EPR of Mn^{2+} in $Pr_2Mg_3(NO_3)_{12} \cdot 24\,H_2O$ Single Crystals

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EPR of Mn^{2+} in $Pr_2Mg_3(NO_3)_{12} \cdot 24\,H_2O$ single crystals has been studied at X-band. Mn^{2+} substitutes two inequivalent Mg^{2+} sites. The spin-Hamiltonian analysis of the EPR spectra is presented at 298 K as well as 77 K.

The hydrated double nitrates with the general formula $M_2''' M_3''(NO_3)_{12} \cdot 24\,H_2O$, where M''' is a trivalent cation (Bi or an ion of the 4f group) and M'' is a divalent cation (Zn, Mg or an ion of the 3d group), form an interesting isomorphous series of salts for Electron Paramagnetic Resonance (EPR) studies of S-state ions (Mn^{2+}, Gd^{3+}). 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 note we describe the EPR of Mn^{2+} in $Pr_2Mg_3(No_3)_{12} \cdot 24\,H_2O$ (hereafter called PMN) single crystals from 298 K down to 77 K.

The crystal structure of Ce compound has been determined by Zalkin et al[1]. The other hydrated double nitrates can be expected to have similar structure. The unit cell of double nitrates is rhombohedral with space group $R\overline{3}$. There are two different divalent cation sites (site I and site II), each of which is octahedrally surrounded by six nearest neighbour oxygens belonging to water molecules. The difference between the two sites is in the degree of symmetry; site I possesses inversion symmetry, while the site II does not. The unit cell contains one divalent ion in site I and two in a site II. The trivalent ion is found at a site of C_{3i} point symmetry.

Single crystals of PMN doped with Mn^{2+} were grown by slow evaporation of the aqueous solution at constant temperature. The Mn^{2+} was introduced into the lattice by adding a small amount (0.1% by weight) of manganese nitrate. The experiments were performed on a Varian V-4502 EPR spectrometer, operating at X-band, provided with 100 kHz field modulation.

From the angular variation studies of the EPR spectra of Mn^{2+} in PMN it was found that the manganese ion substitutes two inequivalent divalent magnesium sites. The spectra of the Mn^{2+}(I) centre were measured for various angles of the magnetic field relative to the *c* axis. Figure 1 shows the angular variation of the allowed fine structure transitions ($\Delta M = \pm 1$) of Mn^{2+} in the zx plane at 298 K for site I. The EPR spectra of Mn^{2+} in PMN at 298 K and 77 K for both sites can be described by a spin-Hamiltonian of the form [2]

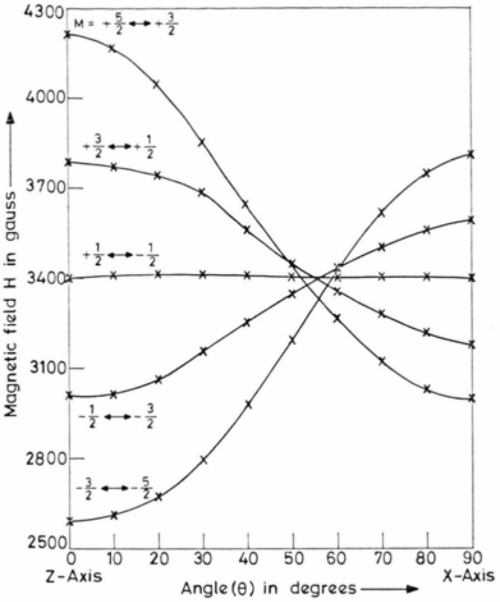

Fig. 1. Angular variation of the fine structure transitions of Mn^{2+} for site I in the zx plane. The solid lines are smooth curves that connect data points from the same transition.

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

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

Using the above spin-Hamiltonian, the Mn^{2+} EPR spectra were analysed and the best fit parameter, thus obtained, are being listed in Table I for both sites at 298 K and 77 K. The signs of the parameters are only relative and have been determined from

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Table I. Spin-Hamiltonian parameters for Mn^{2+} in $Pr_2Mg_3(NO_3)_{12} \cdot 24\,H_2O$ single crystals at 298 K and 77 K. All the crystal field and h.f. parameters are in units of $10^{-4}\ cm^{-1}$.

Spin-Hamiltonian parameters	Site I		Site II	
	298 K	77 K	298 K	77 K
D	-187.6 ± 1	-220.0 ± 1	20.63 ± 2	43.0 ± 2
$a-F$	7.2 ± 1	7.4 ± 1	9.4 ± 1	9.5 ± 1
$g_{\parallel}$	2.0051 $\pm .0005$	2.0049 $\pm .0005$	2.0084 $\pm .0012$	2.0080 $\pm .0012$
$g_{\perp}$	2.0067 $\pm .0008$	2.0065 $\pm .0008$	2.0090 $\pm .0015$	2.0085 $\pm .0015$
A	-89.90 $\pm\ 0.5$	-89.90 $\pm\ 0.5$	-89.40 $\pm\ 1$	-89.50 $\pm\ 1$
B	-89.6 $\pm\ 0.5$	-89.7 $\pm\ 0.5$	-90.0 $\pm\ 1$	-90.0 $\pm\ 1$

the observed second-order hyperfine shift, assuming "A" to be negative. The values of g and A for both Mn^{2+} sites are independent of the temperature within the experimental error. The values of the zero-field splitting parameter D is very different for the two sites and is sensitive to temperature. The observed value of A indicates that Mn^{2+} at both sites is surrounded by six water molecules as the covalency parameter determined from the curve (hyperfine parameter vs covalency) given by Simanek and Müller[3] indicates the characteristic covalency of the $Mn^{2+}-6\,H_2O$ complex. Moreover the line-width of Mn^{2+} in PMN is of the order of 12 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 moments in the water molecules[4].

Brandt et al.[5] have determined the zero-field splitting parameter D of Mn^{2+} in $La_2Mg_3(NO_3)_{12} \cdot 24\,H_2O$ for both sites. It is interesting to note that the values of D for sites I and II obtained in this experiment for PMN : Mn^{2+} are nearly the same as the parameter D of Mn^{2+} in $La_2Mg_3(NO_3)_{12} \cdot 24\,H_2O$. A theoretical interpretation of the latter for site I was given by Chatterjee et al[6]. They concluded that the relativistic second-order effect of Wybourne[7] 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.

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