CHAPTER VIII
CHAPTER - VIII

Theoretical and Experimental Studies on the Chiroptical Activity of Magnetic Dipole Allowed $^8S \rightarrow ^6P$ Transition in Gadolinium Pyrogermanate Single Crystal.

8.1. Introduction

In chapter VII our attempt to calculate the CD spectrum of Pr-DN has met with limited success. A part of the difficulty might have arisen from the fact that none of the Pr$^{3+}$ transitions are directly magnetic dipole allowed. We have therefore attempted another calculation on Gd$^{3+} \, ^8S \rightarrow ^6P$ transitions, where out of the three transitions, the calculation of two, which are directly magnetic dipole allowed, becomes relatively straightforward. Instead of the DG crystal discussed in chapter IV, we have chosen a new system - Gadolinium Pyrogermanate Gd$_2$GeO$_7$; Gd-PG, the reason for choosing this crystal for spectra-structure correlation is that the transitions are well resolved at R.T and the experimental CD shows a distinctive pattern as shown in Fig. 8.1. If one sums up the CD over the components, the CD becomes nearly zero. Secondly, the CD pattern of $^8S_{7/2} \rightarrow ^6P_{7/2}$ is just opposite to that of $^8S_{7/2} \rightarrow ^6P_{5/2}$. This gives an intuitive feeling that the CD pattern is
Fig. 8.1. Room temperature axial absorption (OD) and CD spectra of Gd-PG.
explicable by intra-$^6P$ mixing and thus one can possibly limit the basis set to $^6P$ and $^6I$ group of states only. The discrepancies observed by Bloembergen and others\textsuperscript{203} in TPA intensities of $^8S_{1/2} \rightarrow ^6P_{7/2,5/2,3/2}$ transitions - and the subsequent controversies\textsuperscript{161,162,204} regarding the reasons for it have added further impetus to our work.

8.2. Experimental

The supplied\textsuperscript{151} Gd-PG crystal was treated following the procedure given in Chapter III. The crystal four-fold axis was identified visually and then verified under the polarising microscope and room temperature axial absorption and CD spectra were recorded under the same resolution.

8.3. Calculational Procedures

The site symmetry of Gd$^{3+}$ in Gd-PG is a distorted pentagonal bipyramid\textsuperscript{151}. In our CF calculation, it has been assumed to possess the lowest symmetry (C$_1$). Hence in the CF potential expansion all the terms are allowed. In C$_1$ symmetry, as in our C$_3$ symmetry in K$_3$Pr$_2$(NO$_3$)$_9$, there are two sets of CF parameters, one real and the other, 'imaginary'. This contributes a total of 27 independent even parameters - 15 real and 12 imaginary. Moreover, each parameter is composed of static point charge and ligand polarizability contributions. They are calculated following Richardson\textsuperscript{34a}. We chose our starting wavefunctions...
as the intermediate coupled (IC) states given by Wybourne. The CF matrix elements with these wavefunctions however, are constructed within the $^{6}P_{7/2,5/2,3/2}$ basis. We have followed the procedure of Chapter-III to solve the (36x36) real matrix and obtained the eigen function spanning the irreducible representations of the $C_1$ point group. A significant point has to be noted in this regard. It is that, for half-filled open-shell the diagonal matrix elements of the CF potential, $V_{CF}$ (e.g. $\langle 6_p | V_{CF} | 6_p \rangle$ in Gd$^{3+}$) vanish. This is due to the charge conjugation symmetry of the free ion states (which only changes sign when the holes and particles are interchanged) and due to the proportionality of $V_{CF}$ to the charge of the particles it acts on. Hence the CF contribution to the diagonal matrix element is nil. Whatever CF contribution the off-diagonal elements offer is through the admixture of $6_{P_j}$ states with $6_{D_j}$, since the small contributions from other states are neglected in the IC wavefunctions.

8.4. Results and Discussions

Figure 8.1 describes the room temperature axial absorption and CD spectra for the transitions $^{8}S_{7/2} \rightarrow ^{6}P_{7/2,5/2,3/2}$, one above the other for easy comparison. It can be seen that all the multiplets are completely resolved and their splittings are much higher than corresponding Gd-DG transitions studied before, as expected from the larger magnitude of the CF potential the low symmetry ($C_1$) site offers. Along with the clear CF splittings, the spectrum reveals the interesting CD sign pattern. We
have preferred to confine the discussion to the transitions to $^6\tilde{P}_J$ multiplets because of the following reasons:

1. The spin-orbit coupling operator $L \cdot S$ couples directly the $^6P$ states with $^8S$ because they differ in $L$ by one unit (i.e. $\Delta L = 1$) and also according to the $J$-selection rule ($\Delta J = 0, \pm 1$) the transitions $^8S_{1/2} \rightarrow ^6P_{7/2}$ and $^6P_{5/2}$ are directly magnetic dipole allowed in the free ion itself.

2. Secondly, it is found that both in cubic CaF$_2$:Gd$^{3+}$ and in C$_4v$ site of SrF$_2$:Gd$^{3+}$, CF induced $J$-mixing have been negligible on the $^6P_J$ multiplets.\textsuperscript{200-202}

3. Thirdly, although a full $J$-mixing calculation would have improved the energy level fitting as found by others\textsuperscript{220} it has been observed by us (Chapter - VII) that no unique set of parameters could be found which reproduce the CF splitting and at the same time fitted the observed intensities of different CF bands. The large number of parameters frustrated our attempts for semi-empirical fitting.

4. In view of the number of parameters we did not venture into complicated calculations by taking all other states because in that case much of the simplicity would have been lost. The observed relative CD pattern of $^8S_{7/2} \rightarrow ^6P_{7/2}$ and $^8S_{7/2} \rightarrow ^6P_{5/2}$ components (i.e. that the lowest energy component of $^8S_{7/2} \rightarrow ^6P_{5/2}$ has the same sign as the highest energy component of $^8S_{7/2} \rightarrow ^6P_{5/2}$ transition) gives one the intuitive feeling that the pattern arises through interaction between the two.
Table 8.1 reveals clearly the overall magnitudes of the di-
symmetry factor \( \frac{R_K}{D_K} \) for CP component to component tran-
sitions to the \(^6P_J\) states. It contains the experimental values as well as the values obtained from our CF calculations. The experimental energies of the CF levels are included. The calculated splittings are shown at the top of Figure 8.1. As expected the calculated splittings are in poor agreement with the experimental results. However, the agreement regarding CD pattern is fairly good. Though the calculated magnitudes are lower in general, the relative sign matching is quite remarkable, particularly for \(^6P_{7/2}\) and \(^6P_{5/2}\) states. We, therefore, feel that the distinctive CD pattern of the components of the two transitions is emerging basically from interaction within the \(^6P\)-manifold rather than the inter-group interaction.

The low \( \frac{R_K}{D_K} \) values is partly due to the higher estimation of \( D_K \) in our calculation. It has been observed that the calculated magnitudes of electric dipole moment and magnetic dipole moment are of comparable magnitudes whereas comparison of axial spectrum with polarised spectrum show that MDM E.D.M. If E.D.M's are neglected \( \frac{R_K}{D_K} \) will improve by a factor of two. In view of the energy level pattern of Gd\(^{3+}\) (i.e., high energy of \(^6P\) states and consequently smaller gap between \( f^N \)-states and opposite parity states) the EDM calculated on the basis of Judd-
Ofelt theory can be questioned.

The high observed \( \frac{R_K}{D_K} \) for \( ^8S_{7/2} \rightarrow ^6P_{3/2} \) is unexpected in view of the magnetic-dipole-forbidden character of a \( \Delta S = 2 \).
transition. The calculated pattern is also not in agreement. Several explanations may be offered.

(1) It may arise from quadrupolar contribution to CD. The experimental way of deciding quadrupolar contribution is to compare the single crystal CD with that of random sample. The quadrupolar contribution should vanish for the random samples. Unfortunately, the experiment did not succeed because of large scattering from pelleted powdered sample and intrinsic small CD of the transition.

(2) There could be higher order spin-orbit contribution to the moments of the type discussed by Judd for anomalous TPA intensity for this transition. Before taking such higher order contribution, it will of course be necessary to extend the basis and take CF-induced mixing between different groups.

(3) Judd-Ofelt approximation may not be a good one for 3d$^{3+}$ case.

8.5. Conclusion

Considering the simplicity of the approach, the results achieved are quite encouraging. The limited goal of explaining the distinctive CD pattern of the component transitions of magnetic dipole allowed $^8S_{7/2} \rightarrow ^6P_{7/2,5/2}$ transitions has been achieved. Quantitative evaluation of the CD of $^8S_{7/2} \rightarrow ^6P_{7/2,5/2,3/2}$ group however, needs improved wavefunctions.
Table 8.1. Room temperature Stark-splitting and $R_K/D_K$ of $\text{Gd}_2\text{Ge}_2\text{O}_7$ single crystal.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Stark-splitting in cm$^{-1}$</th>
<th>$R_K/D_K \times 10^4$</th>
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<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Theoretical</td>
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<tr>
<td>$^8S_{7/2} \rightarrow ^6P_{7/2}$</td>
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<tr>
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<td>$^8S_{7/2} \rightarrow ^6P_{3/2}$</td>
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