EPR measurement of Cu^{2+}–Fe^{2+} exchange in $FeSiF_6 \cdot 6H_2O$ at 4.2 K

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Six inequivalent Cu^{2+} EPR spectra were observed at 4.2 K in single crystals of $FeSiF_6 \cdot 6H_2O$. The estimated parameters $g_z \simeq 2.38$ and $\theta \simeq 40°$, where θ is the angle between the ionic z axis and the c axis, differ from those measured in crystals of similar structure. These differences have been explained in terms of an isotropic Cu^{2+}–Fe^{2+} exchange Hamiltonian $JS_1 \cdot S_2$, with $J = + (0.030 \pm 0.003)$ cm^{-1}, which gives a contribution $g_{ex} \simeq - 5.05 J \sin^2 \theta$, where θ is the angle between the external magnetic field and the z axis. Perpendicular to the c axis, an independent estimate of $+ 0.034$ cm^{-1} for J was made from the low-field displacement of a satellite spectrum.

I. INTRODUCTION

At low temperatures, ferrous fluosilicate hexahydrate $FeSiF_6 \cdot 6H_2O$ belongs to the monoclinic space group $C_{2h}^5 (P2_1/c)$.[1] Electron paramagnetic resonance (EPR) measurements on copper-doped materials of this class have been reported in the diamagnetic crystals $ZnGeF_6 \cdot 6H_2O$,[2,3] $ZnTiF_6 \cdot 6H_2O$,[4] and $MgSiF_6 \cdot 6H_2O$.[5] These materials give six inequivalent Cu^{2+} spectra at 4.2 K, each with $g_\parallel = 2.47$ and $g_\perp = 2.10$. Consistent with a "static" Jahn–Teller effect in a basically cubic crystal,[6] the six z axes were found to lie along the tetragonal axes of two cubes, separated by a rotation of roughly 40° about the crystallographic c axis, which forms a common [111] axis for each cube.

The same symmetry was observed in the EPR spectrum of Cu^{2+} in $FeSiF_6 \cdot 6H_2O$, except for the fact that z axes of the Cu^{2+} spectra made angles of only 40° with the c axis, rather than the angle of 55° observed in the diamagnetic crystals.[7] In addition, a lower maximum g value of 2.38 was observed. This was close to the maximum g value 2.40 deduced by Sthanapati *et al.*[8] from powder EPR measurements at 20 K. The crystallographic data for the above materials were essentially similar,[9] and gave no reason for the large differences in the EPR data for $FeSiF_6 \cdot 6H_2O$. The purpose of this paper is to present the EPR results obtained at 4.2 K for Cu^{2+} in $FeSiF_6 \cdot 6H_2O$ and to show that the differences mentioned above are a consequence of the superexchange interaction between the Cu^{2+} ions and their nearest-neighbor host Fe^{2+} ions.

EPR measurements in systems of this type, which consist of a paramagnetic impurity substituted into a non-Kramers' paramagnetic host with a singlet ground state and a large zero-field splitting, have been the subject of recent studies of Moriya and Obata,[10] Gill,[11] and St. John and Myers.[12]

The nature of the low temperature impurity ion spectra observed in such systems depends on the spin–spin relaxation rate of the nearest neighbor host ions. In the case of fast relaxation, the displacement of the impurity spectrum due to exchange depends on an averaged magnetic moment over the thermally populated states of the host ion. This is the situation considered by St. John and Myers.[12] On the other hand, if the spin–spin relaxation rates are sufficiently slow, several sets of displaced spectra may be observed. These consist of a primary spectrum corresponding to all the nearest neighbor host ions being in their ground states, and satellite spectra due to one or more neighbors being in excited states. Satellite spectra of this type have been studied by Gill[11] for Cu^{2+} in $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

The latter situation should occur for Cu^{2+} in $FeSiF_6 \cdot 6H_2O$, since the large lattice strains associated with the static Jahn–Teller effect in Cu^{2+} should make the nearest-neighbor Fe^{2+} ions nonresonant with the bulk of Fe^{2+} ions further removed from Cu^{2+} impurities.[11] In this case, the exchange parameter J may be estimated both from the difference outlined above between the primary spectrum and the spectra observed in isomorphous diamagnetic crystals and also from the displacements of the satellite spectra relative to the primary spectrum. Both methods require that the spin-Hamiltonian parameters for the nearest-neighbor host ions be known, and are limited by our ignorance of the effect of the local lattice distortion near an impurity site on the spin-Hamiltonian parameters of the host ion.

The present experimental study was confined to the low field end of the Cu^{2+} spectrum by the presence of a relatively intense accidental Mn^{2+} impurity spectrum. Even so, sufficient information was obtained to provide a reasonable test of the theory and to obtain a value for J, which was confirmed by measuring the displacement of a satellite spectrum. The experimental results are given in Sec. II, and the theory for estimating J from the known energy-level scheme for $FeSiF_6 \cdot 6H_2O$ is given in Sec. III. This theory is applied to the experimental data in Sec. IV. The results are discussed in Sec. V.

II. EXPERIMENTAL RESULTS

The measurements were carried out at 4.2 K on single crystal samples of $FeSiF_6 \cdot 6H_2O$ doped with Cu^{2+} using standard EPR spectrometers, operating at 24 and 35 GHz. A typical sample of the material was found on analysis to contain 0.2 at. % Cu^{2+}.[13] As in the case of $ZnTiF_6 \cdot 6H_2O$,[4] the measurements were made in three mutually perpendicular crystal planes labeled as follows: Plane 1, which is paral-
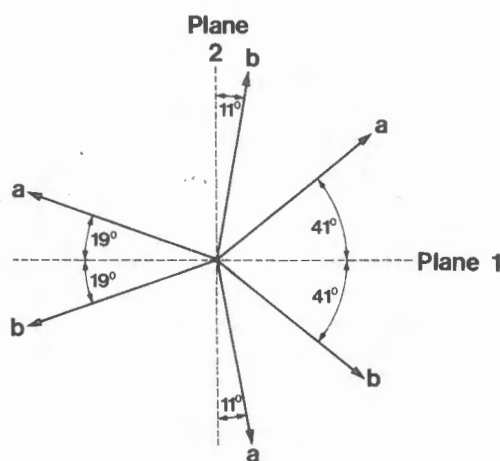
FIG. 1. The projections of the z axes of the six Cu^{2+} spectra onto plane 3 are shown, together with the intersections of planes 1 and 2 with plane 3. The two sets of spectra, labeled a and b, are rotated with respect to each other by an angle of 38° about the c axis of the crystal (see the text). The values of β are given for the measured spectra in planes 1 and 2.

FIG. 2. The low field portion of the Cu^{2+} spectrum in FeSiF₆ · 6H₂0 at 4.2 K and 34.6 GHz in a plane perpendicular to the c axis is shown at a low field extremum. The displacement of the satellite spectrum relative to the primary spectrum is given by ΔH.

lel to a hexagonal face of the crystal; plane 2, which is derived from plane 1 by a rotation of 90° about the c axis; plane 3, which is perpendicular to the c axis.

The EPR spectrum in plane 3 showed an overall 60° rotational symmetry, with six inequivalent Cu^{2+} spectra, as observed previously in ZnGeF₆ · 6H₂O,[3] ZnTiF₆ · 6H₂O,[4] and MgSiF₆ · 6H₂O.[5] With the rotation angle $\beta = 0°$ being arbitrarily chosen to correspond to an orientation in which the external magnetic field was parallel to a hexagonal crystal face, g-value maxima of 2.175 ± 0.010 were observed at the angles $\beta \simeq 11°$, 49°, 71°, 109°, 131°, and 169°. These results are consistent with the existence of two sets of three Cu^{2+} spectra separated by an angular rotation of either 22° or 38°. As in the cases of the diamagnetic lattices,[4,5] the data for planes 1 and 2 were consistent only with a situation in which the projections of the z axes for the two sets of spectra onto plane 3 were separated by the larger angle $\Delta\beta \simeq 38°$. This situation is illustrated in Fig. 1, which shows the projections of the six z axes onto plane 3. A Cu^{2+} spectrum is shown in Fig. 2 for a low-field extremum in plane 3. A partially resolved satellite structure with a relative intensity of approximately 5% of the primary spectrum may be seen on the low-field side of the latter. Measurements at different extrema indicated the lowest hyperfine line of the satellite spectrum was displaced by (252 ± 5) G to the low-field side of the primary spectrum.

The orientation of the crystal in plane 3 was checked by observing the g-value maxima for Ni^{2+} spectrum also present in the crystal. The observed orientations $\beta \simeq 6°$, 66°, and 126° were in agreement with the previously reported measurements on this ion.[14]

In plane 2, equivalent g-value maxima and subsidiary maxima were found on both sides of the c axis, while in plane 1, the g-value maximum was found on one side only, with a subsidiary maximum closer to the c axis on the other side. Diagrams of the symmetries observed for rotations in both planes have been given elsewhere for ZnTiF₆ · 6H₂O.[4]
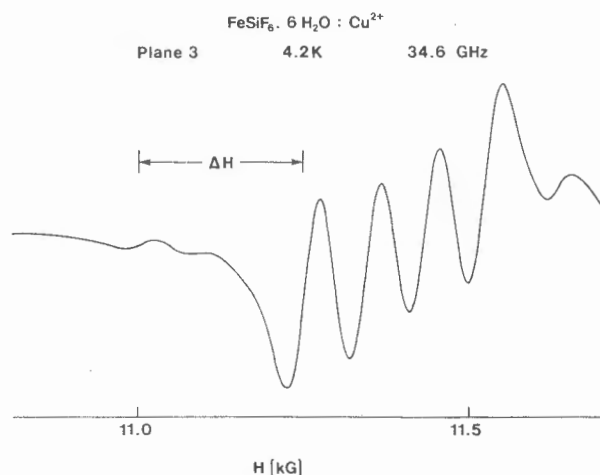
The measured values of the g-value maximum and subsidiary maximum and the angles θ with the crystal c axis in plane 1 were

$$g_1 = 2.360 \pm 0.002, \quad \theta_1 = (39 \pm 1)°,$$
$$g_2 = 2.308 \pm 0.003, \quad \theta_2 = (30 \pm 2)°,$$

and in plane 2 were

$$g_3 = 2.380 \pm 0.002, \quad \theta_3 = (40 \pm 1)°,$$
$$g_4 = 2.289 \pm 0.003, \quad \theta_4 = (22 \pm 2)°.$$

Peak-to-peak linewidths were measured in the range 40–50 G, while the mean hyperfine structure constant A for the unresolved Cu^{63} $(I = 3/2)$ and Cu^{65} $(I = 3/2)$ hyperfine lines was found to be (91 ± 1) G for the g-value maxima in all three planes.

III. THEORY

A. The energy-level scheme of Fe²⁺ in FeSiF₆ · 6H₂O

In FeSiF₆ · 6H₂O, each Fe^{2+} ion is surrounded by a slightly distorted octahedron of water molecules.[9,15] The distortion is essentially trigonal, with lower symmetry components present in the low temperature monoclinic phase.[1,9] The presence of at least six inequivalent Fe^{2+} sites at 4.2 K was confirmed by a nuclear magnetic resonance study.[16] Experimental estimates of the angle between the crystal c axis and the z axes of the six Fe^{2+} sites varied between 1° and 4°.[17–19] The effects of this small angle will be ignored in the following theory.

Neglecting small fourth degree terms,[20,21] the spin Hamiltonian describing the ground spin-quintet $(S = 2)$ in FeSiF₆ · 6H₂O at 4.2 K is given by[19,22]

$$\mathscr{H} = DS_z^2 + E(S_x^2 - S_y^2) + G_\parallel S_z \cos\theta + G_\perp S_x \sin\theta, \quad (1)$$

where $G_\parallel = g_\parallel \mu_\beta H$, $G_\perp = g_\perp \mu_\beta H$, the magnetic field is assumed to lie in the xz plane at an angle θ to the z axis, and the experimentally determined parameters were

$$D = 11.88 \text{ cm}^{-1}, \quad E = 0.67 \text{ cm}^{-1}, \quad g_{\parallel} = 1.96. \quad (2)$$

While no direct experimental determination of $g_{\perp}$ has been made, the value 2.0 will be used, based on Palumbo's[23] original fit of Jackson's[24] susceptibility data. Assuming the inequality

$$D \gg E, G_{\parallel}, G_{\perp}. \quad (3)$$

the energies of the spin quintet are given to the second order of perturbation theory by

$$E_0 = -3E^2/D - 3G_{\perp}^2 \sin^2 \theta /D, \quad (4a)$$

$$E_{1\pm} = D \pm (G_{\parallel}^2 \cos^2 \theta + 9E^2)^{1/2} + 7G_{\perp}^2 \sin^2 \theta /6D, \quad (4b)$$

$$E_{2\pm} = 4D \pm 2G_{\parallel} \cos \theta + 3E^2/2D + G_{\perp}^2 \sin^2 \theta /3D. \quad (4c)$$

B. The effect of impurity-host exchange

Following the molecular field approach of St. John and Myers,[12] the superexchange interaction between an impurity ion of spin S' and its z nearest neighbor host ions of spin S may be written

$$\mathcal{H}_{ex} \simeq zJ S' \cdot \langle S \rangle, \quad (5)$$

where

$$\langle S \rangle = \langle \partial E /\partial H \rangle /g\mu_\beta.$$

For the primary EPR spectrum at 4.2 K, all the nearest-neighbor host ions are in their ground state, so that

$$\langle \partial E /\partial H \rangle_p = \partial E_0/\partial H = -6g_{\perp}^2 \mu_\beta^2 \, {}^2H \sin^2 \theta /D. \quad (6)$$

In a first-order approach, only the diagonal portion of $\mathcal{H}_{ex}$ is retained, and is expressed in terms of an effective g value as follows:

$$\mathcal{H}_{ex} \simeq zJ \langle S_z \rangle S'_z = g_{ex}\mu_\beta HS'_z. \quad (7)$$

Assuming that $g_{\parallel} \simeq g_{\perp} \simeq g$ for Fe^{2+}, Eqs. (5) through (7) give the following g-value shift for the primary Cu^{2+} spectrum:

$$(g_{ex})_p \simeq -6zJg \sin^2 \theta /D. \quad (8)$$

The most intense satellite spectrum would correspond to one of the six nearest-neighbor Fe^{2+} ions occupying the first excited state with energy E_{1-} given by Eq. (4b). In this case the mean energy $\langle E \rangle_s$ of the six neighbors is

$$\langle E \rangle_s = (5E_0 + E_{1-})/6. \quad (9)$$

Following the same procedure used above for the primary spectrum, and assuming in addition that $9E^2 \gg G_{\parallel}^2 \cos^2 \theta$, the following g-value shift is obtained for the secondary spectrum:

$$(g_{ex})_s \simeq -(zJg/18)[(83 \sin^2 \theta /D) - (\cos^2 \theta /E)], \quad (10)$$

which leads to the difference

$$\Delta g_{ex} = (g_{ex})_s - (g_{ex})_p \simeq (zJg/18)$$
$$\times [(25 \sin^2 \theta /D) + (\cos^2 \theta /E)]. \quad (11)$$

It should be noted that the low symmetry parameter E does not enter the expression for $(g_{ex})_p$ given in Eq. (8), nor that given above for Δg_{ex} when $\theta = 90°$. The displacements in these cases should therefore be insensitive to the low symmetry components of the local distortion produced by the impurity ion.

IV. DETERMINATION OF J

Following the approach used by St. John and Myers,[13] the observed g value may be written as

$$g_{obs} = g_{dia} + g_{ex}, \quad (12)$$

where g_{dia} is that value which would be observed in a diamagnetic crystal of the same structure and g_{ex} is given by Eq. (8) for the primary spectrum. Inserting the values $z = 6$, $g = 2.0$, and $D = 11.88 \text{ cm}^{-1}$ from Sec. III A gives

$$g_{ex} \simeq -5.05J \sin^2 \theta, \quad (13)$$

g_{dia} is assumed to be the same as in $ZnGeF_6 \cdot 6H_2O$, $ZnTiF_6 \cdot 6H_2O$, and $MgSiF_6 \cdot 6H_2O$, where the 4.2 K spectra of which are described by the parameters

$$g_{\parallel} = 2.47, \quad g_{\perp} = 2.10, \quad \alpha = 55°, \quad (14)$$

where $g_{\parallel}$ and $g_{\perp}$ are the principal values of the tensor g_{dia} and α is the angle between the z axis of each Cu^{2+} spectrum and c axis of the crystal.[3–5]

For an arbitrary angle δ between the external magnetic field and the z axis for a particular Cu^{2+} spectrum, g_{dia} is given by

$$g_{dia}^2 = g_{\parallel}^2 \cos^2 \delta + g_{\perp}^2 \sin^2 \delta, \quad (15)$$

where $g_{\parallel}$ and $g_{\perp}$ have the values given in Eq. (14). The angle δ cannot be measured directly, but may be deduced from the measured rotation θ from the c axis and the projection β of the angle δ onto plane 3. As indicated in Fig. 1, β has the values 19° and 41° for the measured spectra in plane 1, and the values 11° and 49° in plane 2. For the low field extremum in plane 3 (for which $\theta = 90°$), $\beta = 0°$. The angle δ is related to α, β, and θ as follows:

$$\cos \delta = \cos \alpha \cos \theta + \sin \alpha \sin \theta \cos \beta. \quad (16)$$
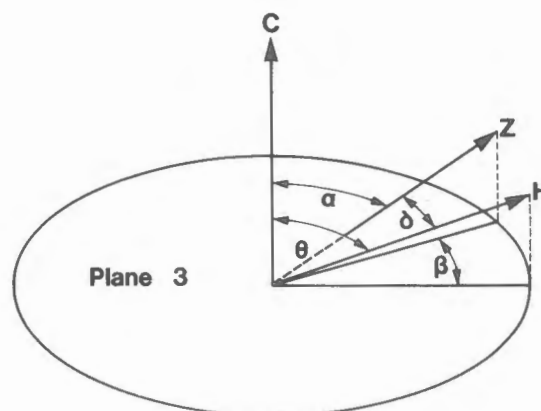
These angles are shown schematically in Fig. 3.

FIG. 3. The angles α, β, θ, and δ used in the text are illustrated for a typical Cu^{2+} spectrum. The z axis of the Cu^{2+} spectrum, the direction of the magnetic field at a g-value maximum, and their projections onto plane 3 are shown, together with the c axis of the crystal.

TABLE I. The calculation of J from measurements of g-value extrema.

Spectrum	β^a	θ^a	δ^a	$g_{dia}{}^b$	$g_{obs}{}^c$	g_{ex}	J (cm^{-1})
Plane 1							
g_1	19	39	21	2.425	2.360	−0.065	0.032 ± 0.005
g_2	41	30	36	2.348	2.308	−0.040	0.032 ± 0.008
Plane 2							
g_3	11	40	17	2.440	2.380	−0.060	0.029 ± 0.004
g_4	49	22	43	2.305	2.289	−0.016	≈ 0.02
Plane 3							
g_5	0	90	35	2.355	2.175	−0.018	≈ 0.04

[a] Errors of $\pm 1°$ were estimated for β and θ in planes 1 and 2. With $\alpha = (55 \pm 1)°$ in Eq. (16), the errors in δ were found to be less than $\pm 0.5°$. In plane 3, where $\delta = 90° - \alpha$, the error in δ was $\pm 1°$.
[b] The calculation of g_{dia} was made from Eq. (16), assuming that $g_{\parallel} = 2.470 \pm 0.005$ and $g_{\perp} = 2.100 \pm 0.005$. The errors in g_{dia} were found to be ± 0.006 for planes 1 and 2 and ± 0.012 for plane 3.
[c] The errors in g_{obs} are given in Sec. III.

Estimates of J, together with the values of β, θ, δ, g_{dia}, g_{obs}, and g_{ex}, are given in Table I for the low field extrema of the various Cu²⁺ spectra in the three planes of measurement. The EPR data for the primary spectrum, is satisfactorily explained by the value

$$J = + (0.030 \pm 0.003) \text{cm}^{-1}, \tag{17}$$

where the positive sign indicates antiferromagnetic coupling.

The angular dependencies of g_{dia}, g_{ex}, and their sum g_{tot} are shown in Fig. 4 for rotation in a plane containing the crystal c axis and the z axis for one Cu²⁺ spectrum. The lowering of the observed g value and the shifting of the extrema by about 15° may be clearly seen. While this plane of rotation is one for which $\beta = 0°$, the behavior of the lowest field spectra in planes 1 and 2, where $\beta = 19°$ and 11°, respectively, should be similar. In plane 3, where $\theta = 90°$, g_{ex} should be constant for all orientations, giving the maximum shift of 0.18 units towards higher fields.
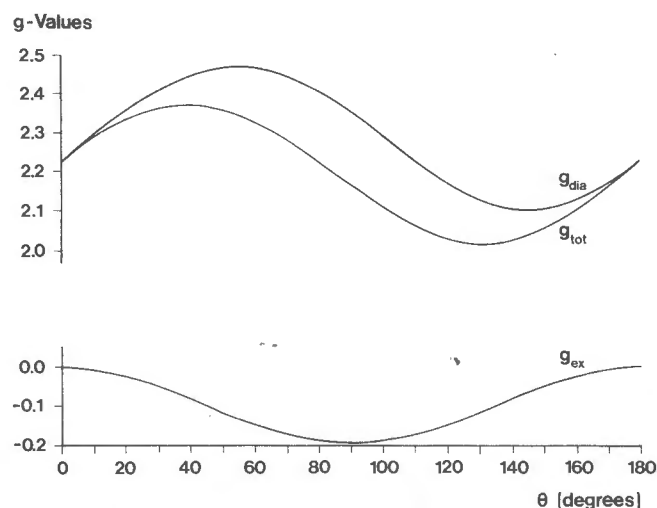

g-Values

FIG. 4. The angular dependencies of g_{ex}, g_{dia}, and g_{tot} are shown for rotation in a plane containing the c axis of the crystal and the z axis for one Cu²⁺ spectrum. The angle of rotation θ is measured from the c axis. The main features of g_{tot} compared to g_{dia} are the lowering of the g value and the occurrence of the maximum g value about 15° closer to the c axis.

An independent estimate of J may be made from the low-field displacement of the satellite spectrum by (252 ± 5) G, which may be seen in Fig. 2. This shift is equivalent to a g shift $\Delta g_{ex} = 0.048 \pm 0.001$. Inserting the values $z = 6$, $g = 2.0$, $D = 11.88$ cm^{-1}, and $E = 0.67$ cm^{-1} [see Eq. (2)] into Eq. (11) give the theoretical result

$$\Delta g_{ex} = J(1.40 - 2.40 \cos^2 \theta). \tag{18}$$

For plane 3, $\theta = 90°$ and $g = g_{\perp}$ for Fe²⁺. With an error of ± 0.1 assumed for g, the value obtained for J is

$$J = + (0.034 \pm 0.002) \text{cm}^{-1}, \tag{19}$$

which is in excellent agreement with the value given in Eq. (17). It should be noted that both values are inversely proportional to D, which may differ from the value given above for an undistorted crystal.

V. DISCUSSION

The main purpose of this work, which was to explain the anomalous g values observed in the EPR of Cu²⁺ in FeSiF₆ · 6H₂O, led to the determination of the exchange parameter $J = + 0.032$ cm^{-1} for Cu²⁺–Fe²⁺ coupling, a value confirmed by measurements on the displacement of a satellite spectrum. This value may be compared to those of $+ 0.029$ and 0.074 cm^{-1} determined, respectively, from the pair spectra of Co²⁺ and Ni²⁺ doped MgSiF₆ · 6H₂O crystals,[25,26] and to that of $+ 0.006$ cm^{-1} for Mn²⁺–Fe²⁺ coupling obtained in a current study of Mn²⁺ in FeSiF₆ · 6H₂O.[27]

The similarity of magnetic interactions in fluosilicate crystals with the C_{2h}^5 structure to those between nearest neighbor X–Y pairs in the double nitrate series has been pointed out by Francis and Culvahouse. In a thorough investigation of all possible pair combinations involving Mn²⁺, Ni²⁺ and Co²⁺ in La₂Zn₃(NO₃)₁₂ · 24H₂O, Culvahouse et al.[28-31] were able to present a theory for X–Y coupling based (in the first approximation) on the following assumptions:

(i) that only e_g electrons are involved in the exchange process;

(ii) that the orbital exchange parameters are independent of the number of $3d$ electrons.

Because of the local distortion of the crystal produced by a "Jahn–Teller" ion such as Cu²⁺, it is not clear how well the second assumption would apply in the present case. It would be useful for comparison purposes to measure the pair spectra of Mn²⁺, Ni²⁺, or Co²⁺ in FeSiF₆ · 6H₂O.

Dipolar contributions to the Cu²⁺–Fe²⁺ coupling were neglected in the theory presented in this paper. Since the effective magnetic moments of the lowest Fe²⁺ states, which may be found from Eqs. (4b) and (4c), are considerably less than 2, the magnitude of the nearest-neighbor dipolar coupling should be smaller than the 0.002 cm^{-1} calculated for Ni²⁺ pairs in MgSiF₆ · 6H₂O.

Much work remains to be done on the FeSiF₆ · 6H₂O: Cu²⁺ system. At 4.2 K, the Cu²⁺ spectrum needs to be measured in a sample free of Mn²⁺ in order to confirm the angular dependence of g_{tot} given in Fig. 4 over the whole range. Even more important would be a study of displacements, line shapes, and linewidths with temperature of the type car-

ried out by Gill[11] on Cu^{2+} in $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. In Fe-SiF$_6$ · 6H$_2$O, temperature-dependent displacements should occur for two quite different reasons:

(i). the effect on the exchange coupling of increasing the populations of the upper states of the Fe^{2+} spin quintet;

(ii). the averaging of the "pseudo" Jahn–Teller distortions, which has been measured in diamagnetic crystals with this structure.[2–5]

ACKNOWLEDGMENTS

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