Variable-temperature EPR study of an Fe^{3+}-doped diammonium indium pentachloride monohydrate single crystal

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X-band ($\sim$9.25 GHz) electron-paramagnetic-resonance (EPR) measurements have been made on a single crystal of Fe^{3+}-doped $(NH_4)_2InCl_5 \cdot H_2O$ in the temperature range 4–295 K. The values of the spin-Hamiltonian parameters (SHP) for the Fe^{3+} ion have been determined from line positions at various temperatures, using a rigorous least-squares-fitting procedure. The absolute signs of the SHP are determined fom the relative intensities of the EPR lines at 4 K. The temperature dependences of the parameters b_2^0 and b_2^2, as estimated here, have been found to be continuous, fitting well quadratic functions in temperature, in the range 4–295 K. The present accurate determination of SHP's corrects the previously reported controversy, i.e., a discontinuous behavior of the SHP b_2^0 with respect to temperature, leading incorrectly to the prediction of a kink at 240 K.

I. INTRODUCTION

Diammonium indium pentachloride monohydrate, $(NH_4)_2InCl_5 \cdot H_2O$ (hereafter DIPM), is an interesting substance for experimental studies for several reasons: (i) It provides an excellent host lattice for electron-paramagnetic-resonance (EPR) studies of the ferric (Fe^{3+}) ion because both the indium salt and the analogous iron salt are readily crystallizable from respective aqueous solutions as isomorphous compounds with known structures containing discrete molecular ions.[1] (ii) It is a salt amenable to Pound's method of nuclear alignment[2] because In nuclei possess a large nuclear electric quadrupole moment as well as a large magnetic moment, and there exist several known γ-active In isotopes. (iii) The symmetry possessed by DIPM crystal is appropriate to an experimental investigation of the effect of nuclear recoil on intermediate-state reorientation of aligned nuclei.[3] (iv) Magnetic susceptibility, heat capacity,[4] and Mössbauer spectroscopic studies[5] on DIPM indicate that this salt has some unique properties in comparison with other members of the series $A_2FeX_5 \cdot H_2O$ (A = K,Rb,Cs,NH₄ and X = Cl,Br).[6] (v) There exists a discrepancy in the interpretation of the data in a previously reported EPR study by Partiti and Rechenberg;[7] the plot of the spin-Hamiltonian parameter (SHP) b_2^0 against temperature exhibited a kink at 240 K. (This is contrary to the present measurements; see Sec. V.)

Several EPR studies of Fe^{3+}-doped DIPM have been reported in the literature. Cole and Garrett[8] reported a preliminary measurement at 295 and 77 K. The spin-Hamiltonian parameters of the Fe^{3+} ion in DIPM lattice were estimated at room temperature (RT) by the use of EPR line positions by Misra and Sharp.[9] More recently, a variable-temperature study was made by Partiti and Rechenberg[7] in the temperature range 100–295 K; they found a 15% increase in the absolute value of the SHP b_2^0 as estimated by them when the sample was cooled from RT to 100 K, assuming the value of b_2^2 to remain un-

changed over this temperature range. In particular, Partiti and Rechenberg[7] recorded spectra for the orientation of the external magnetic field (**B**) parallel to the crystal b and c axes in the range 100–295 K. They evaluated the SHP b_2^0 from EPR line positions as recorded for **B**||**b** or for **B**||**c**, but not both simultaneously, assuming without *convincing* justification that the values of the other SHP's are invariant with temperature. (It is well known that evaluation of SHP's from line positions observed for only one orientation of **B** can lead to serious inaccuracies.[10]) The resulting values of b_2^0 exhibited a kink at 240 K as a function of temperature. They interpreted this to be due to reorientation of NH_4^+ ions.[7] (It should here be pointed out that the x-ray data do not indicate the occurrence of any phase transition in DIPM around 240 K.) Further, they reported that one Fe^{3+} EPR line for **B**||**b** disappeared completely at 235 K, without realizing that this line had instead moved in its position, as the present data indicate, since they did not record angular variation of EPR line positions by varying the orientation of **B**.

To our knowledge, no EPR studies have been carried out on a Fe^{3+}-doped DIPM single crystal below 77 K. It is the purpose of this paper to report an extensive variable-temperature X-band EPR study on a Fe^{3+}-doped DIPM single crystal between liquid-helium temperature (LHT) and RT (4–295 K). The values of the spin-Hamiltonian parameters of the Fe^{3+} ion will be determined accurately at various temperatures over this temperature range by a simultaneous fitting of all the allowed EPR line positions observed for several orientations of the external Zeeman field in the magnetic ZX plane, using a least-squares-fitting procedure, evaluating the required eigenvalues and eigenvectors on a digital computer. The absolute signs of SHP's will be determined from the relative intensities of lines at 4 K. The temperature dependences of b_2^0 and b_2^2 will be exploited to fit to quadratic functions over the temperature range 4–295 K. Particular attention will be focused on the investigation of the kink in the $b_2^0 - T$ plot reported by Partiti *et al.*[7]

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II. CRYSTAL STRUCTURE AND EXPERIMENTAL DETAILS

The crystal structure of the isomorphous salts $(NH_4)_2FeCl_5 \cdot H_2O$ and $(NH_4)_2InCl_5 \cdot H_2O$ have been studied by x-ray diffraction by Lindqvist[11] and by Klug, Kummer, and Alexander.[12] It is orthorhombic bipyramidal (space group $D_{2h}^{16}\text{-}P_{nma}$). The dimensions of the unit cell for the iron salt are $a = 1.410$ nm, $b = 1.017$ nm, and $c = 0.716$ nm $(a:b:c = 1.387:1.0:0.704)$, whereas those for the indium salt are $a = 1.368$ nm, $b = 0.988$ nm, and $c = 0.702$ nm $(a:b:c = 1.385:1.0:0.710)$.[12] The lattice is constituted by NH_4^+ ions and $(MCl_5 \cdot H_2O)^{2-}$ ions, where $M = $ Fe or In, the latter forming a complex of octahedral symmetry. The octahedra are distorted due to unequal sizes of the Cl^- ion and the H_2O molecule, the latter being situated at a definite corner of the $(MCl_5 \cdot H_0O)^{2-}$ octahedron. There are four formula units per unit cell.

Single crystals of DIPM were prepared by slow evaporation of an aqueous solution of calculated amounts of ammonium chloride, indium chloride, and ferric chloride so as to have a starting ratio of one Fe^{3+} ion for every ten In^{3+} ions, noting that not all Fe^{3+} ions enter into the crystal lattice in the same ratio to In^{3+} ions as they are in the solution. The solution was made slightly acidic with hydrochloric acid in order to prevent hydrolysis. The concentration of the Fe^{3+} ions is exhibited by the degree of yellowness of the solution. A crystal of approximate size $1.5 \times 2.0 \times 2.5$ mm^3 was chosen for the present measurements.

An X-band Varian V4502 spectrometer was employed to record the EPR spectra, using a 100-kHz field modulation for RT measurements and a 200-Hz field modulation for measurements at temperatures below RT. The calibration of the magnetic field was accomplished by the use of a Bruker (B-NM20) gaussmeter. The temperature of the sample was varied by a heater resistor inside the liquid-helium cryostat. The temperatures were determined by measuring the resistances of the platinum and germanium resistors in the liquid-nitrogen (LNT) and liquid-helium (LHT) ranges, respectively.

III. EPR SPECTRA

The EPR spectra were recorded at RT for the external magnetic-field (**B**) orientation in the magnetic ZY plane; the orientation of **B** was varied at 3° intervals. By comparing the respective EPR spectra, the presence of two magnetically inequivalent, but crystallographically equivalent Fe^{3+} ions, referred to as ions I and II, was found. The magnetic X, Y, and Z axes, corresponding to a magnetically inequivalent Fe^{3+} ion, exhibiting extrema of the respective allowed lines ($\Delta M = \pm 1$; M is the electronic magnetic quantum number) positions, were chosen according to the usual convention of maximum splitting of lines for the orientation of **B** along the Z axis and the minimum splitting along the Y axis. The angular variation of the EPR line positions for various orientation of **B** revealed that the magnetic ZY planes for the two magnetically inequivalent ions I and II were coincident with the crystallographic ac plane; the Z_1 axis was found to make
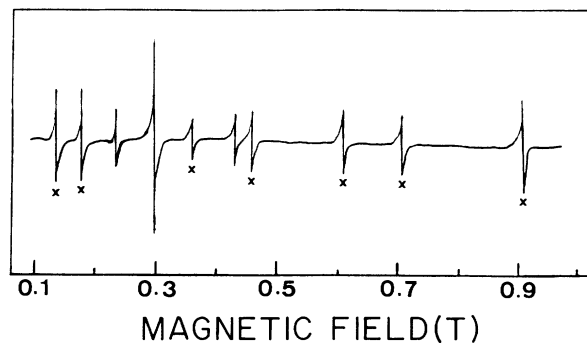

FIG. 1. First-derivative EPR spectrum of the Fe^{3+} ion in a DIPM single crystal at 295 K for $B\|Z_I$. The $\times$'s represent the allowed EPR lines belonging to Fe^{3+} ion I; the remaining lines belong to ion II.

angle of $\sim 39°$ with the a axis. The Y_{II} and Z_{II} axes were found to make angles of $\sim 10°$ with the Z_I and Y_I, respectively. The X_I and X_{II} axes were coincident with the b axis. (Here the subscripts I and II indicate the two magnetically inequivalent ions.) A typical spectrum indicating the various transitions at RT for $B\|Z_I$ is shown in Fig. 1. The intensities of the lines belonging to the two inequivalent Fe^{3+} ions for the orientations of **B** along their respective Z axes were found to be equal, implying that the two magnetically inequivalent Fe^{3+} ions substituted with equal preferences at the respective In^{3+} sites.
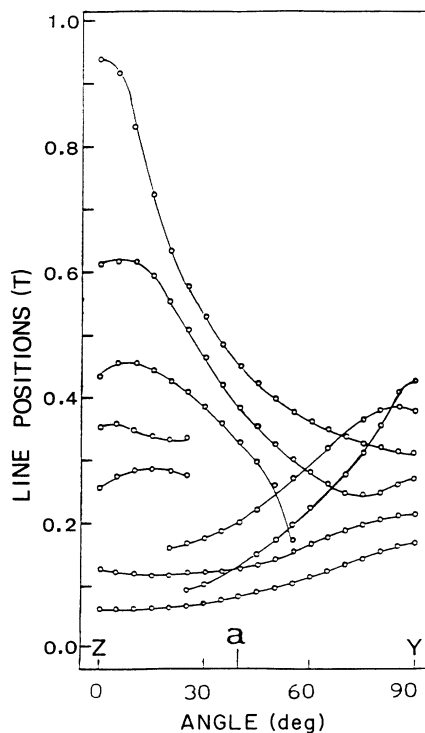

FIG. 2. The angular variation of the EPR line positions for Fe^{3+} in DIPM for the orientation of **B** in the magnetic ZY plane for ion I at 4 K. The circles represent experimental data, while the continuous lines connect the data points belonging to the same transition.

Upon lowering the temperature from 295 to 4 K and recording the EPR spectra for various orientations of **B** in the magnetic ZY plane for ion I, it was found that the general features of the EPR spectra remained the same, except that the overall splitting for any ion for **B** parallel to its magnetic Z axis increased continuously with lowering temperature; as well, some lines moved in their positions. This indicated a monotonic increase in the absolute value of the zero-field splitting parameter, b_2^0, implying in turn that the crystal did not undergo any structural phase transition over the temperature range 4–295 K. The angular variation of the EPR line positions at 4 K for Fe^{3+} ion I for the orientation of **B** in the magnetic ZY plane in DIPM is displayed in Fig. 2.

IV. SPIN HAMILTONIAN AND EVALUATION OF PARAMETERS

A spin Hamiltonian appropriate to orthorhombic symmetry was chosen to fit the EPR line positions of Fe^{3+} in DIPM:[13,14]

$$\mathcal{H} = \mu_B(g_{zz}B_zS_z + g_{xx}B_xS_x + g_{yy}B_yS_y)$$
$$+ \tfrac{1}{3}(b_2^0O_2^0 + b_2^2O_2^2)$$
$$+ \tfrac{1}{60}(b_4^0O_4^0 + b_4^2O_4^2 + b_4^4O_4^4) \ . \tag{4.1}$$

In Eq. (4.1) μ_B is the Bohr magneton, S ($=\tfrac{5}{2}$) is the electron spin of the Fe^{3+} ion, g_{zz}, g_{xx}, and g_{yy} are the spectroscopic splitting factors, the b_l^m are the fine-structure spin-Hamiltonian parameters (SHP's), and the O_l^m are the spin operators as defined by Abragam and Bleaney.[13]

The SHP's for the Fe^{3+} ion in a DIPM host crystal were evaluated at various temperatures in the range 4–295 K, by the use of a least-squares-fitting (LSF) procedure,[15] fitting simultaneously all EPR line positions recorded for the orientations of **B** in the magnetic ZY

plane, and employing numerical diagonalizations of the Fe^{3+} 6×6 spin-Hamiltonian matrix on a digital computer. The errors in the evaluation of SHP's were determined by the use of a statistical method.[16] The resulting SHP values for Fe^{3+} ion I in DIPM at 4, 20, 77, and 295 K are listed in Table I. The values of the SHP's evaluated for Fe^{3+} ion II are expected to be the same as that for Fe^{3+} ion I, within the experimental error, because of the physical equivalence of the two ions, the only difference being in the orientations of the principal axes of the various tensors.

The absolute signs of the parameters were determined from the relative intensities of the lines at LHT. In the spectrum for **B**$\|Z_I$, as the temperature was lowered to LHT, the intensity of the highest-field line decreased relative to that of the lowest-field line. This indicated that the absolute sign of b_2^0 was negative in the present case.[13] The signs of the other fine-structure parameters (b_l^m), relative to that of b_2^0, as yielded by the LSF procedure, are correct.

V. TEMPERATURE DEPENDENCE OF THE SPIN-HAMILTONIAN PARAMETERS

The values of SHP's for Fe^{3+} in DIPM have been presently estimated at every 10-K interval in the temperature range 4–295 K. From these values, it is seen that there are increases of 14%, 2%, and 18%, respectively, in the absolute values of b_2^0, b_2^2, and b_4^0, upon cooling the sample from 295 to 4 K; on the other hand, there are decreases of 9% and 3%, respectively, in the values of b_4^2 and b_4^4. The b_2^0 and b_2^2 dependences on temperature are exhibited in Fig. 3.

It is found that the temperature dependences of both b_2^0 and b_2^2 fit reasonably well, in the temperature range 4–295 K, to the quadratic function, $a + bT + cT^2$, with the coefficients a, b, and c being equal to 5.192 GHz,

TABLE I. The spin-Hamiltonian parameters (SHP's) for Fe^{3+} ion I in a DIPM host at various temperatures. (Because of the physical equivalence of ions I and II, the same values of SHP's are expected for ion II.) The units of b_l^m are GHz, while the g values are dimensionless. Here χ^2 $(GHz^2) \equiv \sum_i(\Delta E_1 - h\nu_i)^2$, where ΔE_1 and $h\nu_i$ are, respectively, the experimental and calculated energy differences between the energy levels participating in resonance, the index i covers all the resonant line positions used simultaneously in the least-squares fitting as recorded for the orientations of **B** in the magnetic ZY plane; h and ν_i are, respectively, the Planck's constant and klystron frequency for the ith line. n is the number of the resonant lines fitted simultaneously. The parameter errors are estimated by the use of a statistical method (Ref. 16). The sign of b_2^0 has been determined to be negative from the intensity ratio between the high- and low-field lines at LHT; it is taken into account that the relative signs of all b_l^m, as yielded by the LSF procedure, are correct.

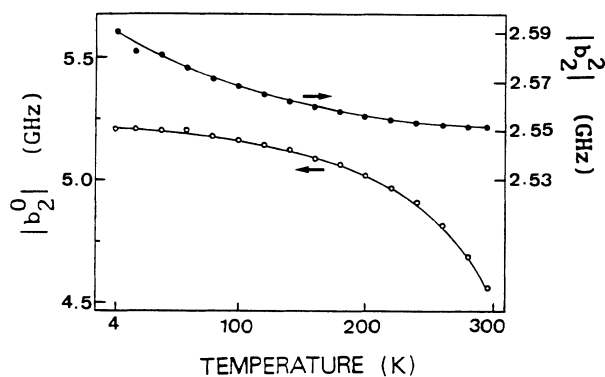| Parameters	295 K	77 K	20 K	4 K
g_{zz}	2.012 ± 0.004	2.017 ± 0.003	2.019 ± 0.002	2.020 ± 0.004
g_{yy}	2.015 ± 0.005	2.019 ± 0.002	2.020 ± 0.003	2.021 ± 0.003
b_2^0	-4.563 ± 0.003	-5.182 ± 0.002	-5.201 ± 0.003	-5.205 ± 0.002
b_2^2	2.551 ± 0.002	2.576 ± 0.004	2.587 ± 0.005	2.590 ± 0.003
b_4^0	0.032 ± 0.005	0.039 ± 0.002	0.037 ± 0.003	0.038 ± 0.002
b_4^2	0.021 ± 0.002	0.014 ± 0.003	0.018 ± 0.005	0.019 ± 0.001
b_4^4	0.217 ± 0.003	0.208 ± 0.005	0.213 ± 0.002	0.211 ± 0.002
n	102	96	96	96
χ^2	0.35	0.41	0.56	0.36

FIG. 3. Variation of the spin-Hamiltonian parameters b_2^0 and b_2^2 as functions of temperature for Fe^{3+} in the DIPM crystal. The open and solid circles represent the absolute values of b_2^0 and b_2^2, respectively. The continuous lines represent the least-squares fit to the respective quadratic functions in temperature.

6.023×10^{-4} GHz/K, and -8.659×10^{-6} GHz/K^2, respectively, for b_2^0, while they are equal to 2.591 GHz, -1.915×10^{-4} GHz/K and 1.699×10^{-7} GHz/K^2, respectively, for b_2^2. Similar quadratic temperature dependences of b_l^m have also been reported for Gd^{3+}-doped $LaAlO_3$ (Ref. 17) and $LiYF_4$ (Ref. 18). In order to explain these dependences, it is noted that early theoretical approaches[19,20] yield an expression for b_2^0 in the form

$$b_2^0 = C_1 A_2^0 + C_2 (A_2^0)^2 , \qquad (5.1)$$

where the A_l^m are the crystal-field parameters,[21] and the coefficients C_1, C_2 depend on a number of mechanisms; in particular, the spin-orbit coupling and the spin-spin interaction. However, C_1 and C_2 are not significantly dependent upon temperature.[17] Thus, the temperature dependence of b_l^m is mainly due to those of A_l^m. Finally, for the quadratic temperature dependence of b_l^m, it is necessary that the A_l^m be predominantly linear in temperature in the range 4–295 K.

It should be noted that Partiti and Rechenberg[7] reported a discontinuous behavior of the value of b_2^0 against temperature in range of 295–100 K, leading to the occurrence of a kink at 240 K. This misleading result is obviously due to their incorrect estimation of b_2^0. This happened because b_2^0 was estimated by them from the EPR line positions recorded either for $B\|b$, or for $B\|c$, rather than from a simultaneous fitting of a large number of line positions obtained for several different orientations of B. (They only stated that the SHP's evaluated from the line positions for $B\|b$ were the same as those evaluated from line positions for $B\|c$.) Further, the value of b_2^0 was evaluated by them with the *unjustifiable* assumption that all other SHP's are temperature independent.

VI. CONCLUDING REMARKS

From the angular variation and temperature dependence of the EPR spectra, the values of the spin-Hamiltonian parameters (SHP's) have been determined at various temperatures, using a least-squares-fitting procedure, fitting simultaneously a large number of line positions recorded for several orientations of the external magnetic field. The absolute sign of b_2^0 has been determined to be negative from the relative intensities of lines at 4 K. The temperature dependences of b_2^0 and b_2^2 are found to be continuous, and to fit to the quadratic functions of temperature in the range 4–295 K. This continuous behavior is in contradiction to the previously reported discontinuous behavior deduced by Partiti and Rechenberg,[7] who reported a kink in b_2^0 versus temperature plot at 240 K because of an incorrect evaluation of the parameter b_2^0.

[1]H. P. Klug, D. Kummer, and L. Alexander, J. Am. Chem. Soc. 70, 3064 (1948).

[2]J. M. Daniels, *Oriented Nuclei, Polarized Targets, and Beams* (Academic, New York, 1965).

[3]S. K. Misra, Phys. Rev. B 1, 63 (1970).

[4]J. N. McElearney and S. Merchant, Inorg. Chem. 17, 1207 (1978).

[5]C. S. M. Partiti, H. R. Rechenberg, and J. P. Sanchez, J. Phys. C 21, 5828 (1988).

[6]R. Carlin and F. Palacio, Coord. Chem. Rev. 65, 141 (1985).

[7]C. S. M. Partiti and H. R. Rechenberg, J. Phys. Chem. Solids 50, 1023 (1989).

[8]G. M. Cole and B. B. Garrett, Inorg. Chem. 13, 2680 (1974).

[9]S. K. Misra and G. R. Sharp, J. Chem. Phys. 66, 4172 (1977).

[10]S. K. Misra and G. R. Sharp, J. Mag. Reson. 23, 191 (1976).

[11]I. Lindqvist, Ark. Kemi Mineral. Geol. 29, 1 (1946).

[12]H. P. Klug, E. Kummer, and L. Alexander, J. Am. Chem. Soc. 70, 3064 (1948).

[13]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[14]S. K. Misra and C. Rudowicz, Phys. Status Solidi B 147, 677 (1988).

[15]S. K. Misra, J. Mag. Reson. 23, 403 (1976).

[16]S. K. Misra and S. Subramanian, J. Phys. 15, 7199 (1982).

[17]W. Low and A. Zusman, Phys. Rev. 130, 144 (1963).

[18]L. E. Misiak, S. K. Misra, and P. Mikolajczak, Phys. Rev. B 38, 8673 (1988).

[19]M. H. L. Pryce, Phys. Rev. 80, 1107 (1950).

[20]H. Watanabe, Prog. Theor. Phys. (Kyoto) 18, 405 (1957).

[21]M. T. Hutchings, Solid State Phys. 16, 227 (1964).