CHAPTER - IV

Chiro-optical Studies on Gadolinium-Diglycollate (Gd$^{3+}$:DG) single crystal.

4.1. A brief overview of Gd$^{3+}$-spectroscopy

The ground state of Gd$^{3+}$ is $^8S_{7/2}$, the only ground level among the lanthanides which has an 'S' character. A $^S$-state has zero orbital angular momentum (L=0) and in first approximation, it does not interact with the crystal field. The $^S$ level is thus nearly degenerate and only under very high resolution it shows up a structure of few cm$^{-1}$ which is due to the simultaneous action of both crystal field and spin-orbit (S-O) coupling. In Gd$^{3+}$ the nearest excited states are so much away ($\sim 30000$ cm$^{-1}$) that even higher order S-O perturbation, which is generally high for lanthanides compared to the transition metal ions, is not sufficient to bring about large splitting of $^8S_{7/2}$ ground state. For complete removal of the Kramers' degeneracy one has to apply magnetic field. Unlike in transition metals, S-O perturbation in lanthanides is much greater than the crystal field (CF). Therefore Russel-Saundar's coupling is insufficient in lanthanides. One has to apply intermediate coupling approximation where each intermediate coupled state is a combination of Russel-Saundar's states.
Spin-orbit coupling mixes states with \( L \neq 0 \) which then splits up under the second order perturbation of CF. For example, in LaCl\(_3\) host, the \( ^4S \) level of Nd\(^{3+}\) and Er\(^{3+}\) show splittings of 4.01 and 24.17 cm\(^{-1}\) respectively while the \( ^5S \) level of Ho\(^{3+}\) splits up to only 2.23 cm\(^{-1}\). Because of this, S-state (ground) ions in general and Gd\(^{3+}\) in particular could be little understood. The nature of the interaction which causes the small but definite ground state splitting of the ion continues to baffle the spectroscopists even today.

Among the fourteen lanthanides, Gadolinium is unique in the sense that it has no visible or infrared absorption or fluorescence. A majority of the work on Gd\(^{3+}\) spectroscopy reported so far deal with the CF energy level calculation. \(^{196-198}\) Intensity calculations for the UV transitions have been very few. \(^{199}\) Detrio studied Gd\(^{3+}\) in CaF\(_2\) and SrF\(_2\) crystals and reported polarized Zeeman spectra at low temperatures. \(^{200}\) It has been observed that trivalent ions having an effective S-ground state can substitute divalent Ca in CaF\(_2\) without any significant disturbance of the local cubic symmetry. The cubic site of CaF\(_2\) does not allow electric dipole transitions and so one can measure magnetic dipole and electric quadrupole contributions, free from the interference by electric dipole. He has come to the conclusion that magnetic dipole mechanism is operative in CaF\(_2\) : Gd\(^{3+}\). The electric dipole contribution to \( C_{4v} \) site in SrF\(_2\) : Gd\(^{3+}\) has been analysed in the light of Judd-Ofelt theory. The effects of CF-induced J-mixing
were investigated both for cubic and for $C_{4v}$ symmetry. The effect has been found to be negligible on the $^6P_J$ multiplets. Transitions to $^6I_J$ multiplets are nearly pure electric dipole in origin and are dominated by the sixth rank terms in $\text{CF}$. 

Measurements of $4f \rightarrow 4f$ two-photon absorption (TPA) spectra in $\text{Gd}^{3+} : \text{LaF}_3$ and $\text{Eu}^{2+} : \text{CaF}_2$ have recently been reported. \cite{161,203,204} It has been concluded that quantitative measurements of relative TPA cross sections uniquely test a prediction of the Judd-Ofelt method which does not involve phenomenological parameters. The observations revealed widespread and severe discrepancies with the angular momentum selection rules ($\Delta L, \Delta J \leq 2$), relative intensities and polarization dependence predicted by a standard second-order theory of TPA. \cite{160} Subsequent analysis however demonstrated that the discrepancies could be explained in quantitative detail by expanding TPA theory to include third and fourth-order contributions which take into account spin-orbit and CF interactions among higher lying opposite parity configurations which serve as intermediate states. \cite{161,204}

Very recently a third-order process involving ligand excited states has been reported. \cite{162} It is the ligand polarization mechanism, popularly known as 'Dynamic Coupling' mechanism in one-photon processes. It has been estimated that for TPA within the $f^7$ configuration of $\text{Gd}^{3+} : \text{CaF}_2$, this mechanism makes a contribution comparable to the third-order static CF process.

Radiationless transitions between the various $J$-states of lanthanide ions may occur by simultaneous emission of several
phonons (quantized crystal lattice vibrations). This is due to the interaction of the electronic levels of the lanthanide ion with the vibrations of the host lattice. The overall electronic symmetry is expected to be conserved in a radiationless transition. Several groups have reported the luminescence from J-manifold of lanthanide ions in weakly coupled lattice environments. They proposed that the interaction of the lanthanide electronic levels and the vibrations of the host lattice is responsible for nonradiative transitions. This needs simultaneous emission of several phonons which conserve the energy of the transition. Gadolinium is the exception among lanthanides in the sense that it has hardly any superimposed crystal vibrations not it has any local vibrational mode acting. And thus strong fluorescence is observed even for the hydrated salts. The 7 msec relaxation time for the $^6P_{7/2}$ state in GdCl$_3$·6H$_2$O is not affected by interactions with the lattice.

4.1.2. Purpose of the present study:

We have already indicated in Chapter II (2.1.3) that by a comparative study of polarized and axial spectra of an axially symmetric crystal, one can detect the magnetic dipole transitions. Since the axial crystal field is insufficient to lift the $^8S_{7/2}$ degeneracy, this simple experimental test for finding the nature of the dipolar transition is inapplicable for most Gd$^{3+}$ crystals. However, magnetic field can be used to lift the degeneracy in a
cubic crystal and provide the necessary axis required for polarization study. But to have a meaningful Zeeman spectra, the Zeeman splitting should be greater than the band width, and at the same time, it should not exceed the CF splitting. These are difficult to fulfill.

An useful alternative way to gain information on the nature of the transitions operative in axial crystals is to study the circular dichroism (CD) spectra coupled with absorption. Such studies offer an elegant alternative to separate magnetic dipolar contribution from a mixed dipolar transition. This has been successfully applied for the first time by Sen et al in single crystals of Eu-DG complexes. Here we follow the same technique to look into the nature of moments for the $^8S_{7/2} \rightarrow ^6P_J$, $^6D_J$, and $^6I_J$ transitions in Gd$^{3+}$-diglycollate (Gd$^{3+}$:DG) single crystal. The set of transitions provide large variation of $\Delta J$ and $\Delta L$ values, and hence are ideal for studying the influence of $\Delta J$ and $\Delta L$ on the CD/OD ratio.
4.2. Crystal Structure:

The crystal structures of the isostructural Trisodium-tris(diglycollato) lanthanide (III) di(sodium perchlorate) hexahydrate, \( \text{Na}_3 \text{Ln}(\text{OCOCCH}_2\text{CH}_2\text{OCO})_3\text{2NaClO}_4 \cdot 6\text{H}_2\text{O} \) have been determined from X-ray intensity data. The crystals are trigo­

The unit cell dimensions for the \( \text{Gd}^{3+} \) compound are \( a = 9.73\text{Å} \) and \( c = 28.18\text{Å} \). Three molecular units consist the unit cell (\( Z=3 \)). The ligand \( (-\text{OCOCCH}_2\text{CH}_2\text{OCO})^- \) has three possible coordinating groups and acts as a tridentate ligand. The central lanthanide ions must be nine-coordinated. The unit cell structure consists of layers perpendicular to the \( c \)-axis. The layers contain the negatively charged mono-nuclear diglycollate complexes and the perchlorate ions. These layers are alternated by layers of \( \text{Na}^+ \) ions, \( \text{Gd}^{3+} \) ion and water molecules.

Each lanthanide ion is coordinated to six carboxylic oxy­

Each ether oxygen occupy one of the three two-­
fold axes which pass through the centres of the rectangular faces of the prism. The symmetry of the complex then, becomes 32 (point group \( D_3 \)). The structure of the isostructural \( \text{Ln-DG} \), for example is shown in Fig. 4.1. In general, the distance between the \( \text{Ln}^{3+} \) ion and the carboxylic oxygen is significantly shorter
Fig. 4.1. A view down the trigonal axis of the \( \text{Ln(oxydiacetate)}_3^{3-} \) complex as it exists in crystalline \( \text{Na}_3 \text{Ln(oxydiacetate)}_3 \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O} \). The six nearest neighbour \( \text{ClO}_4^- \) ions are also shown.
than that between Ln$^{3+}$-ion and the ether oxygen. The diglycolla-
te ions form two identical five membered rings with the Ln$^{3+}$ ion
and the ligand molecule lying approximately in the plane defined
by its two carboxylic oxygen and the Ln$^{3+}$-ion. The C$_3$-axis of
the trigonal prism coincides with the three-fold axis of the
crystal. The nearest neighbour distance is more than 8.9Å in all
cases.

4.3. CD Spectral analysis and CF splitting of the states ($^6P_J$, $^6D_J$ and $^6I_J$) of Gd$^{3+}$ diglycollate (Gd$^{3+}$-DG) crystal.

The axial absorption and CD spectra were taken under com-
parable resolution and are shown in the Fig. 4.2. The spectrum
is composed of three groups of transitions $^8S_{7/2} \rightarrow ^6P_J$, $^6P_J$ and
$^6I_J$. Resolution in the spectrum could have been improved by
applying magnetic field with simultaneous lowering of temperature.
Such high resolution spectra in conjunction with a suitable theo-
retical model is a powerful means for spectra-structure correla-
tion. Notwithstanding the importance of high resolution spectra, we
mean to concentrate on the low resolution CD spectra. The crystal
structure is determined at RT, but the RT CD spectrum is not
sufficiently resolved, specially for $^6I_J$ groups. The resolution
is better at 4K due to narrowing of line-width, but then a
phase transition sets in at 110K; the structure of the low-
temperature phase has not been well investigated and hence, the
theoretical parameters, which are large in number for low symme-
try, remain uncertain. We have therefore addressed ourselves to
Fig. 4.2 — Room-temperature absorption (lower) and circular dichroism (upper) corresponding to the $^8S_{7/2} \rightarrow ^2I_{9/2}$ (A) and $^8S_{7/2} \rightarrow ^6P_{7/2}^0D_{7/2}$ (B) groups of transitions in the single crystal.
the question for spectra-structure correlation in Chapter VII and VIII for Pr-DH and Gd-PG crystals - while this low-resolution study is confined to throwing light on $\Delta J$ selection rule proposed before and $\Delta L$ selection rule proposed now, for gross term-to-term transitions. These selection rules are admittedly approximate, for they ignore the effect of crystal field and only deal with relative gross magnitudes, but not the signs, of term-to-term transitions.

Circular Dichroism study, as has already been pointed out, is an elegant means to get the magnetic dipole moment contribution for a mixed dipolar transition. For the $K$-th band, the rotational strength ($R_K$) is the scalar product of electric dipole and magnetic dipole moments and the dipole strength ($D_K$) is the sum of their absolute squares, neglecting higher order moments whose contributions are much less. To get an idea of the relative magnetic dipolar contribution to the total moment of a free ion term-to-term transition, the basic assumption one has to make is that CD for such transitions are proportional to the total (i.e., summed over all CF components) electric dipole transition moment ($P$) and total magnetic dipole transition moment ($M$). If one further makes an assumption that the total intensity or the oscillator strength is proportional to $P^2$ (neglecting $M^2$, which is relatively small in most cases), a rough correlation can be made for observed relative $R_K/\sqrt{D_K}$ values with the respective magnetic dipole moments ($M$) calculated from the free ion wavefunctions given by Wybourne. Of course for purely magnetic dipole allowed
transitions, $^8S_{7/2} \rightarrow ^6P_{7/2}, ^6P_{5/2}$, this assumption is less than valid since P and M are then of comparable magnitudes.

McCaffery and Mason, while discussing the optical activity of metal complexes argued that instead of $R_K/\mu^2$ the calculated values should correlate better with $R_K/\Delta D_K$, where $\Delta D_K$ is the difference between dipole strengths of the optically active complex and that of a symmetric inactive one. Though it is difficult to find a rigorous justification behind their argument, we include both the sets for comparison. $\Delta D_K$ for our case is the difference between the dipole strengths of Gd-DG and the symmetric, optically inactive Gd$^{3+}$ aqua-ion.

It is evident from the data and the spectra that $R_K/\mu^2$ values for transitions to $^6P_J$ and $^6D_J$ groups are much higher than those for the $^6I_J$ group. Reason for this is not difficult to find. In the free ion the transitions $^8S \rightarrow ^6P$, $^8S \rightarrow ^6D$ and $^8S \rightarrow ^6I$ have decreasing order of magnetic dipole character.

Magnetic dipole transition primarily occurs between states having same L and S i.e., $\Delta L = 0$, $\Delta S = 0$. Now, the spin-orbit coupling operator $(L, S)$ couples directly the states which differ in L by one unit. Therefore this operator mixes the $^8S$, $^6P$ and $^6D$ states in the free ion wavefunction and thus, the transitions $^8S \rightarrow ^6P$ and $^6D$ get weak magnetic dipole allowedness in the free ion itself. On the other hand, in a perturbation approach, six-steps are needed to mix $^6I$ states with $^8S$, and in consequence, the probability for $^8S \rightarrow ^6I$ transition is very low. The same general argument will make $R_K/\mu^2$ values for $^8S \rightarrow ^6D$ transitions less than that for $^8S \rightarrow ^6P$ transition.
The calculated values (M) based on exact free ion wave-function (of Wybourne), however, are less in agreement with relation $R_K/\sqrt{D_K}$, or even $R_K/\sqrt{4D_K}$ values, as shown in Table 4.1. Several explanation may be offered: (1) The $^8S \rightarrow ^6P$ transition are primarily magnetic dipole allowed, and here neglecting $M^2$ from $\mathbf{p}^2+M^2$ in the expression of $D_K$ is not justified. Secondly, parity all-electric quadrupolar transition may contribute a part of the observed rotational strength as pointed out by Richardson. Indeed, for such heavy atoms as lanthanides, the electric quadrupolar and magnetic dipolar moments at times may be of comparable orders of magnitudes. Moreover, gradient of crystal field might be significant for these cases.

Let us now turn to the $\Delta J$ selection rule. In accordance with the $J$-selection rule for a magnetic dipole transition, i.e., $\Delta J = 0, \pm 1$, the CD for $^8S_{7/2} \rightarrow ^6P_{3/2}$ transition has been found to be weak. In case of $^6I$ group of transitions, the CD/\sqrt{D_D}$ for $^8S_{7/2} \rightarrow ^6I_{7/2}$ is relatively large but not $^8S_{7/2} \rightarrow ^6I_{9/2}$. It is weak and is of comparable intensity with the $^8S_{7/2} \rightarrow ^6I_{13/2,15/2,17/2}$ transitions. If intensity for $^8S_{7/2} \rightarrow ^6I_{9/2}$ was prominent, CD could have been used as a valuable diagnostic tool for cases of close lying $J$-levels. Unfortunately CF-induced $J$-mixing of states of same $L$, as $J$-levels get closer, puts a limitation over the $J$ selection rule in the present case.

4.4. Conclusion:

The general conclusion drawn from these observations can be summarised as follows. As expected, the CD/Absorption ratio
is large for $\Delta L = |1\rangle, |2\rangle$ compared to $\Delta L \gg 2$. The proximity of $J$ levels with small $L$ in case of Gd$^{3+}$ causes violation of the simple $\Delta J = 0, \pm 1$ selection rule. It is possible that reasons for observing breakdown of the strict $\Delta J$ selection rule in this case are similar to those put forward for two-photon absorption $^{161,162}$ and resonance second harmonic generation $^{162a}$ in analogous Gd$^{3+}$ crystals.
Table 4.1. Calculated magnetic dipole moments, $R_K/D_K^{1/2}$ and $R_K/(\Delta D_K^{1/2})$, for different transitions in the Gd$^{III}$-DG single crystal.

<table>
<thead>
<tr>
<th>band position (nm)</th>
<th>$2S+1L_J$</th>
<th>Calc. magnetic dipole moments$^a$ (SI units)</th>
<th>$R_K/D_K^{1/2}$ (SI units)</th>
<th>$R_K/(\Delta D_K^{1/2})$ (SI units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>244.6</td>
<td>$^6D_{3/2}$ $^6D_{5/2}$</td>
<td>$3.3 \times 10^{-11}$ ($^6D_{5/2}$)</td>
<td>$1.35 \times 10^{-12}$</td>
<td>$3.86 \times 10^{-12}$</td>
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<tr>
<td>245.0</td>
<td>$^6D_{7/2}$ $^6D_{1/2}$</td>
<td>$5.7 \times 10^{-11}$ ($^6D_{7/2}$)</td>
<td>$2.22 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>253.0$^b$</td>
<td>$^6D_{9/2}$</td>
<td>$1.2 \times 10^{-11}$</td>
<td>$1.74 \times 10^{-12}$</td>
<td>$1.98 \times 10^{-12}$</td>
</tr>
<tr>
<td>273.3$^b$</td>
<td>$^6I_{13/2}$ $^6I_{15/2}$ $^6I_{11/2}$</td>
<td>-</td>
<td>$3.9 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>276.3</td>
<td>$^6I_{17/2}$ $^6I_{9/2}$</td>
<td>-</td>
<td>$2.1 \times 10^{-13}$</td>
<td>$4.13 \times 10^{-13}$</td>
</tr>
<tr>
<td>276.8</td>
<td>$^6I_{7/2}$</td>
<td>-</td>
<td>$2.7 \times 10^{-13}$</td>
<td>$2.4 \times 10^{-14}$</td>
</tr>
<tr>
<td>279.2</td>
<td>$^6I_{11/2}$</td>
<td>-</td>
<td>$3.9 \times 10^{-13}$</td>
<td>$2.05 \times 10^{-13}$</td>
</tr>
<tr>
<td>279.4</td>
<td>$^6I_{7/2}$</td>
<td>-</td>
<td>$1.2 \times 10^{-13}$</td>
<td>$2.4 \times 10^{-14}$</td>
</tr>
<tr>
<td>306.5$^b$</td>
<td>$^6F_{7/2}$</td>
<td>$1.6 \times 10^{-10}$</td>
<td>$4.8 \times 10^{-12}$</td>
<td>$1.33 \times 10^{-11}$</td>
</tr>
<tr>
<td>312.2$^b$</td>
<td>$^6F_{5/2}$</td>
<td>$1.32 \times 10^{-10}$</td>
<td>$3.6 \times 10^{-12}$</td>
<td>$7.44 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

$^b$ When either or both of the absorption and Gd bands remain unresolved, the CF components are considered as a composite case. $^c$ For the aquo ion the bands are not resolved and the single-crystal bands are summed accordingly. $\Delta D_K$ is the difference in dipole strength between that of the chiral single crystal and that of the symmetric Gd$^{III}$-aquo ion.