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Electron-nuclear double resonance of Fe^{3+} in guanidinium aluminum sulfate hexahydrate

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Electron-nuclear double resonance (ENDOR) measurements of the S-state ion $^{57}Fe^{3+}$ have been performed in guanidinium aluminum sulfate hexahydrate $[C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O]$ single crystal at liquid-helium temperature. ENDOR frequencies for the two Fe^{3+} sites in the unit cell were measured for various orientations of the external magnetic field. All the frequencies observed for each site were simultaneously fitted in a rigorous least-squares fitting procedure to evaluate the hyperfine parameters A, B, $U_{\|}$, $U_{\perp}$, and g_n for $^{57}Fe^{3+}$. It is found that these parameters, as evaluated from the data for the two sites, agree within experimental errors. Further, the ratio of $|(A-B)/A|$ to $eqQ/\hbar$ (as found by Mössbauer spectroscopy for the first excited state of ^{57}Fe) in $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ is in agreement with those found for the hosts rutile (TiO_2) and octaethylhemin. This supports the analysis of Schlaak [Ber. Bunsenges. Phys. Chem. **79**, 1016 (1975)] predicting a linear dependence of $|(A-B)/A|$ on Q' $(=\frac{1}{2}eqQ/\hbar)$, the coefficient of the term $[I_z^2-I(I+1)/3]$ in the spin Hamiltonian.

I. INTRODUCTION

The purpose of this paper is to describe electron-nuclear double resonance (ENDOR) studies on a $^{57}Fe^{3+}$-doped single crystal of guanidinium aluminum sulfate hexahydrate $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ (GASH) in order to obtain accurate values of the $^{57}Fe^{3+}$ hyperfine parameters in GASH. The electron paramagnetic resonance (EPR) spectra of ^{57}Fe-enriched samples can sometimes also exhibit resolved hyperfine structure, e.g., in hydrated double nitrate crystals,[1] α-quartz,[2] foresterite (Mg_2SiO_4),[3] CaO and MgO,[4] and rutile (TiO_2).[5] On the other hand, the values of the hyperfine parameters using the ENDOR technique are not only improved by two significant figures over the ordinary EPR method,[6] the ENDOR technique also enables one to determine additional hyperfine parameters of smaller magnitude, e.g., $U_{\|}$, $U_{\perp}$, and g_n.

Relatively few ENDOR measurements have been reported to date on $^{57}Fe^{3+}$-doped single crystals. These are, for example, those performed in the host lattices of Si,[7] CaO,[8] MgO,[9] SnO,[10] and RbAl and RbGa sulfate alums.[6] The crystalline electric field at the Fe^{3+} site in MgO and CaO is of octahedral symmetry, while in SnO it is strongly rhombic. On the other hand, it is of trigonal symmetry in RbAl and RbGa sulfate alums, as well as in GASH. However, in GASH the trigonal distortion is much larger than that in sulfate alums.[6]

Another motivation for this study has been provided by the linear relationship that exists between $|(A-B)/A|$ and $eqQ/\hbar$, as discussed by Schlaak.[11] For ^{57}Fe the former quantity can be determined from ENDOR measurements (the ground-state nuclear spin is $\frac{1}{2}$), while the latter from Mössbauer measurements on the first excited state of ^{57}Fe (nuclear spin is $\frac{3}{2}$). Such Mössbauer studies have already been reported, e.g., by Nicholson and Burns[12] in $BaTiO_3$, $Y_3Ga(CaO_4)_3$, TiO_2, Al_2O_3, GASH, ZnO, $AlCl_3 \cdot 6H_2O$, and beryl $[Be_3Al_2(SiO_3)_6]$. It would then be interesting to see if this proposed linearity is indeed verified by comparing the ENDOR and Mössbauer results on the same host lattice for $^{57}Fe^{3+}$.

II. CRYSTAL STRUCTURE AND SAMPLE PREPARATION

GASH is a trigonal crystal with space group C_{3v}-$P31m$, with three molecules per unit cell.[13] The Al^{3+} ions, which are substituted by Fe^{3+} ions, lie on threefold axes, and are surrounded by slightly distorted octahedra constituted by the water molecules. The guanidinium ions lie above and below the octahedra, and are loosely bound.[14] Two of the Al^{3+} ions in the unit cell are equivalent, and are said to belong to site II; the third Al^{3+} ion belongs to site I. The unit-cell parameters are $a = 11.745$ Å and $c = 8.592$ Å.[15]

The crystals were grown by slow evaporation of an aqueous solution containing calculated stoichiometric amounts of guanidinium sulfate $[HNC(NH_2)_2]_2 \cdot H_2SO_4$, aluminum sulfate $[Al_2(SO_4)_3]$, and ferric sulfate $[Fe_2(SO_4)_3]$. $Fe_2(SO_4)_3$ was prepared by dissolving ^{57}Fe metal (enriched to 90%) in a sufficient amount of dilute sulfuric acid and then adding hydrogen peroxide to convert all ferrous (Fe^{2+}) ions to ferric (Fe^{3+}) ions. The solution was made slightly acidic with sulfuric acid to prevent hydrolysis of the ferric ion. The amount of $Fe_2(SO_4)_3$ used was such that there was one Fe^{3+} ion for every ten Al^{3+} ions in the solution. However, in the crystals only one-tenth of this amount enters.[16] At first, small platelets formed on the surface of the solution, later they sank to the bottom; these were then allowed to grow in place. The crystals grew as hexagonal plates with normals parallel to the *c* axis.

III. EXPERIMENTAL ARRANGEMENT AND DETAILS OF MEASUREMENT

The ENDOR measurements were carried out at 4.2 K on a conventional superheterodyne *X*-band spectrometer (at about 9.5 GHz). The ENDOR signal was detected by frequency modulating the radio-frequency (rf) waves, switching off the magnetic field modulation at the same time. The crystal was placed inside a rectangular TE_{101} cavity such that the microwave magnetic field is vertical at the sample, while the static magnetic field could be rotated in the horizontal plane. The sample could be rotated about a horizontal axis. For the present measurements the rf was varied up to 100 MHz. This was accomplished as follows. The rf was produced by a Hewlett-Packard 8601A sweep generator covering the range 0.1—110 MHz. The rf could be power amplified either by a rf communication amplifier, type RF805, in the range 50 KHz—80 MHz, up to a maximum of 10 W, or by an ENI amplifier, type 403L, in the range 150 KHz—250 MHz, up to a maximum of 3 W. The single-loop coil carrying the rf waves was placed inside the cavity and it was a part of the inner conductor of the 50-Ω coaxial supply cable to match the output impedance of the power amplifier.

For ENDOR measurements several EPR lines (below or about 5 kG) corresponding to the sites I and II at angles $-1°$, $1.2°$, $24°$, $89°$, and $91.2°$ from the *c* axis in the ac plane were saturated. It should be noted that as the amount of $^{57}\mathrm{Fe}$ was rather high (about 1%) in the GASH sample used, it was possible to observe some ENDOR lines corresponding to the "other" site when an EPR line corresponding to a particular site was saturated. This is due to mutual spin interactions between $^{57}\mathrm{Fe}$ ions belonging to different sites. The intensities of ENDOR lines corresponding to the other site were, of course, smaller. Usually, if an EPR line $M \leftrightarrow (M-1)$ is saturated, nuclear transitions $m,M' \leftrightarrow (m-1),M'$ with $M'=M$, and $M-1$ are observed. (M and m are the electronic and nuclear quantum numbers, respectively.) In the present case, additional ENDOR transitions with $M' \neq M$ or $M-1$ are observed. This is fortuitous, since this way it was possible to observe those ENDOR transitions for which the M' correspond to EPR lines that occur above 5 kG. (Other researchers have also observed this favorable phenomenon, e.g., Schrama *et al.*[17] However, in the present case the phenomenon seems to be even more pronounced.) The present data corresponding to each site could be reasonably well fitted, with the exception of very few "spurious" lines, to appropriate hyperfine parameters.

IV. SPIN HAMILTONIAN

The spin Hamiltonian for the electron-nuclear spin-coupled system of $^{57}\mathrm{Fe}^{3+}$ in the C_{3v} point-group symmetry of GASH for either site (I or II) can be expressed as

$$\mathscr{H}=\mathscr{H}_f+\mathscr{H}_{\mathrm{hf}}\,, \tag{4.1}$$

where[16]

$$\mathscr{H}_f=g_{\parallel}\mu_B H_z S_z+g_{\perp}\mu_B(H_x S_x+H_y S_y) +B_2^0 O_2^0+B_4^0 O_4^0+B_4^3 O_4^3+B_4^{-3} O_4^{-3} \tag{4.2}$$

and

$$\mathscr{H}_{\mathrm{hf}}= A_0^0 T_0^0(\vec{\mathrm{S}},\vec{\mathrm{I}}\,)+A_2^0 T_2^0(\vec{\mathrm{S}},\vec{\mathrm{I}}\,)+U_{\parallel}T_{\parallel}(\vec{\mathrm{S}},\vec{\mathrm{I}}\,) +U_{\perp}T_{\perp}(\vec{\mathrm{S}},\vec{\mathrm{I}}\,)-g_n\beta_n\vec{\mathrm{H}}\cdot\vec{\mathrm{I}}\ . \tag{4.3}$$

In Eq. (4.1), $\mathscr{H}_f$ represents the fine-structure part of the spin Hamiltonian $\mathscr{H}$, while $\mathscr{H}_{\mathrm{hf}}$ represents the hyperfine part of $\mathscr{H}$. In (4.2), $g_{\parallel}$ and $g_{\perp}$ are the *g* factors for Fe^{3+}, parallel and perpendicular to the *c* axis of the crystal (coincident with the *z* axis), $\vec{\mathrm{H}}$ is the external magnetic field, $S(=\frac{5}{2})$ is the electronic spin, and O_l^m are the spin operators as defined by Abragam and Bleaney.[18] x,y,z are the axes along which the overall splitting of the $\Delta M=\pm 1$ fine-structure lines (M is the electronic quantum number) exhibits maxima, the splitting being maximum along z. The (fine-structure) EPR spectrum is axially symmetric.[16] For further details of the EPR spectrum of Fe^{3+} in GASH at *X* band, see Ref. 16, which also lists the values of the parameters $g_{\parallel}$, $g_{\perp}$, B_2^0, B_4^0, B_4^3, and B_4^{-3} for the two sites.

In Eq. (4.3) the electron-nuclear spin operators $T(\vec{\mathrm{S}},\vec{\mathrm{I}}\,)$ are defined as follows:

$$\begin{aligned}
T_0^0(\vec{\mathrm{S}},\vec{\mathrm{I}}\,)&=S_1^0 I_1^0-S_1^1 I_1^{-1}-S_1^{-1}I_1^1\\
&=\vec{\mathrm{S}}\cdot\vec{\mathrm{I}}=S_z I_z+S_x I_x+S_y I_y\ ,\\
T_2^0(\vec{\mathrm{S}},\vec{\mathrm{I}}\,)&=2S_1^0 I_1^0+S_1^1 I_1^{-1}+S_1^{-1}I_1^1\\
&=2S_z I_z-S_x I_x-S_y I_y\ ,\\
T_{\parallel}(\vec{\mathrm{S}},\vec{\mathrm{I}}\,)&=S_3^0 I_1^0=5S_z^3 I_z-3S(S+1)S_z I_z+S_z I_z\ ,\\
T_{\perp}(\vec{\mathrm{S}},\vec{\mathrm{I}}\,)&=S_3^1 I_1^{-1}+S_3^{-1}I_1^1\\
&=-\frac{\sqrt{6}}{4}S_+[5S_z^2+5S_z+2-S(S+1)]I_-\\
&\quad-\frac{\sqrt{6}}{4}S_-[5S_z^2-5S_z+2-S(S+1)]I_+\ .
\end{aligned} \tag{4.4}$$

In Eqs. (4.4), $I(=\frac{1}{2})$ is the nuclear spin, S_l^m and I_l^m are functions of (S_x,S_y,S_z) and (I_x,I_y,I_z), respectively, and each transforms as the spherical harmonic Y_l^m under rotations. The matrix elements of S_l^m or I_l^m, can be calculated according to the prescriptions of Edmonds[19] as follows:

$$\langle S,M\,|\,S_l^m\,|\,S,M'\rangle=(-1)^{S-M}\langle S||S_l||S\rangle\begin{bmatrix} S & l & S\\ -M & m & M'\end{bmatrix},$$

and a similar expression for I_l^m. Finally, $S_{\pm}=(S_x\pm iS_y)$ and $I_{\pm}=(I_x\pm iI_y)$. The operators T_0^0 and T_2^0 together are equivalent to operator terms $S_z I_z$ and $(S_x I_x+S_y I_y)$, while $T_{\parallel}$ and $T_{\perp}$ are consistent with the terms of the type $S^3 I$ appropriate to trigonal symmetry.[6,20]

V. EVALUATION OF PARAMETERS

As far as the EPR measurements are concerned, a thorough study at X band on a single crystal of Fe^{3+}-doped GASH from room temperature down to liquid-helium temperature has already been reported by Misra and Sharp.[16] The fine-structure parameters were evaluated by the use of a rigorous least-squares-fitting (LSF) method,[21] fitting simultaneously all resonant line positions obtained for several orientations of the external magnetic field in the ac plane.

As far as the evaluation of the hyperfine parameters from the present ENDOR data is concerned, an extension of the LSF technique for purely electronic systems, as given in Ref. 21, was used so as to take into account the electron-nuclear spin-coupled system of the $^{57}Fe^{3+}$ ion. The details of this extension are well described by Misra.[22] Briefly, in this method, all ENDOR frequencies obtained for several orientations of the external magnetic field are simultaneously fitted in an LSF procedure. The differences of the energy levels participating in resonance, as computed using a set of hyperfine parameters for the particular iteration, are compared with the corresponding ENDOR frequencies, starting with an initially chosen set of hyperfine parameters. (The fine-structure parameters used are those already determined by EPR, i.e., those reported in Ref. 16.) The "χ^2" value, which depends upon the squares of the differences between the calculated energy-level separations and corresponding ENDOR frequencies, appropriately weighted, is minimized iteratively by modifying the vector, constituted by the hyperfine parameters as its components. The required derivatives of the χ^2 depend upon the eigenvalues and eigenvectors of the spin-Hamiltonian matrix, which are evaluated on a computer using numerical techniques. The errors of the parameters, corresponding to the minimum of the χ^2 value, are estimated using a statistical method;[23] specifically, these are the diagonal matrix elements of the inverse of one-half the matrix, whose elements are the second derivatives of χ^2 with respect to the parameters.

The hyperfine parameters A_0^0, A_2^0, $U_{||}$, $U_{\perp}$, and g_n were evaluated from separate simultaneous fittings of all observed ENDOR frequencies for the two sites corresponding to saturation of their respective EPR lines. The resulting values are listed in Table I, which also lists the more commonly known parameters A and B (which depend on A_0^0 and A_2^0).

TABLE I. Fine-structure parameters (in MHz, except for g_n which is dimensionless) as estimated from ENDOR data for $^{57}Fe^{3+}$ in GASH for the two sites occupied by $^{57}Fe^{3+}$.

Parameters	Site I	Site II
A_0^0	-31.7701 ± 0.0767	-31.6073 ± 0.1216
A_2^0	-0.3488 ± 0.0383	-0.4273 ± 0.0618
$(A)^a$	-32.4677	-32.4619
$(B)^b$	-31.4213	-31.1800
$U_{\|\|}$	0.0112 ± 0.0032	0.0120 ± 0.0032
$U_{\perp}$	-0.0651 ± 0.0134	-0.0880 ± 0.0219
g_n	-0.0994 ± 0.0092	-0.0961 ± 0.0092

[a] $A=A_0^0+2A_2^0$.

[b] $B=A_0^0-A_2^0$.

VI. DISCUSSION OF RESULTS

It is clearly seen from Table I that the values of the parameters A_0^0, A_2^0, $U_{||}$, $U_{\perp}$, and g_n as determined from the data for the two sites agree within experimental errors. Furthermore, the g_n values are also in agreement, within their experimental errors, with the value 0.090 604 ±0.000 009 as reported by Schwenk from nuclear magnetic resonance measurements.[24]

The value of $eqQ/\hbar$ for GASH, as determined by Nicholson and Burns[12] from Mössbauer data for the first excited state of ^{57}Fe, is 14±3 MHz. Thus, the ratios $|(A-B)/A|/eqQ/\hbar$ for GASH are 0.0023 and 0.0028 MHz^{-1} for sites I and II, respectively, as calculated using the values of A and B from Table I. There are only two hosts for which the experimental values of A, B, and $eqQ/\hbar$ (obtained by Mössbauer spectroscopy in the same way as that for the present case) are available. The only ones for which they are available are octaethylhemin and rutile (TiO_2). These are, for TiO_2,[5,12] $A_x=-28.8$ MHz, $A_y=-27.6$ MHz, $A_z=-28.2$ MHz, and $eqQ/\hbar=6.9$ MHz; and for octaethylhemin,[25] $A=16.24$ MHz, $B=15.08$ MHz, and $eqQ/\hbar=21.58$ MHz. Using these values it is found that the ratio $|(A-B)/A|/eqQ/\hbar$ is 0.0030 and 0.0033 for TiO_2 and octaethylhemin hosts, respectively, which is in agreement, within experimental error, to that found for GASH. This lends support to the linear relationship between $|(A-B)/A|$ and $eqQ/\hbar$ as discussed by Schlaak.[11]

VII. CONCLUDING REMARKS

More ENDOR measurements on $^{57}Fe^{3+}$ in various hosts should be performed. This would further test the linearity between $|(A-B)/A|$ and $eqQ/\hbar$ proposed by Schlaak,[11] although this is confirmed by the three hosts considered in Sec. VI. Moreover, it would help in classifying the spin-Hamiltonian parameters. As mentioned by Brisson and Manoogian[6] the attempts of Nicholson and Burns[12] to classify some Fe^{3+}-doped crystals on the basis of b_2^0 values (determined by EPR) and quadrupole splitting $eqQ/\hbar$ (determined by Mössbauer spectroscopy) were only partially successful as the signs of the parameters were not known in many cases.

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