It may be noted that for N_2^+ and H_2^+, Propst and Luscher observe no ejected electrons with energies beyond the limit predicted for ground-state ions, in agreement with our conclusion that these beams are in the ground state. No data of this nature for NO^+ or N^+ are available.

SUMMARY

The Auger electron yields for electronically excited ions have been shown to be larger than the yields for the corresponding ground-state ions for NO^+ and O_2^+. This effect must be taken into account when the electron yields for these ions are measured, and when the measured yields are used in calculations of the properties of aggregate phenomena, such as gas discharges. It would also appear that excited-state effects must be accounted for in the application of particle multipliers as current amplifiers. More generally, measurement of the Auger electron yield from a metal surface bombarded by positive ions provides a convenient means of detecting long-lived electronically excited ions in the ion beam. The Auger emission acts as an ionization potential (or E_R) detector which is only incidentally sensitive to ion mass and velocity. This method, while incapable of providing quantitative information concerning the numbers of excited ions present allows considerable information to be gained regarding the states involved.

PHYSICAL REVIEW VOLUME 169, NUMBER 2 10 MAY 1968

Nuclear Electric-Field-Gradient Determination in Single Crystals of $Fe(NH_4SO_4)_2 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$†

Kailash Chandra and S. P. Puri
Department of Physics, University of Roorkee, Roorkee, India

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Single-crystal Mössbauer studies have been carried out on $Fe(NH_4SO_4)_2 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ to determine the five independent parameters of the nuclear electric-field-gradient (EFG) tensor, viz., its principal values, asymmetry parameter, and coupling constant, and the direction cosines of the EFG axes with respect to the crystal axes. Furthermore, in view of the agreement of the observed and calculated values of the absorption-peak-area ratios, the anisotropy of the Lamb-Mössbauer fraction for both these cases does not appear to be significant. It is concluded that in the case of $Fe(NH_4SO_4)_2 \cdot 6H_2O$, the principal axes of the EFG tensor are not coincident with those of the susceptibility tensor.

1. INTRODUCTION

The Mössbauer effect in Fe^{57} has been extensively used to study a wide variety of ionic ferrous compounds.[1] When an iron atom is present in a crystalline field of symmetry lower than cubic, the 14.4-keV first excited state of Fe^{57} generally splits into two levels, giving a quadrupole-split two-line absorption spectrum. These lines are of equal intensity only for a randomly oriented polycrystalline sample, provided the anisotropy in the Lamb-Mössbauer recoilless factor is not significant. The electric field gradient (EFG), represented as a traceless, symmetric tensor of second rank,[2] depends upon the electronic state of the atom. The sign of the quadrupole coupling constant as well as the ground-state orbital wave function can be inferred from the single-crystal absorption spectra by analyzing the line intensities as a function of orientation[3]; and from the absorption spectra obtained with a polarized source[4] and magnetic perturbation technique.[5] Furthermore, from the Zeeman-split spectrum, the sign of e^2qQ has been determined in a few cases.[6]

The purpose here is to report the determination of all five parameters of the EFG tensor for the first excited state of Fe^{57} in single crystals of $Fe(NH_4SO_4)_2 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$. The method employed was first suggested and utilized by Zory.[7] It is based on the fact that the emission and absorption probabilities of both hyperfine components are dependent upon the γ-ray direction with respect to the EFG axes.[8]

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† Supported by the Council of Scientific and Industrial Research, New Delhi, India.

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2. CRYSTAL STRUCTURES

$Fe(NH_4SO_4)_2 \cdot 6H_2O$ is a monoclinic crystal, space group $P2_{1/a}$, with unit-cell dimensions $a=9.28$, $b=12.58$, and $c=6.22$ Å, and $\beta=106°\ 50'$.[9] A unit cell contains two equivalent Fe^{++} ions at (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0); these ions are in a spin-free state and are surrounded by a distorted octahedron formed from six water molecules. These octahedra get transformed into each other by a rotation of 180° about the **b** axis, disregarding the translation, for it is the orientation of the sites relative to the crystal axes which is important. The projection diagram along [010] for $Mg(NH_4SO_4)_2 \cdot 6H_2O$ which is isomorphous to the Fe compound, is shown in Fig. 1.

The crystal structure of $FeSO_4 \cdot 7H_2O$ has been investigated by Baur[10]; its projection diagram along [010] is given in Fig. 2. It crystallizes in monoclinic crystals, space group $P2_{1/c}$, with unit-cell dimensions $a=14.07$, $b=6.503$, and $c=11.041$ Å, $\beta=105°\ 34'$. There are four molecules per unit cell, with Fe^{++} ions at (a) $(0,0,0)$, $(0,\frac{1}{2},\frac{1}{2})$ and (d) $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$, forming a face-centered arrangement. Positions (a) and (d) have the point symmetry $\bar{1}$, as have the other two special positions (b) and (c).

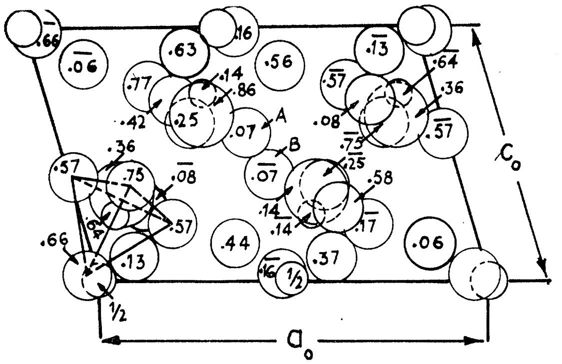

FIG. 1. Projection of the monoclinic structure of

$Mg(NH_4SO_4)_2 \cdot 6H_2O$

on its *b* face. Oxygen atoms of the sulfate ions near the origin are connected by light lines. The NH_4^+ ions are shown as the largest circles, the magnesium atoms by circles slightly larger than the (smallest) sulfur circles. Water molecules are the heavily ringed circles.

3. EXPERIMENTAL

Single crystals of these compounds were grown from solution by recrystallization for the second or even the third time. The preliminary selection was done by examination under a polarizing microscope and later by x rays. A thin coating of liquid paraffin was used so as to avoid oxidation by the atmosphere. The crystal axes were identified from the habits[11] and confirmed by the optical data. Orientation was done on a goniometer head. The large crystals were ground down to $0.5 \times 0.5 \times 0.04$ cm^3 size.

A constant-velocity mechanical device employing a motor-driven cam was used to take the Mössbauer spectra. The source was a standard Co^{57} in copper matrix with an initial activity of 1 mCi.

TABLE I. Single-crystal absorption-peak-area ratios for different orientations. Principal values of EFG, assuming $Q=+0.30$ b. For $Fe(NH_4SO_4)_2 \cdot 6H_2O$ (in units of 10^{17} V/cm^2), $V_{xx}=-0.8$, $V_{yy}=-4.53$, $V_{zz}=5.33$; for $FeSO_4 \cdot 7H_2O$, $V_{xx}=-4.5$, $V_{yy}=-5.5$, $V_{zz}=10.0$.

			$Fe(NH_4SO_4)_2 \cdot 6H_2O$		$FeSO_4 \cdot 7H_2O$	
	Θ	Φ	Expt (300°K)	Calc (a_3/b_1)	Expt (300°K)	Calc[a] (a_3/b_1)
(1)	0	0	0.98	1.00	0.74	0.72
(2)	$\frac{1}{2}\pi$	0	1.15	1.15	1.00	0.92
(3)	$\frac{1}{2}\pi$	$\frac{1}{4}\pi$	2.10	2.16	1.80	1.82
(4)	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0.91	0.88	1.60	1.57
(5)	$\frac{1}{2}\pi$	$-\frac{1}{4}\pi$	0.54	0.47	0.78	0.78
(6)	$\frac{1}{4}\pi$	$\frac{1}{2}\pi$	0.90	0.94[a]	0.83	1.04
(7)	$\frac{1}{4}\pi$	0	1.10	1.07[a]	0.88	0.80
(8)	Powder		0.96	1.00[a]	0.97	1.00

[a] Calculated assuming the isotropy of the recoilless factor.

4. METHOD OF ANALYSIS

The presence of an electric field gradient leads to a splitting of the 14.4-keV state into two levels. The separation between the two absorption peaks is

$$\Delta E_Q = \tfrac{1}{2}e^2\,|\,q\,|\,Q[1+\tfrac{1}{3}\eta^2]^{1/2}, \qquad (1)$$

where the symbols have their usual meaning. The EFG parameters are determined from the experimental data by comparing the absorption-peak areas.

TABLE II. Direction cosines of EFG axes with respect to the crystallographic axes (**a′**, **b**, **c**) as calculated from the positional coordinates of H_2O molecules.

Direction cosine	$Fe(NH_4SO_4)_2 \cdot 6H_2O$	$FeSO_4 \cdot 7H_2O$ Site *A*	Site *B*
$Z_{a'}$	0.663	0.759	0.144
Z_b	0.472	0.346	0.124
Z_c	0.589	0.552	0.981
$Y_{a'}$	−0.642	−0.677	−0.899
Y_b	−0.363	0.121	0.431
Y_c	0.693	0.726	0.077
$X_{a'}$	−0.610	−0.183	0.414
X_b	0.772	0.924	0.894
X_c	−0.179	−0.328	−0.171

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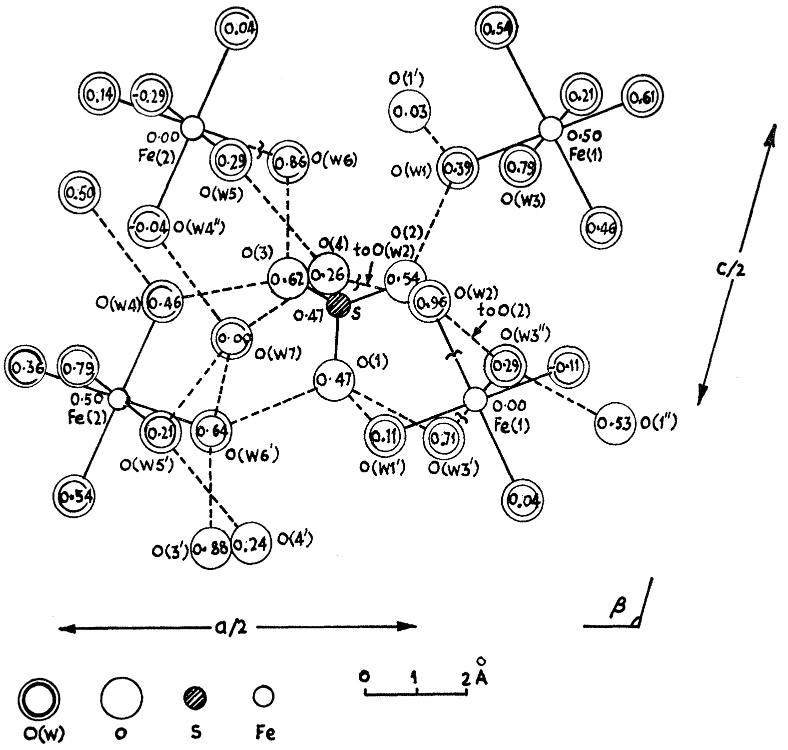

FIG. 2. Projection of the monoclinic structure of $FeSO_4 \cdot 7H_2O$ in the [010] direction.

Designating these by $\mathcal{A}_3$ and $\mathcal{A}_1$ for the higher-energy and lower-energy peaks respectively, it has been shown by Zory[7] that for a monochromatic, unpolarized source and a single-crystal absorber with i equivalent sites[12] per unit cell, the area ratio is

$$\mathcal{A}_3/\mathcal{A}_1=\Big[\sum_i^{\text{sites}} p_3(\theta_i,\phi_i)f'(\theta_i,\phi_i)\Big/\sum_i p_1(\theta_i,\phi_i)f'(\theta_i,\phi_i)\Big], \tag{2}$$

where $p_n(\theta_i,\phi_i)$ is the relative angular-dependent absorption probability for transition n, and $f'(\theta_i,\phi_i)$ is the Lamb-Mössbauer fraction of the absorbing nucleus in the (θ_i,ϕ_i) direction. (θ,ϕ) are the polar and azimuthal angles of the incident unpolarized beam with respect to the EFG axes $\hat{X}_i$, $\hat{Y}_i$, $\hat{Z}_i$ (Fig. 3). The crystal axes ($\mathbf{a}'$, $\mathbf{b}$, $\mathbf{c}$) are mutually orthogonal.

The expressions for the relative absorption probabilities for p_3 and p_1 were derived[7] by utilizing the fact that the 14.4-keV γ ray is a magnetic dipolar radiation. In terms of the known experimental angles Θ, Φ and the unknown Euler angles relating site i to axes ($\mathbf{a}'$, $\mathbf{b}$, $\mathbf{c}$), we get the expression for $\mathcal{A}_3/\mathcal{A}_1$, based on the assumption that $f'(\theta_i,\phi_i)$ is isotropic:

$$\frac{\mathcal{A}_3}{\mathcal{A}_1}=\frac{\sum_{\text{sites}}\{4[\frac{1}{3}(3+\eta^2)]^{1/2}+[3K-1+\eta K']\}}{\sum_{\text{sites}}\{4[\frac{1}{3}(3+\eta^2)]^{1/2}-[3K-1+\eta K']\}}, \tag{3}$$

where

$$K=\sin^2\Theta[(\cos^2\Phi)Z_{a'}^2+(\sin^2\Phi)Z_c^2]+(\cos^2\Theta)Z_b^2+(\sin^2\Theta\sin2\Phi)Z_{a'}Z_c+\sin2\Theta[(\sin\Phi)Z_cZ_b+(\cos\Phi)Z_{a'}Z_b]$$

and

$$K'=\sin^2\Theta[(\cos^2\Phi)(X_{a'}^2-Y_{a'}^2)+(\sin^2\Phi)(X_c^2-Y_c^2)]+(\cos^2\Theta)(X_b^2-Y_b^2)+(\sin^2\Theta\sin2\Phi)(X_{a'}X_c-Y_{a'}Y_c)+\sin2\Theta[(\cos\Phi)(X_{a'}X_b-Y_{a'}Y_b)+(\sin\Phi)(X_cX_b-Y_cY_b)].$$

The symbols $X_{a'}$, Y_b, and Z_c, etc. denote the direction cosines $\hat{X}\cdot\mathbf{a}'$, $\hat{Y}\cdot\mathbf{b}$, and $\hat{Z}\cdot\mathbf{c}$, etc. Equation (3) is utilized to find the EFG parameters from experimental data in both these cases.

5. EXPERIMENTAL OBSERVATIONS AND RESULTS

A. Ferrous Ammonium Sulphate Hexahydrate

The distances and angles[13] of three sets of water molecules surrounding the Fe^{++} are given in Fig. 4. The angles between the different axes of octahedron are nearly 90°, and these directions are taken as the

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[12] Two crystal sites are considered to be equivalent when the surrounding environments of the absorbing nuclei are the same but differ in orientation.

[13] As no x-ray data are available for $Fe(NH_4SO_4)_2 \cdot 6H_2O$, the distances and angles referred to here are those for its isomorphous salt (Ref. 9) $Zn(NH_4SO_4)_2 \cdot 6H_2O$.

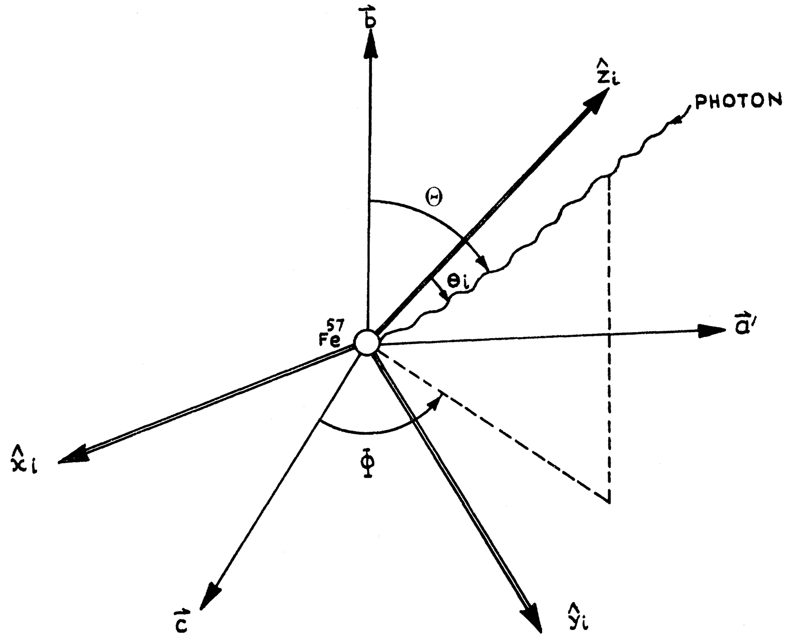

FIG. 3. Schematics of the absorption of the 14.4-keV γ ray by Fe^{57}.

axes of the EFG. The experimental values and calculations of the area ratios on the basis of Eq. (3) are compared in Table I. The following specifications of EFG parameters were assumed:

(i) The $OW(9)$-$OW(9)$ direction is the major axis, i.e., the $\hat{Z}$ axis of the EFG, whereas the $OW(7)$-$OW(7)$ and $OW(8)$-$OW(8)$ directions correspond to the $\hat{Y}$ and $\hat{X}$ axes, respectively. The direction cosines of $(\hat{X}, \hat{Y}, \hat{Z})$ relative to the $(\mathbf{a}', \mathbf{b}, \mathbf{c})$ axes are given in Table II.

(ii) The ratio of the higher-energy experimental peak occurring at $\approx$1.95 mm/sec to the lower-energy one at $\approx$0.15 mm/sec is $\mathcal{a}_3/\mathcal{a}_1$ and not $\mathcal{a}_1/\mathcal{a}_3$. This implies that the $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ transition is higher in energy than the $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$ transition. Taking $Q=0.30$ b,[14] we find from Eq. (1) that $eq=+5.33\times10^{17}$ V/cm^2 (300°K).

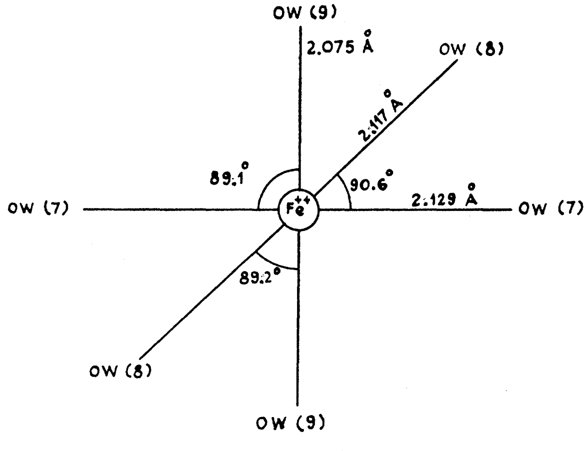

FIG. 4. Schematics of Zn(NH$_4$SO$_4$)$_2$·6H$_2$O[isomorphous with Fe(NH$_4$SO$_4$)$_2$·6H$_2$O] crystal showing distances between the water molecules around Fe^{++} and angles between octahedron axes.

(iii) $\eta=0.7$. For the measurements in the orientations (1) through (5), it can be shown that $p_3(\theta_1, \phi_1)=p_3(\theta_2, \phi_2)$ and $p_1(\theta_1, \phi_1)=p_1(\theta_2, \phi_2)$, with the consequence that $f'(\theta_i, \phi_i)$ cancels out of Eq. (3), so that the calculations are valid even in the presence of anisotropy. But in view of the agreement between experiment and calculations, the anisotropy of f' does not appear significant. The assignment of parameters is quite unique since the same set of five parameters of the EFG tensor is able to satisfy the observations at all seven settings.

B. Ferrous Sulphate Heptahydrate

There are four molecules per unit cell, and these form two distinct sites A and B (each site includes the site having the point symmetry $\bar{1}$). The schematics of the arrangement of six water molecules around Fe^{++} are given in Fig. 5(a) and Fig. 5(b) for each set separately. Likewise in this case, the angles between the different axes of the octahedron are nearly 90°, and these directions are taken as the axes of the EFG. The direction cosines of $(\hat{X}, \hat{Y}, \hat{Z})$ relative to $(\mathbf{a}', \mathbf{b}, \mathbf{c})$ are given in Table II. The observed absorption-peak-area ratios for different orientations, along with the calculated values, are given in Table I. The calcula-

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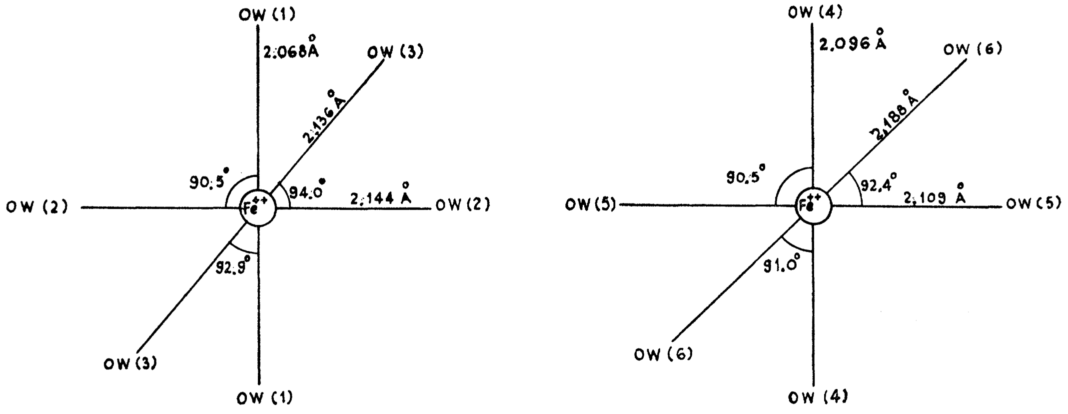
[14] A paper by A. H. Muir, Jr., H. Wiedersich, and J. O. Artman appeared in the abstracts of the International Conference on Hyperfine Interactions Detected by Nuclear Radiation, Asilomar, Pacific Grove, Calif., 1967, Paper I-18 (unpublished), which suggested that Artman's Q value of 0.41 b [Phys. Rev. **143**, 541 (1966)] should be reduced to 0.30 b, more in accord with previous data.



(a) Site A

(b) Site B

FIG. 5. The schematic arrangement for $FeSO_4 \cdot 7H_2O$ crystal showing distances between H_2O molecules around Fe^{++} and angles between the octahedron axes for site A and site B.

tions are based on the following assumptions regarding the EFG axes and asymmetry parameters:

(i) For site A, the $OW(1)$–$OW(1)$ direction is the $\hat{Z}$ axis, $OW(2)$–$OW(2)$ the Y axis, and $OW(3)$–$OW(3)$ the X axis. For site B, $OW(4)$–$OW(4)$ is the $\hat{Z}$ axis, $OW(5)$–$OW(5)$ the $\hat{X}$ axis, and $OW(6)$–$OW(6)$ the Y axis.

(ii) The ratio of the higher-energy experimental peak occurring at $\approx +2.56$ mm/sec to the lower-energy one at ≈ -0.56 mm/sec is $\mathcal{A}_3/\mathcal{A}_1$ and not $\mathcal{A}_1/\mathcal{A}_3$, implying that sign of q is positive. The value of $eq = +1.0 \times 10^{18}$ V/cm^2 (300°K).

(iii) Asymmetry parameter $\eta = 0.1$ for sites A and B. It may be remarked that f' does not cancel out of Eq. (3) for any orientation (1) to (7), since for the two distinct sites A and B, the relative absorption probabilities are different. In view of the agreement between the observed and calculated values (based on the assumption of isotropic f'), one concludes that for $FeSO_4 \cdot 7H_2O$ the anisotropy in the Lamb-Mössbauer fraction does not appear to be appreciable at room temperature. The assignment of the parameters is all the more unique since the requirement was more stringent because of the presence of two sites A and B per unit cell.

6. DISCUSSION

The sign of the nuclear quadrupole coupling constant, and on that basis the conclusion that the ground-state orbital wave function is a singlet $|xy\rangle$ both in the case of $Fe(NH_4SO_4)_2 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$, agrees with that given by Ingalls[15] and Grant *et al.*[5] By means of the magnetic perturbation technique, Grant *et al.* had set the lower limit of $\eta > 0.7$ for $Fe(NH_4SO_4)_2 \cdot 6H_2O$ which tallies with our value of η. The large asymmetry arises from the asymmetric distribution of NH_4^+ ions around Fe^{++}.

Measurements of magnetic anisotropy and susceptibility of single crystals of $Fe(NH_4SO_4)_2 \cdot 6H_2O$ had been reported and accounted for by a number of workers.[16–18] Thakurta and Mukhopadhyay[18] infer that the magnetic ellipsoids of the crystals are roughly reduced to oblate spheroids about the χ_2 axis, which has the minimum susceptibility. Furthermore the **b** axis coincides with the principal susceptibility, and the angle between **a** and χ_2 axes is $\approx -37°$. The principal axes of the EFG tensor as determined here do not coincide with those of the susceptibility tensor; this was also the case with $FeCl_2 \cdot 4H_2O$.[7] No report of the measurement of the magnetic anisotropy of $FeSO_4 \cdot 7H_2O$ exists in the literature.

ACKNOWLEDGMENTS

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