



ESTIMATION OF THE ENERGY LEVELS OF DI-AMMONIUM D-TARTRATE DOPED WITH GADOLINIUM ION

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ABSTRACT

This paper is an endeavor to appraise the energy levels of the $4f^7$ configuration to the ground state splitting of the trivalent gadolinium ion in di-ammonium D- tartrate single crystals. The energy levels of Gd^{3+} ion in 8S state are split in the presence of the crystalline electric field with either monoclinic or orthorhombic symmetry. The optical absorption spectra of Gd^{3+} ions in single crystals of di-ammonium D- tartrate are also recorded at room temperature. The energy levels of the $4f^7$ configuration were estimated and compared with those observed by experiment. The values of $E^1=6253\pm 12$, $E^2=41\pm 0.26$, $E^3=692\pm 3.1$ and $\zeta_{4f}=1525\pm 20\text{ cm}^{-1}$, $\alpha=29.98\text{ cm}^{-1}$, $\beta=-106.36$ and $\gamma=955$ are found to give the best over-all agreement between experimentally observed and calculated levels. Using spin-orbit and spin-spin contributions the mean error was decreased to 34.32 cm^{-1} . Assuming non-hydrogenic ratio the intermediate-coupling free ion estimation can be easily done.

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Keywords: Optical absorption; Crystal field; Slater parameters; Configuration Interaction; Spin- Orbit Coupling Constant.

INTRODUCTION

Optical spectroscopy gives the electronic structure of rare earth ions in the single crystals, knowledge of the energy levels and crystal field parameters as well as better understanding of the physical interactions present in the system [1-4]. Trivalent gadolinium belongs to the $4f^7$ configuration. This arrangement belongs to the half-filled shell of equivalent electrons. Trivalent gadolinium belongs to the $4f^7$ configuration. According to Hund's rule, the ground state of Gd^{3+} ion is $^8S_{7/2}$. The trivalent gadolinium ion is unique among the trivalent rare earths as it gives a large number of distinctive characteristic properties that are not found in any other trivalent lanthanide ions. The optical spectra of Gd^{3+} ion in crystalline field have long been of considerable interest for spectroscopists [5-12]. In ions having half filled shell because of less knowledge of ground state splitting, researchers have serious problem in the crystal field theory [13-18] The little progress has



been made in obtaining more explanation for splitting of ground state of trivalent gadolinium in so many crystalline environments using EPR (Electron paramagnetic resonance) technique [19-26].

Because of specific characteristics of half filled shells the energy levels of a multiplet will not be split in the Russel-Saunders approximation of neglecting second-order spin-orbit interactions (small splitting due to first-order spin-orbit interactions could occur). In some cases quite large splitting are observed [7-8, 27]. The order in which the levels of a multiplet occur will be determined by the intermediate coupling and will be sensitive to the magnitude of Coulombic and spin-orbit parameters and to which the energy level calculations are done [28]. Dieke and Leopold [7] explained first time successfully the optical absorption spectrum of $GdCl_3 \cdot 6H_2O$. The explanations was further extended by Hellwege, Huffner and Schmidt [8] to the shorter wave lengths and have reported absorption line groups for all levels of the lowest excited multiplets 6P , 6I and 6D .

In the present paper we shall focus our study on the explanation of the ground state splitting of Gd^{3+} ion. Optical absorption study on Gd^{3+} ion in di-ammonium D- tartrate single crystals has been done at room temperature. The purpose of the present study is to first review some of the special properties of half filled shells and then consider the estimation of the energy levels of the $4f^7$ configuration.

EXPERIMENTAL

Single crystals of DADT were grown by slow evaporation of an aqueous solution of di-ammonium D- tartrate. The Gd^{3+} impurity was added by mixing 0.02 mole % of Gadolinium Oxide (Gd_2O_3). After a few days well developed single crystals of Gd^{3+} doped DADT with well-defined faces were selected for investigation. The optical absorption spectra have been recorded on a Unicam-5625 spectrophotometer in the wavelength range 195-325 nm at room temperature.

OPTICAL ABSORPTION STUDIES

The optical spectra of Gd^{3+} crystals have been the subject of interest to a number of workers [5-6, 9-11]. The vibronic structure is comparatively absent in the absorption spectra of Gd^{3+} ion unlike other rare earth ions, therefore this study is well suited for the study of pure electronic properties. In the ground state (${}^8S_{7/2}$) of Gd^{3+} ion the crystal-field splitting is negligibly small ($\sim 1 \text{ cm}^{-1}$), therefore it can usually be neglected in the optical absorption study. Above the ground level two excited energy levels found around 32000 cm^{-1} , are ${}^6P_{7/2}$



and ${}^6P_{5/2}$ [11] However, no crystal-field splitting is expected in pure $4f^7$ configuration in Russell-Saunders coupling, both levels show splittings of about 100 cm^{-1} .

The absorption spectra of rare earth hosts containing very small percentage of rare earth ion is in the form of well-resolved groups of lines. Each group exhibits a transition to a level which is characterized by a definite value of J, the quantum number corresponding to the total angular momentum. In the presence of crystalline electric field the level is split in $(2J+1)$ components. The group of lines is usually arranged by Russell-Saunders Coupling (LS) but the considerable deviation is seen from the Lande interval rule. In rare earth salts the crystal-field splitting is much less than the spin-orbit splitting, which in turn is much less than the Coulomb splitting [4].

Coulomb and spin-orbit interaction matrices were calculated by Nielson and Koster [29-30]. The energy levels of configuration $4f^7$ for Gd^{3+} ion can be determined by diagonalization of the combined matrices for Coulomb and spin-orbit interaction. Coulomb interaction matrix elements may be expressed in terms of Racah parameters (E^1 , E^2 and E^3) [31] and spin-orbit interaction matrix elements are given in terms of spin-orbit coupling constant (ζ_{4f}). The energies of the multiplets being linearly dependent to the Coulomb parameters but the splitting between multiplets are quadratic function of ζ_{4f} . The optical spectra observed by earlier workers for Gd^{3+} doped systems has revealed only 15 of the 327 SLJ states in $4f^7$ configuration [8, 27, and 31]. These states are related with four multiplets, 8S ${}^6P(DI)$, therefore it is not suitable to fix the parameters by least-square methods.

Optical absorption spectrum of Gd^{3+} in di-ammonium D- tartrate single crystals recorded at room temperature in the wavelength range 195-325 nm is shown in Fig. 1. The recorded optical spectra consist of twelve absorption bands located at 197.59 (50609), 201.08 (49731), 208.87 (47877), 228.21 (43819), 244.06 (40974), 254.81 (39245), 267.17 (37429), 282.76 (35366), 290.01 (34482), 305.32 (32753), 310.16 (32241) and 319.29 (31319) nm (cm^{-1}) respectively.

RESULTS AND DISCUSSION

The Gd^{3+} has simpler optical spectrum in comparison to other trivalent rare earth ions. It has been known for many years that the absorption spectrum of Gd^{3+} ion lies entirely in ultraviolet region [32]. A very close correlation between the energies of the centers of gravity of the bands and the energies of the transition was observed by earlier workers [8, 33] during studying of solution absorption spectrum of Gd^{3+} ion. In addition several absorption bands



were identified near 50000 cm^{-1} which appeared to be characteristic of Gd^{3+} . These bands have not been reported previously. The correlations between calculated and observed intensities were used for assignments of energy levels [33].

In the present study, lowest observed absorption band is observed at approximately at 31000 cm^{-1} . The detection of the excited states around at 43000 cm^{-1} may be hampered by the absorption of the radiation by the host crystal [32]. The transitions to the different multiplets were observed by earlier workers [27-28, 31 and 34]. The bands observed at 31319, 32241, 32753, 34482, 35366, 37429, 39245, 40974, 43819 and 47877 cm^{-1} have been assigned to ${}^6\text{P}_{7/2}$, ${}^6\text{P}_{5/2}$, ${}^6\text{P}_{3/2}$, ${}^6\text{I}_{7/2}$, ${}^6\text{I}_{17/2}$, ${}^6\text{I}_{15/2}$, ${}^6\text{D}_{9/2}$, ${}^6\text{D}_{1/2}$, ${}^6\text{D}_{7/2}$ and ${}^6\text{D}_{3/2}$ respectively [27, 34]. The absorption band at 49731 cm^{-1} may be assigned to ${}^6\text{D}_{5/2}$ [35]. The last band located at has 50609 cm^{-1} has been found to correspond to ${}^6\text{G}$ state [32]. For gadolinium it is known that all of the components of multiplets ${}^6\text{P}$, ${}^6\text{I}$ and ${}^6\text{D}$ are purely L-S states [8, 33].

The calculated energy values of different levels and experimentally observed are given in **Table 1**. The ${}^6\text{G}$ State was calculated at 50000 cm^{-1} [32]. In the present work a band is calculated at 50609 cm^{-1} which can be assumed the ${}^6\text{G}$ State. This ${}^6\text{G}$ State in our case is observed at 49996 cm^{-1} , which is very near to calculated value 50609 cm^{-1} . No structure due to the Stark components of the ${}^8\text{S}_{7/2}$ ground state was observed. In the present work (at room temperature) all the levels of ${}^6\text{P}$, ${}^6\text{I}$ and ${}^6\text{D}$ multiplets are not split as shown in **Table 1**. To observe rest of the levels we will have to go at lower temperature probably at liquid-nitrogen or liquid -helium temperature.

The splitting found in the present study indicates the possibility of a strong spin-orbit coupling between the states of various classes. The spin-orbit and Slater parameters give the information about the energy and exact order multiplicity. Therefore, by diagonalizing the Hamiltonian having Coulombic and spin-orbit interactions including all states for f^7 someone can easily estimate these parameters [32]. We can define an approximate value of spin-orbit coupling constants and Slater parameters (F_k). It is observed earlier [33] that all these parameters along with α , β and γ may play a valuable role in assigning energy levels for Gd^{3+} ion. The energies for ${}^6\text{P}$ state are very sensitive to parameter γ [33]. The first assignments were done by Cook and Dieke [27] Dikke and Liopold [31] for the levels belonging to levels ${}^6\text{P}_{7/2}$, ${}^6\text{P}_{5/2}$ and ${}^6\text{P}_{3/2}$ and ${}^6\text{P}_{7/2}$, ${}^6\text{P}_{5/2}$ and ${}^6\text{I}_{7/2}$ respectively in different gadolinium crystals. Runciman [34] and Lacroix [36] observed the levels of ${}^6\text{P}$ multiplet experimentally and also formed the basic theoretical methods also. In all these calculations $4f$ wave functions were assumed to be hydrogenic. The absorption spectrum of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ was recalculated by



Hellwege, Hufner and Schmidt [8]. Using suitable values of Slater parameters and ζ_{4f} Wybourne [35] calculated the multiplet splittings agreed with the data observed by Hellwege et al [8]. The correlation between the experimental result of Hellwege et al [8] and calculated free ion energies by using electrostatic and spin-orbit parameters taken by Runciman [34] and Wybourne [35] suggests that it should be possible to get a better fit to the data. Assuming 4f wave functions to be hydrogenic the Racah parameters have the following values in terms of Slater integral [34]:

$$E^1=14.68 F_2, E^2=0.077 F_2, E^3=1.484 F_2.$$

A correction term $\alpha L(L+1)$ is included in the calculation of the intermediate coupling energy levels to account for the odd-parity configuration. The energy eigen values of the matrices containing both electrostatic and spin-orbit matrix elements were obtained [34] using the following expression:

$$\zeta_{4f}=1625, \zeta_{4f}/F_2=4$$

The better agreement between calculated data and experimental one is possible by freely varying all the four parameters. By freely varying all four parameters and fitting the data for DADT, we obtained:

$E^1=6253\pm 12$, $E^2=41\pm 0.26$, $E^3=692\pm 3.1$ and $\zeta_{4f}=1525\pm 20 \text{ cm}^{-1}$, $\alpha=29.98 \text{ cm}^{-1}$, $\beta=-106.36$ and $\gamma=955$. Here α , β and γ are interaction parameters.

The above values of the parameters are found to give the best agreement between experimentally observed and calculated energy levels. This agreement indicates the choice of the spin-orbit coupling constant is indeed reasonable. The important thing is to be mark that no account has been considered for configuration interaction, which may be appreciable. A complete consideration would include a fruitful discussion of crystal field splitting for the LSJ levels which may be difficult because of absence of first order splitting due to the crystal field. The experimental positions for center of gravity of the multiplets are only in fair agreement with the calculated one. Therefore the coulomb parameters require some modification. To reduce this difference we need some adjustment in the electrostatic energy of the multiplets. This may be due to either the choice of the electrostatic parameters is inappropriate or because of appreciable interaction with other odd-parity configurations. The calculated and experimental energy levels are compared in Table 1. It is clear that the levels of the ${}^6(\text{PDI})$ are calculated to be in the same order as obtained by Hellwege et al [8] and earlier workers. The low temperature EPR and optical studies of Gd^{3+} in DADT are in progress and the results will be published later.



CONCLUSIONS

In this paper we report the absorption spectrum of Gd^{3+} in di-ammonium D- tartrate single crystals recorded at room temperature in the wavelength range from 195-325 nm. The energy levels have been determined including the effects of all the states of f^7 configuration using 12 experimentally observed barycenters belonging to the states of 8S , 6P , 6I and 6D multiplets. As the observed transition for Gd^{3+} ion lie above 3100 cm^{-1} , it is assumed that $4f^7$ configuration is perturbed by the $4f^75d^2$ configuration. In the least-squares method the Slater, spin-orbit and configuration interaction parameters were assumed to be freely varying.

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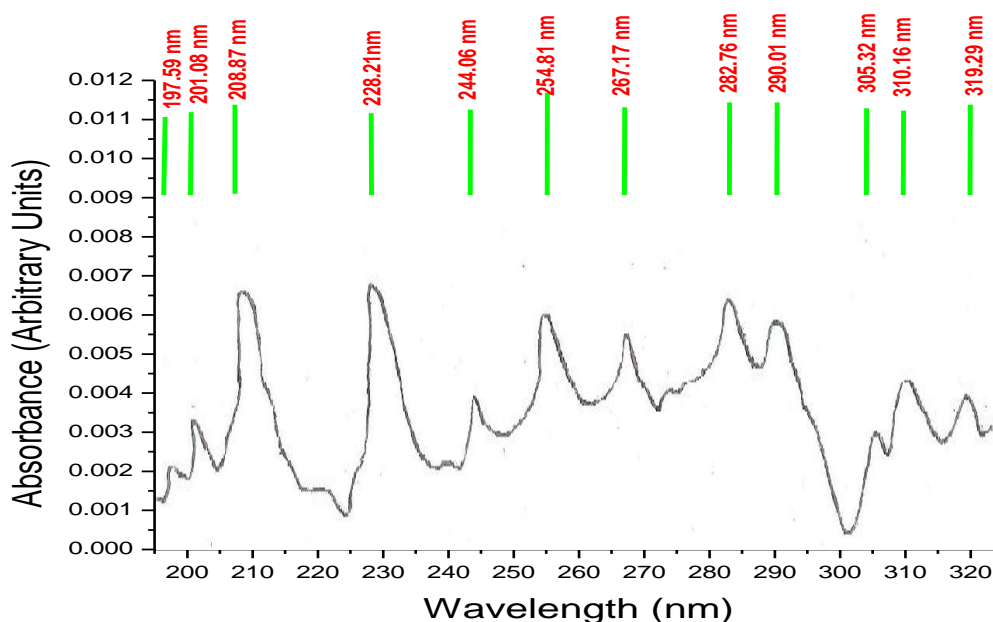


Fig.1: Scanned optical absorption spectrum of Gd^{3+} in di-ammonium D-tartrate (DADT) at Room Temperature in the wavelength ranges 195-325 nm.



Table1 Energy level assignments of Gd^{3+} in di-ammonium D-tartrate (DADT) single crystals

(Uncertainties are given in bracket).

Quantum state (SLJ)	Calculated (cm^{-1})	Experimental (cm^{-1})
$^8S_{7/2}$	0	0
$^6P_{7/2}$	31585 (10)	31319 (15)
$^6P_{5/2}$	32899 (11)	32241 (12)
$^6P_{3/2}$	34195 (12)	32753 (10)
$^6I_{7/2}$	34765 (15)	34482 (12)
$^6I_{9/2}$	34995 (14)	-
$^6I_{17/2}$	35299 (11)	35366 (11)
$^6I_{11/2}$	35114 (13)	-
$^6I_{13/2}$	35565 (12)	-
$^6I_{15/2}$	37211 (15)	37429 (13)
$^6D_{9/2}$	39011 (14)	39245 (12)
$^6D_{1/2}$	41158 (12)	40974 (15)
$^6D_{7/2}$	43654 (16)	43819 (11)



${}^6D_{3/2}$	46654 (14)	47877 (12)
${}^6D_{5/2}$	48990 (12)	49731 (12)
6G	49996 (13)	50609 (14)

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