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ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} AND Gd^{3+} IN $Nd_3Mg_3(NO_3)_{12} \cdot 24H_2O$ SINGLE CRYSTALS

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The electron paramagnetic resonance (EPR) of Mn^{2+} and Gd^{3+} doped in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$ single crystals has been studied at the X-band. Mn^{2+} substitutes for two Mg^{2+} sites, while Gd^{3+} substitutes for single type of Nd^{3+} sites. The spin-Hamiltonian analysis of the EPR spectra is presented for 298 K and 77 K.

1. *Introduction*

The electron paramagnetic resonance (EPR) studies required the presence of unpaired electrons in the sample to be investigated. In general, these are not present in the pure material but can be introduced by doping with paramagnetic substances such as the transition elements of 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 at low magnetic fields for two reasons: (a) the zero-field splitting is zero to the first order and (b) only higher-order effects permit lifting the degeneracy of the fundamental states (^6S and ^8S). Therefore, a detailded 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 an ion 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

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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 the present paper we describe EPR of Mn^{2+} and Gd^{3+} in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$(NMN) single crystals at 298 K and at 77 K. The EPR of Gd^{3+} in NMN was reported earlier only for room temperature [1].

2. *Crystal structure*

The crystal structure of $Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$ has been determined by Zalkin et al. [2]. The other hydrated double nitrates can be expected to have similar structure. The primitive cell containing one formula unit is rhombohedral with dimension $a = 13.165$ Å and $\alpha = 49.37°$. The space group is $R\bar{3}$. The corresponding hexagonal cell containing three formula units has dimension $a = 11.004$ Å, $c = 34.592$ Å. The rhombohedral unit cell contains three divalent ions situated at two different lattice sites. One of them occupies a site with the point symmetry C_{3i} (Y sites 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 rest of the atoms are in a position of the general type. Culvahouse et al. [3] has shown that one Zn^{2+} lies on the body centre of the cell (Y site) and two Zn^{2+} at special positions $\pm(x, x, x)$ $(x = 0.399)$ which are along the long diagonal of the rhombohedron and $34.18x$ Å to either side of the centre of the cell (X site). There are two trivalent ions along this diagonal and 8.54 Å 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 the central ion a nearly regular octahedral $M''(H_2O)_6^{2+}$ complex. Each trivalent ion is coordinated by 12 oxygens belonging to six nitrate ions, located at the corners of a somewhat irregular icosahedron.

3. *Experimental*

Single crystals of NMN doped with Mn^{2+} and Gd^{3+} were grown by slow evaporation of an aqueous solution of $Nd(NO_3)_3 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$, mixed in stoichiometric ratios, at room temperature. The Mn^{2+} and Gd^{3+} were introduced into the lattice by adding a small amont (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. The crystals were mounted on quartz rods and angular variation studies were performed using a Varian E-229 goniometer.

4. *Results and discussion*

4.1. Mn^{2+}

For an arbitrary orientation, the EPR spectrum consists of a number of lines corresponding to allowed and forbidden transitions. Angular variation studies of Mn^{2+} spectra reveal the presence of two inequivalent Mn^{2+} centre of unequal intensity. The Mn^{2+} substitutes for Mg^{2+} and shows the spectrum of two Mn^{2+} complexes. The spectrum having large intensity is due to Mn^{2+} substituting for Mg^{2+} at site II while spectrum having low intensity is due to Mn^{2+} at site I (Fig. 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 were located by searching the directions of extrema in the spread of the spectrum. It was found that the principal z axis of two Mn^{2+} complexes are along the trigonal axis (c axis) and x axis is perpendicular to the 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 (Fig. 1). 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. Fig. 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 the z axis as θ changes. The lines collapse to a very small spread at an orientation $\theta = 52.7°$ away from the z axis. As θ increases further, the lines cross each other and spread out to a second maximum at $\theta = 90°$ (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 Mg^{2+} sites. Experiments were also performed

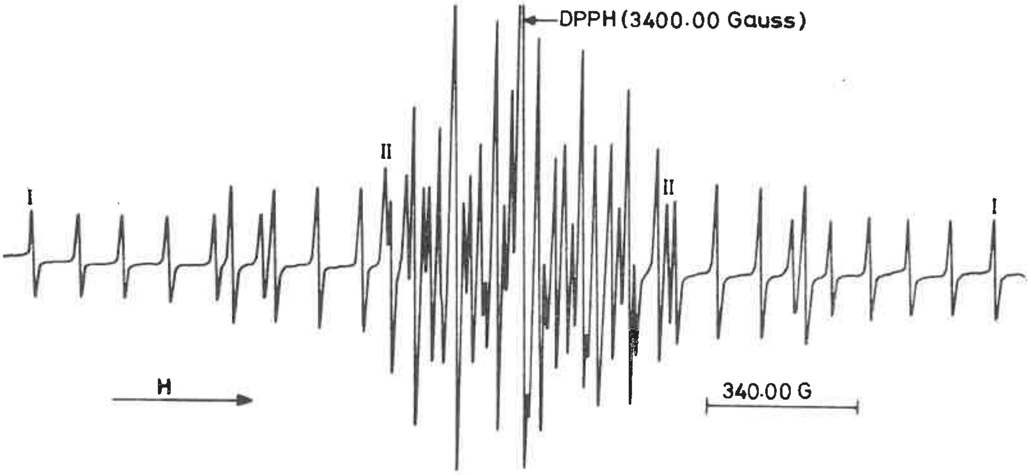

Fig. 1. EPR spectrum of Mn^{2+} in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$ single crystals at 298 K. The magnetic field is along the c axis. The position of extreme hyperfine lines of Mn^{2+} complexes for two sites are designated by I and II respectively

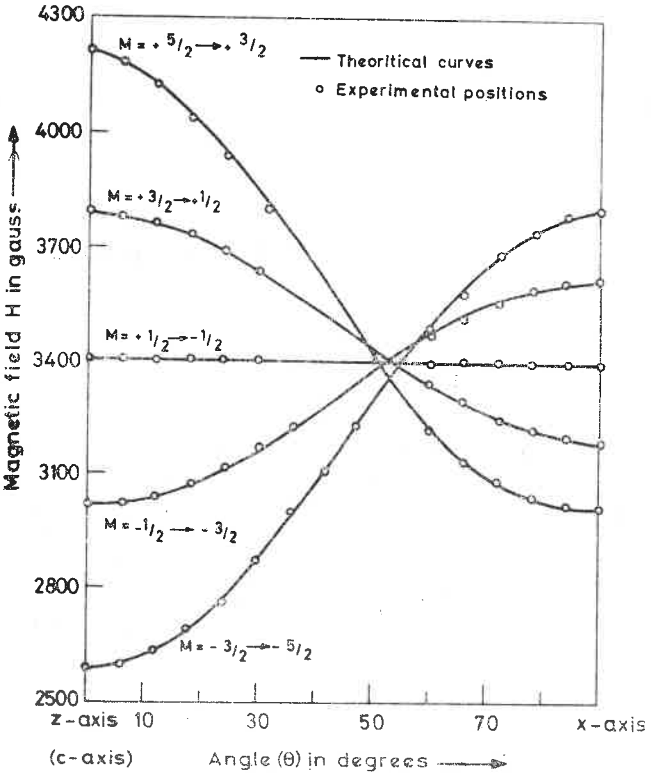

Fig. 2. Angular dependence of allowed fine structure transitions ($\Delta M + \pm 1$) of Mn^{2+} for site I in the zx plane at 298 K

at 77 K in order to observe the effect of paramagnetic Nd^{3+} ions on Mn^{2+} spectra. However, at this temperature no effect on the spectrum was observed and experiments at 4.2 K were not possible.

The EPR spectrum of Mn^{2+} for both sites can be described by the spin-Hamiltonian of the form [4]

$$\begin{aligned}\mathcal{H} &= \beta g_{\parallel} H_z S_z + \beta g_{\perp}(H_x S_x + H_y S_y) + D(S_z^2 - 35/12) - (7/36)(a-F) \\ &\times (S_z^4 - (95/14)S_x^2 + 81/16) + AI_zS_z + B(S_xI_x + S_yI_y) + (a\sqrt{2}/36) \\ &\times \{S_z[S_+^3 \exp(-3i\Phi) + S_-^3 \exp(3i\Phi)] + [S_+^3 \exp(-3i\Phi) + S_-^3 \exp(3i\Phi)]S_z\},\end{aligned}$$

where the z axis is parallel to the trigonal 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 listed in Table I for both sites at 298 K and 77 K. The signs of the parameters (given in Table I) are relative. Since the hyperfine splitting constant is always found to be negative for a manganese ion

TABLE I

Spin-Hamiltonian parameters for Mn^{2+} in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$ single crystals at 298 K and 77 K. All 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	298K	77 K
D	-187.2 ± 1	220.0 ± 1	19.4 ± 2	-54.6 ± 2
$a-F$	8.5 ± 1	9.4 ± 1	9.3 ± 1	9.4 ± 1
$g_{\parallel}$	2.0031 ± 0.0005	2.003 ± 0.0005	2.002 ± 0.001	2.001 ± 0.001
$g_{\perp}$	2.0066 ± 0.0005	2.006 ± 0.0005	2.009 ± 0.002	2.009 ± 0.002
A	-89.9 ± 0.5	-90.0 ± 0.5	-98.0 ± 1	-89.3 ± 1
B	-89.8 ± 0.5	-89.8 ± 0.5	-89.2 ± 1	-89.5 ± 1

[5, 6] 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[7].

The g-factor for both the sites is found to be isotropic and independent of temperature, any anisotropy being within the experimental error. The small deviation from free spin value may be attributed to the effects of covalent bonding [8] although it is difficult to extract any meaningful covalency parameter out of it.

The value of the hyperfine splitting constant for both the sites is found to be almost isotropic and independent of temperature, any anisotropy being within the experimental error. It was recognized that nearest neighbour interactions are dominating for hyperfine splitting in contrast to other EPR parameters like D, a and g values where long range interactions can be important [9]. The determination of the hyperfine splitting constant in the EPR spectra of Mn^{2+} makes it possible to evaluate the nature of the bond between the manganese ion and its immediate surrounding. Van Wieringen [10] has shown that the hyperfine splitting of Mn^{2+} decreases with increasing covalency of the magnetic complex. The relation between hyperfine parameter (average hyperfine splitting) and the local bonding of the Mn^{2+} and the nearest neighbour ligands was put phenomenologically on a more quantitative basis by plotting hyperfine parameters versus Pauling's covalency parameter [11–14]. The plots are almost linear. Here, the covalency parameters are derived from the electronegativity of Mn^{2+} and ligands and the number of ligands, using the expression developed by Hannay and Smyth [15]. The hyperfine parameter in these plots were obtained experimentally from a series of crystals in which Mn^{2+} is surrounded by the same type of ligands (it is interesting to note that hyperfine splitting is almost idependent of the host cation in a series of isomorphous crystals). It is well established that Mn^{2+} in Tutton salts [16], fluosilicate [17], struvite [18], GASH [19] and perchlorates [20] where it is surrounded by six water molecules, the average value of the hyperfine splitting is observed 90.0×10^{-4} cm^{-1} which corresponds to a covalency of 7% from the curve (hyperfine parameter vs covalency) given by Simanek and Müller [14]. The observed value of the hyperfine splitting in NMN : Mn^{2+} indicates that Mn^{2+}

at both sites is surrounded by six water molecules since the average value of hyperfine splitting corresponds to a covalency parameter of 7 % which is characteristic of $Mn(H_2O)_6^{2+}$ complex. Moreover, the linewidth of Mn^{2+} in NMN 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 moments in the water molecules [8].

From Table I it can be seen that the value of the 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 I 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 [21]. 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 [22, 23]. 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 the [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 [21] and for Mn^{2+} in $MgSeO_4 \cdot 6H_2O$ single crystals [24]. In a theoretical analysis of the ground state splitting of the S-state ion it is generally recognized that more than one mechanism is required to account for the magnitude of the parameter D. Brandt et al. [25] have determined the zero-field splitting parameter D of Mn^{2+} in LMN for both sites. It is interesting to note the value of D for site I and site II obtained in this experiment for NMN : 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. [26]. They concluded that the relativistic second-order effect of Wybourne [27] yields the major contribution to the value of the zero-field splitting parameter D. Their calculated values are in good agreement with the observed values for site I.

4.2. Gd^{3+}

An angular variation study of the EPR spectrum of Gd^{3+} in NMN reveal the presence of a single set of a seven line spectrum at 298 K. 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 a single type of site. Figure 3 shows the angular variation of the fine structure transition ($\Delta M = \pm 1$) with the magnetic field in the zx plane. From Fig. 3 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 [28]. Measurements at 77 K were made to observe the effect of paramagnetic Nd^{3+} ions on the Gd^{3+} spectra. However, at this temperature no effect on the spectrum was observed except an increase in the spread of the spectrum. This increase is probably due to the thermal contraction and vibrational mechanism of the crystal. The experiments at 4.2 K were not possible.

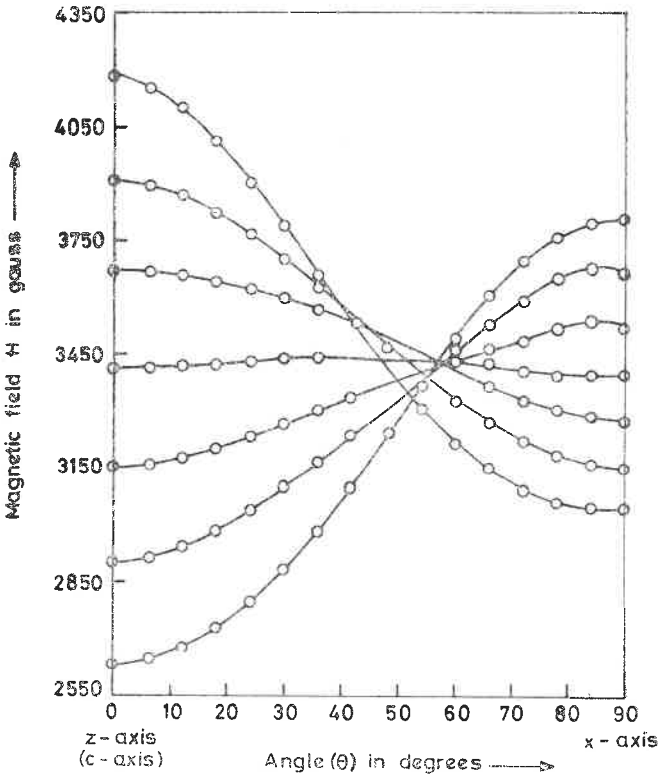

Fig. 3. Angular variation of EPR spectrum in the *zx* plane for Gd^{3+} in $Nd_2Mg_3(NO_3)_{12}\cdot 24H_2O$ at 298 K. The solid lines are smooth curves that connect data points from the same transition

The EPR spectra of Gd^{3+} in NMN can be described by the spin-Hamiltonian [29]

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

with $b_2^0 = 3B_2^0$, $b_4^0 = 60B_4^0$, $b_6^0 = 1260B_6^0$, $b_6^6 = 1260B_6^6$, where the symbols have their usual meaning and $S = 7/2$ for Gd^{3+}. Using the above spin-Hamiltonian (neglecting the small term in b_6^6 since they are very small and have matrix elements only between

TABLE II

Spin-Hamiltonian parameters for Gd^{3+} in $Nd_2Mg_3(NO_3)_{12}\cdot 24H_2O$ single crystals at 298 K and at 77 K. All crystal field parameters are in units of 10^{-4} cm^{-1}

Spin-Hamiltonian parameters	298 K	77 K
b_2^0	116.6 ± 1	128.4 ± 1
b_4^0	0.276 ± 0.001	0.471 ± 0.001
b_6^0	0.4 ± 0.002	0.84 ± 0.002
$g_{\parallel}$	1.9915 ± 0.0005	1.9910 ± 0.0005
$g_{\perp}$	1.9918 ± 0.0005	1.9916 ± 0.0005

states for which $\Delta M = \pm 6$), Gd^{3+} EPR spectra are analysed and the best-fit parameters thus obtained are listed in Table II. The absolute sign of b_2^0 could not be determined since the measurements made here are only down to 77 K. Assuming b_2^0 to be positive the relative sign of b_m^n parameters are found.

Following the calculations of Lacroix [30] explaining the deviation of the g value from the free electron g value, the parameter α, 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 α values are computed for both the temperatures and are found to be 0.194 ± 0.004 at 298 K and 0.198 ± 0.004 at 77 K. The value of α was found to be the same at both temperatures (within the experimental error), indicating constancy of the admixture of the ${}^6P_{7/2}$ state with the ${}^8S_{7/2}$ state down to 77 K.

5. *Conclusions*

The electron paramagnetic resonance of Mn^{2+} and Gd^{3+} in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$ single crystals is studied. The data presented permit one to assert that in NMN, Mn^{2+} ions substitutes for two inequivalent Mg^{2+} sites and Mn atoms (and consequently Mg atoms) are surrounded by water molecules. The Gd atoms (and consequently the Nd atoms) in NMN crystals are localized in a position of single type with a magnetic multiplicity factor equal to one and structure multiplicity factor (K_α) equal to two ($K_\alpha = 1$ is excluded by the chemical formula of the double nitrate, and $K_\alpha > 2$ does not conform with magnetic multiplicity factor). These results are in agreement with the crystallographic data on double nitrates.

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