

EPR of Mn^{2+} -doped $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$: Mn^{2+} - Ni^{2+} exchange constant

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X-band EPR measurements on Mn^{2+} -doped isostructural single crystals of paramagnetic $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and diamagnetic $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ have been made at room, liquid-nitrogen, and liquid-helium temperatures. The spin-Hamiltonian parameters are evaluated from the data using a rigorous least-squares-fitting program suitable for electron-nuclear spin-coupled systems. Using the g shift in the paramagnetic lattice from that in the diamagnetic lattice a value of 4.293 GHz for the Mn^{2+} - Ni^{2+} exchange constant in $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ is estimated. For $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ host the linewidths exhibit temperature and magnetic field dependence. The temperature dependence of the zero-field splitting parameter b_2^0 for both hosts is found to be linear, thus being explained as mainly due to the thermal expansion of the lattice.

EPR studies of Mn^{2+} -doped single crystals of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (hereafter MSO) have been reported by Janakiraman and Upreti¹ and Hayashi and Ono.² These measurements were, however, confined to room temperature only, and the spin-Hamiltonian parameters were estimated, using perturbation expressions, from resonant line positions obtained for the external magnetic field orientation being along the Z and/or X axis only. On the other hand, Bramley and Starch,³ estimated the spin-Hamiltonian parameters of Mn^{2+} in the MSO lattice at room temperature from zero magnetic field resonance (ZFR), using a powder sample. In Refs. 1–3, the individual values of all the spin-Hamiltonian parameters could not be evaluated, due to the use of perturbation expressions for eigenvalues. Further, Bramley and Starch³ cast doubt on the accuracy of the spin-Hamiltonian parameters obtained from EPR data, due to the uncertainty in measuring the frequency and the magnetic field intensity, misalignment of the crystalline sample, and the use of perturbation expressions in the evaluation of parameters. One of the motivations, in this continuing series of measurements, is to minimize these errors. In the present work the magnetic field intensity has been measured precisely by the use of a digital NMR gaussmeter (model B-NM-20 Bruker). (A calibration curve related the measured magnetic field intensity at the position of the probe to that at the actual position of the sample. Measurements of the magnetic field intensity and frequency were further verified using DPPH line position.) Moreover, a rigorous computer technique for the evaluation of spin-Hamiltonian parameters using exact numerical diagonalization of the spin-Hamiltonian matrix (instead of perturbation theory), fitting simultaneously all line positions obtained for various orientations of the external magnetic field to evaluate the spin-Hamiltonian parameters for electron-nuclear spin-coupled systems has recently been published.⁴ All these considerations make it worthwhile to reinvestigate the Mn^{2+} -doped MSO sample by EPR.

EPR measurements on Mn^{2+} -doped single crystals of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (hereafter NSO) have been previously reported by Misra and Mikolajczak.⁵ These were, however, performed on a sample of *arbitrary* shape, although the spin-

Hamiltonian parameters were evaluated from the data using a rigorous least-squares-fitting computer technique.⁴ On the other hand, at liquid-helium temperature a paramagnetic sample becomes magnetized and the demagnetization factor cannot be estimated for a sample of arbitrary shape, making it impossible to estimate the Mn^{2+} - Ni^{2+} exchange constant from the shift of the g value in the paramagnetic lattice from that in the isostructural diamagnetic lattice. (For more details, see Refs. 6 and 7.) Further, the determination of the exchange constant requires the values of the zero-field splitting parameter β_2^0 and the g factor for Ni^{2+} in NSO (see further on in this paper). Fortunately, these values have been reported by Ono.⁸

The purpose of this paper is twofold: (i) to determine more accurately the spin-Hamiltonian parameters for Mn^{2+} in MSO at room, liquid-nitrogen, and liquid-helium temperatures; and (ii) to estimate the exchange-interaction constant between Mn^{2+} - Ni^{2+} in the paramagnetic lattice of NSO, by measuring, at liquid-helium temperature, the shift of g value in the NSO lattice of a spherical sample (so that the demagnetization factor is zero^{6,7}) from that in the isostructural diamagnetic lattice of MSO. Similar investigations have already been reported for $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Ref. 6) and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Ref. 7).

The (isostructural) crystals of MSO and NSO have a unit cell of orthorhombic symmetry,⁹ containing four formula units related to each other by the operation of the space group $P2_12_12_1$. Each Ni^{2+} , or Mg^{2+} , ion is surrounded by a distorted octahedron of six water molecules. The seventh water molecule is not coordinated with the Ni^{2+} , or Mg^{2+} , ion but instead fills what would otherwise be a hole in the structure. The unit-cell dimensions are⁹ for MSO $a = 11.91$, $b = 12.01$, and $c = 6.87$ Å, and for NSO $a = 11.86$, $b = 12.08$, and $c = 6.81$ Å. The four Mg^{2+} , or Ni^{2+} , sites in the unit cell are magnetically inequivalent. This is also reflected in the EPR spectra.

Single crystals of Mn^{2+} -doped MSO and NSO were grown by slow evaporation at room temperature of solutions of MSO and NSO, respectively, each containing stoichiometric amount of 0.1% of MnSO_4 .

The spin-Hamiltonian appropriate to orthorhombic symmetry is¹⁰

$$\mathcal{H} = \mu_B \vec{H} \cdot \vec{g} \cdot \vec{S} + \sum_{m=0,2} \frac{1}{3} b_2^m O_2^m + \sum_{m=0,2,4} \frac{1}{60} b_4^m O_4^m + A S_z I_z + B (S_x I_x + S_y I_y) + Q' [I_z^2 - \frac{1}{3} I(I+1)] + Q'' (I_x^2 - I_y^2) \quad (1)$$

Here, g , b_l^m , A , B , Q' , and Q'' are the spin-Hamiltonian parameters, O_l^m are the spin operators (Ref. 10), μ_B is the Bohr magneton, H is the external magnetic field, S ($=\frac{5}{2}$) and I ($=\frac{5}{2}$) are the electron and nuclear spins, respectively, for the Mn^{2+} ion. The X , Y , and Z axes are coincident with the principal axes of the zero-field splitting parameter b_2^0 , so that the overall splitting of the spectra is maximum along the Z axis, while it is minimum along the Y axis.

The experimental arrangement has been described in Ref. 5. EPR spectra were recorded for the external magnetic field orientation in the ZX plane at 5° intervals both from the Z and X axes for the MSO sample at room, liquid-nitrogen, and liquid-helium temperatures. As mentioned previously, there is observed an overlap of EPR spectra corresponding to four magnetically inequivalent sites. For any one inequivalent Mn^{2+} ion, along its Z axis, five well-separated sets of fine structure lines ($\Delta M = \pm 1$; M is the electronic quantum number) appeared, each set being split into six hyperfine lines ($\Delta m = 0$; m is the nuclear quantum number). The intensities of lines around the center of the spectrum are almost symmetric, and the linewidth remains the same throughout the spectrum (see below for more details). Some other lines with smaller intensities (about half), mostly corresponding to the transition $M = \pm \frac{3}{2} \leftrightarrow M = \pm \frac{1}{2}$ and $M = +\frac{1}{2} \leftrightarrow -\frac{1}{2}$, belonging to the other sites, were also observed. The angular variation of the spectrum corresponding to one inequivalent site at room temperature is shown in Fig. 1. As the temperature of measurement was lowered, the overall splitting of the spectrum increased, indicating an increase of the zero-field parameter b_2^0 (see below for more details).

EPR spectra for spherical crystal of Mn^{2+} -doped NSO were recorded at room, liquid-nitrogen, and liquid-helium temperatures in the ZX plane. The spherical samples were prepared by blowing the soft cubic-shaped samples on emery paper. The shape and angular variation of the spectra are the same as those reported by Misra and Mikolajczak.⁵ The linewidths and intensities of the lines (see below) vary considerably with the intensity of the external magnetic field. The similarity of the EPR spectra of the two samples (except for the differences in the linewidths and intensities caused by the presence of the paramagnetic Ni^{2+} ion in the NSO lattice) confirms that the MSO and NSO crystals are indeed isostructural).

The Mn^{2+} spin-Hamiltonian parameters for both the samples were evaluated by fitting simultaneously all resonant line positions observed in the ZX plane up to 30° around each axis.⁴ The fitting gives the correct relative signs of the parameters. The absolute signs were determined by measuring the intensity of the highest-field sextet relative to the lowest-field sextet along the Z axis, as the temperature is lowered from room down to the liquid-helium temperature. These values were found to be 1.10, 1.08, and 0.30 at 295, 85, and 3 K, respectively, for MSO, and 0.43, 0.41, and 0.10 at 295, 85, and 2 K, respectively, for NSO. They indicate that the sign of b_2^0 is negative for both the samples.¹⁰ A negative sign has been chosen for A and B in conformity with the hyperfine data,¹¹ and errors are calculated by the use of a statistical method.¹² Table I lists the parameter values for the MSO and NSO hosts. The parameters, as reported by the other researchers¹⁻³ for MSO, have also been included in Table I for comparison. The sign of b_2^0 for MSO, as given in Refs. 1-3 is, of course, incorrect, since

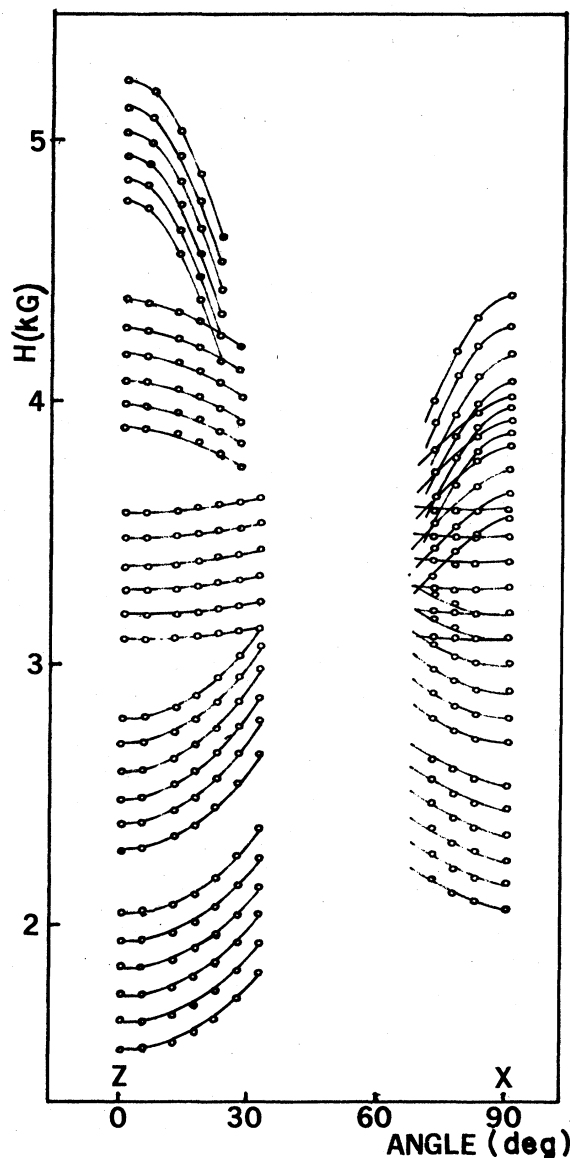


FIG. 1. Angular variation of X-band spectra in the ZX plane for the Mn^{2+} -doped MSO host at room temperature. The circles represent the experimental resonant-line positions, and the solid lines are smooth curves that connect data points for the same transition. Only spectra corresponding to one inequivalent Mn^{2+} ion have been exhibited.

the room-temperature data cannot yield the absolute sign of parameters. On the other hand, the magnitude of the room-temperature values of b_2^0 for MSO, determined in the present work, agree with those reported in Refs. 1-3 within 8%.

The observed EPR linewidths for the MSO sample did not exhibit significant variation, either for different orientations, or for different intensities of the external magnetic field, or at different temperatures. They are generally of the order of 12 G. In the case of NSO, as has been observed in other Ni^{2+} salts,^{6,7,13} the linewidths are magnetic-field-intensity dependent. The reason for this is the nonzero magnetic moment of the host Ni^{2+} ions; this is described well in Ref. 13. The EPR linewidths, as a function of the magnetic field intensity for both the samples at liquid-helium temperature

TABLE I. Values of the spin-Hamiltonian parameters for Mn^{2+} -doped MSO and NSO hosts (each 0.1% by weight). n is the number of points used in each fitting. The parameters b_1^m , Q' , Q'' , A , and B are expressed in units of GHz. A negative sign has been assumed for the values of A and B (Ref. 11). The indicated errors are calculated by the use of a statistical method (Ref. 12). The room-temperature values of the parameters for MSO, as reported in Refs. 1, 2, and 3, have also been included for comparison.

Temperature	MSO			NSO		
	295 K	85 K	3 K	295 K	85 K	2 K
g_{zz}	2.002 ± 0.002	1.996 ± 0.002	2.006 ± 0.002	2.003 ± 0.005	2.000 ± 0.005	2.000 ± 0.005
g_{xx}	1.968 ± 0.002	1.998 ± 0.002	1.963 ± 0.002
b_2^0	-1.118 ± 0.002	-1.241 ± 0.002	-1.292 ± 0.002	1.154 ± 0.014	1.200	1.181 ± 0.002
b_2^2	0.367 ± 0.005	0.254 ± 0.007	0.670 ± 0.007	0.266 ± 0.028	≈ 0.000	0.183 ± 0.002
b_4^0	0.004 ± 0.001	0.006 ± 0.001	0.007 ± 0.001	≈ 0.0003
b_4^2	-0.203 ± 0.023	-0.590 ± 0.038	-0.173 ± 0.047	0.014 ± 0.040
b_4^4	0.243 ± 0.027	0.430 ± 0.044	0.336 ± 0.049	0.012 ± 0.045
Q'	-0.018 ± 0.006	-0.003 ± 0.039	-0.013 ± 0.012	-0.009 ± 0.010
Q''	-0.017 ± 0.012	-0.005 ± 0.114	-0.011 ± 0.032	-0.002 ± 0.014
A	-0.268 ± 0.004	-0.276 ± 0.004	-0.277 ± 0.004	-0.258 ± 0.014	0.265	-0.026 ± 0.030
B	-0.267 ± 0.004	-0.258 ± 0.004	-0.271 ± 0.004	-0.244 ± 0.028	...	-0.265 ± 0.004
n	217	155	155	192
				232
				141

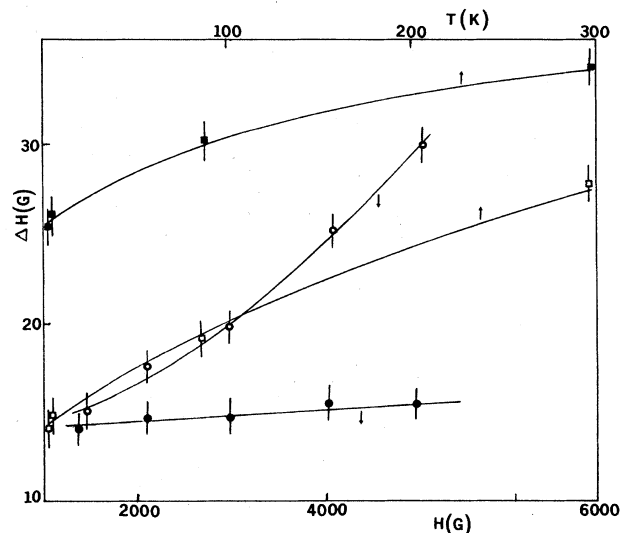


FIG. 2. Variation of the average linewidth: (i) of various sextets as a function of magnetic field intensity at liquid-helium temperature for the orientation of the external magnetic field along the Z axis for the MSO and NSO hosts (the open circles represent the NSO host, while the solid circles represent the MSO host; the abscissa scale is shown at the bottom), and (ii) of the highest- and lowest-field sextets for the NSO host as a function of temperature (the solid squares represent the highest-field sextet while the open squares represent the lowest-field sextet; the abscissa scale is shown on the top).

are exhibited in Fig. 2. The temperature variation of the average of width of the lines corresponding to the lowest- and highest-field sextets for NSO is also shown in Fig. 2. These average linewidths decrease as the temperature is lowered.

Shift of the g value in a paramagnetic lattice from its value in an isostructural diamagnetic lattice has been observed previously by several researchers.¹⁴⁻¹⁷ This phenomenon has been explained by Hutchings and Wolf¹⁴ and Hutchings, Windsor, and Wolf.¹⁵ Using this shift, they estimated the exchange interaction between Eu^{3+} , Fe^{3+} , and Gd^{3+} in europium gallium garnet crystals. Further, St. John and Myers¹⁶ have estimated the exchange integral between Ni^{2+} and several other paramagnetic ions, e.g., Co^{2+} and Cu^{2+} , in $NiSO_4 \cdot 6H_2O$ using the same procedure.

Recently, Misra, and Kahrizi^{6,7} estimated the Mn^{2+} - Ni^{2+} exchange interaction in $NiK_2(SO_4)_2 \cdot 6H_2O$ ⁶ and $Ni(CH_3COO)_2 \cdot 4H_2O$ ⁷ (for more details see Refs. 6 and 7). The following expression relates the g factors as observed in the paramagnetic and isostructural diamagnetic host lattices:

$$g_{obs} = g + J^2(g + g_1) / (\beta_2^0)^2 \quad (2)$$

In (2) g_{obs} and g are, respectively, the spectroscopic splitting factors of the Mn^{2+} ion in the paramagnetic lattice of NSO and its isostructural diamagnetic lattice of MSO, while $g_1 (= 2.2)$ and $\beta_2^0 (= 105 \text{ GHz})$ are, respectively, the g value and the zero-field splitting parameter of Ni^{2+} in NSO lattice (as measured by Ono⁸). Using the above relation and the values in Table I, the exchange interaction constant between Mn^{2+} and Ni^{2+} ions in NSO is estimated to be 4.293 GHz.

The temperature variation of the spin-Hamiltonian parameters of S -state ions for simple cubic systems have been in-

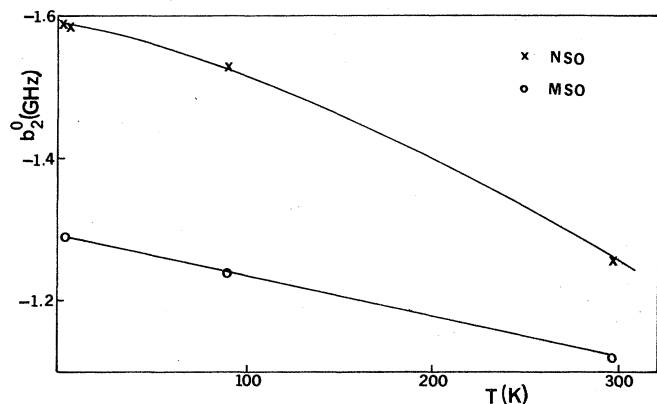


FIG. 3. Variation of the zero-field splitting parameter b_2^0 as a function of temperature for the MSO and NSO hosts.

investigated theoretically and experimentally by several workers.¹⁸⁻²² Simanek and Orbach²⁰ calculated the temperature dependence of the hyperfine parameters A and B using Debye approximation which is in good accord with their experimental results on Mn^{2+} in MgO . Serway²¹ has investigated the temperature dependence of the spin-Hamiltonian parameters of Mn^{2+} in the trigonal site of $CaCO_3$ in terms of implicit (thermal expansion) and explicit (lattice vibration) effects. Geifman and Glinchak²² have studied the temperature dependence of the crystal-field parameters of Fe^{3+} and

Mn^{2+} in Al_2O_3 .

The temperature variation of b_2^0 of Mn^{2+} -doped MSO and NSO lattices is plotted in Fig. 3 from room temperature down to liquid-helium temperature. The magnitude of b_2^0 increases linearly as the temperature is lowered, indicating the contraction of the lattice in both these hosts. Geifman and Glinchak²² have found the temperature variation of the parameter b_2^0 as a function of temperature as follows:

$$b_2^0(T) = b_2^0(0)[1 - 6\alpha(T - T_0)] \quad (3)$$

In (3) $b_2^0(0)$ is the value of b_2^0 at T_0 (usually room temperature) and α is the coefficient of linear thermal expansion. The above expression has been derived, assuming that the thermal expansion is the dominating mechanism and, that the coordinates of the ions surrounding the Mn^{2+} ion are linear in temperature, i.e., $\Delta R = \alpha T$. Also it has been assumed that b_2^0 is proportional to the square of the axial crystal-field potential.

Equation (3) shows that b_2^0 is linear in T . This is certainly borne out by the present values for both the hosts, as can be seen from Fig. 3. From this, one may be tempted to speculate that the thermal expansion is the dominant mechanism to determine the temperature variation of the zero-field-splitting parameter, and that b_2^0 depends predominantly upon the coordinates of the surrounding ions.

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