Mössbauer Study of the Magnetic Field Dependence of the Spin Flop in α-Fe_2O_3 near the Morin Transition

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It is found that an external magnetic field applied in the basal (111) plane of a single crystal of α-Fe_2O_3 causes the Morin transition temperature to be depressed. The detection of the transition was accomplished by observing the appearance of one of the two $\Delta m=0$ lines in the Mössbauer spectrum of Fe^{57} as the crystal warmed through the transition region. From the measurements, the temperature dependence of the antiferromagnetic anisotropy energy can be determined and compared with that predicted on the basis of the Dzyaloshinsky treatment of the weak ferromagnetism in α-Fe_2O_3.

I. INTRODUCTION

THE magnetic properties of hematite, α-Fe_2O_3, have been a subject of wide-spread interest and intensive investigation for many years. Most of this interest is due to the fact that α-Fe_2O_3, a rhombohedral antiferromagnet, exhibits a weak ferromagnetism between about 260°K and its Néel point of 950°K. Below 260°K the spin orientation of the antiferromagnet is parallel to the [111] crystallographic axis, while above 260°K it is perpendicular to the [111] direction.[1] The existence of the weak ferromagnetism is thought to be a result of canting of the two magnetic sublattices of the antiferromagnet and has received a thermodynamic justification by Dzyaloshinsky and Moriya.[2,3] At the temperature of the transition between the two phases, usually referred to as the Morin transition,[4] the dipolar and fine structure anisotropy forces (which are responsible for the spin orientation in the crystal) are of comparable magnitude and opposite in sign.

If a strong magnetic field (60–70 kOe) is applied along the [111] direction at temperatures well below the Morin transition, the antiferromagnetic structure of α-Fe_2O_3 can be induced to "flop" into the high temperature configuration. This spin-flop has been observed in an antiferromagnetic resonance experiment,[5,6] by means of the Mössbauer effect,[7] and in the magnetization study of a hematite single crystal.[8,9] Moreover, the induced transition for this particular configuration of applied magnetic field and crystal axes can be explained in terms of the thermodynamic arguments of Dzyaloshinsky.

Magnetization studies with the applied magnetic field oriented in other directions give a more complicated behavior.[8,9] Nevertheless, they can be interpreted in terms of two induced transitions which are predicted from the Dzyaloshinsky theory. Starting with the low temperature antiferromagnetic phase a spin flop to the weak ferromagnetic state occurs when some critical magnetic field strength is applied. As the applied field strength is increased further a second transition back to the original antiferromagnetic phase is predicted to occur at a second critical field. The critical fields are dependent upon the orientation of the applied field with respect to the crystallographic axes. In this investigation the first of these transitions (antiferromagnetic to weak ferromagnetic) is observed directly using the Mössbauer effect. With the applied magnetic field in the basal (111) plane, the spin-flop temperature is measured as a function of magnetic field, from which the temperature dependence of the anisotropy energy can be determined for temperatures near the Morin transition.

II. EXPERIMENTAL

Synthetic single crystals of α-Fe_2O_3 of 99.6% purity were used for the present study.[10] The crystals were thin platelets about $\frac{1}{4}$ in. in diameter and 0.002 in. thickness with the [111] direction perpendicular to the crystal plane.

The observation of the spin-flop by the Mössbauer effect is based on the angular dependence of the relative spectral-line intensities for a single-crystal absorber. The two lines in the Mössbauer spectrum of ^{57}Fe corresponding to $\Delta m=0$ transitions have intensities proportional to $\sin^2\theta$, where θ is the angle between the spin orientation axis and the γ-ray direction. The crystal was oriented so that the γ radiation propagated along the [111] axis. Thus, the two $\Delta m=0$ lines were absent below the Morin transition temperature and appeared

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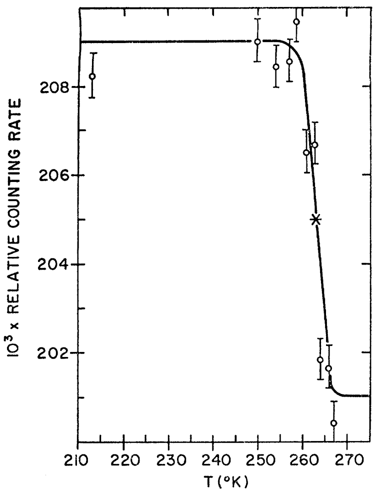

FIG. 1. The appearance of a $\Delta m=0$ transition in the Mössbauer spectrum of a single crystal of α-Fe_2O_3 as it is warmed through the the Morin transition in zero applied magnetic field.

on warming through the transition. The spin-flop temperature was measured by setting the Mössbauer spectrometer to the resonance velocity of one of the $\Delta m=0$ lines and measuring the intensity of transmitted radiation as a function of temperature while the crystal was warmed through the transition. All measurements were made by first cooling the crystal until the antiferromagnetic state was achieved and then warming through the spin flop.

The results of the measurements at 0 and 5000 Oe applied parallel to the (111) plane are shown in Figs. 1 and 2. From these it is clear that with the magnetic field turned on the spin flop occurs at a lower temperature than the zero-field transition temperature. Measurements were also made at several other fields up to 9000 Oe. The transition temperatures, determined at various fields from the inflection points (denoted by *) of plots such as Fig. 1 are listed in Table I.

III. DISCUSSION

The experimental results can be explained by following the argument given by Kaneko and Abe[8] for the field dependence of the magnetization of α-Fe_2O_3. The Dzyaloshinsky treatment of weak ferromagnetic materials[2] applies Landau's theory of second-order phase transitions[11] to these materials and results in an expression for the thermodynamic potential in terms of the magnetic interaction parameters and the orientation of the antiferromagnetic sublattices in the crystal. At the Morin transition temperature T_M the thermodynamic potentials of the two phases are equal under equilibrium conditions:

$$\Phi(\theta=0°)_{T_M}=\Phi(\theta=90°)_{T_M}, \qquad (1)$$

where θ is the angle between the [111] axis and an antiferromagnetic spin axis vector. In the presence of an

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TABLE I. Antiferromagnetic to weak ferromagnetic spin-flop transition temperatures for different magnetic field strengths applied perpendicular to the [111] axis in α-Fe_2O_3 together with the corresponding anisotropy energies determined with the Dzyaloshinsky thermodynamic treatment of weak ferromagnetism.

H_x (kOe)	T_M (°K)	$-(a+g/2)\times10^{-4}$ erg/g
0.0	263±1	0.835
2.5	256±1	1.03
5.0	254±1	1.22
7.0	253±1	1.37
7.5	252±1	1.41
9.0	246±1	1.52

applied magnetic field the same relation holds:

$$\Phi(0°,H)_{T_M}=\Phi(90°,H)_{T_M}. \qquad (2)$$

With the magnetic field applied in the basal plane H_x, the thermodynamic potential can be expanded[2,8,9]:

$$\Phi(\theta,H_x)=\frac{a}{2}\cos^2\theta+\frac{g}{4}\cos^4\theta -d\cos\theta\sin^3\theta-\frac{1}{2}\frac{(q\sin\theta+H_x)^2}{B+J\cos^2\theta}, \qquad (3)$$

where the notation is the same as that used by Dzyaloshinsky,[2] and the small anisotropy of the weak ferromagnetic moment has been neglected ($m_y=0$). The coefficients in the expansion correspond to magnetic interaction energies and mixed interactions of fourth order have been retained. From the expansion it is found that at a given temperature a transition between the two phases $\theta=0°$ and $\theta=90°$ will occur at critical magnetic field strengths of[8]

$$H_{xc}^{\pm}=\frac{-q\pm\left[q^2-\frac{BJ}{B+J}\left(\frac{q^2}{B}+a+\frac{g}{2}\right)\right]^{1/2}}{J/(J+B)}. \qquad (4)$$

Thus, at temperatures below the normal Morin transition, the antiferromagnetic phase will be induced to flop

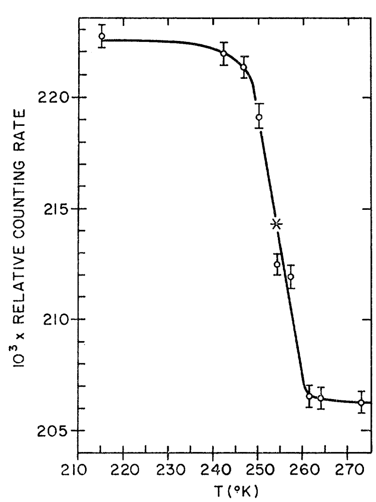

FIG. 2. The appearance of a $\Delta m=0$ transition in the Mössbauer spectrum of a single crystal of α-Fe_2O_3 as it is warmed through the Morin transition with a magnetic field of 5000 Oe applied in the (111) plane.

to the weak ferromagnetic phase at the critical magnetic field H_{xc}^{+}, and at a higher critical field H_{xc}^{-} it will flop back to the antiferromagnetic phase. Without the inclusion of the fourth-order mixed-interaction term only one critical field is obtained and transitions from the antiferromagnetic to the weak ferromagnetic phase would be expected to occur at temperatures above the Morin transition. Consequently, the results in Table I, which show a decrease in T_M with increasing H_x, can be explained only if the fourth-order term is retained in the expansion of the thermodynamic potential.

From magnetic-susceptibility measurements[8] the magnetic interaction parameters B, J, and q can be determined to be 5.2×10^4 erg/g, -1.03×10^4 erg/g, and 2.08×10^4 erg/g at 295°K. In addition, if spin-flop experiments are performed with the applied field perpendicular to the [111] direction, the magnetic anisotropy energy $(a+g/2)$ for α-Fe_2O_3 can be evaluated. The present experiments with the applied field perpendicular to the [111] direction also can be used to arrive at values for the anisotropy energy. Using the previously determined values of B, J, and q together with the measured transition temperatures for different applied magnetic fields, the anisotropy energies in Table I were determined. It was assumed that the values of J, q, and B were independent of temperature near the Morin transition. Actually, the parameter q is temperature-dependent but can be reasonably assumed constant over the small temperature range considered here because of the high Néel point in comparison with T_M.[8]

The results for the anisotropy energy obtained in this work are plotted in Fig. 3 together with some of the results obtained by Kaneko and Abe[7] which were obtained with the spin-flop field applied parallel to the [111] direction in a natural single crystal of α-Fe_2O_3. The two sets of results obtained by quite different techniques and with different orientations of the spin-flop field can be connected with a smooth curve.

Kaczér and Shalnikova[9] have observed substantially the same effect as reported here using torque measurements. Using very pure single crystals of α-Fe_2O_3 they

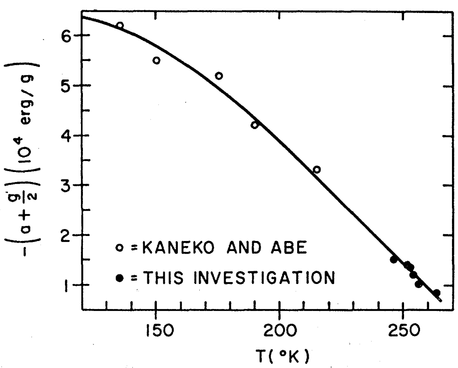

FIG. 3. The temperature dependence of the anisotropy energy of α-Fe_2O_3 near the Morin transition. Comparison is made with magnetic-susceptibility data from Ref. 7.

observed a depression of the Morin transition in the presence of an external magnetic field. From a study of the dependence of the critical magnetic field strength as a function of its orientation with respect to the crystal axes, they were also able to show that the mixed invarient mentioned above had to be retained in the Dzyaloshinsky treatment in order to explain the experimental results. Their result of the field dependence of the Morin transition upon external magnetic field of -1.5 kOe/deg, extrapolated from data taken with the applied magnetic field not parallel to the (111) plane, is a little larger than that indicated by the data in Table I. However, the qualitative features of these three experiments, the magnetization study of Kaneko and Abe, the torque measurements of Kaczér and Shalnikova, and the present results, are consistent with Dzyaloshinsky's thermodynamic approach to the description of the magnetic behavior of α-Fe_2O_3 with the inclusion of the fourth-order mixed invarient.

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