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Linear Chains with a Ferromagnetic Interaction in $RbFeCl_3$

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The temperature dependence of the electric field gradient of $RbFeCl_3$ has been measured in the range 4.2–300 °K ($T_N = 2.55$ °K). These results are analyzed together with the parallel and perpendicular susceptibilities observed by Achiwa. The Hamiltonian describing the system contains a single-ion crystal field term and an anisotropic bilinear interaction between nearest-neighbor Fe^{2+} pairs along the c axis. A best fit is obtained assuming a ferromagnetic pair interaction $J_{\parallel} = 5 \pm 1$ and $J_{\perp} = 11 \pm 2$ cm^{-1}, with the spins lying in the basal plane. At low temperatures ($T < T_N$) the correlation length along the chains (parallel to the c axis) is long enough for a one-dimensional spin-wave theory to be applicable. This assumes that the magnetic properties are predominantly determined by excitations propagating along the chains. Using this approach the magnetic moment per Fe^{2+} ion at 0 °K is calculated to be $2.2\mu_B$, as compared with $2\mu_B$ observed by Davidson *et al.* by neutron scattering.

I. INTRODUCTION

Recently several substances have been found to possess one-dimensional antiferromagnetic chains.[1] Theoretical models exist that describe the thermal and magnetic properties of such systems.[2] Steiner *et al.* have found indications for the existence of ferromagnetic chains in $CsNiF_3$.[3] Here we report the results of Mössbauer measurements on $RbFeCl_3$ which have been correlated with the susceptibility measurements done by Achiwa.[4] The experimental results are consistent with the existence of linear chains with a ferromagnetic interaction and spins perpendicular to the crystallographic axis, as observed by neutron diffraction by Davidson *et al.*[5]

The space group of hexagonal $RbFeCl_3$ is D_{6h}^4. The Rb and Cl ions form a hcp lattice, and the Fe^{2+} ions occupy the octahedral interstices surrounded by six Cl^- ions. The octahedra form an infinite chain along the hexagonal axis. There is a much stronger magnetic interaction between the Fe^{2+} ions along the c axis than between those in the same layers perpendicular to this axis. This results in a very low transition temperature ($T_N = 2.55$ °K)[5] into a three-dimensional ordered state. For temperatures above T_N, the intrachain interactions solely determine the magnetic properties of this crystal.

In $RbFeCl_3$ the axial crystalline field at the Fe^{2+} ion is of the same order of magnitude as the spin-orbit interaction. The combination of these two interactions determines the single-ion anisotropy energy and the form of the magnetic interaction between pairs of Fe^{2+} ions. This problem is dealt with in Sec. II. In Sec. III we develop the theory of the magnetic properties in the paramagnetic phase of $RbFeCl_3$, using the basic system of a pair of interacting Fe^{2+} ions. In Sec. IV the one-dimensional spin-wave theory for the ferromagnetic chain is used to describe the elementary excitations of $RbFeCl_3$ in its ordered phase. It is shown that this theory correctly explains the observed value of the zero-point magnetic moment per Fe^{2+} ion.

II. SINGLE-ION AND MAGNETIC INTERACTIONS

The single-ion anisotropy plays an important role in determining the magnetic properties of $RbFeCl_3$. Each Fe^{2+} ion is subjected to the crystalline field produced chiefly by the distorted octahedron of Cl^- neighboring ions. The situation is similar to other cases of $(FeCl_6)^{4-}$ octahedra.[6] In the weak-field approximation that is applicable here the ^5D term of Fe^{2+} is split by the cubic component of the crystalline field. The lower-lying $^5T_{2g}$ level is further split by the spin-orbit interaction and the residual trigonal component of the crystal field. The perturbing Hamiltonian for the $^5T_{2g}$ level has the form $\mathcal{H} = -\Delta(L_z^2 - 2) - \lambda \vec{L} \cdot \vec{S}$, where Δ measures the axial crystal field strength, λ is the spin-orbit coupling constant, and $L = 2$, $S = 2$. The sign of Δ can be determined from Mössbauer studies on the Fe^{2+} ion in a single crystal. The ground state of the Fe^{2+} ion in the crystal is a singlet for $\Delta > 0$ and a doublet for $\Delta < 0$. The sign of the V_{zz} component of the electric field gradient (EFG) is negative for the singlet and positive for the doublet. For an axially symmetric EFG and a thin absorber, the sign of V_{zz} can be determined from the ratio of the intensities of the two transitions of the ^{57m}Fe nucle-

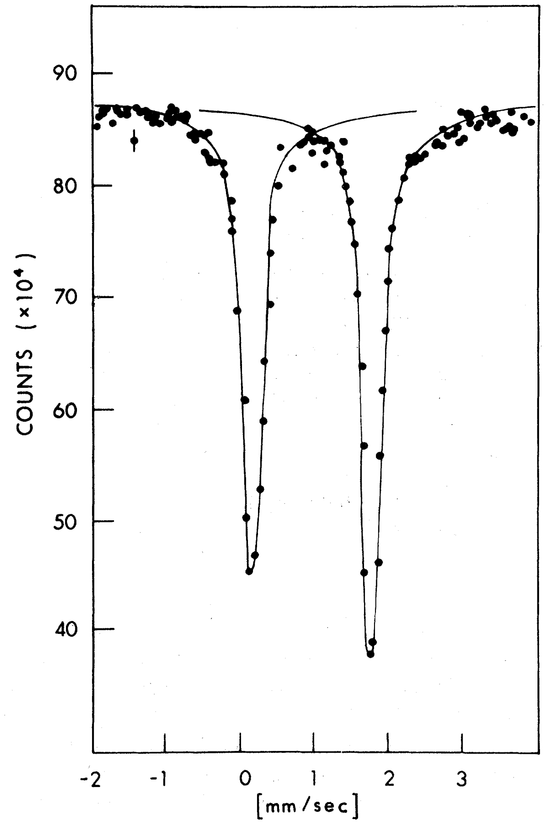

FIG. 1. Typical Mössbauer spectrum of $RbFeCl_3$, $T = 174.5$ °K.

us[7]: $\pm\frac{3}{2} \to \pm\frac{1}{2}$ and $\pm\frac{1}{2} \to \pm\frac{1}{2}$.

The Mössbauer measurements were of $RbFeCl_3$ single crystals and powdered samples for the temperature range 4.2–300 °K. $RbFeCl_3$ possesses a cleavage plane which contains the c axis. Crystals were cut with the EFG principal axis (z axis) in the plane. Down to 4.2 °K the Mössbauer spectrum of $RbFeCl_3$ shows a well-defined quadrupole splitting (Q.S.) with a value of 1.47 mm/sec at room temperature (r.t.). The spectra were recorded and analyzed by a nonlinear-least-squares program (Fig. 1). In addition, measurements at different angles between the γ ray and the z axis were carried out at r.t., where the magnetic interactions are negligible. From these measurements on single crystals it was found that $V_{zz} < 0$, and thus $\Delta > 0$.

We now turn to the problem of determining the magnetic contribution to the Hamiltonian. It is observed (see Sec. III) that in the low-temperature region ($T < 70$ °K) the experimental results for the EFG could not be explained by a single-ion Hamiltonian alone. The exchange interaction between the Fe^{2+} ions must be introduced. Although the $^5T_{2g}$ level of Fe^{2+} is orbitally degenerate, it has been proven experimentally[8] that a Heisenberg interaction between the *real spins* of the ions is adequate to explain many magnetic properties. Thus we assume the magnetic interaction between two Fe^{2+} ions to be of the form

$$\mathcal{H}_{ij} = -2J'_{ij}\vec{S}_i \cdot \vec{S}_j \ . \qquad (1)$$

Now, for $|\Delta/\lambda| \lesssim 1$, the three lowest single-ion levels (a singlet and a doublet separated by a few cm^{-1}) lie well below the other levels, so that at low temperatures the basic system is described by an effective $s = 1$. In order to transform from the real spin to effective-spin systems, the conversion factors[9] are used: $\alpha_\parallel s_z = S_z$; $\alpha_\perp s_x = S_x$; $\alpha_\perp s_y = S_y$. Then the exchange Hamiltonian for a pair of Fe^{2+} ions, both in the ground $s = 1$ state, takes the form

$$\mathcal{H}_{ij} = -2\alpha_\parallel^2 J'_{ij} s_i^z s_j^z - 2\alpha_\perp^2 J'_{ij}(s_i^x s_j^x + s_i^y s_j^y) \ . \qquad (2)$$

Denoting $J_\parallel^{ij} = \alpha_\parallel^2 J'_{ij}$, $J_\perp^{ij} = \alpha_\perp^2 J'_{ij}$, we see that a measure of the anisotropy in the magnetic interaction is given by $\alpha_\parallel^2/\alpha_\perp^2$.

In Fig. 2 $\alpha_\parallel^2/\alpha_\perp^2$ is plotted vs Δ/λ. For Δ/λ outside the plotted region the admixture of upper single-ion levels is large enough for the fictitious $s = 1$ approximation to break down. It is observed that for Δ/λ negative (positive), $J_\perp > J_\parallel$ ($J_\perp < J_\parallel$). Thus for Δ/λ negative the spins tend to point in the x-y plane, while for Δ/λ positive they point in the z direction. We can now write the total Hamiltonian appropriate for the lowest $s = 1$ state of Fe^{2+} interacting ions in $RbFeCl_3$ in the form

$$\mathcal{H} = D\sum_i (s_i^z)^2 - \sum_{\langle ij\rangle}{}' \left[2J_\parallel s_i^z s_j^z + J_\perp(s_i^+ s_j^- + s_i^- s_j^+)\right]$$
$$- g_\parallel \mu_B H_0^z \sum_i s_i^z - \tfrac{1}{2} g_\perp \mu_B H_0^\perp \sum_i (s_i^- + s_i^+) \ , \qquad (3)$$

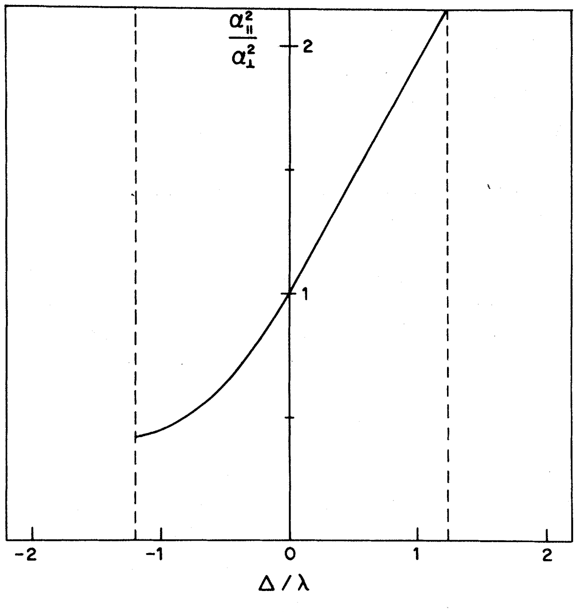

FIG. 2. $\alpha_\parallel^2/\alpha_\perp^2$ vs Δ/λ.

where $g_\parallel$ and $g_\perp$ are the gyromagnetic factors, μ_B is the Bohr magneton, and H_0^z and $H_0^\perp$ are the components of the external magnetic field. The magnetic interaction is assumed to be taken between nearest neighbors (nn) only because of their proximity relative to other neighboring Fe^{2+} ions in $RbFeCl_3$.

The elementary excitations of the system described by this Hamiltonian can be treated in two ways, each applicable in a rather different regime. The first assumes that the linear chain can be substituted by a set of interacting pairs of Fe^{2+} ions with no interaction between the pairs. This simple model provides a good description of the magnetic properties of $RbFeCl_3$ in the temperature region above the three-dimensional ordering temperature. It has the obvious advantage of facilitating the calculation of thermodynamic functions, especially in a case such as this, where the spin dimensionality $s > \frac{1}{2}$ and a single-ion anisotropy are present. It should also be stressed that neither exact nor numerical calculations are available for such systems.

The other approach is applicable for $T < T_N$, where the correlation length along the chains is long. Then the elementary excitations are predominantly spin waves propagating along the chains.

III. PARAMAGNETIC REGION

In order to explain the Mössbauer effect and the magnetic susceptibilities for $T > T_N$ we may adopt a cluster model.[10,11] Basically, such a model assumes a magnetic interaction of the form given by Eq. (3) for the ions within a cluster, and the interaction with the rest of the magnetic ions in the crystal is represented by an effective field. The appropriate cluster for $RbFeCl_3$ can be taken as a pair of nn Fe^{2+} ions along the chain. It was observed by Davidson *et al.*[5] that the correlation length between Fe^{2+} ions along the chain is about 2–3 Å at 20 °K, corresponding to the distance between *a pair of ions*. Thus the magnetic Hamiltonian of Eq. (3) can be substituted by[12]

$$\mathcal{H}_{12} = D[(s_1^z)^2 + (s_2^z)^2] - [2J_\parallel s_1^z s_2^z + J_\perp(s_1^+ s_2^- + s_1^- s_2^+)] - g_\parallel \mu_B H^z(s_1^z + s_2^z) - \tfrac{1}{2} g_\perp \mu_B H^\perp(s_1^+ + s_2^+ + s_1^- + s_2^-) . \tag{4}$$

Here $\vec{H} = \vec{H}^0 + \vec{H}_{eff}$, where $\vec{H}_{eff}$ (which is due to all other magnetic ions) is proportional to the magnetization. In the paramagnetic region the magnetization vanishes, in spite of the fact that there might be some short-range order along the chains. This results in $\vec{H}_{eff} = 0$, and $\mathcal{H}_{12}$ reduces into a simple pair Hamiltonian (including a Zeeman term). There might still arise the possibility of assuming the basic cluster as consisting of more than two ions. This approach was utilized by Bonner and Fisher[13] for the case of a finite one-dimensional chain of spins with $s = \frac{1}{2}$. The computational complications in the anisotropic case with $s = 1$ treated here are great even for a four-spin system.

We can show, however, that the pair system gives comparable results for the magnetic susceptibility, as does an exact expansion in a simplified case. Consider the case of a one-dimensional chain with a Heisenberg interaction: $\mathcal{H} = -2J \times \sum_{ij} \vec{S}_i \cdot \vec{S}_j$. The high-temperature expansion for the magnetic susceptibility was derived by Rushbrook and Wood.[14] Using their results we have calculated $(k_B T \chi)^{-1}$ vs $k_B T J^{-1}$ for the spin dimensionalities $s = \frac{1}{2}$ and 1. The results are shown in dashed lines in Fig. 3. For comparison, the same function is calculated using the pair Hamiltonian $(\mathcal{H}_{12} = -2J\vec{S}_1 \cdot \vec{S}_2)$, and the results are shown in solid lines in Fig. 3. For high temperatures $(kT/J \gg 1)$ both models tend to the same value, while for low temperatures $(kT/J \sim 1)$ they deviate by some 20%. However, it should be remembered that for this region the high-temperature expansion

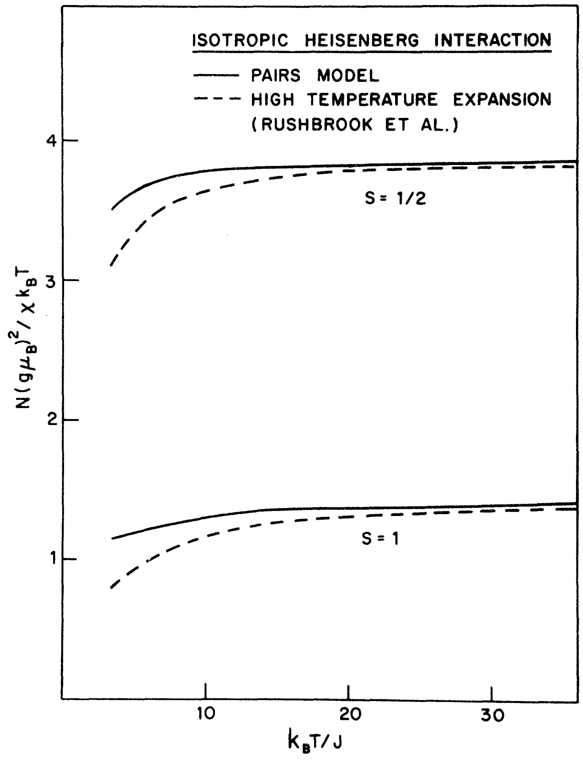

FIG. 3. $N(g\mu_B)^2/\chi k_B T$ vs $k_B T/J$ for a ferromagnetic interaction. For $s = 1$ we have taken six terms in the high-temperature expansion; for $s = \frac{1}{2}$ ten terms were considered in the high-temperature expansion. For kT/J around unity, the high-temperature expansion is no more reliable. Solid line—pairs model. Dashed line—high temperature expansion (Rushbrook *et al.*).

is no more reliable.

In view of these considerations it is expected that the pair Hamiltonian of Eq. (4) (with $\vec{H}=\vec{H}_0$) would yield satisfactory results for the magnetic susceptibilities and EFG in the region $T > T_N$. We thus proceed by diagonalizing $\mathcal{H}_{12}$ in the case of a magnetic field parallel to the crystallographic c axis ($H_0^{\perp}=0$, $H_0^{z}\neq 0$). The resulting eigenvalues and eigenfunctions are as follows:

$$E_1 = 2D - 2J_{\parallel} - 2g_{\parallel}\mu_B H_0\,, \quad \psi_1 = |1,1\rangle\,;$$

$$E_2 = 2D - 2J_{\parallel} + 2g_{\parallel}\mu_B H_0\,, \quad \psi_2 = |-1,-1\rangle\,;$$

$$E_3 = D - 2J_{\perp} - g_{\parallel}\mu_B H_0\,, \quad \psi_3 = \frac{1}{\sqrt{2}}(|1,0\rangle + |0,1\rangle)\,;$$

$$E_4 = D + 2J_{\perp} - g_{\parallel}\mu_B H_0\,, \quad \psi_4 = \frac{1}{\sqrt{2}}(|1,0\rangle - |0,1\rangle)\,;$$

$$E_5 = D - 2J_{\perp} + g_{\parallel}\mu_B H_0\,, \quad \psi_5 = \frac{1}{\sqrt{2}}(|-1,0\rangle + |0,-1\rangle)\,;$$

$$E_6 = D + 2J_{\perp} + g_{\parallel}\mu_B H_0\,, \quad \psi_6 = \frac{1}{\sqrt{2}}(|-1,0\rangle - |0,-1\rangle)\,;$$

and eigenvalues

$$\begin{aligned} &E_7 = 2D + 2J_{\parallel}\,,\\ &E_{8,9} = D + J_{\parallel} \pm [(D+J_{\parallel})^2 + 8J_{\perp}^2]^{1/2}\,, \end{aligned} \tag{5}$$

with eigenfunctions

$$\psi_7 = \frac{1}{\sqrt{2}}(|1,-1\rangle + |-1,1\rangle)\,,$$

$$\psi_8 = C_1\left(|1,-1\rangle + \frac{D + J_{\parallel} - [(D+J_{\parallel})^2 + 8J_{\perp}^2]^{1/2}}{2J_{\perp}}\,|0,0\rangle + |-1,1\rangle\right),$$

$$\psi_9 = C_2\left(|1,-1\rangle + \frac{D + J_{\parallel} + [(D+J_{\parallel})^2 + 8J_{\perp}^2]^{1/2}}{2J_{\perp}}\,|0,0\rangle + |-1,1\rangle\right),$$

$$C_1 = \left(2 + \frac{\{D + J_{\parallel} - [(D+J_{\parallel})^2 + 8J_{\perp}^2]^{1/2}\}^2}{4J_{\perp}^2}\right)^{-1/2},$$

$$C_2 = \left(2 + \frac{\{D + J_{\parallel} + [(D+J_{\parallel})^2 + 8J_{\perp}^2]^{1/2}\}^2}{4J_{\perp}^2}\right)^{-1/2}$$

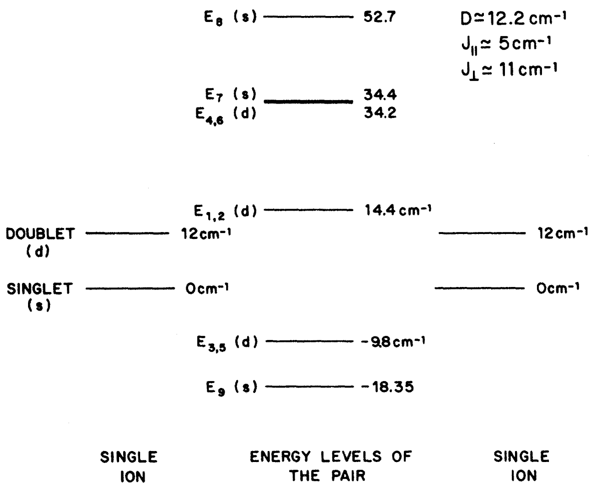

FIG. 4. Energy levels for a pair of nn Fe^{2+} ions. The numbers indicated correspond to the levels given in Eq. (5) with $H_0 = 0$.

The energy-level scheme for a pair of nn Fe^{2+} ions is shown in Fig. 4. The parameters D, $J_{\parallel}$, and $J_{\perp}$ used to calculate the energy levels are those obtained by the best fit to the experimental results. For zero external field there is no magnetization as expected, since there is no long-range order. The parallel susceptibility at zero field is given by

$$\chi_{\parallel}|_{H_0=0} = \frac{2N}{k_B T}(g_{\parallel}\mu_B)^2\left\{\left[2\exp\left(-\frac{2D-2J_{\parallel}}{k_B T}\right) + e^{-D/k_B T}\cosh\left(\frac{2J_{\perp}}{k_B T}\right)\right]\right\}\Big/ Z\,, \tag{6}$$

where

$$\begin{aligned} Z = {} & 4e^{-2D/k_B T}\cosh\left(\frac{2J_{\parallel}}{k_B T}\right) + 4e^{-D/k_B T}\cosh\left(\frac{2J_{\perp}}{k_B T}\right) \\ & - \exp\left(-\frac{2D+2J_{\parallel}}{k_B T}\right) \\ & + 2\exp\left(-\frac{D+J_{\parallel}}{k_B T}\right)\cosh\left(\frac{[(D+J_{\parallel})^2 + 8J_{\perp}^2]^{1/2}}{k_B T}\right). \end{aligned}$$

In Appendix A we have calculated the perpendicular susceptibility using the perturbation theory, for the case $H_0 \to 0$. In Fig. 5 the calculated susceptibilities were compared with the experimental data of Ref. 4.

The quadrupole splitting in an axial symmetric EFG is given by[15]

$$\Delta E_Q = \tfrac{1}{7} e^2 Q \langle r_{3d}^{-3}\rangle_{\text{eff}} \langle L_z^2 - 2\rangle_T + \tfrac{1}{2} e^2 Q q_{\text{latt}}\,,$$

where $\langle r_{3d}^{-3}\rangle_{\text{eff}}$ includes both covalency and antishielding corrections. We have calculated the thermal average of $L_z^2 - 2$ for the lower three levels using Hamiltonian (2). The results are given in Appendix B. $\langle r_{3d}^{-3}\rangle_{\text{eff}}$ assumes the value of $3.7 a_0^{-3}$ by fitting the experimental results with $Q = 0.21$ b.[16] If we assume a larger $Q \sim 0.24$ b, then $\langle r_{3d}^{-3}\rangle_{\text{eff}} \sim 3.24 a_0^{-3}$, so that from an experimental point of view only the product can be determined. The lattice contribution to the EFG was evaluated following Ingalls[15] and was estimated to be ~ 0.03

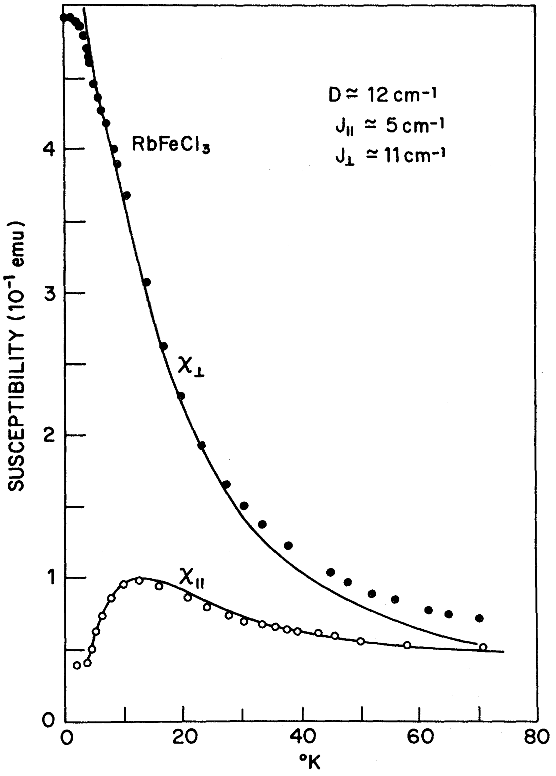

FIG. 5. Parallel and perpendicular susceptibility vs temperature. Experimental data—Ref. 4. Solid line—theoretical fit (present work).

mm/sec.

In Fig. 6 the experimentally observed Q.S. as a function of temperature is compared with calculation. The contribution of the ground ($s=1$) state was computed by using the formulas of Appendix B. The contribution of the higher *single-ion* states is calculated without magnetic interaction. The total calculated Q.S. is shown by the solid line. By fitting the susceptibilities and Mössbauer measurements, the following values are obtained for the ground-state interaction parameters: $D=12.2 \pm 1\ \mathrm{cm}^{-1}$, $J_{\parallel}=5\pm 1\ \mathrm{cm}^{-1}$, $J_{\perp}=11\pm 2\ \mathrm{cm}^{-1}$, $g_{\parallel}=3.52 \pm 0.10$, $g_{\perp}=2.90\pm 0.25$.

The uncertainties in these parameters indicate the ranges over which a good fit is obtained. We obtain, in turn, for the single Fe^{2+} ion $-\Delta/\lambda \sim 0.75-0.80$, $\lambda=78\pm 5\ \mathrm{cm}^{-1}$. The calculated ratio of the conversion factors is $\alpha_{\parallel}^2/\alpha_{\perp}^2=0.52$, yielding $J_{\parallel}\alpha_{\perp}^2 \sim J_{\perp}\alpha_{\parallel}^2$, as expected.[8]

IV. ORDERED STATE

At low temperatures (around T_N) the correlation length along the chains (parallel to the c axis) is long enough to make a one-dimensional spin-wave theory applicable. Since the magnetic interaction between Fe^{2+} ions along the chain is much stronger than the interchain interaction, the magnetic properties are predominantly determined by excitations propagating along the chain. In the three-dimensional ordered state the spin waves propagating in directions perpendicular to the chains are expected to have energies much smaller than those along the chain. Such behavior is expected to be found in all one-dimensional magnetic systems that undergo a phase transition at low temperatures (e.g., $RbNiCl_3$ and $CsNiCl_3$, recently treated along these lines[17]).

The Hamiltonian (1) is written in the crystallographic coordinates. Since the equilibrium direction of the spins along a given chain is perpendicular to the crystallographic c axis, the Hamiltonian should be transformed into the local spin coordinates. Also, since the spins along the chain order ferromagnetically the dipolar interaction should be introduced. Generally, it is smaller relative to other sources of anisotropy, but in the present case it brings about a finite energy gap in the spin-wave spectrum at $k=0$. The dipolar interaction is given by[18]

$$\mathcal{H}_d=\sum_{ij}\frac{g^2\mu_B^2}{r_{ij}^3}\left[\vec{s}_i\cdot\vec{s}_j-3r_{ij}^{-2}(\vec{s}_i\cdot\vec{r}_{ij})(\vec{s}_j\cdot\vec{r}_{ij})\right] .$$

After transforming to the local spin axis (ξ, η, ζ) and using the Holstein–Primakoff approximation, one obtains

$$\begin{aligned}\mathcal{H}&=E_0+\sum_k A_k a_k^{\dagger}a_k+\sum_k \tfrac{1}{2}B_k(a_k^{\dagger}a_{-k}^{\dagger}+a_k a_{-k}) ,\\ E_0&=DN-\tfrac{1}{2}DN\sin^2\theta-Ng_{\parallel}\mu_B H_0^z\cos\theta\\ &\quad -Ng_{\perp}\mu_B H_0^x\sin\theta+4N(J_{\parallel}\cos^2\theta+J_{\perp}\sin^2\theta)\\ &\qquad -NE(0)\left(\tfrac{1}{2}-\tfrac{3}{4}\sin^2\theta\right) ,\end{aligned} \tag{7}$$

where θ is the angle between the ζ and z axes and

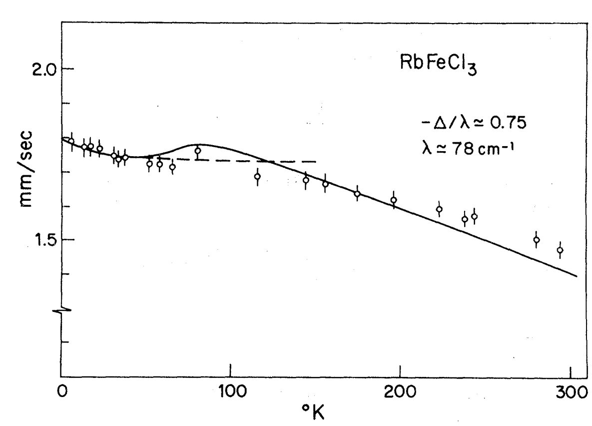

FIG. 6. Quadrupole splitting vs temperature. Dashed line—contribution from ground state ($s=1$) with magnetic interaction. Solid line—total Q.S. including perturbation from excited states.

N is the number of spins in a particular chain.

Here also

$$E(0)=(1.202\cdots)\,\frac{(g_\perp\mu_B)^2}{r^3}\ ,$$

and r is the distance between magnetic atoms along the chain.

Further, here we have

$$\begin{aligned}A_k={}&-8(J_\parallel\cos^2\theta+J_\perp\sin^2\theta)\\&+4\cos(kr)\,[J_\parallel\sin^2\theta\ +J_\perp(\cos^2\theta+1)]\\&+g_\parallel\mu_B H_0^z\cos\theta+3D\sin^2\theta-2D+g_\perp\mu_B H_0^x\sin\theta\\&+2E_k(\tfrac{1}{2}-\tfrac{3}{4}\sin^2\theta)-E(0)\,(\sin^2\theta-2\cos^2\theta)\ ,\end{aligned}$$

$$E_k=2\sum_j E_{0j}e^{ik\cdot r_{0j}}\ ,$$

$$E_{ij}=-\frac{1}{4}\,\frac{(g_\perp\mu_B)^2}{r_{ij}^3}\left[1-3\left(\frac{r_{ij}^z}{r_{ij}}\right)^2\right],$$

$$B_k=D\sin^2\theta-4\cos(kr)\,(J_\perp-J_\parallel)\sin^2\theta-3E_k\sin^2\theta\ .$$

The minimum energy condition (minimum in E_0 with respect to θ) is obtained for $\sin\theta=1$ when $H^z=0$. Linear terms in $a^\dagger$ and a do not appear since their coefficient is identically zero (a result of the minimum imposed on E_0).[19]

The Hamiltonian (6) is diagonalized using a Boguliubov transformation[18]:

$$\begin{aligned}&\mathcal{H}=E_0-\frac{1}{2}\sum_k A_k+\sum_k\epsilon_k\ (c_k^\dagger c_k+\tfrac{1}{2})\ ,\\&\epsilon_k=(A_k^2-B_k^2)^{1/2}\ ,\end{aligned}\tag{8}$$

with the conditions

$$A_k>0\ ,\quad A_k>B_k\ .$$

All the thermodynamic properties can be derived from the partition function

$$Z=\exp\left(-\frac{E_0-\frac{1}{2}\sum_k(A_k-\epsilon_k)}{k_BT}\right)\times\prod_k\left[1-\exp\left(-\frac{\epsilon_k}{k_BT}\right)\right]^{-1}.\tag{9}$$

The magnetization (perpendicular to the chain) is given by

$$\begin{aligned}&M(T)=-\frac{\partial E_0}{\partial H_0^x}+\frac{1}{2}\sum_k\frac{\partial A_k}{\partial H_0^x}-\sum_k\frac{\partial\epsilon_k}{\partial H_0^x}\left(n_k+\frac{1}{2}\right)\ ,\\&n_k=\frac{1}{e^{\epsilon_k/k_BT}-1}\ .\end{aligned}\tag{10}$$

For the single-ion magnetic moment at zero temperature we have

$$\langle s^\zeta\rangle_{T=0}=\tfrac{3}{2}g_\perp\mu_B-\frac{g_\perp\mu_B}{2\pi}\int_0^\pi\frac{A_Q\,dQ}{(A_Q^2-B_Q^2)^{1/2}}\ ,\tag{11}$$

where

$$A_Q=D+8J_\perp-4\cos Q\,(J_\perp+J_\parallel)-\tfrac{1}{2}(E_Q)-E(0)\ ,$$

$$B_Q=D+4\cos Q\,(J_\perp-J_\parallel)-3E_Q\ .$$

With the values of $g_\perp$, D, $J_\parallel$, and $J_\perp$ found in Sec. III we obtain

$$\langle s^\zeta\rangle_{T=0}=(2.2\pm0.2)\mu_B$$

(the integral is computed numerically).

Recently, neutron scattering measurements made by Davidson *et al.*[5] gave a value of $(1.6-2)\mu_B$ for the magnetic moment of the Fe^{2+} ion extrapolated to 0 °K. Although the calculated value is larger than the experimental one it indicates the importance of the zero-point spin deviations in reducing the magnetic moment from its maximum expected value $\langle s^\zeta\rangle_{\max}=2.90\mu_B$.

We conclude that $\mathrm{RbFeCl_3}$ is an example of a compound where ferromagnetic interaction between pairs of neighboring ions affects considerably the magnetic properties over a wide temperature range (above T_N). Below T_N the magnetic properties are predominantly determined by spin-wave excitations propagating along the chain.

ACKNOWLEDGMENT

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APPENDIX A: CALCULATION OF PERPENDICULAR SUSCEPTIBILITY ($s=1$) FOR A PAIR OF INTERACTING SPINS IN THE LIMIT $H_0^\perp\to0$

We will use perturbation theory for the calculation of the eigenvalues of the pair Hamiltonian with spin equal to 1 in the presence of a perpendicular magnetic field. Since there are degenerate levels, we will use perturbation theory for degenerate levels. It is possible to apply perturbation theory since we are interested in the limit $H_0^\perp\to0$.

The perturbation term is

$$V=(\tfrac{1}{2}h)\,(s_1^++s_2^++s_1^-+s_2^-)\ ,\tag{A1}$$

where $h=g_\perp\mu_B H_0^\perp$.

Only terms of the form

$$\sum_m\frac{\langle n|V|m\rangle\langle m|V|n'\rangle}{E_n^0-E_m^0}$$

contribute. The first-order terms are zero. After doing the calculation we obtain the following energy eigenvalues:

$$E_1=2D-2J_\parallel+\frac{h^2}{D-2J_\parallel+2J_\perp}\ ,$$

$$E_2=E_1\ ,$$

$$E_3=D-2J_\perp+\frac{h^2}{2J_\parallel-2J-D}$$

$$+\frac{2h^2C_1^2\{D+J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2} + 2J_\perp\}^2}{\{-2J_\perp - J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2}\}4J_\perp^2}$$

$$+\frac{2h^2C_2^2\{D+J_\| + [(D+J_\|)^2+8J_\perp^2]^{1/2} + 2J_\perp\}^2}{4J_\perp^2\{-2J_\perp - J_\| + [(D+J_\|)^2+8J_\perp^2]^{1/2}\}}$$

$$+\frac{h^2}{-D-2J_\perp-2J_\|} ,$$

$$E_4 = D+2J_\perp ,$$

$$E_5 = D-2J_\perp+\frac{h^2}{-2J_\perp-D+2J_\|} , \tag{A2}$$

$$E_6 = E_4 ,$$

$$E_7 = 2D+2J_\| + \frac{h^2}{D+2J_\|+2J_\perp} ,$$

$$E_8 = D+J_\| + [(D+J_\|)^2+8J_\perp^2]^{1/2}$$

$$+\frac{2h^2C_1^2\{D+J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2} + 2J_\perp\}^2}{4J_\perp^2\{2J_\perp + J_\| + [(D+J_\|)^2+8J_\perp^2]^{1/2}\}} ,$$

$$E_9 = D+J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2}$$

$$+\frac{2h^2C_2^2\{D+J_\| + [(D+J_\|)^2+8J_\perp^2]^{1/2} + 2J_\perp\}^2}{4J_\perp^2\{2J_\perp + J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2}\}} .$$

C_1 and C_2 are given in Eq. (5).

The partition function is given by

$$Z = z^{N/2} , \tag{A3}$$

where

$$z = \sum_{i=1}^{g} e^{-E_i/k_BT} .$$

Then we obtain for the magnetization

$$M(T) = k_BT\,\frac{\partial \ln Z}{\partial H_0} , \tag{A4}$$

$$M(T) = \frac{N}{2}\,\frac{h}{Z}\left[-\frac{2e^{-E_7/k_BT}}{D+2J_\|+2J_\perp} + 2a_1e^{-E_8/k_BT} + 2b_1e^{-E_9/k_BT} - \frac{4e^{-E_1/k_BT}}{D-2J_\|+2J_\perp}\right.$$
$$\left. -2\left(\frac{2}{-2J_\perp-D+2J_\|} - \frac{1}{D+2J_\|+2J_\perp} + a_1 + b_1\right)e^{-E_3/k_BT}\right] ,$$

where

$$a_1 = \frac{2\{D+J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2} + 2J_\perp\}^2}{\{8J_\perp^2 + (D+J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2})^2\}\{-2J_\perp - J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2}\}} ,$$

$$b_1 = \frac{2\{D+J_\| + [(D+J_\|)^2+8J_\perp^2]^{1/2} + 2J_\perp\}^2}{\{8J_\perp^2 + (D+J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2})^2\}\{-2J_\perp - J_\| + [(D+J_\|)^2+8J_\perp^2]^{1/2}\}} .$$

The susceptibility is obtained from

$$\chi_\perp = \left.\frac{M(T)}{H_0^\perp}\right|_{H_0^\perp \to > 0} :$$

$$\chi_\perp = 2N(g_\perp\mu_B)^2\,\frac{R_1+R_2-R_3-R_4-R_5}{Z} ,$$

$$Z = 2\exp\left(-\frac{2D-2J_\|}{k_BT}\right) + 2\exp\left(-\frac{D-2J_\perp}{k_BT}\right)$$
$$+ 2\exp\left(-\frac{D+2J_\perp}{k_BT}\right) + \exp\left(-\frac{2D+2J_\|}{k_BT}\right)$$
$$+ 2\exp\left(-\frac{D+J_\|}{k_BT}\right)\cosh\left(\frac{[(D+J_\|)^2+8J_\perp^2]^{1/2}}{k_BT}\right) ,$$

$$R_1 = \frac{a_1}{2}\exp\left(-\frac{D+J_\| + [(D+J_\|)^2+8J_\perp^2]^{1/2}}{k_BT}\right) , \tag{A5}$$

$$R_2 = \frac{b_1}{2}\exp\left(-\frac{D+J_\| - [(D+J_\|)^2+8J_\perp^2]^{1/2}}{k_BT}\right) ,$$

$$R_3 = \frac{1}{D-2J_\|+2J_\perp}\exp\left(-\frac{2D-2J_\|}{k_BT}\right) ,$$

$$R_4 = \left(\frac{1}{-2J_\perp-D+2J_\|} - \frac{1}{2(D+2J_\|+2J_\perp)} + \frac{a_1}{2} + \frac{b_1}{2}\right)$$
$$\times\exp\left(-\frac{D-2J_\perp}{k_BT}\right) ,$$

$$R_5 = \frac{1}{2(D+2J_\|+2J_\perp)}\exp\left(-\frac{2D+2J_\|}{k_BT}\right) .$$

APPENDIX B: CALCULATION OF 3*d* ELECTRON CONTRIBUTION TO EFG

In axial symmetric field the EFG is given by

$$V_{zz} = (\tfrac{1}{7}2e)\,\langle r^{-3}\rangle_{\text{eff}}\,\langle L_z^2 - 2\rangle_T ,$$

$$\langle L_z^2 - 2\rangle_T = \frac{(P_+ + P_-)X + QY}{Z} ,$$

$$X=\frac{1}{2}\left[2\exp\left(-\frac{2D-2J_{\parallel}}{k_BT}\right)+\exp\left(-\frac{D+2J_{\perp}}{k_BT}\right)+\exp\left(-\frac{D-2J_{\perp}}{k_BT}\right)+\exp\left(-\frac{2D+2J_{\parallel}}{k_BT}\right)+\frac{8J_{\perp}^2}{8J_{\perp}^2+\{D+J_{\parallel}-[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}\}^2}\right.$$

$$\left.\times\exp\left(-\frac{D+J_{\parallel}+[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}}{k_BT}\right)+\frac{8J_{\perp}^2}{8J_{\perp}^2+\{D+J_{\parallel}+[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}\}}\exp\left(-\frac{D+J_{\parallel}-[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}}{k_BT}\right)\right],$$

$$Y=\exp\left(-\frac{D+2J_{\perp}}{k_BT}\right)+\exp\left(-\frac{D-2J_{\perp}}{k_BT}\right)+\frac{\{D+J_{\parallel}-[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}\}^2}{8J_{\perp}^2+\{D+J_{\parallel}-[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}\}^2}\exp\left(-\frac{D+J_{\parallel}+[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}}{k_BT}\right)$$

$$+\frac{\{D+J_{\parallel}+[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}\}^2}{8J_{\perp}^2+\{D+J_{\parallel}+[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}\}^2}\exp\left(-\frac{D+J_{\parallel}-[(D+J_{\parallel})^2+8J_{\perp}^2]^{1/2}}{k_BT}\right).$$

With $E_1=E_{-1}$ and E_0 denoting the energies of the three lowest levels of the single-ion Hamiltonian $\mathcal{H}=-\Delta\times(L_g^2-2)-\lambda\vec{L}\cdot\vec{S}$ the numerical factors P and Q assume the values

$$P_{\pm}=1-3\left(\frac{3\lambda^2}{(E_{\pm 1}+\Delta)^2}+\frac{2\lambda^2}{(2\lambda+E_{\pm 1}+\Delta)^2}+1\right)^{-1},\qquad Q=\frac{-2(\Delta+E_0+\lambda)^2+6\lambda^2}{(\Delta+E_0+\lambda)^2+6\lambda^2}.$$

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[19] Since we have taken dipolar interaction merely along the chains, the sums are easy to carry out. The behavior at $k=0$ is well defined since we are looking at a closed ring and there is no dependence on the position of the magnetic ion (no surface effect).