Neutron Diffraction Study of the Magnetic Structure of Hematite to 41 kbar*†

T. G. WORLTON
Idaho Nuclear Corporation, Idaho Falls, Idaho
AND
D. L. DECKER
Brigham Young University, Provo, Utah

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Time-of-flight neutron diffraction has been used to study the pressure dependence of the magnetic moment direction in α-Fe_2O_3 to 41 kbar. The pressure dependence of the magnetic moment direction at room temperature is found to be in agreement with the pressure dependence calculated from measurements of the quadrupole splitting at high pressure by Vaughan and Drickamer, using the Mössbauer effect. It is found that the spin direction varies slowly and continuously with pressure above 14 kbar, with no well-defined Morin transition occurring at room temperature. The large pressure dependence of the Morin transition at lower pressures is well accounted for by Searle's theory based on the magnetoelastic effect. The slow variation of the spin direction at higher pressures must be accounted for by higher-order contributions to the anisotropy energy.

INTRODUCTION

HEMATITE is an antiferromagnetic material that has two stable spin states. Between 960 and 250°K, the spins of the four magnetic Fe^{3+} ions are perpendicular to the rhombohedral axis of the unit cell and alternate in direction within the (111) planes in a $+--+$ sequence.[1] When the temperature is lowered below the Morin transition temperature ($\sim$250°K), the spins suddenly rotate 90° to a $+--+$ spin alignment along the [111] rhombohedral axis. In this low-temperature antiferromagnetic state, the spins are perfectly collinear, but in the upper antiferromagnetic state the spins are canted slightly towards one another about the rhombohedral axis.[2] This canting of the moments results in a small ferromagnetic moment perpendicular to the rhombohedral axis that can be measured to determine the Morin temperature T_M.[3] The quadrupole splitting observed in the Mössbauer effect is directly dependent on the angle θ between the antiferromagnetic axis and the axis of the crystal field,[4] in this case the crystal axis. However, it has been shown[5] that the α-Fe_2O_3 quadrupole splitting is also extremely sensitive to small changes in the ferric ion position parameter so that the Mössbauer effect cannot give an independent measurement of either quantity. Neutron diffraction measurements, on the other hand, are very sensitive to θ but relatively insensitive to small changes in position parameter and other variables. Thus this neutron diffraction study of hematite as a function of pressure was undertaken to determine the relation of θ to temperature and pressure.

The spin angle is normally determined from neutron diffraction measurements by measuring the intensity of the two large magnetic peaks from the (111) and (100) planes, which are entirely magnetic in origin.[1] The scattered intensity from the (111) planes is proportional to $\sin^2\theta$, while the scattering from the (100) planes is proportional to $0.908\cos^2\theta+0.546\sin^2\theta$, where θ is the angle between the magnetic moments and the crystal axis. Thus the (111) magnetic peak intensity goes from a maximum in the high-temperature phase ($\theta=90°$) to zero in the low-temperature phase ($\theta=0°$).

Several experiments have been carried out recently that have shown that T_M initially increases with pressure at the rate of 3.8 ± 0.3°K/kbar.[6–9] The present experiment (which has been reported briefly[8]) indicates that above 6 kbar the transition increases at the rate of only 1.0 ± 0.3°K/kbar.

This observed change of slope at 6 kbar is in good agreement with a theory recently proposed by Searle[10] based on the magnetoelastic coupling that he estimated using the magnetostriction measurements of Urquhart and Goldman.[11] Searle shows that the magnetoelastic effect could cause a 3°K/kbar increase in T_M, and that the effect should disappear at 5.6 kbar. Subtraction of the magnetoelastic contribution to changes in T_M from the experimental data leaves a slope of approximately 1°K/kbar, which agrees with the data above 6 kbar. This 1°K/kbar slope must now be accounted for by other effects.

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[1] C. G. Shull, W. A. Strausser, and E. O. Wollan, Phys. Rev. **83**, 333 (1951).

[2] I. Dzyaloshinsky, J. Phys. Chem. Solids **4**, 241 (1958).

[3] F. J. Morin, Phys. Rev. **78**, 819 (1950).

[4] G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press Inc., New York, 1964).

[5] R. W. Vaughan and H. G. Drickamer, J. Chem. Phys. **47**, 1530 (1967).

[6] R. C. Wayne and D. H. Anderson, Phys. Rev. **155**, 496 (1967).

[7] H. Umebayashi, B. C. Frazer, G. Shirane, and W. B. Daniels, Phys. Letters **22**, 407 (1966).

[8] T. G. Worlton, R. B. Bennion, and R. M. Brugger, Phys. Letters **24A**, 653 (1967).

[9] N. Kawai, F. Ono, and K. H. Hirooka, J. Appl. Phys. **39**, 712 (1968).

[10] C. W. Searle, Phys. Letters **25A**, 256 (1967).

[11] H. A. Urquhart and J. E. Goldman, Phys. Rev. **101**, 1443 (1956).

The present experiment shows, however, that increasing the pressure does not simply raise the Morin transition temperature. As pressure is increased at room temperature the angle between the spins and the rhombohedral axis begins to decrease at about 5-kbar pressure and decreases rapidly, going from 90° at 5 kbar to 53° at 14 kbar. At pressures greater than 14 kbar the spin angle changes much more slowly. The spin angle was measured to be 43° at 41 kbar. The transition also spreads out in temperature as pressure is increased. A change of spin angle that took place in a temperature range of ~3° at atmospheric pressure is spread over ~200° at 25 kbar.

The neutron diffraction data is an intensity measurement so that only the statistical average of the spin angle is obtained. However, the lack of line broadening in the quadrupole splitting data of Vaughan and Drickamer[5] indicates that most of the spins have the same alignment. It is thus apparent that the Morin transition, as such, is not meaningful at very high pressures because there is not a sudden rotation of spins, but instead a continuous change of spin angle.

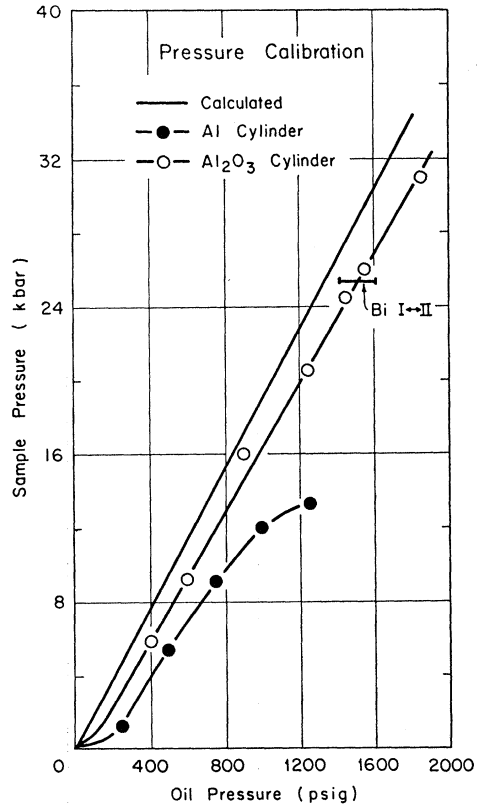

FIG. 1. Calibration of the MTR pressure system using two different containment cylinders. The data points were obtained by measuring the lattice parameters of a NaCl marker and from the electrical resistance of the Bi I–II transition. The upper line indicates the pressure calculated from force per unit area neglecting friction.

EXPERIMENT

Time-of-flight neutron diffraction measurements were made on two samples of powdered bulk α-Fe_2O_3 under pressure using the MTR time-of-flight diffractometer.[12,13] Most of the measurements were made on a commercial "Baker-analyzed" α-Fe_2O_3 powder of 99.9% purity. This sample had a Morin temperature of 250°K with an initial slope of $\partial T_M/\partial P = 3.8$°K/kbar. Part of the measurements were made on a very pure synthetic power of α-Fe_2O_3 obtained from Dr. D. H. Anderson at Sandia Laboratory. This sample had a Morin temperature of 260°K with an initial slope of $\partial T_M/\partial P = 3.6$°K/kbar.

High pressures were generated in a double-ended piston cylinder device. Some measurements were made using a 2-in.-diam cylinder of 7075-T6 aluminum with a 0.250-in.-diam sample chamber. This cylinder would contain pressures up to 13.5 kbar before failing by plastic flow. For experiments at higher pressures a 1.25-in.-diam cylinder of sintered Al_2O_3, which also had a 0.250-in.-diam sample chamber, was used. This cylinder was supported by steel binding rings that had slots cut through them to pass the neutron beam. This cell will hold pressures up to 45 kbar.

Pressures were calibrated by using NaCl powder mixed with the sample as a marker. Measured values of the lattice parameter of NaCl were used to obtain the pressure from Decker's calculations.[14] The pressure calibration curves for the two cylinders are shown in Fig. 1. A calibration point based on the bismuth I–II transition is also included in the figure. In measurements below 10 kbar the sample and NaCl were mixed in liquid CS_2 to give a good hydrostatic environment, but for pressures above 10 kbar no attempt was made to use a hydrostatic pressure medium. These α-Fe_2O_3 samples with their NaCl marker were enclosed in lead capsules that transmitted the pressure and provided lubrication for the pistons.

Counters at scattering angles of 30°, 60°, and 90° were used. The data from the 60° and 90° counters were limited to lattice spacings less than 3.5 Å because of the limited time between bursts. With the 30° counters, lattice spacings up to 8 Å could be observed. A resolution of $\Delta d/d < 0.018$ is obtained for determining lattice spacings from 0.8 to 7.8 Å by combining the data from the three sets of counters. The intensity of the diffraction peaks was calculated using an IBM 7044 computer. The program calculates the integrated peak intensity and makes corrections for background and for counter efficiencies.

[12] R. M. Brugger, R. B. Bennion, T. G. Worlton, and E. R. Peterson, *Research Applications of Nuclear Pulsed Systems* (International Atomic Energy Agency, Vienna, 1967), p. 35. Also available as USAEC Report No. IDO-17170 (unpublished).

[13] R. M. Brugger, R. B. Bennion, and T. G. Worlton, Phys. Letters **24A**, 714 (1967).

[14] D. L. Decker, J. Appl. Phys. **37**, 5012 (1966); **36**, 157 (1965).

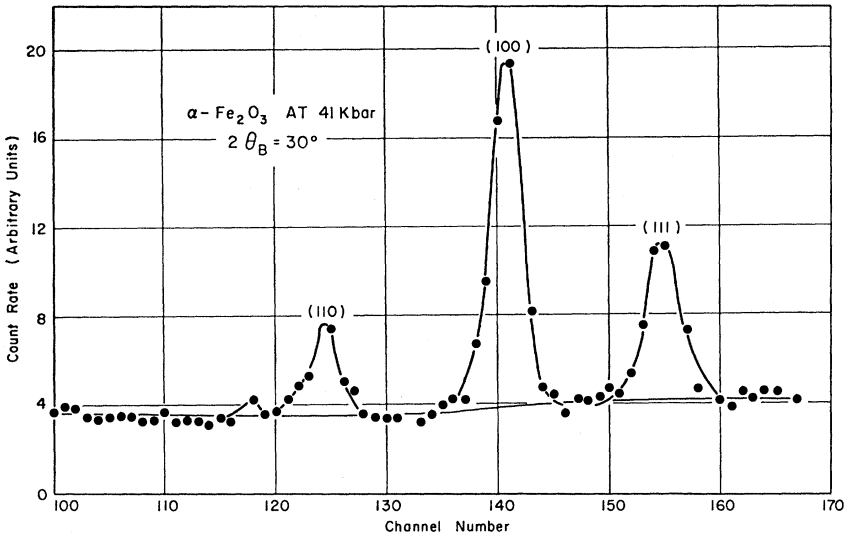

FIG. 2. Time-of-flight neutron diffraction data obtained at the $2\theta_B=30°$ scattering angle in a 9-h scan of α-Fe_2O_3 at 41 kbar. Ferric oxide peaks are indexed in the rhombohedral system. The small peak to the left of the (110) is due to the Al_2O_3 pressure vessel.

Diffraction patterns were obtained for α-Fe_2O_3 at room temperature for pressures up to 41 kbar. Weak diffraction peaks from the Al_2O_3 cylinder appear in the data at 30°, but the slotted binding rings provide adequate collimation to eliminate such peaks from the 60° and 90° data. Typical raw data are illustrated by Fig. 2, which shows a portion of the 30° data taken in a 9-h scan of α-Fe_2O_3 under a press load of 2450 psi. This was the shortest of the room-temperature scans. The other room-temperature scans had better statistical accuracy because of their longer counting times. The small peak to the left of the (110) peak in Fig. 2 is due to the Al_2O_3 pressure cell. The angle θ between the spins and the [111] axis was determined from the intensity of the (111) and (100) magnetic peaks using the angular factors $\langle q^2(111)\rangle=\sin^2\theta$ and $\langle q^2(100)\rangle=0.546\sin^2\theta+0.908\cos^2\theta$. The resultant angles are plotted as a function of pressure in Fig. 3.

The quadrupole splitting recently measured by Vaughan and Drickamer to 200 kbar[5] contains an angular factor $(3\cos^2\theta-1)$ in addition to a strong dependence of the electric field gradient on the ferric ion position parameter. Calculations of θ from Mössbauer-effect data of Vaughan and Drickamer were made assuming that the electric field gradient remains constant with pressure. Results of these calculations are plotted in Fig. 3 together with the neutron diffraction results at room temperature. Agreement between the two measurements seems to be good. This is a strong indication that there is very little change in the ferric

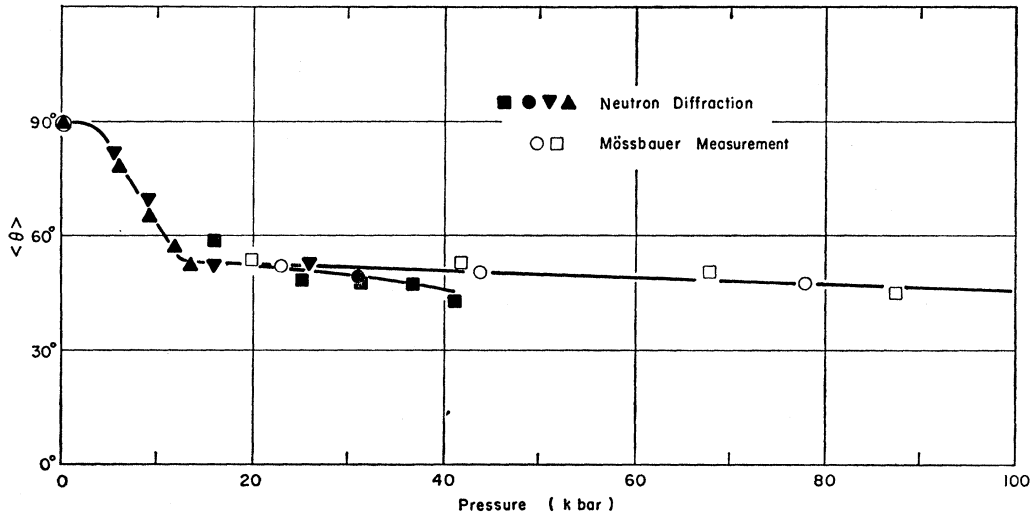

FIG. 3. Pressure dependence at room temperature of the angle θ between the antiferromagnetic axis and the crystal axis. The closed points were determined by neutron diffraction and the open points from Mössbauer-effect measurements of Vaughan and Drickamer (see Ref. 5).

ion position parameter with pressure. No change of the position parameter could be detected from the neutron diffraction data. Calculations using Vaughan and Drickamer's measurements carried out at pressures up to 200 kbar seem to indicate that the spin direction continues to rotate very slowly from 40 to 200 kbar. Vaughan and Drickamer searched for a peak broadening, which would be an indication of the simultaneous existence of both antiferromagnetic phases, but saw none. This indicates that what we have observed is really a slow rotation of the spins and not just a statistical phenomenon where part of the spins have flipped 90° and part have not flipped.

Measurements were also made of the spin angle as a function of temperature for several pressures. When the angle $\theta=45°$ is chosen as the criterion for determining the point of the Morin transition the phase diagram shown in Fig. 4 results. The dashed line indicates that there is no longer a well-defined spin flip, but just a slow rotation of spins at high pressure.

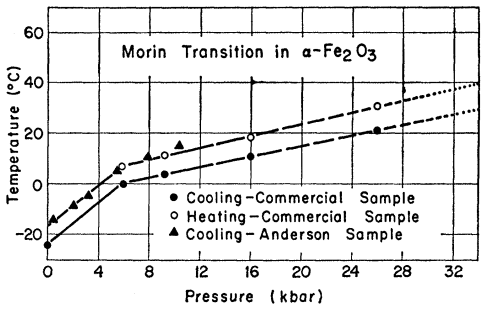

FIG. 4. Pressure dependence of the Morin transition for two samples of powdered α-Fe_2O_3 determined by neutron diffraction. Some data were taken both on cooling and heating. Note the change of slope at 6 kbar.

DISCUSSION OF RESULTS

The favored spin orientation in a magnetic crystal is determined by the anisotropy energy. Dzyaloshinsky developed a phenomenological theory for the free energy of hematite derived from symmetry considerations. According to his theory the free energy can be expressed as

$$\Phi=\tfrac{1}{2}A\cos^2\theta+\tfrac{1}{4}G\cos^4\theta+D\cos\theta\sin^3\theta\sin3\phi$$
$$-(Q^2/2B)\sin^2\theta+E\cos6\theta\sin^6\theta, \quad (1)$$

where A, G, D, Q, E, and B are parameters that are functions of temperature and pressure, θ is the angle between the antiferromagnetic axis and the z axis, and ϕ is an azimuthal angle measured from one of the C_2 axes.

In most of the calculations that have been made, all of the parameters have been assumed negligible in comparison to A. This simplifies the problem considerably. In this case if $A>0$ the favored angle is $\theta=0$, and if $A<0$ the favored angle is $\theta=90°$. It was shown by Artman *et al.*[15] that if A were composed of contributions from the magnetic dipolar anisotropy and the single-ion anisotropy, the different temperature dependences of these two contributions would cause the anisotropy energy to change signs and the spins to flip at about 270°K, which is very close to the observed Morin transition temperature. This good agreement indicates that the other parameters in (1) must be small at atmospheric pressure. The slow change of θ with pressure and temperature at high pressure, however, indicates that the higher-order terms in (1) are no longer small compared to A. For instance, an increase in D with pressure would cause intermediate angles to be favored since the term $D\sin^3\theta\cos\theta\sin3\phi$ favors an angle $\theta=60°$.[16]

Searle's calculations[10] based on the magnetoelastic effect appear to give a good explanation of the rapid initial increase of T_M with pressure. However, since this effect was shown to disappear at about 5.6 kbar it does not explain the anomalous behavior of the spins at higher pressure.

It is suggested here that the washing out of the Morin transition is due to an increase in one of the higher-order anisotropy energy terms such as $D\sin^3\theta\cos\theta\sin3\phi$ with pressure. The physical origin of this term is not known. Perhaps other types of experiments at high pressure will be able to show what change in anisotropy energy is responsible for the slow variation of θ with pressure. Since the neutron diffraction results are in good agreement with the Mössbauer-effect results when the electric field gradient is assumed constant, it appears that the ferric ion position parameter changes very slowly, if at all, with pressure.

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[15] J. O. Artman, J. C. Murphy, and S. Foner, Phys. Rev. **138**, A912 (1965).

[16] T. G. Worlton, Doctoral Dissertation, Brigham Young University, Provo, Utah, 1967 (unpublished).