Magnetic structure of α-$FeC_2O_4 \cdot 2D_2O$

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Long-range spin ordering has been studied in the quasi-one-dimensional antiferromagnet α-$FeC_2O_4 \cdot 2D_2O$ by neutron diffraction on a powdered sample above and below $T_N = 11.7$ K. Data at 14 K show essentially the room-temperature chemical structure. The space group is $C2/c$, $Z = 4$, and unit cell dimensions are $a = 11.700$ Å, $b = 5.568$ Å, and $c = 9.847$ Å with $\beta = 128.05°$. Magnetic peaks appear at T_N and data at 10.5 K show doubling of the unit cell along the b direction, the chain axis. The ordered structure belongs to the magnetic space group $P_{2b}2/n$ with spins parallel to the b axis. Cancellation of certain interchain interactions gives the structure a pronounced two-dimensional character. At $T_2 = 9.5$ K a discontinuous transition to a second magnetic phase occurs with additional doubling of the unit cell in the a direction. Below T_2 the symmetry of the magnetic structure is reduced to triclinic, $P_{2s}\bar{1}$ with the spins deviating slightly from the b axis.

INTRODUCTION

The experimental study of one- or two-dimensional magnetism in three-dimensional crystals is inevitably limited by interchain or interlayer interactions. In the case of antiferromagnetic layer structures, however, the interactions between adjacent layers can be effectively cancelled,[1,2] under certain symmetries. Any ordering in the interlayer direction must be caused either by interactions between next-nearest-neighbor layers or by magnetostrictive effects. Nearly ideal two-dimensional behavior found in compounds with the K_2NiF_4 (Refs. 1 and 2) or the $Ni(NH_3)_2Ni(CN)_4 \cdot 2C_{12}H_{10}$ (Ref. 3) structures is believed to arise in this way. In quasi-one-dimensional magnets, however, cancellation effects are not likely to produce nearly ideal isolation of the chains. Because interchain interactions now extend in two dimensions, even if interactions of nearest-neighbor chains are cancelled, next-nearest-neighbor chains are not very far apart. However, even partial cancellation can lead to a quite interesting situation. Under certain symmetry, it is possible that the dominant interchain interactions can only produce 2D magnetic lattices and that there is cancellation of interactions between adjacent layers thus formed. In such a case we may be able to see a crossover from 1D to 2D behavior before the crystal actually orders in three dimensions.

The monoclinic α-phase of ferrous oxalate dihydrate, α-$FeC_2O_4 \cdot 2H_2O$, may be an example of such a system. According to x-ray diffraction measurements,[4,5] it belongs to the space group $C2/c$ and the Fe^{2+} ions occupy four special positions in a unit cell having the dimensions $a = 12.00$ Å, $b = 5.57$ Å, and $c = 9.91$ Å with $\beta = 128.43°$. Oxalate bridges in this structure link Fe^{2+} ions in chains extending along the b direction and mediate a dominant antiferromagnetic intrachain superexchange interaction. Because of the base-centered lattice structure (C), the interchain interactions in the (001) plane may be readily shown to cancel. Other interchain interactions also compete with one another raising the possibility of intermediate quasi-2D behavior. Powder susceptibility data[6] exhibit the broad rounded maximum typical of 1D antiferromagnets with $T_{max} \sim 40$ K. Above T_{max}, these data are well reproduced by the Heisenberg linear chain model with $S = 2$, $g = 2.49$, and $J/k = -4.8$ K. However, an even better fit of χ_p extending down to ~ 20 K can be obtained using the 1D Ising model with an effective spin $S' = 1/2$ suggesting that anisotropic effects are important. The Ising-like anisotropy appears to arise from a crystalline field splitting of the Fe^{2+} ion energies which leaves an Ising-like doublet or quasi-doublet as the lowest states.

The heat capacity of α-$FeC_2O_4 \cdot 2H_2O$ was found[6] to pass through a small λ-type peak at 11.7 K, the temperature at which $d\chi_p/dT$ also shows a pronounced maximum. These anomalies indicate the onset of antiferromagnetic long-range order below $T_N = 11.7$ K. About 90% of the available spin entropy in α-$FeC_2O_4 \cdot 2H_2O$ is removed as short-range order in linear chains on cooling down to T_N. It is clearly of interest to determine the kind of magnetic structure assumed by α-$FeC_2O_4 \cdot 2H_2O$ below T_N.

In this paper we report the results of a neutron diffraction study of powdered α-$FeC_2O_4 \cdot 2D_2O$ which confirms the ordering at $T_N = 11.7$ K but also reveals the appearance of a second magnetically ordered phase at $T_2 = 9.5$ K. The structures of both phases have been determined.

Neutron diffraction measurements were performed on a powder diffractometer at the High Flux Beam Reactor in Brookhaven National Laboratory. Data were taken every 0.1° in angle 2θ with the sample axis frozen. Neutrons of wavelength 2.35 Å were used.

RESULTS AND DISCUSSION

Figure 1 shows the neutron diffraction pattern for powdered α-$FeC_2O_4 \cdot 2D_2O$ at 14 K ($> T_N$). The peaks found are due to nuclear scattering alone although a noticeable

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increase in the background level at lower θ is probably attributable to short-range order effects. We can account for all observed peaks by assuming essentially the same chemical structure as determined for the hydrate at room temperature by x rays. The lattice constants are now found to be $a = 11.700$ Å, $b = 5.568$ Å, and $c = 9.847$ Å with $\beta = 128.05°$. Using standard methods[7] and neglecting the Debye–Waller factor, good agreement with the observed peak intensities was achieved as will be seen from the fit of the simulated pattern in Fig. 1. The R factor, defined as $R = \Sigma|I_{\text{calc}} - I_{\text{obs}}|/\Sigma I_{\text{obs}}$, is 2.9% with a set of fractional atomic coordinates given in the inset in Fig. 1.

As the temperature was lowered to 10.5 K, new peaks appeared, as shown in Fig. 2, while the intensities and positions of the nuclear peaks remained unchanged. We infer that the sample is in a magnetically ordered state at 10.5 K. Magnetic peaks were found to disappear at ~ 12 K. This is consistent with the observation of a λ peak in C_p at $T_N = 11.7$ K. All of the magnetic peaks are successfully indexed with half integer k's. We conclude that the primitive translation b should now be primed, forming a P_{2b} magnetic lattice with the same lattice constants as those of the monoclinic Bravais lattice C. This is consistent with the previous observations that the linear chains of Fe^{2+} ions in α-$FeC_2O_4 \cdot 2H_2O$ lie along the b direction and that the intrachain nearest-neighbor interaction J is antiferromagnetic in sign. We further infer that the magnetic moments lie along the b axis because the (0 1/2 0) peak is absent.

Assuming the magnetic structure to be collinear, we now consider possible configurations of up/down orientations of the four magnetic moments in a chemical unit cell. We refer to the four positions as $1 = (0, y, 1/4)$, $2 = (0, \bar{y}, 3/4)$, $3 = (1/2, 1/2 + y, 1/4)$, and $4 = (1/2, 1/2 - y, 3/4)$. These are indicated in Fig. 3(a). The positions created by applying a primed translation b' to the position n will be labeled $\hat{n}$. Thus, for example, $\hat{1} = (0, 1 + y, 1/4)$. The magnetic moment at site n will be called simply spin n and the exchange integral between ions at n and m becomes J_{nm}. We note that there are only four possible configurations because we may fix both spin-1 and spin-3 in up positions without loss of generality. This leaves four configurations depending upon the up/down status of spin-2 and spin-4. They may be designated (uuuu), (uuud), (uduu), and (udud).

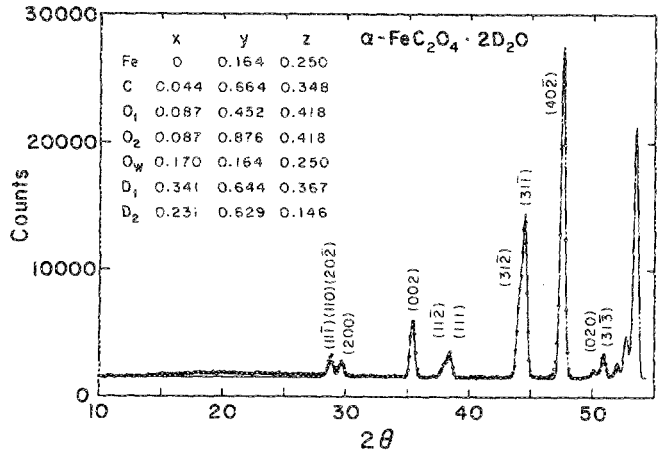

FIG. 1. Neutron diffraction pattern for powdered α-$FeC_2O_4 \cdot 2D_2O$ at 14 K ($> T_N$) for $10° \leqslant 2\theta \leqslant 55°$.

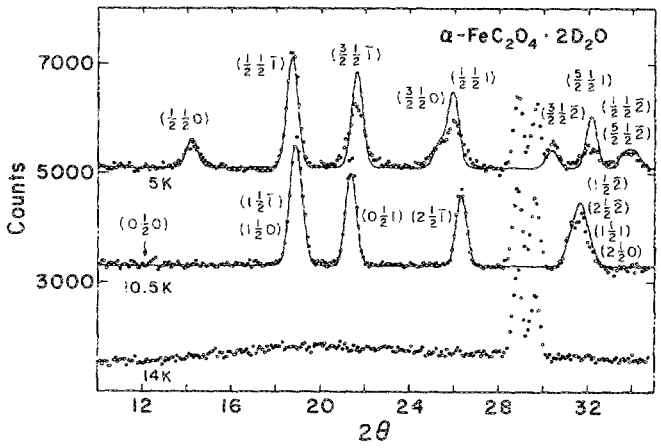

FIG. 2. Neutron diffraction pattern for powdered α-$FeC_2O_4 \cdot 2D_2O$ at 14 K, 10.5 K ($< T_N$), and 5 K ($< T_2$). The 10.5 and 5 K curves are shifted upward by arbitrary amounts.

Which one of the four configurations is actually realized is probably dictated by the magnitudes and signs of the interchain interactions. In the case of antiferromagnetic chains, however, the distinction between antiferromagnetic and ferromagnetic interchain interactions is not very clear. For example, in the (100) plane J_{12} and $J_{\hat{1}2}$ compete if they are both of the same sign. If J_{12} is dominant and antiferromagnetic, spins 1 and 2 will be antiparallel. The same will be true, however, with dominant ferromagnetic $J_{\hat{1}2}$. For our purposes it is adequate to define the net interchain interaction as antiferromagnetic if two nearest spins in adjacent chains are antiparallel. With this in mind we find that there are three (net) interchain interaction paths, J_{12}, J_{13}, and J_{14}. Applying the above definition we determine the signs (AF or F) of the interactions for each possible spin configuration. In each

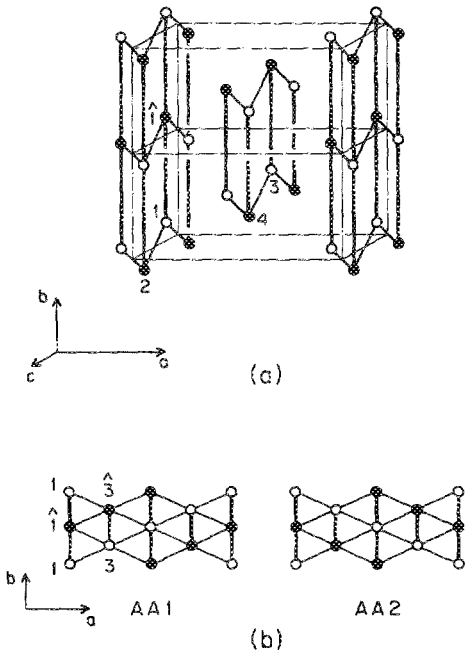

FIG. 3. Spin structures of magnetically ordered α-$FeC_2O_4 \cdot 2D_2O$. (a) $T_2 < T < T_N$ (udud) model. (b) $T < T_2$, AA-1 and AA-2 models.

case only one type of interaction is effective in the ordered state, the other two being cancelled. Thus with (uuuu) we expect J_{12}(F) acting in the (100) plane. The others are: (uuud), J_{14}(AF), ($\bar{1}$01); (uduu), J_{14}(F), ($\bar{1}$01); (udud), J_{12}(AF), (100).

The intensities of the allowed magnetic peaks have been calculated for each configuration using standard formulas.[7] Very reasonable agreement with the observed values is obtained for the (udud) model. The R factor is 7.6%. A simulated diffraction pattern for this model is shown as a solid curve in Fig. 2. The (udud) spin configuration is illustrated in Fig. 3(a). It belongs to the magnetic space group $P_{2b}2/n$. The antiferromagnetic linear chains are coupled antiferromagnetically in the (100) plane. The nearest-neighbor interactions between adjacent planes cancel in the ordered state giving the structure a pronounced 2D character. Its significance in the thermodynamic properties near T_N will be discussed in a later publication.

In Fig. 2 we see that the diffraction pattern observed at 5 K is very different from that at 10.5 K. New peaks appear at $2\theta \sim 14°$ and 30.4° while others are shifted or changed in shape. This change in the diffraction pattern occurs almost discontinuously at $T_2 = 9.5$ K where small anomalies have been noted[5] in χ_p and C_p. A new magnetic structure evidently emerges below T_2. It is possible to index the magnetic peaks below T_2 with half integer values for h as well as k, indicating that the primitive translations in both the a and b directions are now primed. In determining the magnetic structure we again assume collinearity. We further assume that spin-1 and spin-2 remain antiparallel below T_2. This seems reasonable in light of the effective 2D magnetic lattice formation in the (100) plane discussed above. We find two possible structures AA1 and AA2 depending on the orientation of spin-3 [see Fig. 3(b)]. These two structures can be transformed into one another by twofold rotation about the b axis. Therefore, they are merely two domains of the same structure. This also means that the twofold symmetry is broken and the symmetry of the structure lowered to triclinic. The magnetic space group appropriate to this model is $P_{2s}\bar{1}$. For convenience of indexing, however, we use the monoclinic chemical unit cell in the remaining discussion. It should be noted that the reflections (hkl) and $(\bar{h}k\bar{l})$ are no longer equivalent. In calculating intensities it is necessary to take an average of $|F_{hkl}|^2$ and $|F_{\bar{h}k\bar{l}}|^2$ where F_{hkl} and $F_{\bar{h}k\bar{l}}$ are the corresponding structure factors.

The simulated diffraction pattern calculated for this model is compared with the data at 5 K in Fig. 2. The agreement is good with $R = 12.8\%$. All other possible collinear structures with the quadrupled cell were tested, but the results were much less satisfactory. As noted above, the twofold rotational symmetry is broken in the low-temperature phase. Therefore, the moments need not align parallel to the b axis. It is, in fact, possible to reduce the R factor by tipping the moments away from the b direction. A minimum value, $R = 9.8\%$, was found for a tipping angle of 5°.

The cause of the transition at T_2 is still unclear. One might speculate that a magnetostrictive effect removes the degeneracy of J_{13} and $J_{\bar{1}3}$. The deformation of the crystal, in this case, might be too small to be detected. The transition must be discontinuous because not all of the symmetry elements of the triclinic phase are present in the monoclinic phase. As Landau[8] has pointed out, a continuous phase transition is impossible under these circumstances. This is demonstrated by the abrupt change of the diffraction pattern at T_2. The corresponding anomaly in C_p is very small, indicating that very little energy is involved in the transition. This is understandable, because the interactions between adjacent (100) layers are effectively cancelled.

Comparing intensities of nuclear and magnetic peaks, we have calculated the magnitude of the magnetic moment of the Fe^{2+} ion in each phase. One obtains $4.7 \pm 0.3\mu_B$ for the udud structure at 10.5 K and $4.8 \pm 0.4\mu_B$ for the AA structures at 5 K. These are reasonable values for Fe^{2+} ions with nearly quenched orbital angular momenta. The very steep rise of the sublattice magnetization below T_N appears to reflect the pronounced 2D Ising character in this system.

Since this work was completed, we have learned of another neutron study of α-$FeC_2O_4 \cdot 2D_2O$ by Sledzinska *et al.*[9] Their results at 4.2 K agree with ours at 5 K and they too attribute them to the AA model spin structure. They also conclude that the ordered moments should deviate from the b direction and estimate the angle to be 12.9°. Sledzinska *et al.* made no measurements that would have enabled them to detect the high-temperature ordered phase which we have found between $T_2 = 9.5$ K and $T_N = 11.7$ K. They quote a value of $T_N = 16$ K determined by intensity measurement of the (1/2 1/2 $\bar{1}$) reflection during warming from 4.2 K. This is almost certainly too high.

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