

## Electron paramagnetic resonance of $Mn^{2+}$ and $Gd^{3+}$ in $Pr_2Zn_3(NO_3)_{12} \cdot 24 H_2O$ single crystals

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**Abstract.** The electron paramagnetic resonance of  $Mn^{2+}$  and  $Gd^{3+}$  doped in  $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$  single crystals has been studied at X-band.  $Mn^{2+}$  substitutes for two  $Zn^{2+}$  sites, while  $Gd^{3+}$  substitutes for single type of  $Pr^{3+}$  sites. The spin-Hamiltonian analysis of the EPR spectra is presented at 298 K as well as 77 K.

**Keywords.** Electron paramagnetic resonance;  $Mn^{2+}$ ;  $Gd^{3+}$ ;  $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$ .

### 1. Introduction

The electron paramagnetic resonance (EPR) studies require the presence of unpaired electrons in the sample to be studied. In general, these are not present in the pure material but can be introduced by doping with paramagnetic substances such as the transition elements or by radiation damage. Among all the ions which exhibit EPR spectrum, the  $d^5$  and  $f^7$  ions ( $S$ -state ions) are particularly interesting when one is concerned with the local symmetry of the environment of the ion. In fact, all sublevels of  $S$ -state are generally observed in low magnetic fields for the two reasons: (a) the zero-field splitting is zero to the first order and (b) only higher-order effects permit lifting of the degeneracy of the fundamental states ( $^6S$  and  $^8S$ ). Therefore, a detailed study of the angular variation of the paramagnetic resonance absorption lines permits one to establish the point symmetry around the magnetic ion.

The hydrated double nitrates of the rare earth elements form an interesting series of salts for EPR studies. Their general formula is  $M_2''' M_3'' (NO_3)_{12} \cdot 24H_2O$ , where  $M'''$  is a trivalent cation (Bi or anion of the  $4f$  group) and  $M''$  is a divalent cation (Zn, Mg or an ion of the  $3d$  group). Although the trivalent lanthanide ions are generally paramagnetic, their spin-lattice relaxation times are so much shorter than those of the  $S$ -state ions (at sufficiently high temperature) that the magnetic interaction between the paramagnetic ions and the  $S$ -state ions are averaged essentially to zero with the consequence that magnetic resonance absorption by the  $S$ -state ion can be observed without extensive broadening. In this paper we describe EPR of  $Mn^{2+}$  and  $Gd^{3+}$  in  $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$  (PZN) single crystals from 298 K down to 77 K. The EPR of  $Gd^{3+}$  in PZN was reported earlier (Misumi *et al* 1974) only at room temperature.

## 2. Crystal structure

The crystal structure of  $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$  has been determined by Zalkin *et al* (1963). The other hydrated double nitrates can be expected to have similar structure. The primitive cell containing one formula unit is rhombohedral with dimension  $a=13.165\text{ \AA}$  and  $\alpha=49.37^\circ$ . The space group is  $R\bar{3}$ . The corresponding hexagonal cell containing three formula units has dimension  $a=11.004\text{ \AA}$ ,  $c=34.592\text{ \AA}$ . The rhombohedral unit cell contains three divalent ions situated at two different lattice sites. One of them occupies site with the point symmetry  $C_{3i}$  (Y site or site I) and other two divalent ions occupy lattice sites with the point symmetry  $C_3$  (X site or site II). The trivalent ion is found at a site of  $C_{3i}$  point symmetry and the rest of the atoms are in position of the general type. Culvahouse *et al* (1961) have shown that one  $\text{Zn}^{2+}$  lies on the body centre of the cell (Y site) and two  $\text{Zn}^{2+}$  at special positions  $\pm(x, x, x)$  ( $x=0.399$ ) which are along the long diagonal of the rhombohedron and  $34.18x\text{ \AA}$  to either side of the centre of the cell (X site). There are two trivalent ions along this diagonal and  $8.54\text{ \AA}$  to either side of the centre of the cell. The long diagonal of the rhombohedron is along the trigonal axis. The divalent ions are surrounded by six water molecules forming together with central ion a nearly regular octahedral  $M''(\text{H}_2\text{O})_6^{2+}$  complex. 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  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$  were grown by slow evaporation of aqueous solution of  $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , mixed in stoichiometric ratios, at room temperature. The  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$  were introduced into the lattice by adding a small amount (0.1% by weight) of manganese and gadolinium nitrates. The double nitrates grow in flat hexagonal plates, the plane of which is perpendicular to the trigonal axis. The experiments were performed on Varian V-4502 EPR spectrometer, operating at X-band, provided with 100 kHz field modulation. As a reference for magnetic field strength the resonance line of DPPH with  $g=2.0036$  is used. The magnetic field at DPPH resonance was measured with the help of a Varian F-8A fluxmeter while the frequency of proton signal is measured by Systronics Type 701 frequency counter.

## 4. Results and discussion

### 4.1. $\text{Mn}^{2+}$

$\text{Mn}^{2+}$  has  $3d^5$  electronic configuration and accordingly the Hund's rule ground state is  ${}^6S_{5/2}$ . In a crystalline field of low symmetry the ground state is split into three Kramers doublets. An external magnetic field lifts the degeneracy of the doublets, producing six energy levels. The EPR spectrum of a given  $\text{Mn}^{2+}$  centre should consist of five anisotropic fine structure transitions ( $\Delta M = \pm 1$ ). The nuclear spin of  ${}^{55}\text{Mn}$  (natural abundance 100%) is  $\frac{5}{2}$ . Therefore, the total hyperfine structure consists of six lines ( $\Delta m = 0$ ) of equal intensity for each fine structure transition.

For an arbitrary orientation of the magnetic field the EPR spectrum consists of a number of lines corresponding to allowed and forbidden transitions (figure 1). Angular variation studies of  $Mn^{2+}$  spectra reveal the presence of two inequivalent  $Mn^{2+}$  centre of unequal intensity. The  $Mn^{2+}$  substitutes for  $Zn^{2+}$  and shows the spectrum of two  $Mn^{2+}$  complexes. The spectrum having large intensity is due to  $Mn^{2+}$  substituting for  $Zn^{2+}$  at site II while spectrum having low intensity is due to  $Mn^{2+}$  at site I (figure 1). The  $Mn^{2+}$  centre occupying the site II is more intense because there are twice as many X sites as Y sites. The principal axes of the spectra

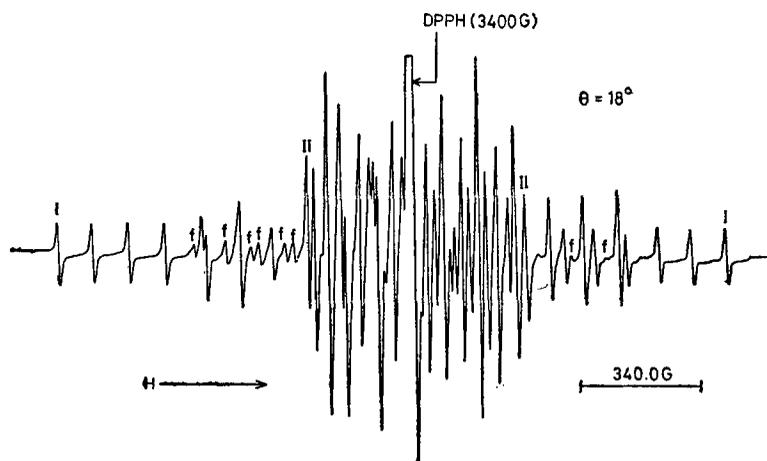


Figure 1. EPR spectrum of  $Mn^{2+}$  in  $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$  single crystals at 298 K. The lines designated by *f* are forbidden hyperfine transitions. The positions of extreme hyperfine lines of  $Mn^{2+}$  complexes for two sites are designated by I and II respectively.

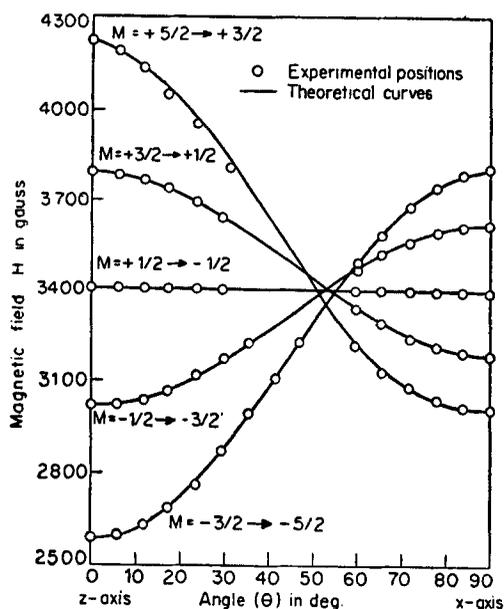


Figure 2. Angular dependence of allowed fine structure transitions ( $\Delta M = \pm 1$ ) of  $Mn^{2+}$  for site I in the *zx* plane at 298 K.

were located by searching the directions of extrema in the spread of the spectrum. It was found that principal  $z$  axis of two  $Mn^{2+}$  complexes are along the trigonal axis ( $c$  axis) and  $x$  axis is perpendicular to trigonal axis. For a field applied along the trigonal axis, each type of  $Mn^{2+}$  complexes produces an EPR spectrum consisting of five nearly equally spaced sets of six nearly equal spaced hyperfine components. The spectra of  $Mn^{2+}$  showing large zero-field splitting (site I) were measured for various angles of the magnetic field relative to the  $c$  axis. Figure 2 shows the angular variation of the allowed fine structure transitions ( $\Delta M = \pm 1$ ) in the  $zx$  plane for site I. It is seen from the angular variation plot in the  $zx$  plane that fine structure transition lines move in rapidly from  $z$  axis as  $\theta$  changes. The lines collapse to a very small spread at an orientation  $\theta = 52.7^\circ$  away from the  $z$  axis. As  $\theta$  increases further, the lines cross each other and spread out to a second maximum at  $\theta = 90^\circ$  ( $x$  axis). A  $\pi/3$  rotational symmetry of the spectrum was observed when the crystal was rotated about the trigonal axis. The  $g$  value, however, shows no angular variation in this plane. The observed behaviour of the spectrum is consistent with the trigonal symmetry of the  $Zn^{2+}$  sites.

The EPR spectrum of  $Mn^{2+}$  for both sites can be described by the spin-Hamiltonian of the form (Geschwind 1961)

$$\mathcal{H} = \beta g_{\parallel} H_z S_z + \beta g_{\perp} (H_x S_x + H_y S_y) + D \left( S_z^2 - \frac{35}{12} \right) - \frac{7}{36} (a - F) \left( S_z^4 - \frac{95}{14} S_x^2 + \frac{81}{16} \right) + A I_z S_z + B (S_x I_x + S_y I_y) + \frac{a(2)^{1/2}}{36} \{ S_z [S_+^3 \exp(-3i\phi) + S_-^3 \exp(3i\phi)] + (S_+^3 \exp(-3i\phi) + S_-^3 \exp(3i\phi)) S_z \}$$

where the  $z$  axis is parallel to the trigonal symmetry axis of the crystal. The symbols have their usual meaning and  $S = I = 5/2$  for  $Mn^{2+}$ .

Using the above spin-Hamiltonian the  $Mn^{2+}$  EPR spectra are analysed and the best-fit parameters, thus obtained, are being listed in table 1 for both sites at 298 K and 77 K. The signs of the parameters given in the table are relative. Since the hyperfine splitting constant is always found to be negative for a manganese ion (Watson and Freeman 1961, Richardson *et al* 1970), this sign is taken for  $A$  in this case as well. The examination of the magnitude of the splitting of the hyperfine sextets appearing at high fields and low fields when the magnetic field is parallel to  $z$  axis attributes a sign to the axial parameter  $D$  (Low 1960).

The value of  $g$  and  $A$  for both the sites are independent of temperature within the experimental error. The work of Van Wieringen (1955) shows that the magnitude of the hyperfine coupling constant depends on the amount of covalent bonding in the crystal. That is, the greater the covalent bonding the smaller will be the hyperfine splitting. Plots of the hyperfine parameter  $A$  (average hyperfine coupling constant) for  $Mn^{2+}$  as a function of covalency or ionicity parameters have been given for simple crystal systems (Matumura 1959, Henning 1967, Simanek and Müller 1970). The observed value of  $A$  indicates that  $Mn^{2+}$  at both the sites are surrounded by six water molecules as the covalency parameter determined from the curve (hyperfine parameter vs covalency) given by Simanek and Müller (1970) indicates the characteristic

**Table 1.** Spin-Hamiltonian parameters for  $Mn^{2+}$  in  $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$  single crystals at 298 K and 77 K. All the crystal field and h.f. parameters are in units of  $10^{-4} \text{ cm}^{-1}$ .

Spin Hamiltonian parameters	Site I		Site II	
	298 K	77 K	298 K	77 K
$D$	$-188.0 \pm 1$	$-218.1 \pm 1$	$18.0 \pm 2$	$-40.0 \pm 2$
$a-F$	$7.3 \pm 1$	$7.5 \pm 1$	$8.8 \pm 1$	$9.4 \pm 1$
$g_{\parallel}$	$2.0068 \pm 0.0005$	$2.0066 \pm 0.0005$	$2.004 \pm 0.001$	$2.004 \pm 0.001$
$g_{\perp}$	$2.007 \pm 0.0005$	$2.007 \pm 0.0005$	$2.006 \pm 0.002$	$2.0058 \pm 0.002$
$A$	$-89.2 \pm 0.5$	$-89.3 \pm 0.5$	$-89.5 \pm 1$	$-89.5 \pm 1$
$B$	$-90.0 \pm 0.5$	$-90.0 \pm 0.5$	$-90.0 \pm 1$	$-90.0 \pm 1$

covalency of  $Mn^{2+}-6H_2O$  complex. Moreover, the line width of  $Mn^{2+}$  in PZN is of the order of 11 gauss. In hydrated crystals, an appreciable degree of line broadening of the order of 10 gauss can originate due to local magnetic fields of the proton nuclear moments in the water molecules (Abragam and Bleaney 1970).

From table 1 it can be seen that the value of zero-field splitting parameter  $D$  is very different for the two sites and is sensitive to temperature. The relative insensitivity of the parameter  $D$  of site I to temperature illustrated by the value in table 1 has also been noted for  $Ni^{2+}$  in  $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$  (LMN) and  $La_2Zn_3(NO_3)_{12} \cdot 24H_2O$  (LZN) as well (Dixon and Culvahouse 1971). The value of  $D$  increases as temperature decreases. An increase in the value of  $D$  at low temperature can probably be explained as due to thermal contraction and vibrational mechanism of the lattice (Walsh 1959, Geifman and Glinchuk 1971). The differing values of  $D$  for  $Mn^{2+}$  at two sites indicate that the two sites differ greatly in the static crystal field seen by the ions. The crystal field is presumed to be due to an octahedron of water molecules oriented with  $[111]$  axis along the trigonal axis of the crystal, and it appears that the octahedron is nearly perfect for site II and have appreciable trigonal distortion for the site I. The large difference in the  $D$  value is also observed for  $Ni^{2+}$  doped LMN, LZN single crystals (Dixon and Culvahouse 1971) and for  $Mn^{2+}$  in  $MgSeO_4 \cdot 6H_2O$  single crystals (Jain 1976). In theoretical analysis of the ground state splitting of the  $S$ -state ion it is generally recognised that more than one mechanism is required to account for the magnitude of the parameter  $D$ . Brandt *et al* (1965) have determined the zero field splitting parameter  $D$  of  $Mn^{2+}$  in LMN for both sites. It is interesting to note that the value of  $D$  for site I and site II obtained in this experiment for PZN: $Mn^{2+}$  are nearly the same as the parameter  $D$  of  $Mn^{2+}$  in LMN. A theoretical interpretation of the latter for site I was given by Chatterjee *et al* (1976). They concluded that the relativistic second-order effect of Wybourne (1966) yields the major contribution to the value of the zero-field splitting parameter  $D$ . Their calculated values are in agreement with the observed values for site I.

#### 4.2. $Gd^{3+}$

$Gd^{3+}$  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.

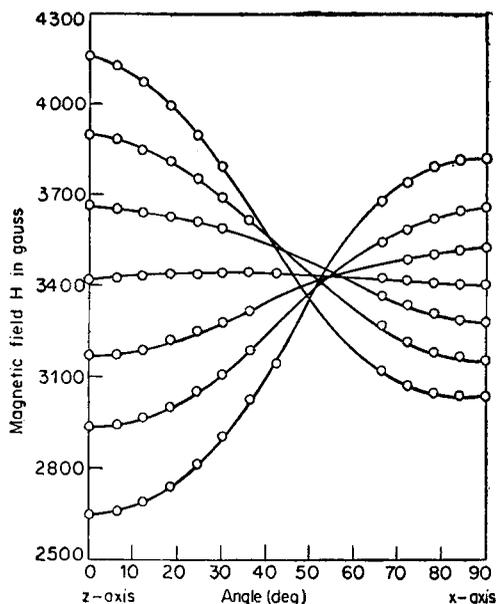
Angular variation study of EPR spectrum of  $Gd^{3+}$  in PZN reveal the presence of a single set of seven line spectrum at 298K. The presence of only one set of spectra down to liquid nitrogen temperature, corresponding to  $\Delta M = \pm 1$  transition shows that  $Gd^{3+}$  substitutes only single type of site. Figure 3 shows the angular variation of the fine structure transitions ( $\Delta M = \pm 1$ ) with magnetic field in  $zx$  plane. From the figure it can be seen that the maximum fine structure separation of the absorption lines occurs when the field is parallel to the trigonal axis of the crystal. The subsidiary maxima occur when the magnetic field is perpendicular to the  $c$  axis. The angular variation of the spectrum in the  $xy$  plane (plane perpendicular to the  $c$  axis) shows a periodicity of  $\pi/3$ . This is consistent with  $C_{3i}$  symmetry as well as  $C_{3h}$  symmetry (Buckmaster *et al* 1968).

The EPR spectra of  $Gd^{3+}$  in PZN can be described by the spin-Hamiltonian (Elliott and Stevens 1953).

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6$$

with  $b_2^0 = 3B_2^0$ ,  $b_4^0 = 60 B_4^0$ ,  $b_6^0 = 1260 B_6^0$ ,  $b_6^6 = 1260 B_6^6$  where the symbols have their usual meaning.

Using the above spin-Hamiltonian (neglecting the small term in  $b_6^6$  since they are very small and have matrix elements only between states for which  $\Delta M = \pm 6$ ),  $Gd^{3+}$  EPR spectra are analysed and the best-fit parameters thus obtained are being listed in table 2. The absolute sign of  $b_2^0$  could not be determined since the measurements made here are only down to 77K. Assuming  $b_2^0$  to be positive the relative sign of  $b_n^m$  parameters are found.



**Figure 3.** Angular variation of EPR spectrum in  $zx$  plane for  $Gd^{3+}$  in  $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$  at 298 K. The solid lines are smooth curves that connect data points from the same transition.

**Table 2.** Spin-Hamiltonian parameters for  $Gd^{3+}$  in  $Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$  at 298 K and 77 K. The  $b_n^m$  parameters are given in units of  $10^{-4} \text{ cm}^{-1}$ .

Spin-Hamiltonian parameters	298 K	77 K
$b_2^0$	$114.60 \pm 1$	$123.70 \pm 1$
$b_4^0$	$0.592 \pm 0.001$	$0.750 \pm 0.001$
$b_6^0$	$0.293 \pm 0.002$	$0.600 \pm 0.002$
$g_{\parallel}$	$1.9925 \pm 0.0005$	$1.9924 \pm 0.0005$
$g_{\perp}$	$1.9940 \pm 0.0005$	$1.9938 \pm 0.0005$

Following the calculations of Lacroix (1957) explaining the deviation of the  $g$  value from the free electron  $g$  value, the parameter  $\alpha$ , which determines the mixture of the excited  ${}^6P_{7/2}$  with the ground  ${}^8S_{7/2}$ , is given by

$$g = (1 - \alpha^2) g_s + \alpha^2 g_p$$

where  $g_s = 2.0023$  and  $g_p = 1.716$  are the  $g$  values for the  ${}^8S_{7/2}$  and  ${}^6P_{7/2}$  states respectively. Using the  $g_{\parallel}$  values, the  $\alpha$  values are computed for both the temperatures and are found to be  $0.185 \pm 0.004$  at 298 K and  $0.186 \pm 0.004$  at 77 K. The value of  $\alpha$  was found to be the same at both the temperature (within the experimental error), indicating constancy of admixture of the  ${}^6P_{7/2}$  state with  ${}^8S_{7/2}$  state down to 77 K.

## Conclusion

We have observed the electron paramagnetic resonance of  $Mn^{2+}$  and  $Gd^{3+}$  in PZN. The data presented permit one to assert that in PZN,  $Mn^{2+}$  ions substitute for two inequivalent  $Zn^{2+}$  sites and Mn atoms (and consequently Zn atoms) are surrounded by water molecules. The Gd atoms (and consequently the Pr atom) in PZN crystals are localized at identical sites.

## References

- Abraham A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon Press) p. 217
- Brandt B M, Van Ormondt D and Thalhammer T 1965 *Phys. Lett.* **19** 549
- Buckmaster H A, Dering J C and Fry D J I 1968 *J. Phys.* **C1** 599
- Chatterjee R, Smith M R and Buckmaster H A 1976 *Can. J. Phys.* **54** 1224
- Culvahouse J W, Unruh W and Sapp R C 1961 *Phys. Rev.* **121** 1370
- Dixon R T and Culvahouse J W 1971 *Phys. Rev.* **B3** 2279
- Elliott R J and Stevens K W H 1953 *Proc. R. Soc. (London)* **A219** 387
- Geifman I N and Glinchuk M D 1971 *Soviet Phys. Solid State* **13** 872
- Geschwind S 1961 *Phys. Rev.* **121** 363
- Henning J C M 1967 *Phys. Lett.* **A24** 40
- Jain V K 1976 Ph.D. Thesis, Indian Institute of Technology, Kanpur

- Lacroix R 1957 *Helv. Phys. Acta* **30** 374  
Low W 1960 *Paramagnetic Resonance in Solids (Solid State Phys. Suppl. 2)* (New York: Academic Press)  
Matumura O 1959 *J. Phys. Soc. Jpn.* **14** 108  
Misumi S, Isobe T and Higa T 1974 *Nippon Kagaku Kaishi* **10** 1829  
Richardson R J, Lee S and Menne T J 1970 *Phys. Rev.* **B2** 2295  
Simanek E and Müller K A 1970 *J. Phys. Chem. Solids* **31** 1027  
Van Wieringen J S 1955 *Disc. Faraday Soc.* **19** 118  
Walsh W M 1959 *Phys. Rev.* **114** 1473  
Watson R E and Freeman A J 1961 *Phys. Rev.* **123** 2027  
Wybourne B G 1966 *Phys. Rev.* **148** 317  
Zalkin A, Forrester J D and Templeton D H 1963 *J. Chem. Phys.* **39** 2881