

High order electron paramagnetic resonance transitions of Gd^{3+} in $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$ single crystals

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Abstract. Electron paramagnetic resonance of Gd^{3+} in $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$ single crystals has been studied at ~ 9.45 GHz and at 285 K. In addition to the allowed fine structure lines ($\Delta M = \pm 1$) some weak low field lines identified as $\Delta M = \pm 2$ transitions have been observed.

Keywords. Electron paramagnetic resonance; trivalent gadolinium ion; praseodymium zinc nitrate hydrate; high order transitions.

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1. Introduction

The electron paramagnetic resonance (EPR) of Gd^{3+} doped in $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$ single crystals (hereafter called PZN) has been previously studied at 298 K as well as 77 K (Misumi *et al* 1974; Jain and Srinivasan 1978). However, the weak lines occurring at the low magnetic field side of the allowed ($\Delta M = \pm 1$) fine structure lines in the EPR spectra of Gd^{3+} in PZN has not been studied earlier. In this paper we present the results of the investigation of the low field lines arising from the $\Delta M = \pm 2$ fine structure transition of Gd^{3+} complexes in PZN single crystals.

2. Crystal structure

The crystal structure of $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ has earlier been determined by Zalkin *et al* (1963). It is assumed that PZN also has a similar structure. The primitive cell of $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ containing one formula unit is rhombohedral with space group $R\bar{3}$ (Zalkin *et al* 1963 and Anderson *et al* 1977). The unit cell contains three divalent ions situated at two different lattice sites. One of them occupies a site with the point symmetry C_{3i} and the other two divalent ions occupy lattice sites with the point symmetry C_3 . The trivalent ion is found at a site of C_{3i} point symmetry and the remaining atoms are in positions of the general type. Each trivalent ion is coordinated with 12 oxygens belonging to six nitrate ions, located at the corners of a somewhat irregular icosahedron.

3. Experimental

Single crystals of PZN doped with Gd^{3+} were grown at room temperature by slow evaporation of an aqueous solution of $Pr(NO_3)_3 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ mixed in stoichiometric ratios. Gd^{3+} was introduced into the host lattice by adding a small amount (0.1 wt %) of gadolinium nitrate. The double nitrates grow in flat hexagonal plates, the plane of which is perpendicular to the trigonal axis.

EPR was measured at 285 K using a JEOL JES-FE3X homodyne X-band spectrometer equipped with TE_{011} cylindrical cavity and 100 kHz field modulation. DPPH with $g = 2.0036$ was used for marking the magnetic field. The crystals were mounted on a quartz rod. The angular variation was studied using a sample angular rotating device (JES-UCR-2X).

4. Results and discussion

For an arbitrary orientation of the crystal, the EPR spectrum consists of a single set of seven lines between $\sim 0.26 T$ and $\sim 0.41 T$ which arise from the allowed fine structure transitions ($\Delta M = \pm 1$) of the Gd^{3+} centres (formed by the substitution of Pr^{3+} by Gd^{3+}). In addition, there are many weak lines below $\sim 0.23 T$ (figure 1). 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 when the external magnetic field is parallel to the trigonal axis (c -axis) of the crystal. This axis can be located accurately from the external morphology of the crystal.
- (ii) The subsidiary maxima (x -axis) occur when the magnetic field is perpendicular to the c -axis. However at this orientation all the observed transitions ($\Delta M = \pm 1$) do not attain an extremum.
- (iii) The angular variation of the spectrum in the xy plane (plane perpendicular to the c -axis) shows a periodicity of $2\pi/3$.

The EPR spectra of Gd^{3+} corresponding to a trigonal symmetry and with z axis parallel to the c axis can be described by the spin-hamiltonian (Buckmaster *et al* 1972).

$$\mathcal{H} = \beta S \vec{g} \mathbf{B} + \frac{1}{3} b_2^0 O_2^0 + \frac{1}{60} b_4^0 O_4^0 + \frac{1}{1260} b_6^0 O_6^0 + \frac{1}{3} b_4^3 O_4^3 + \frac{1}{36} b_6^3 O_6^3 + \frac{1}{1260} b_6^6 O_6^6, \quad (1)$$

where the symbols have their usual meaning and $S = 7/2$ for Gd^{3+} . The crystal field parameters b_4^3 and b_6^3 are indentially zero for C_{3i} symmetry (Buckmaster *et al* 1968).

Spin-hamiltonian parameters are taken from (Jain and Srinivasan 1978).

To identify the observed low field lines higher-order EPR transitions ($\Delta M > \pm 1$) have been studied for the Gd^{3+} centre. For this purpose we have used the expression for the line positions given by Jain (1984) considering the predominant $b_2^0 O_2^0$ term up to the third order perturbation.

The field position $B_{M \rightarrow M-R}$ at which a line due to the EPR transition ($M \rightarrow M - R$)

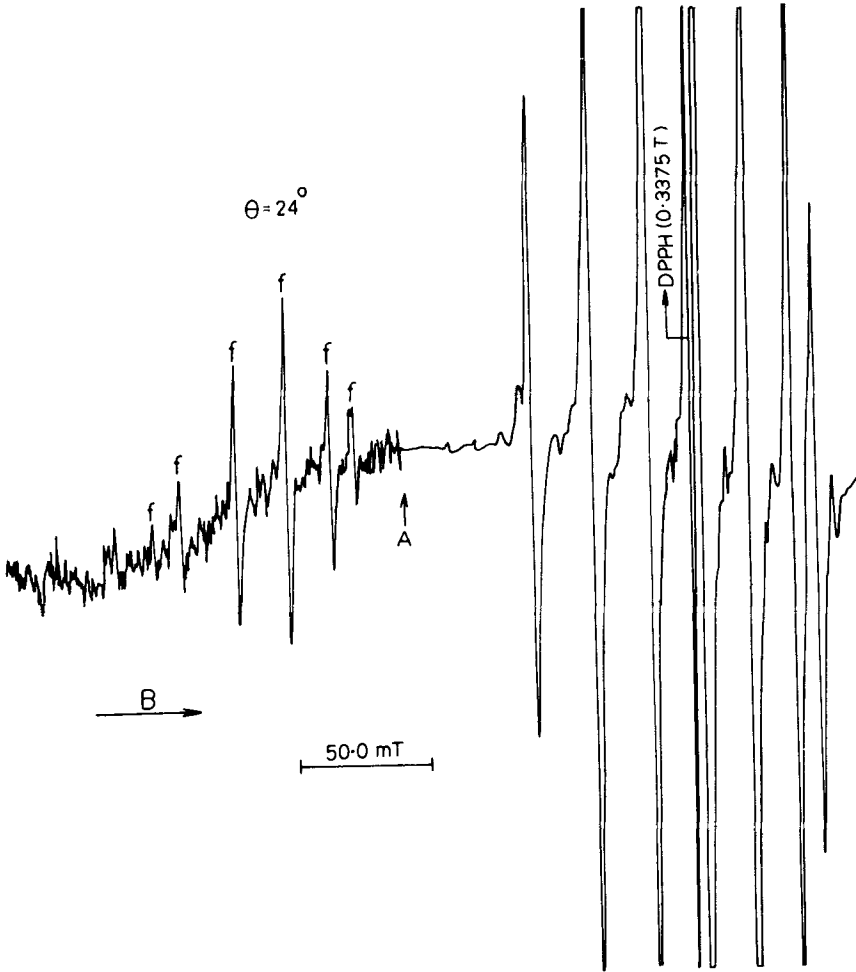


Figure 1. EPR spectrum of Gd^{3+} in $Pr_2Zn_3(NO_3) \cdot 24H_2O$ single crystals at 285 K; with B at 24° to the z axis. The lines designated by f are forbidden transitions. The forbidden transitions are amplified by a factor of 10. The weak lines on the high magnetic field side of A are due to Mn^{2+} impurities.

occurs is given by Jain (1984) assuming g to be isotropic.

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

where

$$\begin{aligned}
 T &= -6M^2 + 6MR - 2R^2 - 1 + 2S(S+1), \\
 U &= 24M^2 - 24MR + 8R^2 + 1 - 4S(S+1), \\
 V &= (2M - R)[-80M^2 - 40R^2 + 80MR - 14 + 24S(S+1)], \\
 W &= (2M - R)[20M^2 + 10R^2 - 20MR + 14 - 12S(S+1)], \\
 X &= (2M - R)[20M^2 + 10R^2 - 20MR + 5 - 8S(S+1)],
 \end{aligned}$$

and $M = \frac{7}{2}, \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}; R = 1, 2, 3, 4, 5, 6.$

The angular variation of the spectrum of the Gd^{3+} complex in zx plane, obtained by substituting the values of $b_2^0 = 114.60 \pm 1$ and $g = 1.9925 \pm 0.0005$ (Jain 1978) in equation (2) is shown in figure 2. When θ is the angle between the external magnetic field and the z axis. The satisfactory 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 ($\Delta M = \pm 1$ transitions) are due to $\Delta M = \pm 2$ transitions.

The appearance of $\Delta M = \pm 2$ transitions in the ESR spectra of Gd^{3+} is connected with the crystalline field symmetry. The presence of the off-diagonal terms in the spin-hamiltonian gives rise to admixture into the pure states when the external magnetic field B is not along the symmetry axis. The spin states are then best described by the linear combinations of the pure spin states and the normally forbidden $\Delta M = \pm 2$ transitions are allowed. When B is along the symmetry axis, $\Delta M = \pm 2$ transitions are entirely

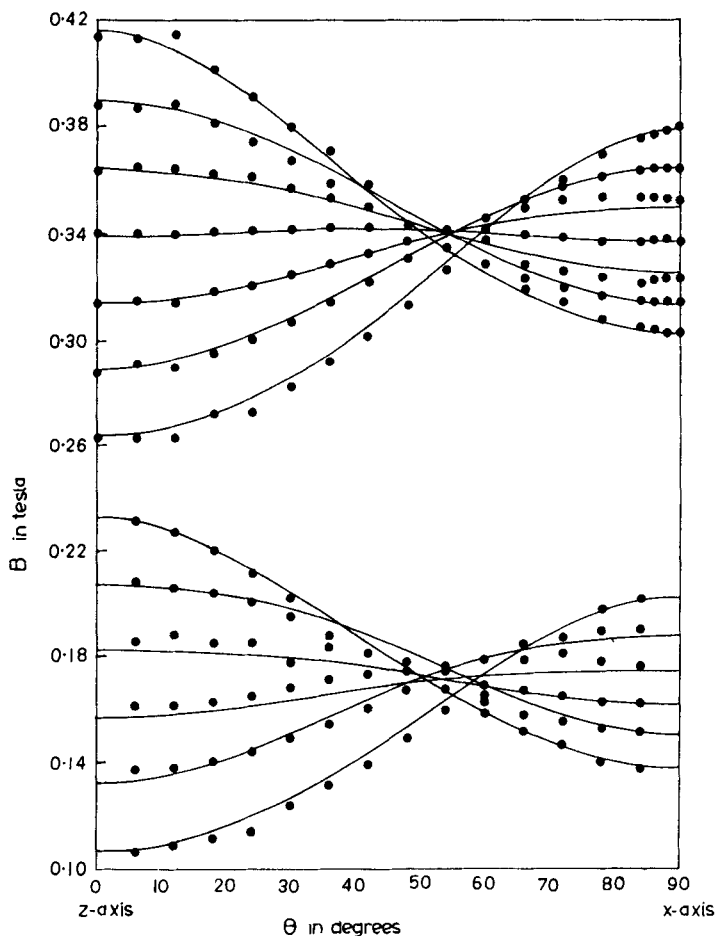


Figure 2. Angular dependence of Gd^{3+} EPR lines in zx plane for $Pr_2Zn(NO_3)_{12} \cdot 24H_2O$ single crystals at 285 K. —: theoretical; ●: experimental.

forbidden and therefore have zero intensity at $\theta = 0^\circ$. At $\theta = 90^\circ$ these transitions are allowed only if the microwave field is parallel to B (Abragam and Bleaney 1970).

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