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Observation of exchange coupling in the EPR spectrum of Mn^{2+} in $FeSiF_6 \cdot 6H_2O$ below 60 K

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The Mn^{2+}-Fe^{2+} superexchange coupling in $FeSiF_6 \cdot 6H_2O$ has been measured from the temperature dependence of the Mn^{2+} EPR spectrum at 9.2 GHz between 4 and 60 K. With the assumption of an exchange Hamiltonian of the form $J\mathbf{S}_1 \cdot \mathbf{S}_2$, the value $J = +(0.0065 \pm 0.0015)\ \mathrm{cm}^{-1}$ was obtained from the deviation of the effective value of $g_\perp$ from 2.000, using the molecular-field method of St. John and Myers. This value for J was in rough agreement with that obtained from the weak temperature dependence observed parallel to the c axis. The linewidth variation for two groups of hyperfine lines was fitted to an expression of the form $T\exp(-\Delta E/k_B T)$, where $\Delta E = 47.5\ \mathrm{cm}^{-1}$ is the mean excitation of the upper Fe^{2+} spin doublet.

I. INTRODUCTION

Ferrous fluorosilicate hexahydrate $FeSiF_6 \cdot 6H_2O$ belongs to the monoclinic space group C_{2h}^5 $(P2_1/c)$ at low temperatures.[1] The weakly coupled Fe^{2+} ions have energy-level schemes characterized by a singlet ground state and a large zero-field splitting. Several detailed studies have been made of the electron-paramagnetic-resonance (EPR) spectra of transition-metal impurities substituted into paramagnetic crystals of this type.[2–4] Moriya and Obata[2] considered the effects of the host ion in terms of an average spin, which displaces the impurity EPR spectrum, and a time-dependent fluctuation, which affects the linewidths. Gill[3] has studied relaxation processes, line shapes, and satellite spectra for a case in which the impurity ion Cu^{2+} causes local strains sufficient to make the neighboring Fe^{2+} ions nonresonant with those further removed. The case of rapid spin-spin relaxation was treated by St. John and Myers[4] by means of a molecular-field method in which the effective host spin was averaged over the thermally populated states, allowing them to measure the Cu^{2+}-Ni^{2+} and V^{2+}-Ni^{2+} superexchange coupling in α-$NiSO_4 \cdot 6H_2O$.

In a recent EPR study of Cu^{2+} in $FeSiF_6 \cdot 6H_2O$ by Rubins and De,[5] anomalously low g values and the presence of a satellite spectrum were explained on the basis of Gill's model for strong local distortions.[3] Unlike Cu^{2+}, which produces a local Jahn-Teller distortion in crystals of this type,[6–8] Mn^{2+} substitutes very easily for Fe^{2+}, probably without appreciable lattice distortion. In this case, the approach of St. John and Myers[4] should be applicable.

The purpose of the work described here was to measure the exchange constant J for the Mn^{2+}-Fe^{2+} coupling in $FeSiF_6 \cdot 6H_2O$. This was done by measuring the temperature dependence of the Mn^{2+} impurity EPR spectrum in single crystals of $FeSiF_6 \cdot 6H_2O$, with the magnetic field both parallel and perpendicular to the crystal c axis. Perpendicular to the c axis, the displacements were an order of magnitude larger than in the parallel orientation. Even though some of the theoretical parameters were not known accurately, measurements in this orientation provided the preferable means of determining J.

Measurements of the EPR spectrum of Mn^{2+} in $FeSiF_6 \cdot 6H_2O$ have been reported at 4.2 K in the parallel orientation, i.e., with the external magnetic field along the c axis of the crystal.[9] Measurements in other orientations were hindered by the complexity of the EPR spectrum, due both to the presence of at least three nonequivalent Mn^{2+} sites and also to intense "forbidden" hyperfine spectra.[10] The z axes of the Mn^{2+} spectra were oriented at about 8° from the c axis. The measured value $g_z \simeq 2.001$ indicated that a negligibly small role was played by Mn^{2+}-Fe^{2+} superexchange in the parallel orientation at 4.2 K.

The organization of this paper is as follows: The theory of exchange displacements in $FeSiF_6 \cdot 6H_2O$ for the parallel and perpendicular orientations is given in Sec. II, while the experimental results and analyses for the two orientations are given in Secs. III A—III C. The results are discussed in Sec. IV.

II. THEORY

Apart from insignificant fourth-degree terms,[11,12] the spin-Hamiltonian for Fe^{2+} in $FeSiF_6 \cdot 6H_2O$ is given by[13,14]

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

where $G_{\|} = g_{\|}\mu_B H$, $G_\perp = g_\perp \mu_B H$, $D = 11.88\ \mathrm{cm}^{-1}$, $E = 0.67\ \mathrm{cm}^{-1}$, $g_{\|} = 1.96$, $g_\perp \simeq 2.0$, and the magnetic field is assumed to lie in the x-z plane at an angle θ to the z axis. Neglecting the small angle of approximately 2° between the z axes of the six inequivalent Fe^{2+} ions and the c axis of the crystal,[9,15,16] and assuming that

$$D \gg E \gg G_{\|},\ \ G_\perp \gg E^2/D \quad (2)$$

the energies of the ground-spin quintet $(S=2)$ are given by

$$E_0 \simeq -3E^2/D - 3G_\perp^2 \sin^2\theta/D \ , \tag{3a}$$

$$E_{1+} \simeq D + 3E + G_{||}^2 \cos^2\theta/6E + 8G_\perp^2 \sin^2\theta/3D \ , \tag{3b}$$

$$E_{1-} \simeq D - 3E - G_{||}^2 \cos^2\theta/6E - G_\perp^2 \sin^2\theta/3D \ . \tag{3c}$$

$$E_{2\pm} \simeq 4D \pm 2G_{||}\cos\theta + 3E^2/2D + G_\perp^2 \sin^2\theta/3D \ . \tag{3d}$$

Following the molecular-field method of St. John and Myers,[4] the exchange interaction between an impurity ion of spin S' and its six nearest-neighbor Fe^{2+} ions may be written as

$$\mathscr{H}_{\text{ex}} \simeq 6JS'_{z'} \langle S_{z'} \rangle \ , \tag{4}$$

where a Heisenberg coupling of the form $J\mathbf{S}\cdot\mathbf{S}'$ is assumed for each pair of nearest-neighbor ions, and $\langle S_{z'} \rangle$, the component of the effective Fe^{2+} spin in an arbitrary direction z', is given by

$$\langle S_{z'} \rangle = (g\mu_B Q)^{-1} \sum_i (\partial E_i/\partial H)\exp(-E_i/k_B T) \ , \tag{5}$$

where $g \simeq 2$ for Fe^{2+}, Q is the partition function, k_B is Boltzmann's constant, and the E_i are given by Eq. (3).

The electronic Zeeman interaction for the impurity ion may be combined with the exchange interaction of Eq. (4) to give an effective Zeeman interaction of the form

$$\mathscr{H}'_{\text{Ze}} \simeq [g' \pm (6J\langle S_{z'} \rangle/\mu_B H)]\mu_B H S'_z \ . \tag{6}$$

where g' is the impurity-ion g value in the z' direction. If the host energy levels E_i are all quadratic in H, then the exchange interaction may be represented by an effective g-value contribution g_{ex}, which depends on temperature. Such a situation occurs for the energy levels of Eq. (3) when $\theta = 90°$. In this case, g_{ex} is given by

$$\begin{aligned} g_{\text{ex}} \simeq -(2Jg_\perp/DQ)\{ & 18\exp(-\beta E_0) \\ & + 2\exp(-\beta E_{1-}) - 16\exp(-\beta E_{1+}) \\ & - 2[\exp(-\beta E_{2-}) + \exp(-\beta E_{2+})]\} \ , \end{aligned} \tag{7}$$

where $\beta = 1/k_B T$. The magnitude of g_{ex} decreases monotonically as the temperature is raised.

When $\theta = 0°$, the E_i are not quadratic in H. Here, the effect of the exchange interaction may be represented by a field shift H_{ex}, which depends on both temperature and microwave frequency. For the energy levels of Eq. (3), H_{ex} is given by

$$\begin{aligned} H_{\text{ex}} \simeq (6J/g_{||}\mu_B Q)\{ & G_{||}(G_{||}^2 + 9E^2)^{-1/2} \\ & \times [\exp(-\beta E_{1-}) - \exp(-\beta E_{1+})] \\ & + 2[\exp(-\beta E_{2-}) - \exp(-\beta E_{2+})]\} \ . \end{aligned} \tag{8}$$

For positive J, this expression has a maximum at a temperature which depends on the relative values of D, E, and $G_{||}$.

III. EXPERIMENTAL RESULTS

A. Equipment

Data were taken at X band using a Varian E109 Series spectrometer. Microwave frequencies were measured to five significant figures with a Hewlett-Packard 5245L oscillator and a 5257A transfer oscillator. Variable temperatures from 3.7 K to room temperature were provided and controlled to about 0.3 K by an Oxford Instruments ESR900 flow-through cryostat and DCT2 temperature controller. Crystals were aligned visually for rotation about an axis perpendicular to the crystallographic c axis. Final orientation of the crystal parallel to the c axis was obtained by maximizing the overlap of the spectra from the nonequivalent magnetic sites and by minimizing the intensities of the forbidden hyperfine lines.

B. The parallel orientation ($\theta = 0°$)

The parallel orientation is advantageous for experimental study since it is the only orientation of the crystal in which the various Mn^{2+} sites are equivalent. In addition, the spin-Hamiltonian parameters of $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ occurring on the right-hand side of Eq. (8) have been measured at 4.2 K in this orientation. For these reasons, the parallel orientation should be ideal, in principle, for determining J. Unfortunately, the measured displacements were very small, the maximum shifts of the EPR lines from their 4-K positions being less than 7G. Since the uncertainties in determining the line centers could be as high as ±2 G, the measurements in this orientation were used only to obtain a rough estimate of J.

In order to organize the data, the groups of hyperfine lines corresponding to the electronic transitions $M \leftrightarrow M-1$, with $M = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$, were denoted groups a, b, c, d, and e, respectively. Since the z axes of the individual Mn^{2+} spectra made angles of about 8° with the crystal c axis, "forbidden" hyperfine lines of appreciable intensities were observed in group c, and weaker ones were present in group b. Because of the overlap of allowed and forbidden spectra in these groups, the measurements were confined to the remaining groups. In Fig. 1 the average displacements for the hyperfine lines of

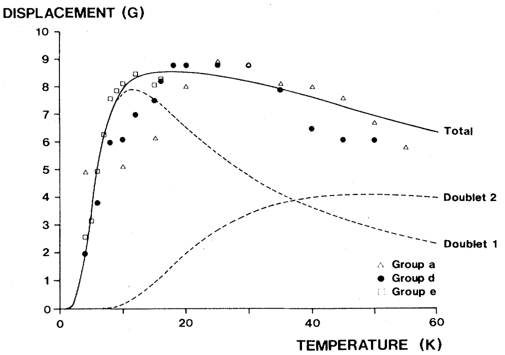

FIG. 1. Average displacements to higher fields for the hyperfine lines of groups a, d, and e plotted against temperature for measurements in the parallel orientation at 9.2 GHz. The experimental errors were estimated to lie between ±0.5 and ±1.0 G. The points were fitted to a theoretical curve with $J = +0.010\ \text{cm}^{-1}$ by the method given in the text. The dashed lines show the contributions to the displacements of the first and second excited Fe^{2+} doublets.

groups a, d, and e have been fitted to the theoretical curve given by Eq. (8), with H set at the central field, 3.3. kG, of the spectrum, and $J=+0.010\ \mathrm{cm}^{-1}$. The dashed curves give the separate contributions of the first and second excited Fe^{2+} doublets to the displacement. The best set of data, that for group d, was used to estimate J, with the 3.8-K point assumed to lie on the theoretical curve. The data for group a were fitted in the range 20—40 K, while the group-e data were fitted to the curve at 10 K. The general form of the theoretical curve, with a rapid change between 4 and 10 K, an extremum near 20 K, and a slow change above 20 K, were observed best in group d. In group e good data were restricted to below 20 K because of overlapping lines. In group a the rapid change below 10 K was not observed.

Linewidth measurements on groups a and d were made between 3.8 and 55 K, above which the overlap of neighboring hyperfine lines affected the results. Below 25 K the results were essentially constant with peak-to-peak linewidths ΔH_0 of approximately 21 G for group a and 28 G for group d. Above 25 K an essentially linear increase of linewidth with temperature was observed for both groups. In Fig. 2 the linewidth increase, given by

$$\Delta H'(T)=\Delta H(T)-\Delta H_0\ , \qquad (9)$$

where $\Delta H(T)$ is the measured width at temperature T, is plotted against temperature for the two groups. The theoretical curve is based on the expression of Moriya and Obata for spin-spin relaxation at low temperatures,[2] i.e.,

$$\Delta H'(T)=CT\exp(\Delta E/k_BT)\ , \qquad (10)$$

where C is a proportionality constant. Since the effective magnetic moment of the upper doublet is an order of magnitude greater than that of the lower doublet at 3.3 kG [see Eq. (3)], ΔE has been taken as $47.5\ \mathrm{cm}^{-1}$, the mean energy of the upper doublet, rather than the energy separation between the two lowest levels, as used by Moriya and Obata.[2] A good fit of the data is obtained with $C=1.2$ G/K.

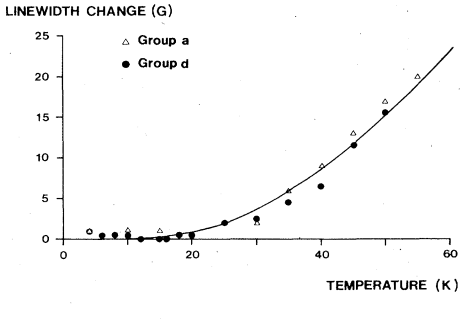

FIG. 2. Increases in the average peak-to-peak linewidths for the hyperfine lines of groups a and d plotted against temperature for measurements in the parallel orientation at 9.2 GHz. The experimental errors were estimated to lie between ±1 and ±2 G. The theoretical curve is of the form $KT\exp(-\Delta E/k_BT)$ with $K=1.2$ G/K and ΔE assumed to be $47.5\ \mathrm{cm}^{-1}$, which is the excitation of the upper Fe^{2+} doublet.

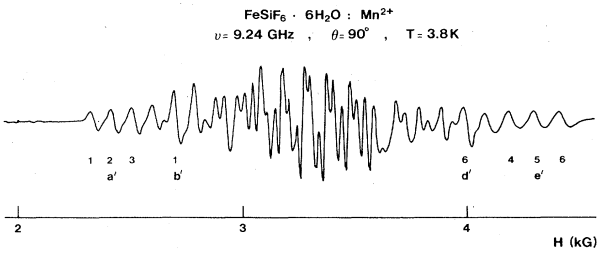

FIG. 3. 3.8-K spectrum of Mn^{2+} in $FeSiF_6\cdot 6H_2O$ perpendicular to the c axis at 9.2 GHz. The measured lines are given the designations used in Table I.

C. Perpendicular to the c axis ($\theta=90°$)

The 3.8-K EPR spectrum of Mn^{2+} in $FeSiF_6\cdot 6H_2O$ is shown in Fig. 3 for the case in which the external field is in the plane of the hexagonal crystal face, perpendicular to the c axis. The lines on which measurements were made are labeled in the same manner as in Table I, which gives the measured fields at 3.8, 10, 15, 20, and 25 K. Starting at low fields, the electronic transitions $M\leftrightarrow M-1$ with $M=-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$ are labeled a', b', c', d', and e', respectively.

The central field H_0 at each temperature was estimated using third-order perturbation theory.[17] Since the EPR spectra from the different Mn^{2+} sites were not equivalent perpendicular to the axis, the measured lines were composites of the spectra from the nonequivalent Mn^{2+} sites. As a result, the error in calculating H_0 was estimated to be as high as ±5 G.

The g-value deviation g_{ex} was obtained from Eq. (7), with the value $g_\perp=2.0$ assumed for Fe^{2+}. Because the effect of Fe^{2+}-Fe^{2+} exchange coupling on the g value is not known in this case, there may be an appreciable error in assuming this value of $g_\perp$.

The exchange coupling constant J may be estimated

TABLE I. Measured fields (peak-to-peak linewidths were 30—40 G for groups a', b', and d', and 45—50 G for group e' and estimated central fields H_0 [errors in H_0 were ±5 G (see text)] at $\theta=90°$ and $\nu=9.242$ GHz for temperatures between 3.8 and 25 K.

	Temperature (K)				
	3.8	10	15	20	25
Line	Resonance field (G)				
$a'1$	2340	2332	2311	2309	2305
$a'2$	2430	2423	2400	2398	2394
$a'3$	2522	2515	2492	2490	2485
$b'1$	2711	2703	2676	2674	2669
$d'6$	4000	3982	3958	3946	3934
$e'4$	4196	4176	4148	4136	4125
$e'5$	4307	4286	4257	4243	4232
$e'6$	4423	4401	4370	4358	4346
H_0	3363	3350	3324	3318	3310

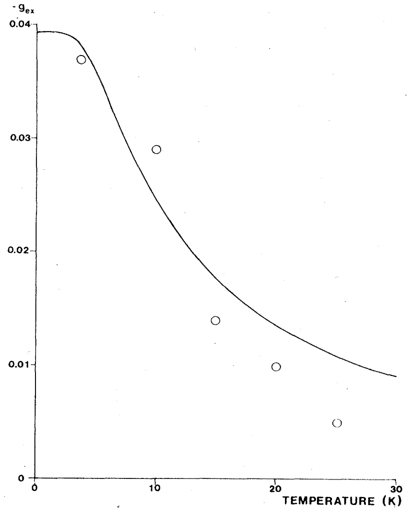

FIG. 4. A plot of the temperature dependence of the exchange contribution to the g value perpendicular to the c axis, assuming $J = +0.0065$ cm^{-1}, is given by the solid curve. The experimental points are the calculated deviations from $g_{\text{dia}} = 2.000$ obtained from the data shown in Table I. The estimated errors in the points are ±0.005.

both from the temperature dependence of the measured g value and from its deviation from the corresponding value g_{dia} in an isomorphous diamagnetic crystal, such as $MgSiF_6 \cdot 6H_2O$ (Ref. 18) and $ZnGeF_6 \cdot 6H_2O$ (Ref. 19). Both methods are combined in Fig. 4, where g_{ex} is plotted against T. The experimental points were obtained from the relationship

$$g_{\text{ex}} = g_{\text{meas}} - g_{\text{dia}} , \tag{11}$$

where g_{meas} was determined from H_0 and g_{dia} was assumed to be 2.000.[18,19] The theoretical curve was based on Eq. (7) with $J = +0.065$ cm^{-1}. With the exchange interaction between two spins written as $J\mathbf{S}_1 \cdot \mathbf{S}_2$, the positive sign refers to antiferromagnetic coupling. Assuming an error of ±0.1 in g, the final result for J was found to be

$$J = +(0.0065 \pm 0.0010) \text{ cm}^{-1} , \tag{12}$$

which is in reasonable agreement with the value $J \simeq +0.010$ cm^{-1} obtained from the data in the parallel orientation.

IV. DISCUSSION

In this work the parameter J for Mn^{2+}-Fe^{2+} superexchange in $FeSiF_6 \cdot 6H_2O$ was determined from the temperature dependence of the Mn^{2+} EPR spectrum. The molecular-field method of St. John and Myers[4] was used to interpret the displacements of the Mn^{2+} lines both parallel and perpendicular to the crystallographic c axis. Because the singlet ground level of Fe^{2+} in $FeSiF_6 \cdot 6H_2O$ is nonmagnetic parallel to the c axis, the effect of exchange was small in this orientation. However, perpendicular to the c axis the effect was an order of magnitude larger, and it was from the data for this orientation that the value $J = +0.0065$ cm^{-1} was obtained.

In order to understand the weak superexchange observed in fluorosilicate crystals of the low-temperature $P2_1/c$ structure, it is useful to measure J for as many different combinations of magnetic ion as possible. Measurements of the type given here may be used to supplement the data obtained from more conventional measurements of EPR pair spectra.

A model for these fluorosilicate lattices, analogous to that for X-Y nearest-neighbor pairs in the double-nitrate series, has been given by Francis and Culvahouse.[20] The most likely superexchange path in the fluorosilicates is of the form M-O-H-F-H-O-M', where M and M' are the magnetic ions and the $[M \cdot 6H_2O]^{2+}$ complexes are connected by hydrogen bonds to a common F^- receptor.[20] (In the double nitrates the central F^- ion is replaced by an O^{2-} ion.) In the most complete investigations to date on weak exchange interactions of this type, Culvahouse *et al.*[21–24] have studied all combinations of interactions between pairs involving Mn^{2+}, Co^{2+}, and Ni^{2+} in $La_2Zn_3(NO_3)_{12} \cdot 24H_2O$. Their theoretical model should be equally applicable to fluorosilicate crystals such as $FeSiF_6 \cdot 6H_2O$ and $MgSiF_6 \cdot 6H_2O$. This model is based in the first approximation on two assumptions:

(i) that the orbital exchange parameters are independent of the number of electrons in the incomplete $3d$ shell;

(ii) that only the e_g shell is involved in the exchange process.

Furthermore, defining the z axes of the two magnetic complexes of the pair in the directions of the water molecules involved in the hydrogen bonds restricts the e_g exchange to the d_θ orbitals only. On the basis of such a theory Culvahouse and Frances[24] obtained an average value of $k_{\theta\theta} = 0.47$ cm^{-1} for the d_θ exchange coupling, with a variation of ±20%.

In the fluorosilicates, the measured exchange parameters for Co^2-Co^{2+} and Ni^{2+}-Ni^{2+} pairs in $MgSiF_6 \cdot 6H_2O$ are consistent with those obtained for the corresponding X-Y pairs in $La_2Zn_3(NO_3)_{12} \cdot 24H_2O$, but with $k_{\theta\theta} = 0.3$ cm^{-1}. The results for Ni^{2+}-Ni^{2+} pairs in $MgTiF_6 \cdot 6H_2O$ lie between those for the two above systems. Given the similarities of the structures, one would expect comparable results in $FeSiF_6 \cdot 6H_2O$ at low temperatures. Using the value $J = 0.0065$ cm^{-1} for Mn^{2+}-Fe^{2+} coupling in the theory of Culvahouse and Francis[20] leads to a value for $k_{\theta\theta}$ of approximately 1 cm^{-1}. However, in order to obtain a direct comparison with the results in $La_2Zn_3(NO_3)_{12} \cdot 24H_2O$ or $MgSiF_6 \cdot 6H_2O$, it would be appropriate to measure Ni^{2+}-Ni^{2+}, Mn^{2+}-Mn^{2+}, or Co^{2+}-Co^{2+} pairs in $FeSiF_6 \cdot 6H_2O$.[25,26]

In the present work, weak EPR lines were observed at both the high- and low-field ends of the main isolated Mn^{2+} spectrum in the parallel orientation at 3.8 K, but insufficient data were available to confirm these spectra as being due to Mn^{2+}-Mn^{2+} pairs.

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