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EPR of Mn^{2+}-doped $Zn(CH_3COO)_2 \cdot 2H_2O$, $Mg(CH_3COO)_2 \cdot 4H_2O$, and $Ni(CH_3COO)_2 \cdot 4H_2O$: Mn^{2+}–Ni^{2+} exchange constant

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X-band EPR measurements on Mn^{2+}-doped single crystals of $Zn(CH_3COO)_2 \cdot 2H_2O$, $Mg(CH_3COO)_2 \cdot 4H_2O$, and $Ni(CH_3COO)_2 \cdot 4H_2O$ have been performed at room, liquid-nitrogen, and liquid-helium temperatures. The spin-Hamiltonian parameters are estimated by the use of a rigorous least-squares-fitting technique especially adapted to electron-nuclear spin-coupled systems, on a digital computer. The Mn^{2+}-Ni^{2+} exchange constant, using the shift of g value in the paramagnetic nickel salt from that in the isostructural magnesium salt at liquid-helium temperature, has been determined to be 3.81 GHz.

I. INTRODUCTION

The present paper reports X-band EPR measurements on three acetates doped with Mn^{2+} at room, liquid-nitrogen, and liquid-helium temperatures. These are zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$, hereafter ZnADH], magnesium acetate tetrahydrate [$Mg(CH_3COO)_2 \cdot 4H_2O$, hereafter MgATH], and nickel acetate tetrahydrate [$Ni(CH_3COO)_2 \cdot 4H_2O$, hereafter NiATH].

An Mn^{2+}-doped ZnADH crystal was investigated previously by the EPR technique by Janakiraman and Upreti.[1] However, their measurements were confined to room temperature only. Moreover, perturbation expressions were used for the estimation of parameters. Thus, values of only a few spin-Hamiltonian parameters could be determined. The absolute signs of the parameters could not be determined as no data were available at liquid-helium temperature. The same comments apply to the unpublished results on an Mn^{2+}-doped MgATH crystal by Manakkil.[2]

As for an Mn^{2+}-doped NiATH crystal, measurements at room, liquid-nitrogen, and liquid-helium temperatures have been reported by Misra and Jalachowski;[3] the spin-Hamiltonian parameters there were rigorously evaluated from the data. However, the sample used was of arbitrary shape, not enabling the determination of the demagnetization factor,[4] which should be taken into account in a paramagnetic lattice, if one were to estimate the guest-host exchange constant.

Recently, a rigorous technique, simultaneously fitting all EPR line positions obtained in a least-squares-fitting procedure, especially suitable for electron-nuclear spin-coupled systems, has been proposed[5] for the evaluation of spin-Hamiltonian parameters. For a crystal sample of a known shape, the demagnetization factor effective at low temperatures can be calculated. Then the shift in the g value at liquid-helium temperature in the paramagnetic lattice due to the guest-host (Mn^{2+}-Ni^{2+}) exchange interaction from that in an isostructural diamagnetic lattice can be definitively ascertained. This will enable the determination of an Mn^{2+}-Ni^{2+} exchange interaction constant, especially since the required value of the zero-field splitting parameter for Ni^{2+} in NiATH has already been estimated.[6]

It is the purpose of the present paper to report more accurate spin-Hamiltonian parameters as evaluated from EPR data for Mn^{2+}-doped single crystals of ZnADH, MgATH, and NiATH at room, liquid-nitrogen, and liquid-helium temperatures. Further, the Mn^{2+}-Ni^{2+} exchange constant has been estimated in the NiATH host. A similar study has been reported on an Mn^{2+}-doped nickel potassium sulfate hexahydrate crystal.[7]

II. DEMAGNETIZATION EFFECT AND g SHIFT DUE TO GUEST-HOST EXCHANGE INTERACTION

According to Ref. 4 the demagnetization factor for a sample of spherical shape is zero. Thus, for the measurements presented here a NiATH sample of spherical shape was chosen. Further, the value of the exchange-interaction constant J between Mn^{2+} and Ni^{2+} ions in NiATH can be expressed as[7–11]

$$|J| = \left(\frac{g_{\text{obs}} - g}{g + g_1} \right)^{1/2} \beta_2^0 \ . \tag{2.1}$$

In Eq. (2.1) g_{obs}, g, and g_1 are the g values as observed for Mn^{2+} in the paramagnetic host (NiATH), for Mn^{2+} in the isostructural diamagnetic host lattice (MgATH), and for Ni^{2+} in NiATH, respectively, while β_2^0 is the zero-field splitting parameter for Ni^{2+} in NiATH.

III. CRYSTAL STRUCTURES AND SAMPLE PREPARATIONS

The structure of a ZnADH crystal was determined by Van Niekerk, Schoening, and Talbot.[12] The unit cell is of dimensions $a = 14.50$, $b = 5.32$, $c = 11.02$ Å and $\beta = 100°0'$; it is monoclinic with space group C_2/c. There are four formula units in the unit cell; the zinc atoms lie on the twofold axis parallel to the b axis. (The site symmetries for all the zinc ions are exactly the same.) The six nearest neighbors of a zinc atom are four oxygen atoms (two pairs: O_1 and O_2) and two water molecules which form a distorted octahedron around the zinc atom. The distances are $d_{Zn\text{-}O_1} = 2.18$ Å, $d_{Zn\text{-}O_2} = 2.17$ Å, and $d_{Zn\text{-}H_2O} = 2.14$ Å. Single crystals were grown by slow evaporation at room temperature of a solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ containing 0.1% (by weight) of $Mn(CH_3COO)_2 \cdot 4H_2O$ in distilled water.

The crystal structures of isostructural crystals NiATH and MgATH were determined by Van Niekerk and Schoening[13] and Shankar, Khubchandani, and Padmanabhan,[14] respectively. These crystals are monoclinic with space group $P2_1/c$, having identical unit-cell dimensions. There are two formula units in the unit cell of dimension: $a = 4.75$, $b = 11.77$, $c = 8.44$ Å, and $\beta = 93°36'$. The nickel or magnesium atoms (indicated below as M) see exactly the same site symmetry, and are surrounded octahedrally by four water molecules and by two oxygen atoms, which belong to two different acetate groups as follows:

$$d_{M\text{-O}_1} = 2.12\ \text{Å}\ ,\quad \angle(\text{O}_1\text{-}M\text{-H}_2\text{O}(1)) = 90°44'\ ,$$

$$d_{M\text{-H}_2\text{O}(1)} = 2.11\ \text{Å}\ ,\quad \angle(\text{O}_1\text{-}M\text{-H}_2\text{O}(2)) = 90°33'\ ,$$

$$d_{M\text{-H}_2\text{O}(2)} = 2.06\ \text{Å}\ ,\quad \angle(\text{H}_2\text{O}(1)\text{-}M\text{-H}_2\text{O}(2)) = 88°03'\ .$$

Single crystals of Mn^{2+}-doped NiATH and MgATH were grown by slow evaporation at room temperature of 0.1% solution by weight of $\text{Mn(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}$ in $\text{Ni(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}$ and $\text{Mg(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}$, respectively.

Spheres of 1–2 mm diameter of paramagnetic lattice NiATH were prepared by blowing the roughly cubic single crystals on emery paper.

IV. EXPERIMENTAL DETAILS, SPIN HAMILTONIAN, AND EVALUATION OF PARAMETERS

The experimental details are the same as those described in Ref. 3. EPR spectra for ZnADH were measured at room, liquid-nitrogen, and liquid-helium temperatures for the magnetic field (H) orientation in the z-x plane. [The axes are defined after Eq. (4.1) below.] With H parallel to either the z or the x axis clearly resolved 30 allowed hyperfine lines ($\Delta M = \pm 1$ and $\Delta m = 0$) were observed (M and m are the electron- and nuclear-spin quantum numbers, respectively). (All Mn^{2+} ions are magnetically equivalent.) At liquid-nitrogen and liquid-helium temperatures the spectra have the same angular variation as at room temperature. As the temperature was lowered the size of overall splitting

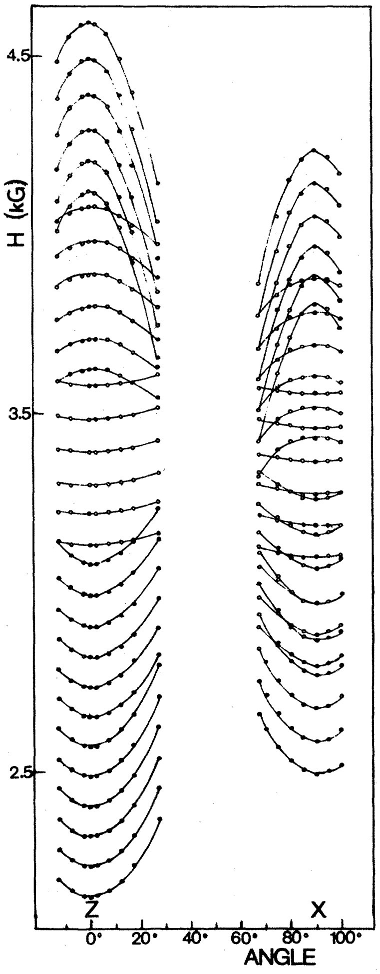

FIG. 1. Angular variation of X-band spectra in the z-x plane for the Mn^{2+}-doped ZnADH host at room temperature. The circles represent the experimental resonant-line positions, and the solid lines are smooth curves that connect data points for the same transition.

TABLE I. Values of spin-Hamiltonian parameters for the Mn^{2+}-doped ZnADH host (0.1 wt.%). n is the number of points used in each fitting. The parameters b_l^m, Q', Q'', A, and B are expressed in units of GHz. A negative sign has been assumed for the value of A. The indicated errors are calculated by use of a statistical method (Ref. 16). The parameters at room temperature (RT), as reported in Ref. 1, have also been included for comparison.

Temperature	295 K	85 K	11 K	Ref. 1 (RT)
g_{zz}	2.000 ± 0.001	2.027 ± 0.001	2.031 ± 0.001	2.001 ± 0.001
g_{xx}	2.001 ± 0.001	2.023 ± 0.001	2.013 ± 0.001	2.001 ± 0.001
b_2^0	−0.702 ± 0.002	−0.941 ± 0.002	−1.037 ± 0.002	0.694 ± 0.001
b_2^2	0.202 ± 0.002	0.436 ± 0.002	0.566 ± 0.002	−0.214 ± 0.004
b_4^0	0.000 ± 0.001	0.002 ± 0.001	0.002 ± 0.001	· · ·
b_4^2	0.037 ± 0.013	0.013 ± 0.013	0.026 ± 0.013	· · ·
b_4^4	0.054 ± 0.013	0.036 ± 0.015	0.134 ± 0.038	· · ·
Q'	0.005 ± 0.002	0.002 ± 0.001	−0.003 ± 0.001	0.001
Q''	0.021 ± 0.009	0.030 ± 0.010	0.008 ± 0.004	0.013
A	−0.251 ± 0.002	−0.254 ± 0.002	−0.247 ± 0.003	−0.251 ± 0.001
B	−0.252 ± 0.002	−0.257 ± 0.002	−0.244 ± 0.004	−0.251 ± 0.001
n	272	262	218	

TABLE II. Values of spin-Hamiltonian parameters for the Mn^{2+}-doped MgATH and NiATH hosts (each 0.1 wt.%). Other details and notations are the same as those given in the caption of Table I.

	MgATH			NiATH		
Temperature	295 K	85 K	2.5 K	295 K	85 K	1.8 K
g_{zz}	1.996 ±0.002	2.019 ±0.002	1.952 ±0.002	1.959 ±0.002	1.960 ±0.002	1.948 ±0.002
g_{xx}	1.993 ±0.002	1.005 ±0.002	1.981 ±0.002	1.971 ±0.002	2.007 ±0.002	1.959 ±0.002
b_2^0	1.160 ±0.002	1.257 ±0.002	1.350 ±0.002	1.272 ±0.003	1.341 ±0.003	1.430 ±0.003
b_2^2	−0.350 ±0.006	−0.594 ±0.006	−0.450 ±0.006	−0.356 ±0.009	−0.298 ±0.009	−0.283 ±0.009
b_4^0	0.017 ±0.002	0.047 ±0.002	0.017 ±0.002	0.016 ±0.002	0.023 ±0.002	0.010 ±0.002
b_4^2	−0.017 ±0.012	−0.332 ±0.026	−0.036 ±0.019	−0.239 ±0.030	−0.200 ±0.046	0.050 ±0.047
b_4^4	−0.071 ±0.027	−0.318 ±0.028	−0.181 ±0.023	−0.099 ±0.041	−0.707 ±0.129	−0.505 ±0.054
Q'	0.016 ±0.006	−0.001 ±0.016	0.018 ±0.006	0.001 ±0.008	0.030 ±0.006	0.008 ±0.008
Q''	0.048 ±0.011	−0.009 ±0.047	0.053 ±0.010	0.047 ±0.013	0.087 ±0.010	0.026 ±0.013
A	−0.250 ±0.004	−0.263 ±0.004	−0.258 ±0.004	−0.264 ±0.004	−0.268 ±0.004	−0.259 ±0.004
B	−0.243 ±0.004	−0.259 ±0.004	−0.255 ±0.004	−0.250 ±0.004	−0.273 ±0.006	−0.269 ±0.004
n	270	256	250	234	186	161

increased and at liquid-helium temperature the five sextets of the hyperfine lines were completely separated. The last sextet of the spectrum was observed down to 11 K, but below this temperature the intensity of these lines diminished rapidly and at 5 K they completely disappeared. The angular variation of EPR spectrum for a Mn^{2+} ion in ZnADH is shown in Fig. 1.

EPR measurements on a Mn^{2+}-doped single crystal of $Mg(CH_3COO)_2 \cdot 4H_2O$ were made at room, liquid-nitrogen, and liquid-helium temperatures in the z-x plane. Thirty well-resolved transition lines were observed along both the z and x axes. (All Mn^{2+} ions are magnetically equivalent.) The overall splitting of the lines increased for this sample also as the temperature was lowered. The angular variation of the spectrum for this sample is similar to that for NiATH (as given in Ref. 3).

The EPR spectra of Mn^{2+}-doped NiATH were recorded at room, liquid-nitrogen, and liquid-helium temperatures. The shape of the spectra, the absolute sign of b_2^0, and the relative sign of parameters and angular variation of resonant lines with respect to the external magnetic field were the same as those reported in Ref. 3 (all Mn^{2+} ions are magnetically equivalent.)

The spin Hamiltonian that corresponds to the monoclinic symmetry[15] is

$$\mathscr{H} = \mu_B \vec{\mathrm{H}} \cdot \vec{g} \cdot \vec{\mathrm{S}} + \sum_{m=0,2} \tfrac{1}{3} b_2^m O_2^m + \sum_{m=0,2,4} \tfrac{1}{60} b_4^m O_4^m + A S_z I_z + B(S_x I_x + S_y I_y) + Q'[I_z^2 - \tfrac{1}{3} I(I+1)] + Q''(I_x^2 - I_y^2) \ . \tag{4.1}$$

Here g, b_l^m, A, B, Q', and Q'' are the spin-Hamiltonian parameters; O_l^m are the spin operators as defined by Abragam and Bleaney,[15] μ_B the Bohr magneton, H the external magnetic field, and S and I the electron and nuclear spins, respectively, corresponding to the Mn atom ($S = I = \frac{5}{2}$).

The x, y, and z axes are so chosen that they coincide with the principal axes of the b_2^m tensor; the overall splitting of the spectra is maximum along the z axis and minimum along the y axis.[3]

The parameters were evaluated by the use of a rigorous least-squares-fitting procedure designed and adapted to the electron-nuclear spin-coupled system of Mn^{2+} by Misra[5] (see also Ref. 7). The spin-Hamiltonian parameters were determined by simultaneously fitting all clearly resolved resonant field positions for at least ten different orientations of the external magnetic field around the principal axes (z and x axes). The fitting gave the correct relative signs of the parameters; the absolute signs were determined from the intensities of lines at liquid-helium temperature.[15] The list of the parameters for ZnADH, MgATH, and NiATH at different temperatures are given in Tables I and II.

The values of these parameters for ZnADH and MgATH are significantly different from those reported previously.[1,2] The fourth-order parameters b_4^m corresponding to cubic-field symmetry, which were neglected by the previous workers,[1,2] are here found to have small but significant values. The absolute sign of b_2^0 was determined from the intensity ratios of the average intensity for the highest-field sextet to that of the lowest one for the external magnetic field orientation along the z axis. These ratios for ZnADH are ~3.7, ~3.6, ~1.5, and ~0.0 at 298, 85, 11, and 3.5 K, respectively, while for MgATH these are 0.8, 0.8, and 2.4 at 298, 85, and 2.5 K, respectively. Thus the absolute sign of b_2^0 is negative for ZnADH while it is positive for MgATH.[15] The errors of parameters were calculated by use of a statistical method.[16] The variation of the largest parameter b_2^0 which predominantly determines the zero-field splitting is shown as a function of temperature in Fig. 2.

The linewidths of Mn^{2+} in ZnADH lattice were of the order of 8 ± 1 G at room temperature for all the lines of the spectra, and showed no magnetic field dependence. As the temperature was decreased to liquid-helium temperature the linewidths increased to about 16 ± 1 G. The reason for such small linewidths is that four of the six ligands surrounding Mn^{2+} are oxygens, which, because of their zero nuclear spin, do not contribute to the dipolar interactions with a Mn^{2+} ion.

For the case of MgATH also, the linewidths were more or less isotropic for all spectra, and are about 20 ± 1 G at room temperature and 18 ± 1 G at liquid-helium temperature.

The linewidths of Mn^{2+} in the paramagnetic lattice of NiATH exhibited some differences from those in the diamag-

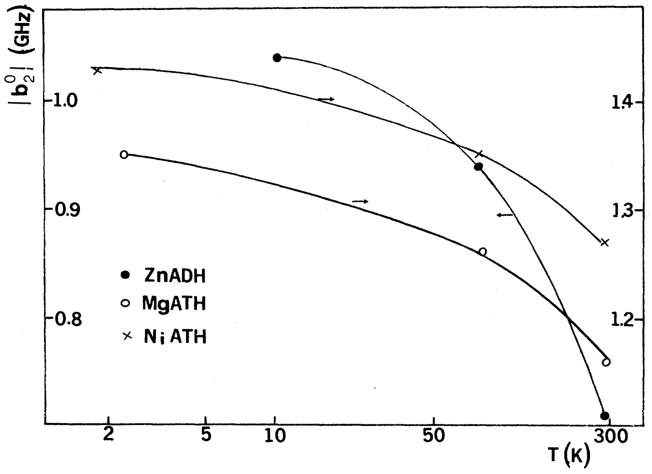

FIG. 2. Variation of zero-field splitting parameter b_2^0 for Mn^{2+}-doped ZnADH, MgATH, and NiATH hosts as a function of temperature.

netic lattices. These are (i) the anisotropy of the widths as a function of orientation of H and (ii) the magnetic field dependence of linewidths (true at all temperatures); for more details see Refs. 3 and 7. The variation of linewidths as a function of magnetic field intensity for the various host lattices is shown in Fig. 3.

V. *g* SHIFT AND Mn^{2+}-Ni^{2+} EXCHANGE CONSTANT

The shift of the g value in the paramagnetic lattice from its value in the isostructural diamagnetic crystal can be explained to be due to the exchange interaction between the Mn^{2+} ion and paramagnetic neighbor ions Ni^{2+}.[8,9] Due to the polarization effect of the Zeeman field, magnetic moments are induced on paramagnetic ions like Ni^{2+} (which have partly filled electron shells, and thus a nonmagnetic ground state). As a result of the interaction of this magnetic moment with the impurity ion (Mn^{2+}) an additional internal field manifests itself at the site of the Mn^{2+} ion, causing a shift of resonance and thus the shift of the the g value from its isolated value.

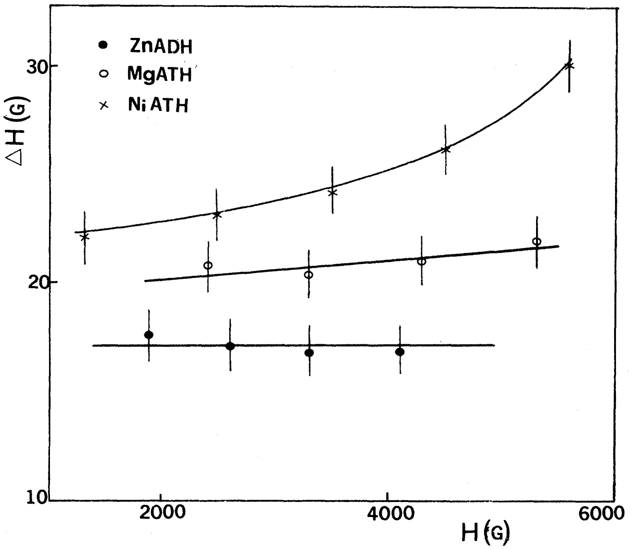

FIG. 3. Variation of linewidths as a function of magnetic field intensity at room temperature for the orientation of the external magnetic field along the z axis for ZnADH, MgATH, and NiATH hosts.

Using Eq. (2.1) and the g values in NiATH and MgATH hosts for Mn^{2+} at liquid-helium temperature, the value of 3.81 GHz for $|J|$ was found for the Mn^{2+}-Ni^{2+} exchange-interaction constant in NiATH at 1.8 K. The required values of g_1 and β_2^0 for Ni^{2+} are 2.24 and 123.15 GHz, respectively, as reported by Schriempf and Friedberg.[6]

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