°K infrared spectra were recorded from 1500 cm$^{-1}$ down to the absorption band edge of the host lattice at 450 cm$^{-1}$. The infrared spectrum is relatively featureless, having only an intense broad band centred at around 750 cm$^{-1}$. As this band is not present in the spectra of CdCl$_2$:Co, it is assigned as a vibronic band of the ferrous ion.

These spectra are too broad and featureless for any detailed analysis to be carried out.

9.4 ANALYSIS OF THE ELECTRONIC TRANSITIONS OF THE FERROUS ION IN CdBr$_2$

The ferrous ion possesses the [Ar]3d$^6$ configuration whose only quintet term $^5D$ is the ground term. In an octahedral crystal field the $^5D$ term splits into an upper doublet $^5Q$ and a lower triplet $^5T_{2g}$. The spin-orbit interaction splits the $^5T_{2g}$ ground manifold into $^T_1^+$,$^T_3^+$,$^T_4^+$ and $^T_5^+$ states, with a $^T_5^+$ state lowest.$^{(46)}$ A $^T_4^+$ triplet and a $^T_3^+$ doublet lie at an energy $-2\lambda$ above the $^T_5^+$ ground state while higher up at $-5\lambda$, lie a $^T_1^+$ singlet and two triplets $^T_4^+$ and $^T_5^+$. Here $\lambda$ is the spin-orbit coupling constant, which is related to the single electron spin-orbit parameter $\xi$ by $\lambda = -\frac{\xi}{4}$. Inclusion of the trigonal crystal field raises the degeneracies further. It splits the $^T_4^+$ and $^T_5^+$ triplets into states labelled by the $\gamma_2^+$,$\gamma_3^+$ and $\gamma_1^+$,$\gamma_3^+$ irreps, while the $^T_1^+$ singlet and the $^T_3^+$ doublet become the $\gamma_1^+$ and $\gamma_3^+$ states respectively of the D$_{3d}$ group.

From EPR studies of divalent iron in CdCl$_2$, Trapp et al.$^{(47)}$ have determined that the $^T_5^+$ ground state is split by the trigonal crystal
field into a $\gamma_1^+$ singlet and a $\gamma_3^+$ doublet, with the latter lying 2.9 cm$^{-1}$ below the former. Because CdBr$_2$ is isostructural with CdCl$_2$, it is reasonable to assume that the $\gamma_3^+$ doublet also lies lowest for CdBr$_2$:Fe.

Several workers have reported evidence of the Jahn-Teller effect in their work with divalent iron. Among them are Ray et al. (48) who studied the far infrared spectra of KMeF$_3$:Fe and Freeman et al. (49) who performed optical studies on Fe$^{2+}$ ions in CdCl$_2$-type crystals. Manifestations of the Jahn-Teller distortion were observed in the optical spectra of CsCdCl$_3$:Fe by Shaha et al. (50). The Jahn-Teller theorem (51) states that a system with an orbitally degenerate ground state will be unstable. A distortion, which will lift this degeneracy, will lower the energy of the system.

No electric dipole electronic transitions are allowed for transition-metal ions in the centrosymmetric D$_{3d}$ sites of CdBr$_2$ and the electronic transitions of cobalt ions in these sites were found to be magnetic dipole allowed (37). However Fig. 9-2 reveals that the lines due to the electronic transitions of the ferrous ions in CdBr$_2$ are electric dipole in character. This can only be accounted for by a lowering in the D$_{3d}$ ferrous ion site symmetry to a noncentrosymmetric one. As the Fe$^{2+}$ ion has a $\gamma_3^+$ doublet lowest, such a distortion could occur through the Jahn-Teller effect resulting in the lifting of the degeneracy of this $\gamma_3^+$ ground state.

The evidence for the Jahn-Teller effect in CdBr$_2$:Fe is the occurrence of electric dipole electronic transitions. These transitions are not much stronger than the magnetic dipole electronic transitions observed for CdBr$_2$:Co and so any static Jahn-Teller distortion present is small, and would only cause a small splitting of the $\gamma_3^+$ ground state. In their EPR studies of CdCl$_2$:Fe, Trapp et al. (47) did not detect any splitting in the ground state of the Fe$^{2+}$ ion. To all intents and purposes therefore, the D$_{3d}$ trigonal crystal field determines the
energy level pattern of the Fe$^{2+}$ ions in CdBr$_2$. Because electric
dipole electronic transitions were observed, the actual Fe$^{2+}$ ion site
symmetry lacks inversion. This means that the states of the Fe$^{2+}$ ions
can be labelled by the irreps of the D$_3$ group which have no parity labels.
The D$_3$ group was chosen because it is the highest subgroup of D$_{3d}$ that
has no centre of symmetry. Moreover a crystalline field of D$_3$
symmetry has the same even terms as that of D$_{3d}$ symmetry. Fig. 9-4
displays the schematic energy levels of the Fe$^{2+}$ ion in CdBr$_2$.

The zero-field 150 K electronic Raman spectrum obtained by Tomblin
comprises a narrow intense line at 491 cm$^{-1}$ and two broad bands, each
of which was resolved into two components. One band has components
at 539 and 550 cm$^{-1}$ while the other at 586 and 602 cm$^{-1}$. On the basis
of the Zeeman-infrared measurements reported below, the former and
latter pairs of components are assigned to electronic transitions to the
trigonal crystal field levels of the spin-orbit $\Gamma'_4$ and $\Gamma'_5$ triplets viz.,
$\Gamma_3(\Gamma'_4)$, $\Gamma_2(\Gamma'_4)$ and $\Gamma_3(\Gamma'_5)$, $\Gamma_1(\Gamma'_5)$ respectively. Fig. 9-4 shows the
$\Gamma'_4$ triplet as being lower in energy than the $\Gamma'_5$ triplet but the alternative
assignment, where the $\Gamma'_5$ triplet is lower, would be equally valid. The
following argument is equally applicable for either assignment. The
491 cm$^{-1}$ is assigned as the electronic transition to the spin-orbit $\Gamma'_1$
state.

An interpretation of the infrared spectra is now attempted. As
mentioned above the Jahn-Teller distortion, which would split the $\Gamma_3$
ground state doublet, could account for the electric dipole electronic
transitions of CdBr$_2$:Fe. In order to lift the degeneracy of this ground
state, the D$_{3d}$ ferrous ion site symmetry has to be reduced to at least
C$_{2h}$ and for electric dipole electronic transitions to occur, this C$_{2h}$
symmetry needs to be further reduced to C$_2$. For such a low symmetry,
electronic transitions to all the excited states are allowed from either
of the two components of the $\Gamma_3$ ground state. However the lines of the
Fig. 9-4: Schematic diagram of the splitting of the $^5T_{2g}(^5D)$ ground term of the Fe$^{2+}$ ion in CdBr$_2$. 

CUBIC FIELD

SPIN-ORBIT COUPLING

TRIGONAL CRYSTAL FIELD

JAHN-TELLER OR ZEEMAN SPLITTING
infrared spectra show polarization indicative of a higher effective symmetry. This is reasonable as the $C_2$ symmetry site would only be a slight modification of the $D_{3d}$ symmetry site. The polarization selection rules were therefore derived for a $D_3$ symmetry.

In the $D_3$ group, the $x, y$ and $z$ components of the electric dipole transition operator transform like $\gamma_3$ and $\gamma_2$ respectively. For axial and $\sigma$ spectra, the relevant direct product

$$\gamma_3 \times \gamma_3 = \gamma_1 + \gamma_2 + \gamma_3$$

(9.1)

indicates that all electronic transitions are allowed from the $\gamma_3(\Gamma_3)$ ground state. However only the transitions to the $\gamma_1(\Gamma_1)$, $\gamma_2(\Gamma_4')$ and $\gamma_1(\Gamma_5')$ states, which were assigned as having frequencies of 491.0, 547.5 and 605 cm$^{-1}$ respectively, were detected. Transitions to the remaining $\gamma_3(\Gamma_4')$ and $\gamma_3(\Gamma_5')$ states were not observed due presumably to their weak intensity. Transitions from the $\gamma_1(\Gamma_5)$ state, which is just above the ground state, are expected but are weak because of its partial depopulation at 150 K.

No electronic transitions were seen in the $\pi$ spectra. From the product representation,

$$\gamma_3 \times \gamma_3 = \gamma_3$$

(9.2)

it follows that transitions from the $\gamma_3(\Gamma_5)$ ground state to the excited singlet levels are forbidden in the $\pi$ spectra. Non-observation of transitions to the $\gamma_3(\Gamma_4')$ and $\gamma_3(\Gamma_5')$ levels is, as for the axial and $\sigma$ spectra, ascribed to their weak intensity.

Due to insufficient information on the Fe$^{2+}$ ion site symmetry, no selection rules governing the electronic Zeeman-infrared transitions were derived. When a 40 kG field was applied along the crystal $c$ axis, a shift of 2.5 cm$^{-1}$ up in energy was recorded for each of the three zero-field 491.0, 547.5 and 605 cm$^{-1}$ electronic lines. Because of their
identical Zeeman shifts, these lines are assigned as electronic transitions to the \( \gamma_1(\Gamma_1), \gamma_2(\Gamma_4'), \) and \( \gamma_1(\Gamma_5') \) levels respectively. These singlet levels are unaffected by the magnetic field and any shift in frequency of the transitions to them is due to a shift in the energy of the lower component of the \( \gamma_3(\Gamma_5') \) ground state. A \( g_\parallel \) value of 2.6±0.5 is evaluated for the \( \gamma_3(\Gamma_5) \) ground state of CdBr\(_2\):Fe from this shift. Trapp et al.\(^{(47)}\) estimated the \( g_\parallel \) value of the ground state of CdCl\(_2\):Fe at 3.68±0.05. A shift of 5 \( \text{cm}^{-1} \) was measured for the zero-field electronic 586 \( \text{cm}^{-1} \) line in the \( 40 \text{ kG} \) Zeeman-Raman spectrum recorded by Tomblin. This line is assigned as the electronic transition to the upper component of the \( \gamma_3(\Gamma_5') \) doublet.

The \( 2^\circ \text{K} \) Zeeman-Raman (\( \mathbf{H} \parallel \mathbf{c} \)) spectrum does not contain the 574 \( \text{cm}^{-1} \) line which appears in the Zeeman-infrared (\( \mathbf{H} \parallel \mathbf{c} \)) spectrum. This line could be attributed to the electronic transition that originated from the upper component of the \( \gamma_3(\Gamma_5) \) ground doublet and terminated on the lower component of the \( \gamma_3(\Gamma_5') \) excited doublet. Depopulation of the former component at \( 2^\circ \text{K} \) would account for the absence of the 574 \( \text{cm}^{-1} \) line in the Zeeman-Raman spectrum. Further work is required to definitely assign this line.
CHAPTER X
OVERALL SUMMARY AND CONCLUSION

Raman scattering and infrared absorption techniques have been successfully employed to obtain spectra of divalent cobalt ions in CsMgCl$_3$ and CsCdCl$_3$. These spectra exhibit electronic lines due to transitions between the spin-orbit and trigonal crystal field levels of the $^4T_{1g} (^4F)$ ground manifold of the cobalt ion. All five single ion electronic transitions were observed for CsMgCl$_3$:Co, while only three electronic transitions were detected for CsCdCl$_3$:Co(2). A crystal field fit was performed using all the 120 states of the 3d$^7$ configuration and agreement to within experimental accuracy was achieved. Oscillator strengths for the magnetic dipole electronic transitions of CsMgCl$_3$:Co were computed using crystal field theory and were found to be sufficiently close to those measured from experiment, to substantiate the identification of these transitions as magnetic dipole in character.

First- and second-order phonon scattering in the Raman spectra of CsMgCl$_3$ and CsCdCl$_3$ hosts has been identified. Vibronic absorptions in the infrared spectra were analysed to give frequencies of peaks in the phonon density of states of these two hosts.

Zeeman-Raman and -infrared investigations were also carried out on the CsMgCl$_3$:Co and CsCdCl$_3$:Co systems. Selection rules, governing the occurrence of electronic transitions between the lowest twelve Zeeman levels, were derived using the group multiplication tables of the appropriate cobalt ion site symmetries. These rules were found to be in agreement with observation. The Zeeman splittings and shifts observed provided information on the magnetic splitting factors of the excited electronic states. The crystal field model was again utilized to evaluate the frequencies and oscillator strengths (for CsMgCl$_3$:Co) of the electronic Zeeman transitions and also the excited state $g$ values. The close agreement between the predicted values of these quantities and
those measured from experiments affirms the adequacy of the crystal field theory for the two systems examined. The Zeeman patterns of the vibronic bands were found to be similar to that of their associated electronic parent lines, thus confirming their identification as vibrationally induced absorptions.

On the experimental side, several improvements and modifications on the existing Zeeman-Raman and -infrared equipment are suggested. The non-observation of splittings of the Zeeman-Raman electronic lines is partly ascribed to the depopulation of the upper component of the zero-field ground state. This could be avoided if the specimens are not cooled to liquid helium temperatures by e.g., enclosing them in an evacuated quartz tube. Problems with the low signal-to-noise ratio of the Zeeman-Raman arrangement could be surmounted if the collection optics used were more efficient. One solution is to mount a convex lens in front of the solenoid's bore so as to collect more of the scattered radiation, thus permitting more of it to pass through the B.O.C. cryostat's windows.

At present Zeeman-infrared spectral runs are restricted to cases where the magnetic field is applied along the infrared radiation beam. A split-solenoidal magnet, similar to the B.O.C. one would permit the field to be directed at right angles to the radiation beam. Electronic Zeeman transitions, which would otherwise be forbidden, could then be observed.

Raman and infrared spectra of KCdCl₃:Co and CsCoCl₃ were also recorded. However no crystal field analysis was attempted due to lack of experimental data. Further work on the CsCoCl₃ crystals would be worthwhile in view of the well-defined polarization of their infrared spectra and also the expected spectral effects due to antiferromagnetic ordering.

An optical investigation of CsCdCl₃:Co has been performed and a
tentative interpretation of the spectra given. Zeeman studies are needed to verify the assignment proposed.

A preliminary research into the transitions of the ferrous ion was undertaken as a continuation to the spectral studies of the cobaltous ion. Electronic transitions within the $^{5}T_{2g} (^{5}D)$ cubic field ground term were observed using Raman and infrared spectroscopy. Infrared measurements reveal that the electronic transitions are principally electric dipole polarized, inferring that the expected inversion symmetry of the ferrous ion sites is not present. This is an indication that the Jahn-Teller effect is operative. A $g_{\parallel}$ value of 2.6±0.5 for the trigonal crystal field ground state of CdBr$_2$:Fe was inferred from Zeeman-infrared studies. A tentative analysis of the spectra recorded has been proposed. This research project is still at its infancy and further work is necessary to fully understand these spectra.
REFERENCES


45. C.W. Tomblin: Private communication.


The programs Oscstrengths/H120 and Oscstrengths/H3942 are written in the B6700 Fortran language and appear on the following pages. The former incorporates the entire 120-dimension energy matrix and is used for $H_{lc}$. In the latter, which is used for $H_{llc}$, the energy matrix comprises two 39-dimension $\gamma_4^+(-\frac{1}{2})$ and $\gamma_4^+(+\frac{1}{2})$ block matrices and a 42-dimension $\gamma_{5,6}^+$ block matrix. They are both used for computing the frequencies, magnetic-dipole oscillator strengths and the $g$ values of the lowest 12 crystal field levels of the Co$^{2+}$ ion from the crystal field parameters for any magnetic field strength.
FILE 61=Ours/H120,UNIT=DISK,RECORD=7260,AREA=13*1,SAVE=1
C******************************************************************************
C MAIN PROGRAM
C CALCULATES OSCILLATOR STRENGTHS FOR CRYSTAL FIELD SPLIT LEVELS
C******************************************************************************
DIMENSION R(7260),F(7260),P(10),S(14400),EC(120),T(1440),CA(12,12)
FORMAT(6F20.8)
FORMAT(7F10.2)
FORMAT(' INPUT PARAMETERS ARE : '/)
FORMAT('/10F12.4/)
FORMAT(' ENERGY LEVELS ARE : '/)
FORMAT('/10F12.4/)
FORMAT(' EIGENVECTORS ARE : '/)
FORMAT('/2OF6.3)
FORMAT(' MATRIX ELEMENT,ITS SQUARE,ASSOC. EIGENVAL. LABEL '/)
FORMAT('/5F20.8,10)
FORMAT('5F20.6 2110)
READ (5,1000) (P(I),I=1,7)
WRITE(6,1001) (P(I),I=1,7)
READ(5,1002) (P(I),I=1,7)
P(I)=-P(I)/535.00 P(9)=P(5)/535.00 P(10)=2.0
WRITE(6,1003) (P(I),I=1,10)
P(6)=P(6)*0.8164965809
READ(5,1004) (P(I),I=1,10)
P(7)=P(7)*1.414213562
READ(5,1011) FIELD
WRITE(6,1010) FIELD
FX=FIELD*0.046685
DO 100 1=1,7260
R(I)=O.O
DO 200 LL=1,7
WRITE(6,1009) LL
FORMAT(/1 **** 1 ,11)
DO 300 I=1,7260
F(J)=O.O
READ(6,110) F(J)
R(J)=R(J)+F(J)
CALL EIGEN(R,S,120,0)
DO 20 K=1,1440,6 KMAX=K+5
WRITE(6,501) (T(I),I=K,KMAX)
WRITE (6,1003)
IP=I*(I+1)/2
EC(I)=R(IP)-R(7260)
WRITE(6,1004) (EC(I),I=1,120)
DO 1400 LO=1,3
DO 600 I=1,7260
R(I)=0.0
DO 700 KL=8,10
IF(LO.EQ.1) LL=KL
IF(LO.EQ.2) LL=KL+3
DO 800 I=1,7260
F(I)=0.0
READ(61=LL) F
IF(LO.EQ.3) GO TO 1700
DO 1600 J=79,120
K=K-108
L=L-108
A(K1,L1)=0.0
B=0.0
DO 1300 I=1,120
DO 1300 J=1,120
KI=(K-1)*120+I
LJ=(L-1)*120+J
IF(I=J) 1100,1200,1200
A(K1,L1)=A(K1,L1)+S(KI)*R(IJ)*S(LJ)
GO TO 1300
IF(LO.EQ.3) 1800,1900,1800
A(K1,L1)=A(K1,L1)+S(KI)*R(JI)*S(LJ)
CONTINUE
B=A(K1,L1)*A(K1,L1)
C=B*EC(L)-B*EC(K)
WRITE(6,1112) EC(K),EC(L),A(K1,L1),B,C,K,L
CONTINUE
WRITE(6,1111) ((A(K1,L1),L1=1,12),K1=1,12)
CONTINUE
LOCK 61
END
PROGRAM OSCSTRENGTHS/H3942

CALCULATES MAGNETIC DIPOLE OSCILLATOR STRENGTHS FOR THE 12 LOWEST CRYSTAL FIELD LEVELS OF COBALT FOR THE CASE OF AN APPLIED MAGNETIC FIELD ALONG THE Z AXIS.

INPUT DATA REQUIRED

FIRST DATA CARD AN INDEX SPECIFYING THE MATRIX ELEMENTS REQUIRED. ITS VALUE IS SET TO 1 FOR ALL THE L + 2S ELEMENTS. ITS VALUE IS SET TO 2 FOR THE S ELEMENTS ONLY. ANY OTHER VALUE GIVES THE OSC. ST. L + 2S EL ONLY.

SECOND DATA CARD THE PARAMETERS DQ, B, C, S, Z, V, AND W.

THIRD DATA CARD THE APPLIED MAGNETIC FIELD IN KILOGAUSS.

CPU TIME 120 SECONDS COST 3.50 DOLLARS
CPU TIME FOR ZERO FIELD 75 SECONDS COST 2.50 DOLLARS

DIMENSION P(10), E(1000), R(1000), S(1800), PP(10), T(168), CED(42, 2), GA(480), LJ(1000), SS(1800), W(168), EG(42), G(480, 2), H(7260), CB(7260).

FORMAT(8F10.6)
FORMAT(1H0, 10F12.4)
FORMAT(1H0, 'TH~ CRYSTAL FIELD PARAMETERS B20, B40, AND B43')
FORMAT(1H0, 'THE PARAMETERS DQ, B, C, S, Z, V, W, K, L, AND M')
FORMAT(1H0, 'GAMMA FOUR MINUS EIGENVALUES')
FORMAT(1H0, 'GAMMA FIVE AND SIX EIGENVALUES')
FORMAT(1H0, 'AN EIGENVALUE OF THE GAMMA 4 MINUS MATRIX', F25.4)
FORMAT(1H0, 'AN EIGENVALUE OF THE GAMMA 5, 6 MATRIX', F25.4)
FORMAT(1H0, 'AN EIGENVALUE OF THE GAMMA 4 PLUS MATRIX', F25.4)
FORMAT(1H0, 'CORR. EIGENVALUE OF THE GAMMA 4 PLUS MATRIX', F25.4)
FORMAT(1H0, 'OSCILLATOR STRENGTHS FOR THE GAMMA 5, 6 MATRIX', F25.4)
FORMAT(1H0, 'OSCILLATOR STRENGTHS FOR THE GAMMA 5, 6 PLUS STATES')
FORMAT(1H0, 'OSCILLATOR STRENGTHS FOR THE GAMMA 5, 6 PLUS STATES')
FORMAT(1H0, 'OSCILLATOR STRENGTHS FOR THE GAMMA FIVE, SIX STATES')
FORMAT(1H0, 'OSCILLATOR STRENGTHS FOR THE GAMMA 5, 6 MINUS STATES')
FORMAT(1H0, 'OSCILLATOR STRENGTHS FOR THE GAMMA 5, 6 PLUS STATES')
FORMAT(1H0, 'OSCILLATOR STRENGTHS FOR THE GAMMA 5, 6 PLUS STATES')
FORMAT(1H0, 'INITIAL STATE', 19X, 'FINAL STATE', 16X, 'MATRIX ELEMENT', 11X, 'OSCILLATOR STRENGTH')
S23=SQR(2.0/3.0)
S2=SQR(2.0)
S107=SQR\(T\left(\frac{10.0}{7.0}\right)\)
READ(5,1025) NS
WRITE(6,1026) NS
READ(5,1000) (P(I),I=1,7)
P(8)=P(4)/535.0
P(9)=P(5)/535.0
P(10)=2.0
WRITE(6,1003)
WRITE(6,1001) (P(I),I=1,10)
P(6)=P(6)*S23
P(7)=P(7)*S2
READ(5,1016) FIELD
WRITE(6,1018) FIELD
FX=FIELD*S0.04668
DO 3200 I=8,10
PP(I)=P(I)*FX
DO 150 JJ=1,2
DO 100 I=1,1000
U(I)=0.0
R(I)=0.0
N=39+(JJ-1)*3
NP=(N*N+N)/2
DO 200 KL=1,7
LL=KL+(JJ-1)*10
READ(70=LL)E
Z=PP(KL)
DO 200 I=1,NP
U(I)=U(I)+E(I)*Z
DO 3300 I=1,10
LL=KL+(JJ-1)*10
READ(70=LL)E
Z=PP(KL)
DO 3300 I=1,NP
U(I)=U(I)+E(I)*Z
DO 3400 I=1,NP
R(I)=R(I)-U(I)
IF(JJ.EQ.2) GO TO 4100
DO 3500 I=1,NP
U(I)=R(I)+2.0*U(I)
CALL EIGEN(U,SS,N,O)
CONTINUE
CALL EIGEN(R,S,N,O)
IF(JJ.EQ.1) ZERO=R(NP)
DO 300 I=1,N
IP=(I*I+I)/2
ED(I,JJ)=R(IP)-ZERO
CONTINUE
IF(FIELD.EQ.O.O) GO TO 350
IF(JJ.EQ.2) GO TO 350
DO 350 1=1,N
IP=(I*I+I)/2
EG(I)=U(IP)-ZERO
CONTINUE
IF(JJ.EQ.1) WRITE(6,1004)
IF(JJ.EQ.2) WRITE(6,1005)
WRITE(6,1006) (ED(I,JJ),I=1,N)
IF(FIELD.EQ.0.0) GO TO 4200
IF(JJ.EQ.1) WRITE(6,1024)
IF(JJ.EQ.1) WRITE(6,1006) (EG(I),I=1,N)
CONTINUE
N4=N*N4
DO 500 I=1,N4
IM=1365+(JJ-1)*231+1
T(I)=S(IM)
IF(FIELD.EQ.0.0) GO TO 450
126 IF(JJ.EQ.2) GO TO 450
127 DO 450 I=1,N4
128 IM=1365+I
129 W(I)=SS(IM)
130 450 CONTINUE
131 DO 700 I=1,1000
132 700 R(I)=0.0
133 IF(NS.EQ.2) GO TO 5200
134 DO 800 KL=8,10
135 LL=KL+(JJ-1)*10
136 READ(70=LL)E
137 Z=P(KL)
138 DO 800 I=1,NP
139 800 R(I)=R(I)+E(I)*Z
140 GO TO 5150
141 5200 LL=JJ*10
142 READ(70=LL)R
143 5150 CONTINUE
144 DO 900 KP=1,2
145 IF(KP.EQ.2,.AND.(FIELD.EQ.0.0)) GO TO 900
146 IF(KP.EQ.2,.AND.(JJ.EQ.2)) GO TO 900
147 IF(JJ.EQ.1,.AND.(KP.EQ.1)) WRITE(6,1017)
148 IF(JJ.EQ.1,.AND.(KP.EQ.2)) WRITE(6,1022)
149 IF(JJ.EQ.2) WRITE(6,1023)
150 WRITE(6,1034)
151 DO 900 K=1,4
152 K35=K+35+(JJ-1)*3
153 DO 900 L=1,4
154 L35=L+35+(JJ-1)*3
155 IF(NS.EQ.1,.OR.(NS.EQ.2)) GO TO 5300
156 IF(K.LT.4,.AND.(K.NE.L)) GO TO 900
157 IF(JJ.EQ.2,.AND.(K.NE.L)) GO TO 900
158 5300 CONTINUE
159 A=0.0
160 D=0.0
161 IF(KP.EQ.2) GO TO 3600
162 DO 1100 I=1,N
163 DO 1100 J=1,I
164 KI=(K-1)*N+I
165 LJ=(L-1)*N+J
166 JI=(I*J-I)/2+J
167 A=A+T(KI)*R(JI)*T(LJ)
168 1100 CONTINUE
169 DO 1150 J=2,N
170 DO 1150 I=1,J-1
171 KI=(K-1)*N+I
172 LJ=(L-1)*N+J
173 IJ=(J*J-J)/2+1
174 A=A+T(KI)*R(IJ)*T(LJ)
175 1150 CONTINUE
176 IF(K.EQ.L) WRITE(6,1011)
177 IF(K.EQ.L) D=2.0*A
178 IF(K.EQ.L) A=A+ED(L35,JJ)
179 WRITE(6,1012) ED(K35,JJ),ED(L35,JJ),A,D
180 GO TO 900
181 3600 CONTINUE
182 DO 4400 I=1,N
183 DO 4400 J=1,I
184 KI=(K-1)*N+I
185 LJ=(L-1)*N+J
186 JI=(I*J-I)/2+J
187 A=A+W(KI)*R(JI)*W(LJ)
188 4400 CONTINUE
189 DO 4450 J=2,N
190 DO 4450 I=1,J-1
191 KI=(K-1)*N+I
\[ LJ = (L-1)^*N + J \]
\[ IJ = (J*J-J)/2 + I \]
\[ A = A + W(KI)^*R(IJ)^*W(LJ) \]

CONTINUE
\[ C = \neg A \]

IF (K.EQ.L) WRITE(6,1011)
IF (K.EQ.L) D = 2.0*C
IF (K.NE.L) D = A + A*EG(L35)
WRITE(6,1012) EG(K35), EG(L35), C, D

CONTINUE
DO 550 I = 1, 480
G(I, JJ) = 0.0
IF (JJ.EQ.2) GO TO 1250
DO 50 I = 1, N
G(I) = 0.0
CONTINUE
DO 600 K = 1, 4
DO 600 I = 1, N
IR = I + (K-1)*120 + (JJ-1)*78
IM = 1365 + (JJ-1)*231 + (K-1)*N + I
G(IR, JJ) = S(IM)
CONTINUE
IF (S.EQ.2) GO TO 5400
DO 1400 I = 1, 7260
H(I) = 0.0
DO 1500 KL = 8, 10
LZ = P(KL)
DO 1500 I = 1, 7260
H(I) = H(I) + B(I)*Z
GO TO 5500
CONTINUE
READ(60=13) H
CONTINUE
DO 1600 JJ = 1, 2
DO 1600 KP = 1, 2
IF ((KP.EQ.2).AND.(FIELD.EQ.0.0)) GO TO 1600
IF ((KP.EQ.1).AND.(JJ.EQ.1)) GO TO 1600
IF ((KP.EQ.1).AND.(JJ.EQ.2)) WRITE(6,1031)
IF ((KP.EQ.2).AND.(JJ.EQ.1)) WRITE(6,1032)
IF ((KP.EQ.2).AND.(JJ.EQ.2)) WRITE(6,1033)
WRITE(6,1034)
JA = 1
N1 = I + (JJ-1)*78
N2 = N1 + 38 + (JJ-1)*3
DO 1600 K = 1, 4
K35 = K + 35 + (JJ-1)*3
DO 1600 L = 1, 4
L35 = L + 35
A = 0.0
DO = 0.0
IF (KP.EQ.2) GO TO 2600
IF (NS.EQ.1).OR.(NS.EQ.2)) GO TO 5700
IF (L.LT.4) GO TO 1600
CONTINUE
DO 1700 I = 79, 120
KI = (K-1)*120 + I
LJ=(L-1)*120+J
IJ=(J*J-J)/2+I
JI=(I*I-I)/2+J
IF(I-J) 2200,2300,2300
A=A+G(KI,JJ)*H(IJ)*G(LJ,JA)
GO TO 1700
A=A+G(KI,JJ)*H(JI)*G(LJ,JA)
CONTINUE
D=A*A*ED(K35,JJ)
WRITE(6,1013) ED(K35,JJ),ED(L35,JA),A,D
GO TO 2600
IF((NS.EQ.1).OR.(NS.EQ.2)) GO TO 5100
IF((JJ.EQ.2).AND.(L.LT.4)) GO TO 1600
IF(JJ.EQ.2) GO TO 5100
IF((K.LT.4).AND.(K.NE.L)) GO TO 1600
CONTINUE
DO 2900 I=N1,N2 DO 2900 J=40,78
KI=(K-1)*120+I
LJ=(L-1)*120+J
IJ=(J*J-J)/2+I
JI=(I*I-I)/2+J
IF(I-J) 2700,2800,2800
A=A+G(KI,JJ)*H(IJ)*GA(LJ)
GO TO 2900
A=A+G(KI,JJ)*H(JI)*GA(LJ)
CONTINUE
IF((JJ.EQ.1).AND.(K.EQ.L)) WRITE(6,1019)
D=A*A*ED(K35,JJ)
IF(JJ.EQ.1) D=A*A*EG(L35)
IF((JJ.EQ.1).AND.(K.EQ.L)) D=2.0*A
WRITE(6,1013) ED(K35,JJ),EG(L35),A,D
CONTINUE
GO TO 1600
CONTINUE
LOCK 60
LOCK 70
STOP
END