

Electron paramagnetic resonance of Gd^{3+} in $Eu_2Zn_3(NO_3)_{12}\cdot 24H_2O$ single crystals

V. K. Jain*

Department Of Physics, M. D. University, Rohtak-12001, India

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Electron paramagnetic resonance of Gd^{3+} in $Eu_2Zn_3(NO_3)_{12}\cdot 24H_2O$ single crystals is studied at ≈ 9.45 GHz and at 298 and 77 K. Gd^{3+} substitutes for the Eu^{3+} site. In addition to the allowed fine structure lines, forbidden transitions ($\Delta M = \pm 2, \pm 3, \pm 4, \pm 5$) are observed. The superposition model is applied to the zero-field splitting parameter b_2^0 .

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1 Introduction

Since Electron paramagnetic resonance (EPR) absorption by Gd^{3+} present as dilute guest is easily detectable even at room temperature, many EPR investigations result in the determination of zero-field splitting (ZFS) parameters. In most of these systems Gd^{3+} ions were coordinated by oxygens or halogens and the ZFS parameter b_2^0 is quite sensitive with respect to small structural changes. The calculations of ZFS follow two lines. In the first, which is referred to as ab-initio calculations, the ZFS is generally reckoned using an electrostatic model of the crystal field, together with one or more of the splitting mechanisms. The second method of estimating ZFS is by the empirical superposition model (SPM) [1]. This paper describes EPR studies of Gd^{3+} present as dilute guest in $Eu_2Zn_3(NO_3)_{12}\cdot 24H_2O$ at 298 and 77 K. The SPM analysis of the ZFS parameter b_2^0 is also presented.

2 Crystal structure

The crystal structure of $Eu_2Mg_3(NO_3)_{12}\cdot 24H_2O$ (EMN) isomorphous to EZN has been studied by Akimov et al. [2]. The primitive cell of EMN containing one formula unit is rhombohedral with lattice constant $a = 1.3116$ nm and $\alpha = 49.34^\circ$. The space group is $R\bar{3}$. The lattice parameters in hexagonal setting are $a = 1.0949$ nm, $c = 3.448$ nm. The rhombohedral unit cell contains three divalent ions, surrounded by six water molecules, situated at two different lattice sites. One occupies the C_{3i} point symmetry and the other two occupy the point symmetry C_3 site. The Eu^{3+} is found at a site of C_3 point symmetry. Each Eu^{3+} is coordinated with twelve oxygen ions belonging to six nitrate ions, located at the corners of a somewhat irregular icosahedron. Eu^{3+} -O bond length varies between 0.2548 nm to 0.2622 nm.

3 Experimental

Single crystals of EZN were grown at ≈ 300 K by slow evaporation of an aqueous solution. The Gd^{3+} was introduced into the host lattice by adding (0.2 wt%) gadolinium nitrate. The crystal grows in flat hexagonal

* Corresponding author: e-mail: liggavansh@yahoo.com

plates, the plane of which is perpendicular to the trigonal axis. The EPR experiments were performed on a JEOL FE-3X homodyne spectrometer operating at ≈ 9.45 GHz equipped with TE_{011} -cylindrical cavity and 100 kHz field modulation. A speck of powdered DPPH used as a field marker (taking $g_{\text{DPPH}} = 2.0036$) was inserted simultaneously into the sample cavity. The angular variation studies were done using a JES-UCR-2X sample angular rotating device. Measurement at liquid nitrogen temperature was made using JES-UCD-2X insertion type dewar.

4 Results and discussion

Gd^{3+} has $4f^7$ electronic configuration and accordingly the Hund's rule ground state is $^8S_{7/2}$. In a crystalline environment of low symmetry the ground state is split into four doublets. An external magnetic field will lift the degeneracy of the doublets producing eight energy levels, which, in an EPR experiment, give rise to a seven line spectrum.

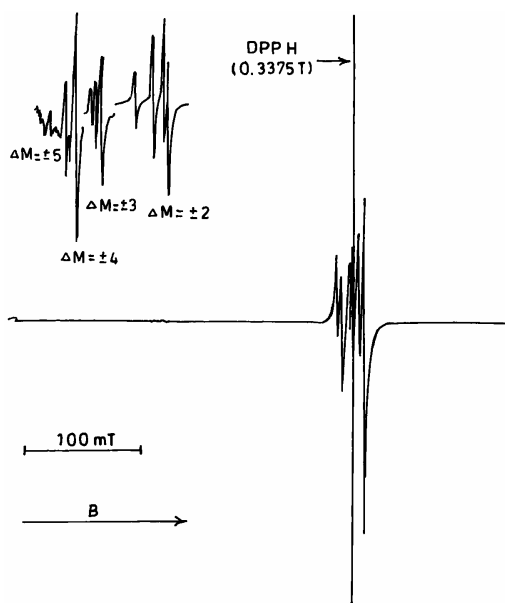


Fig. 1 EPR spectrum of Gd^{3+} in $Eu_2Zn_3(NO_3)_{12} \cdot 24H_2O$ single crystals at 298 K with B at 50° to the z -axis in the zx plane. Forbidden fine structure lines belong to $\Delta M = \pm 2, \pm 3, \pm 4, \pm 5$. Forbidden transitions $\Delta M = \pm 2$ are amplified by a factor of ~ 20 , $\Delta M = \pm 3$ by a factor of ~ 100 and $\Delta M = \pm 4, \pm 5$ by a factor of ~ 250 .

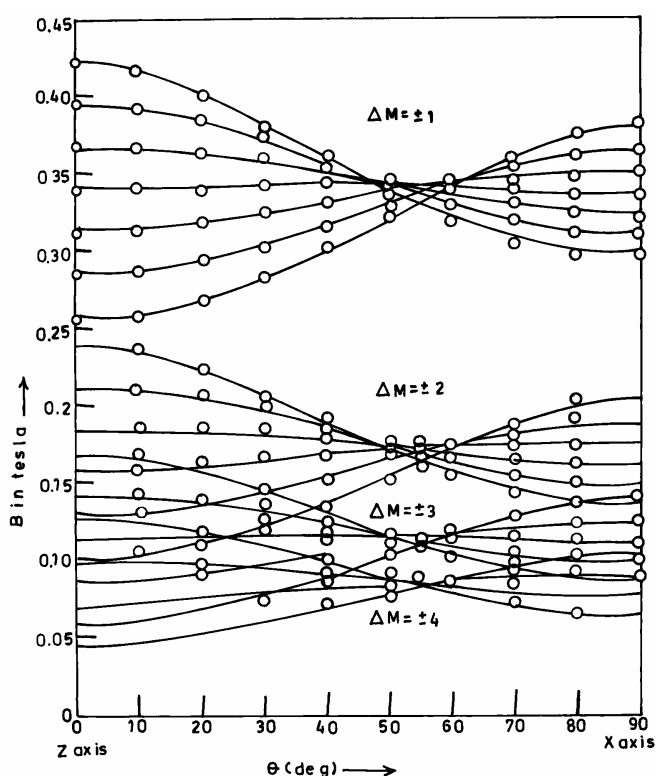


Fig. 2 Angular variation of Gd^{3+} EPR lines in the zx plane for $Eu_2Zn_3(NO_3)_{12} \cdot 24H_2O$ single crystals at ~ 298 K. o - experimental positions, — - theoretical curves.

For an arbitrary orientation of the crystal the EPR spectrum consists of a single set of seven intense lines between ~ 0.254 T and ~ 0.425 T which arise from the allowed fine structure transitions ($\Delta M = \pm 1$) of the Gd^{3+} centre (formed by the substitution of Eu^{3+} by Gd^{3+}). The linewidth of $\Delta M = \pm 1$ transitions at ~ 298 K is ~ 1.6 mT. In addition to these lines there are many weak lines below ~ 0.24 T (Fig.1). The intensity of these weak lines is $\sim 1/10$ to $\sim 1/500$ of the $\Delta M = \pm 1$ transitions. Angular variation studies of the spectrum reveal the following:

- (i) The maximum spread of the spectrum (z axis) corresponding to $\Delta M = \pm 1$ transitions occur when the magnetic field is parallel to the c-axis of the crystal.
- (ii) The subsidiary maxima (x-axis) occur when the magnetic field is at 90° to the c-axis. (iii) The spectrum shows a periodicity of $2\pi/3$ when the crystal is rotated in a plane perpendicular to the c-axis.

The Eu^{3+} ion has $4f^6$ electronic configuration and accordingly Hund's rule ground state is 7F_0 and no EPR is expected for an ion with $J=0$. Experiments at 77 K show an increase in the spread of the spectrum, however no change in g value or linewidth is observed.

The spin-Hamiltonian for Gd^{3+} corresponding to a trigonal symmetry with z-axis parallel to the c-axis is of the form [3]

$$H = \beta_e S \cdot g \cdot B + (1/3) b_2^0 O_2^0 + (1/60) b_4^0 O_4^0 + (1/1260) b_6^0 O_6^0 + (1/3) b_4^3 O_4^3 + (1/36) b_6^3 O_6^3 + (1/360) b_6^6 O_6^6 \quad (1)$$

where the symbols have their usual meaning and $S = 7/2$ for Gd^{3+} . The ZFS parameters b_4^3 and b_6^3 are zero for C_{3h} and C_{3i} symmetry [4]. The parameters obtained for the spin-Hamiltonian at 298 and 77 K are given in Table 1. The signs of the parameters are only relative and have been determined assuming b_2^0 to be positive. The small term in b_6^6 has been ignored.

Table 1 Spin-Hamiltonian parameters of Gd^{3+} in $Eu_2Zn_3(NO_3)_{12} \cdot 24H_2O$. All crystal field parameters are in units of 10^{-4} cm^{-1} .

Spin-Hamiltonian parameters	298 K	77K
b_2^0	130(1)	132(1)
b_4^0	0.50(5)	0.90(5)
b_6^0	0.50(5)	0.40(5)
$g_{ }$	1.9921(3)	1.9920(3)
g_{\perp}	1.9901(5)	1.9910(5)

To identify the observed low field lines we have investigated forbidden EPR transitions ($\Delta M > \pm 1$) for the Gd^{3+} centre. For this third-order perturbation is used to evaluate the position of all the fine structure transitions. The field position at which a line due to the EPR transition occur was obtained by using the eigenvalue of the spin-Hamiltonian (retaining only the predominant $b_2^0 O_2^0$ term) to third order of perturbation [5]. The line position is given by

$$B_{M \rightarrow M-R} = (B_0/R) - \frac{1}{2} b_2^0 (3 \cos^2\theta - 1)(2M-R) - (b_2^0)^2 \sin^4\theta T/8B_0 - (b_2^0)^2 \sin^2\theta \cos^2\theta U/2B_0 - (b_2^0)^3 \sin^2\theta \cos^2\theta (3 \cos^2\theta - 1) V/8B_0^2 - (b_2^0)^3 \sin^4\theta (3 \cos^2\theta - 1) W/32B_0^2 - 3(b_2^0)^3 \sin^4\theta \cos^2\theta X/4B_0^2 \quad (2)$$

where $T = -6M^2 + 6MR - 2R^2 - 1 + 2S(S+1)$, $U = 24M^2 - 24MR + 8R^2 + 1 - 4S(S+1)$, $V = (2M-R)[-80M^2 - 40R^2 + 80MR - 14 + 24S(S+1)]$, $W = (2M-R)[20M^2 - 20MR + 10R^2 + 14 - 12S(S+1)]$, $X = (2M-R)[20M^2 - 20MR + 10R^2 - 20MR + 5 - 8S(S+1)]$, and $M = 7/2, \pm 5/2, \pm 3/2, \pm 1/2$; $R = 1, 2, 3, 4, 5, 6$.

Fig. 2 shows the angular variation of the spectrum in the zx plane. In the figure θ is the angle between the external magnetic field and the z-axis of the Gd^{3+} centre. Because of the low intensity of $\Delta M = \pm 5$ transitions could not be followed while $\Delta M = \pm 3, \pm 4$ transitions are followed for certain orientations. The reasonably good agreement of the calculated angular variation with the experimental one suggests that the weak lines at the low magnetic field side of the allowed fine structure lines are due to forbidden transitions.

Assuming ZFS to be solely due to distortion of the first coordination sphere of oxygens of nitrate ions, the experimental ZFS can be compared with those calculated from the crystal structure data for the pure host compound. The SPM allows such a comparison [1]. The SPM is based on two assumptions: (i) ZFS is due to the close neighbour ions and (ii) ZFS is given by a sum of axially symmetric contributions of the i ligands of MX_i unit. The contributions of more distant neighbours as well as the interaction between the ligands are ignored. The ZFS parameter b_2^0 is written as

$$b_2^0 = \sum K_2^0(\theta_i, \varphi_i) \bar{b}_2(R_i) \quad (3)$$

where $K_2^0 = (1/2)(3 \cos^2\theta - 1)$, the summation runs over all ligands, R_i , θ_i , φ_i are the spherical coordinates of the i -th ligands (paramagnetic ion is placed at the origin). The dependence of $\bar{b}_2(R)$ on the metal ligand distance R can be approximated by

$$\bar{b}_2(R) = \bar{b}_2(R_0)(R_0/R_i)^{t_2} \quad (4)$$

where the power law exponent t_2 is typical of the particular system considered.

SPM analysis has been carried out by taking $R_0 = 0.254$ nm and $t_2 = 1$. The value of R_0 is very near to the shortest Eu-O bond length. Using (3) the value of $\bar{b}_2 = -0.0798$ cm⁻¹ is obtained. In the determination of b_2 for EZN, the crystal structure data of isomorphous EMN have been used. It is assumed that the crystalline structure in the vicinity of the magnetic ion is unchanged from that of the host lattice. It has been shown that if R (metal – ligand bond distance) is greater than the normal impurity-ligand bond distance, the introduction of substitutional impurity gives rise to an inward relaxation while the opposite occurs for R less than the normal impurity-ligand bond distance [6]. The ionic radii of Gd³⁺ and Eu³⁺ are 0.0938 and 0.0950 nm, respectively [7]. Therefore, Gd³⁺ substitution for Eu³⁺ would allow some inward relaxation for oxygen surrounding the trivalent ions. Thus it is a good approximation to take the value of R as the mean of the impurity-ligand and metal-ligand bond distances in the pure host to take into account the lattice relaxation. Thus taking into account relaxation effects of bond lengths only assuming bond angles to remain unchanged on doping with Gd³⁺ in place of Eu³⁺, SPM analysis has been made. The value of the intrinsic parameter \bar{b}_2 is -0.0906 cm⁻¹ for $t_2 = 1$ and $R_0 = 0.254$ nm. The values are consistent with the values obtained for Gd³⁺ surrounded by oxygens [1].

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