Exchange interactions in the quasi-linear-chain antiferromagnet $KFeS_2$

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We report magnetic susceptibility measurements on $KFeS_2$ in the temperature range $4.2 < T < 300$ K. In addition to a curvature of the susceptibility curve $\chi(T)$ near 250 K, we also observe a small sharp maximum at 12.5 K characteristic of linear-chain antiferromagnetism in quasi-one-dimensional systems. The results were interpreted with use of the molecular-field approximation and the temperature-dependent Green's-function method as well as the refined molecular-field theory for the Heisenberg model. The interchain, and intrachain exchange interactions and their ratio ($\eta = 10^{-2}$) which measures the one dimensionality of the system could be estimated and compared with other results. We attribute the positive value of the paramagnetic Curie temperature $\Theta \sim +70$ K to a ferromagnetic exchange interaction J_2 between next-nearest neighbors along the chains, superimposed on the antiferromagnetic exchange J_1 between nearest neighbors. The best fit to the experimental data is obtained for $J_1/k_B \sim 23.6$ K, $J_2/k_B = 41.9$ K, and $J'/k_B = 3.3$ K, with J' being the interchain exchange constant. We suggest that the three-dimensional antiferromagnetism occurs at the Néel temperature $T_N \sim 12.5$ K rather than at 250 K as is usually assumed.

I. INTRODUCTION

The iron sulfur proteins are widely distributed in nature as major components of bioenergetic systems. Such proteins, named ferrodoxins, with linked clusters of FeS_4 tetrahedra have been widely investigated[1–3] since they play important roles in the biochemical reduction and oxidation processes.[4,5] In this respect, it may be desirable to study the magnetic properties of the potassium dithioferrate $KFeS_2$ as a spin-model compound of the ferredoxin. Actually, $KFeS_2$ is a good candidate for a spin analog of the active sites of the ferredoxins, since the basic structure consists of the same tetrahedral FeS_4 chains. Also, in the oxidized state of the two iron ferredoxins, the irons are believed to be antiferromagnetically coupled and this may be well simulated by iron atoms in $KFeS_2$.[6,7]

$KFeS_2$ is a monoclinic crystal with space-group symmetry $C2/c$ (C_{2h}^6) and includes four molecules per unit cell having all Fe at equivalent sites.[8] Mössbauer studies of this material have shown that the iron is in a trivalent state.[9–11] The Fe^{3+} ions are surrounded by a distorted tetrahedron of four S^{2-} ions. It follows that the $(FeS_2)^{1-}$ ions are arranged in chains of FeS_4 tetrahedra parallel to the c axis. The strong covalent bonding ($4s4p^3$) along the c axis expected in this situation agrees with the parallel-to-c axis needle shape of the crystals. Thus, much stronger interaction is expected between Fe^{3+} ions in the chain, with an intrachain iron-iron distance 2.70 Å, than between Fe^{3+} of adjacent chains, with an interchain Fe^{3+}-Fe^{3+} distance 6.6 Å. Then, a one-dimensional nature of iron-iron spin interaction is inferred. The spin arrangement studied by neutron-diffraction experiments[12,13] is illustrated in Fig. 1. The ratio $|J'/J_1|$ with J', the exchange integral between the chains, and J_1, the exchange integral within the chain, is of fundamental interest, since this parameter controls the spatial dimensionality of the magnetic system. Previous determinations of J'/J_1 in $KFeS_2$ have been reported by several authors.[13–15] According to Ref. 14, $\eta = |J'/J_1| \sim 4\times10^{-4}$, presuming linear-spin ordering. In Ref. 13, however, a much larger value is obtained: $\eta \sim 4\times10^{-2}$. This discrepancy mainly comes from different estimations of J_1: 1000 K in Ref. 14 and 66 K in Ref. 13. Results in Ref. 15 give intermediate values $J_1 = 245$ K and $\eta \cong 8.6\times10^{-3}$. It follows that previous determinations of J_1 and η differ by 2 orders of magnitude, so that these parameters can still be considered as unknown.

The purpose of this paper is to report magnetic suscep-

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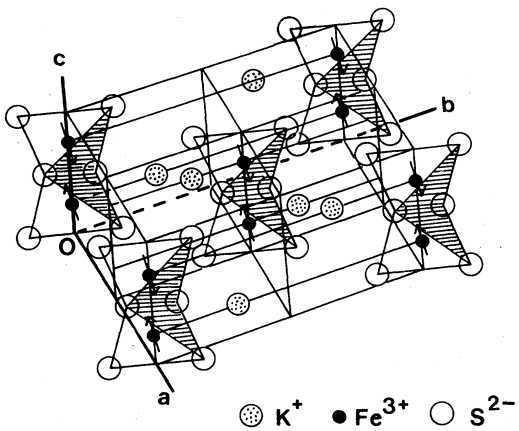

FIG. 1. Magnetic structure of $KFeS_2$, after Ref. 12.

tibility measurements on $KFeS_2$. Our experimental results are then analyzed using the molecular-field approximation and the Green's-function method as well as the refined molecular-field theory for the Heisenberg model, in order to deduce the exchange parameters.

II. EXPERIMENTS

The crystals have been formed by fusing nonoxidized Fe with sulfur and potassium carbonate and leaching the cold product in water. Large single crystals have been grown using the Bridgeman method.[16] Our samples were characterized by x-ray diffraction.

The measurements of the temperature dependence of the magnetic susceptibility $\chi(T)$ have been carried out using a Faraday balance for different samples. The results are reproducible and reported in Fig. 2. They are at variance with previous results obtained by Bronger,[17] but agree, at least qualitatively, with data reported in Ref. 13. The studies in Ref. 13 have been essentially focused on the high-temperature behavior of $\chi(T)$ up to 800 K, with emphasis on a maximum of $\chi(T)$ at $T \sim 700$ K. In this paper, we only consider the low-temperature regime in the range $4.2 < T < 300$ K.

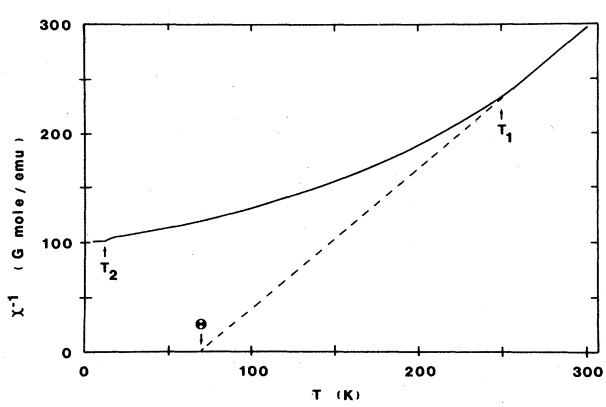

FIG. 2. Inverse of the magnetic susceptibility as a function of temperature for $KFeS_2$. Θ is the paramagnetic Curie temperature. The dashed curve is the extrapolation of the Curie-Weiss law. The solid curve is experimental and departs from the Curie-Weiss law at the transition temperature T_1. An anomaly is evidenced at T_2.

A. Magnetic behavior above the freezing temperature

In the upper range $250 < T < 300$ K a Curie-Weiss law is satisfied, as can be seen in Fig. 2, and we can write

$$\chi(T) = \frac{C}{T - \Theta} \tag{1}$$

with C the Curie constant which we can express as

$$C = \frac{p^2 \mu_B^2}{3k_B} , \tag{2}$$

where p is the effective number of Bohr magnetons μ_B carried by the magnetic ions, and k_B is the Boltzmann constant. In the case of Fe^{3+} ions in the state $^6S_{5/2}$, the theoretical value of p is

$$p_t = g[J(J+1)]^{1/2} = 5.9 \tag{3}$$

since the Landé factor is $g=2$, and the angular momentum $J = S = \frac{5}{2}$. From the fit of the experimental data by Eq. (1), it is possible to derive an effective value p_e for the parameter p entering Eq. (1). The result is

$$p_e \sim 2.5 . \tag{4}$$

This value is much smaller than p_t and in good agreement with the value 2.4 deduced from neutron experiments.[12] Since the experimental value p_e in salts of the iron is quite close to p_t, the very low value of p_e in $KFeS_2$ is a specific property of this compound. In particular, it has been argued, on the basis of multiple scattering $X\alpha$ molecular-orbital calculations, that a large spin-down electron density is transferred from the $3p$ orbitals of sulfur to Fe^{3+} sites.[18] The main difference between the actual configuration of iron in FeS_4^{5-} and a Fe^{3+} free ion, as a result of the covalent Fe—S bond, is the partial occupation of the $3d$ and the $4s$ shells. The $4s$ shell, however, is not significantly polarized, since the $4s\uparrow$ and $4s\downarrow$ populations are almost equal (~ 0.42).[18] The relevant effect which modifies the magnetic properties is then the number N_e of electrons transferred from the sulfur into the $3d\downarrow$ states. In first approximation we can take this effect into account by replacing $S = \frac{5}{2}$ by an effective spin

$$S' = S - N_e/2 . \tag{5}$$

Therefore, we can write

$$p_e = g'[S'(S'+1)]^{1/2} \tag{6}$$

with g' the effective Landé factor, to take into account possible orbital momentum effects associated with the partial occupation of the $3d$ shell. A very similar effect has been studied in europium chalcogenides where Eqs. (5) and (6) have been used to account quantitatively for the magnetic susceptibility data in these materials.[19] In the present case, however, we could not account quantitatively for the experimental value p_e unambiguously. One possibility is to suppose that the electron in the $3d$ bands are in

a pure spin state, with their orbital momentum completely quenched by the crystal-field interaction. In that case, $g'=2$. This assumption is supported by the EPR measurements[20] of the Landé factor in $KFeS_2$. Nevertheless, the value of N_e deduced from Eqs. (4)—(6) with $g'=2$ is $N_e \sim 3.30$, much larger than the value $N_e \sim 1.1$ deduced from the spin-polarized calculation in the Slater $X\alpha$ local-exchange approximation.[18] Another possibility is to suppose that $N_e=1.1$, in agreement with Ref. 18, but then the value of g' deduced from Eqs. (4)—(6) is $g' \sim 1$ and this should be observed by EPR measurements.

According to Eq. (5), $N_e=3.30$ and 1.1 lead to $S'=0.85$ and 1.95, respectively, which represent two extremal values of these parameters S':

$$0.85 < S' < 1.95 \ . \tag{7}$$

Note that the low value of p_e is also consistent with the observed low-hyperfine-field value $H_h \sim 215$ kG from the Mössbauer experiments.[16,21] However, it is difficult, from the Mössbauer experiments alone, to deduce a value of p_e or N_e, because a partial contribution of the zero-point spin fluctuations in the reduction of H_h cannot be precluded.[22]

B. Magnetic behavior below the freezing temperature

We can define the ordering temperature T_1 as the temperature at which a deviation from the Curie-Weiss law takes place, with the onset of a strong curvature of the experimental curve $\chi(T)$: $T_1=250\pm5$ K. The rather large uncertainty in the determination of T_1 arises from the absence of any sharp anomaly of $\chi(T)$ at T_1, in accordance with previous results,[13,17] which is a typical behavior of one-dimensional antiferromagnets. This value of T_1 is in good agreement with those obtained from neutron experiments:[13,14] $T_1 \sim 250$ K from Mössbauer experiments[16] and $T_1 \sim 245$ K from electron-spin-resonance experiments.[22] At a lower temperature, $T_2=12.5$ K, an anomaly in the $\chi(T)$ curve is observed, which has not been reported previously (Fig. 3). This anomaly may be associated with a long-range three-dimensional antiferromagnetic ordering. Theoretically, a one-dimensional system with short-range interactions should not have three-dimensional long-range order at finite temperature as high as 245 K. Our data are qualitatively similar to those observed in the uniaxial crystal tetramethyl ammonium manganese trichloride [$(CH_3)_4NMnCl_3$, or TMMC], which is the classical example of a one-dimensional magnetic system with a three-dimensional phase transition at the Néel temperature 0.84 K.[23] The theory of the magnetic susceptibility in such materials was developed some years ago for an isotropic linear-chain Heisenberg antiferromagnet.[24,25] The model for such an interaction was solved in the limit $S \to \infty$,[24] and also for $S=\frac{1}{2}$, and was further modified[24] to apply to a spin $S=\frac{5}{2}$.[26] The susceptibility χ is then given by

$$\chi = \frac{C}{T}\frac{1+u(K)}{1-u(k)} \ , \quad u(K)=\coth K - 1/K \ , \quad K=-2J_1S'(S'+1)/k_BT \ . \tag{8}$$

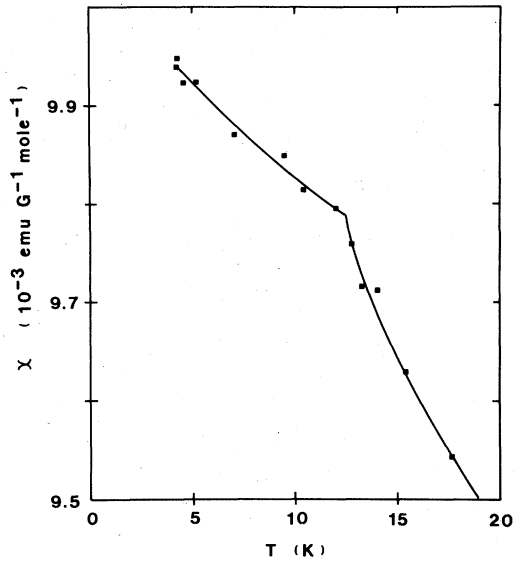

FIG. 3. Magnetic susceptibility as a function of temperature in the vicinity of the temperature T_2; we attribute this to a three-dimensional magnetic ordering.

Equation (8) is the expression derived in Ref. 26, with S replaced by S' as given by Eq. (7), to take covalent effects into account. To derive this expression of $\chi(T)$, it is supposed that the interchain exchange interaction is negligible and that the short-range intrachain exchange interaction is restricted to nearest neighbors; then there is only one exchange integral, J_1, entering Eq. (8). Since the Fe^{3+} spins are coupled antiferromagnetically along the chains,[13,14] J_1 is positive.

At high temperatures, the leading terms in Eq. (8) match the result of Rushbroke and Wood[27] and then $\chi(T)$ satisfies the Curie-Weiss law. The paramagnetic Curie-Weiss temperature Θ defined in Eq. (1) is given by

$$\Theta = -\tfrac{4}{3}J_1S'(S'+1)/k_B \ . \tag{9}$$

Although Eq. (8) with $S'=S$ has proved suitable to reproduce experimental data for some antiferromagnetic chains,[23,28] we did not obtain a satisfactory fit to the experimental curve $\chi(T)$ in the present case. In particular, a positive value of J_1 implies that Θ, in Eq. (9), is negative. To the contrary, the experimental value of Θ is positive: $\Theta \sim +70$ K, which implies a ferromagnetic component to the magnetic susceptibility ignored in Eq. (8). Also, Eq. (8) always leads to a broad maximum of the theoretical curve $\chi(T)$ at $T \sim T_1$. To the contrary, the experimental curve decreases monotonically as a function of temperature. Nevertheless, a marked curvature of the experimental $\chi(T)$ curve takes place at $T \sim T_1$, so that the absence of any broad maximum may also be attributable to a monotonic ferromagnetic component to the magnetic susceptibility which we propose now to calculate by different theoretical approaches.

III. THEORETICAL MODELS

A. Molecular-field approximation (MFA)

The existence of a ferromagnetic contribution to the magnetic properties of $KFeS_2$ has already been reported by authors[9,17] who attributed this effect to impurities. It must be noticed, however, that positive values of Θ imply that the ferromagnetic contribution to $\chi(T)$ is of the Curie-Weiss type. Noninteracting impurities only give a Curie-type contribution, proportional to T^{-1}, which does not account for a positive value of Θ. It does not seem realistic to assume that the amount of magnetic impurities is so large that they can interact between themselves. Therefore, we can presume that the ferromagnetic component of the magnetic interactions is an intrinsic property of the material. Such ferromagnetic interactions can take place between next-nearest neighbors (NNN's) along the c axis, with the exchange constant J_2, or between third-nearest neighbors (interchain coupling J'). Since there are superexchange pathways along the chains, J_2 may be large and of the same order of magnitude as J_1. To the contrary, the metal-ligand chain is effectively separated from all its neighbors by the potassium ions, so that the interchain interaction J' is essentially dipolar in nature. Therefore, we can expect that $J' \ll J_2, J_1$. In that case, Θ takes the form

$$\Theta = \frac{4S'(S'+1)}{3k_B}(J_2 - J_1) ,$$

with the convention $J_2 > 0$ for a NNN ferromagnetic coupling and $J_1 > 0$ for a nearest-neighbor (NN) antiferromagnetic coupling. The one-dimensional antiferromagnetic ordering along the c axis takes place at a temperature T_1, which, in the molecular-field approximation, is given by

$$T_1 = \frac{4S'(S'+1)}{3k_B}(J_1 + J_2) . \tag{10}$$

We can deduce J_1 and J_2 from Eqs. (9) and (10) with $T_1 \sim 250$ K and $\Theta \sim 70$ K for S' in the limits fixed in Eq. (7). We obtain

$$11.7 < J_1/k_B < 43 \text{ K}, \quad 20.9 < J_2/k_B < 76.8 \text{ K} . \tag{11}$$

A three-dimensional ordering is expected at a temperature T_2 given in the molecular-field approximation by $T_2 = 4S'(S'+1)J'/3k_B$.

For $T_2 \sim 12.5$ K, we have

$$1.6 < J'/k_B < 6 \text{ K} . \tag{12}$$

The ratio $\eta = J'/(J_1 + J_2)$ which measures the degree of one dimensionality of the system does not depend on S' in this model and is equal to

$$\eta = \frac{J'}{J_1 + J_2} = \frac{T_2}{T_1} = 0.05 . \tag{13}$$

These values are of the same order of magnitude as the results of Tomkowicz *et al.*,[13] who estimated $J_1/k_B \sim 66$ K, $J' \sim 2.64$ K, and $J'/J_1 = \eta = 0.04$ from the analysis of their data in the framework of models which assume $J_2 = 0$.

B. Refined molecular-field approach

Despite a good experimental linearity of χ^{-1} versus T, short-range spin correlations, neglected in the MFA, can be observed even at room temperature in linear-chain antiferromagnets.[23] In the refined molecular-field theory which takes these spin correlations into account, the intrachain (J_1) and interchain (J') exchange interactions and their ratio (η) are given by[29]

$$\exp\frac{2|J_1|}{k_B T_N} = (4 + Z\eta)/(Z\eta), \quad \eta = |J'|/|J_1| , \tag{14}$$

where Z is the number of neighbors in the ab plane. For Heisenberg antiferromagnetic chain with $J_2 = 0$, it has been established that[30] $J_1 = k_B T(\chi_{\max})/10.6$, with $T(\chi_{\max})$ the temperature at which $\chi(T)$ is maximum. If we assume, as discussed above, that the main effect of the ferromagnetic interactions is only to smear this maximum at T_1, we can estimate $J_1 \sim k_B T_1/10.6$. We then have

$$J_1/k_B = 23.6 \text{ K} . \tag{15}$$

For this value of J_1, in the range predicted by the crude molecular-field approximation defined in Eq. (11), Eqs. (9) and (10) give $J' = 3.3$ K, $J_2/k_B = 41.9$ K, and $S' = 1.26$. Equations (14) and (15) with $T_N = 12.5$ K and $Z = 4$, yields $\eta \sim 0.02$, which is of the same order of magnitude as the results discussed above.

C. Green's-function techniques

A one-dimensional system with short-range interactions can have no long-range order at finite temperatures; hence, any ordering effect must be attributed to interchain coupling. The most reliable estimates of T_N in terms of J' probably comes from random-phase approximation (RPA) and other Green's-function schemes. These may be put in the form[29]

$$k_B T_N / J_1 = \tfrac{4}{3} S'(S'+1) f / I \tag{16}$$

where S has been replaced by S' to take covalent effects into account, and

$$I = N^{-1} \sum_{\vec{q}} [1 - j(\vec{q})/J(0)]^{-1} , \tag{17}$$

in which

$$J(\vec{q}) = \sum_{i,j} J_{ij} e^{-i\vec{q}\cdot\vec{R}_{ij}}$$

is the Fourier transform of the exchange interaction. The quantity f is a factor which depends on the decoupling of the equations of motion for the Green's functions. In the random-phase approximation, $f = 1$. Equations (16) and (17) were first applied successfully to the linear-chain antiferromagnet $Cu(NH_3)_4SO_4 \cdot H_2O$ by Oguchi.[29] If $J_2 \sim 0$, I is simply a function of $\eta = J'/J_1$. Since η is very small, $I(\eta)$ in Eq. (17) can be replaced by its asymptotic limit,[31] $I(\eta) \simeq 0.64/\sqrt{\eta}$, which can be inserted in Eq. (16) to give the RPA expression

$$\eta = [0.54(k_B T_N/J_1)][S'(S'+1)]^{-2} . \tag{18}$$

Equations (7), (15), and (18) with $T_N = 12.5$ K give

$$2\times10^{-3} < \eta < 3.3\times10^{-2} . \tag{19}$$

Other expressions for f have been obtained for other decouplings of the equations of motions.[32] Tahir-Kheli has suggested[33]

$$f = 1 + \frac{S'-1}{3S'}\frac{I-1}{I} \tag{20}$$

to obtain agreement with Padé approximants for the critical temperature in cubic ferromagnets. Once again, S has been replaced by S' with respect to the original formula. Green's-function theories, rigorously correct for classical spins, predict the same ordering temperature for ferromagnetic and antiferromagnetic interactions. Rushbrooke and Wood[27] have shown there is about a 13% difference between Curie and Néel temperatures in the case of a spin-$\frac{1}{2}$, simple-cubic lattice. This difference drops to 1.3% for spin $\frac{5}{2}$. Since $S' > \frac{1}{2}$, there should not be a serious error in applying Eq. (24) to an antiferromagnet. With f given by Eq. (20) instead of unity, Eqs. (18) and (19) are replaced, respectively, by

$$\eta = \left[\frac{2.88 k_B T_N}{J_1}\right]^2 \left[(S'+1)(4S'-1) + \left[(S'+1)^2(4S'-1)^2 - \frac{9(S'^2-1)k_B T_N}{J_1}\right]^{1/2}\right]^{-2} \tag{21}$$

and

$$1.5\times10^{-3} < \eta < 2.87\times10^{-2} . \tag{22}$$

Note that the range determined in the RPA [in Eq. (19)] is included in that of Eq. (22) in the Tahir-Kheli model.

In principle, the Green's-functions method, which contains the wave-number vector, takes the crystal structure into account more precisely than the molecular-field models which contain only the number of neighbors Z. In our particular case, however, the Green's-function methods fail to give an accurate determination of η because η depends strongly on S'. This can be seen from Eqs. (18) and (21), which, in the limit of large S', give $\eta \propto (S')^{-4}$. Note that in the particular case $S' = 1.26$ (see end of Sec. III B), Eq. (21) gives $\eta = 6\times10^{-3}$, while Eq. (18) gives $\eta = 1.0\times10^{-2}$.

IV. DISCUSSION

From the analysis of the magnetic susceptibility as a function of temperature using the molecular-field and Green's-function methods, it has been possible to find the order of magnitude of the exchange parameters in $KFeS_2$. We find that the interchain exchange constant J' is in the range $1.6 < J'/k_B < 6$ K, and that the ratio η of the inter- to intrachain exchange constants which measures the degree of one dimensionality of this system is $\eta \sim 10^{-2}$. These results, in agreement with those of Refs. 13 and 15, seem more reliable than the values $J_1/k_B \sim 1000$ K and $\eta = 5\times10^{-4}$ reported in Ref. 14. The intrachain exchange constants are thus much larger than the interchain exchange constant, emphasizing the one-dimensional nature of this system.

Based on the molecular-field model one could propose, in $KFeS_2$, the situation $|J_2| > |J_1|$ with J_1 and J_2 the NN and NNN intrachain exchange constants, as also proposed for some three-dimensional antiferromagnets such as EuTe.[34] However, the inadequacy of the molecular-field model, which excludes short-range effects, has been noted in linear-chain antiferromagnetic systems. Ferromagnetic impurities have also been suggested to strongly influence the susceptibility measurements in $KFeS_2$. Although their effects have probably been overestimated in previous works, they may influence quantitatively the exchange constants J_2 derived in this paper. Therefore, we do not make any definite conclusion herewith regarding the relative strength of NNN intrachain exchange constants.

The large discrepancies between values of J_1 deduced from neutron experimental data, ranging from 66 (Ref. 13) to 245 K (Ref. 15), evidence the difficulties met to determine this parameter. Note that the lower value of J_1 in our present work, with respect to Ref. 13, comes from the fact that we did not make the approximation $J_2 = 0$. Also, the value $J_1/k_B \sim 254$ K $\sim T_1$ is the consequence of the assumption $T_N = T_1$ in Ref. 15. To the contrary, the values of the exchange constants we have derived in this paper suppose that T_1 is the one-dimensional ordering temperature, with the spins ordering antiferromagnetically along the c axis.

This is the main disagreement between our analysis and previous analyses of neutron experiments[13,15] or of magnetic susceptibility measurements,[14] assuming that T_1 is the Néel temperature T_N at which the three-dimensional ordering occurs. Such a high value of $T_N \sim 250$ K, however, would be very surprising because long-range magnetic ordering does not occur at finite temperature in one-dimensional chains with short-range magnetic interactions. The small value of η in $KFeS_2$ evidence a large anisotropy of the exchange interactions and the quasi-one-dimensional nature of this system. Indeed, the value of $T_N = 12.5$ K measured in this work is in better agreement with the expected and usually observed low values of T_N in quasi-one-dimensional systems. Also, the absence of any marked singularity near 250 K in the susceptibility curve is typical of the behavior predicted for one-dimensional antiferromagnetic transition, and it is associated with the influence of magnetic coupling along individual chains of iron ions upon the bulk susceptibility.

It is possible, however, that strong spin correlations between the chains take place at T_1. Such correlations depend in fact on the easy axis of magnetization. If the spins are polarized in a plane perpendicular to the c axis, adjacent spins in the ab plane have the possibility of being canted by a small angle θ, with a low cost in energy. Therefore, the interchain spin correlations will be smaller at T_1. This is roughly the case in TMMC. To the contrary, if the spins are aligned along the c axis, there are two spin configurations for adjacent spins in the ab plane,

namely ↑ and ↓. This last configuration, however, is associated with a higher energy since $\theta \sim 180°$. Therefore the configuration ↑ has a higher probability and the interchain spin correlations will be stronger in this case. The spin arrangement in $KFeS_2$ is close to this last case. The angle between the magnetic moments and the c axis is small: $\theta \sim 13.6°$.[12] The strong interchain spin correlations, which are expected to take place at T_1 in this configuration, might explain the neutron experimental data, rather than an interchain magnetic ordering.

We now propose to make low-temperature anisotropic measurements using specific heat, magnetic susceptibility, neutron scattering, and other experimental techniques in order to further elucidate the nature of the magnetic ordering and exchange constants in this interesting one-dimensional system.

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