Magnetic structure of $\alpha$-Fe$_2$O$_4$:2D$_2$O

Satoru Simizu, Jiing-Yann Chen, and S. A. Friedberg

Physics Department, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

J. Martinez and G. Shirane

Brookhaven National Laboratory, Upton, New York 11973

Long-range spin ordering has been studied in the quasi-one-dimensional antiferromagnet $\alpha$-Fe$_2$O$_4$:2D$_2$O 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 $\beta = 128.05^\circ$. 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 $P_{21}/$ with spins parallel to the $b$ axis. Cancellation of certain interchain interactions gives the structure a pronounced two-dimensional character. At $T = 9.5$ K a discontinuous transition to a second magnetic phase occurs with additional doubling of the unit cell in the $a$ direction. Below $T_1$ the symmetry of the magnetic structure is reduced to triclinic, $P_{21}$ 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, 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 $K_x$NiF$_4$ (Refs. 1 and 2) or the Ni(NH$_3$)$_2$Ni(CN)$_4$·2C$_2$H$_5$OH (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 $\alpha$-phase of ferrous oxalate dihydrate, $\alpha$-Fe$_2$O$_4$:2H$_2$O, may be an example of such a system. According to x-ray diffraction measurements, 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 $\beta = 128.43^\circ$. 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 exhibit the broad rounded maximum typical of 1D antiferromagnets with $T_{\text{max}} \approx 40$ K. Above $T_{\text{max}}$, these data are well reproduced by the Heisenberg chain model with $S = 2$, $g = 2.49$, and $J/k = -4.8$ K. However, an even better fit of $\chi_p$ extending down to $\approx 20$ 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 $\alpha$-Fe$_2$O$_4$:2H$_2$O was found to pass through a small $\lambda$-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 $\alpha$-Fe$_2$O$_4$:2H$_2$O 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 $\alpha$-Fe$_2$O$_4$:2H$_2$O below $T_N$.

In this paper we report the results of a neutron diffraction study of powdered $\alpha$-Fe$_2$O$_4$:2D$_2$O 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 $\alpha$-Fe$_2$O$_4$:2D$_2$O at 14 K ($> T_N$). The peaks found are due to nuclear scattering alone although a noticeable
increase in the background level at lower $\theta$ 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 $\beta = 128.05^\circ$. Using standard methods 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 $\sim 12$ K. This is consistent with the observation of a $\lambda$ 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 $P_{2_1}$ 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 $\alpha$-Fe$_2$O$_3$-2H$_2$O 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 $\tilde{n}$. Thus, for example, $\tilde{1} = (0, 1 + y, 1/4)$. 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 (uuu), (uud), (udu), and (udud).

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 $J_{13}$ 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 $J_{13}$. 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. 1. Neutron diffraction pattern for powdered $\alpha$-Fe$_2$O$_3$-2D$_2$O at 14 K ($> T_N$) for $10^3 < 2\theta < 35^\circ$.](image1)

![Fig. 2. Neutron diffraction pattern for powdered $\alpha$-Fe$_2$O$_3$-2D$_2$O at 14 K, 10.5 K ($< T_N$), and 5 K ($< T_F$). The 10.5 and 5 K curves are shifted upward by arbitrary amounts.](image2)

![Fig. 3. Spin structures of magnetically ordered $\alpha$-Fe$_2$O$_3$-2D$_2$O. (a) $T_F < T < T_N$ (udud) model. (b) $T < T_F$, AA-1 and AA-2 models.](image3)
case only one type of interaction is effective in the ordered state, the other two being cancelled. Thus with (uuuu) we expect \( J_{12}(\mathcal{F}) \) acting in the (100) plane. The others are: (uuud), \( J_{14}(\mathcal{F}) \), (101); (uudd), \( J_{14}(\mathcal{F}) \), (101); (uuud), \( J_{12}(\mathcal{AF}) \), (100).

The intensities of the allowed magnetic peaks have been calculated for each configuration using standard formulas. Very reasonable agreement with the observed values is obtained for the (uuud) model. The \( R \) factor is 7.6%. A simulated diffraction pattern for this model is shown as a solid curve in Fig. 2. The (uuud) spin configuration is illustrated in Fig. 3(a). It belongs to the magnetic space group \( P_{2a}2/a \). 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\( \theta \approx 14^\circ \) and 30.4° while others are shifted or changed in shape. This change in the diffraction pattern occurs almost discontinuously at \( T_s = 9.5 \) K where small anomalies have been noted\(^ 2 \) in \( \chi_{\rho} \) and \( C_{\rho} \). A new magnetic structure evidently emerges below \( T_s \). It is possible to index the magnetic peaks below \( T_s \) 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 \( T_s \). 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 \( P_{2a}1 \). For convenience of indexing, however, we use the monoclinic chemical unit cell in the remaining discussion. It should be noted that the reflections \((hk0)\) and \((hkl)\) are no longer equivalent. In calculating intensities it is necessary to take an average of \( |F_{hkl}|^2 \) and \( |F_{hkl}|^2 \) where \( F_{hkl} \) and \( F_{hkl} \) 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 \( T_s \) is still unclear. One might speculate that a magnetostriective effect removes the degeneracy of \( J_{14} \) and \( J_{12} \). 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\(^ 4 \) has pointed out, a continuous phase transition is impossible under these circumstances. This is demonstrated by the abrupt change of the diffraction pattern at \( T_s \). 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 \( \text{Fe}^{2+} \) ion in each phase. One obtains 4.7 ± 0.3 \( \mu_B \) for the uuud structure at 10.5 K and 4.8 ± 0.4 \( \mu_B \) for the AA structures at 5 K. These are reasonable values for \( \text{Fe}^{2+} \) 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 \( a-x \text{Fe}_2C_2O_7 \), 2D\( \text{O} \) 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°. Sledzinska et al. made no measurements that would have enabled them to detect the high-temperature ordered phase which we have found between \( T_s = 9.5 \) 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 1) reflection during warming from 4.2 K. This is almost certainly too high.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation grant no. DMR84-05833. Work at Brookhaven National Laboratory was supported by the U.S. Department of Energy under contract no. DE-AC02-76CH00016.

---