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Magnetization and Mössbauer Studies of the Field Dependence of the Morin Transition in Hematite*

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The field dependence of the Morin transition in Hematite, α-Fe$_2$O$_3$, was studied using the rotating sample magnetometer (RSM) and Mössbauer techniques. With fields in the basal plane, (111), as high as 20 kOe, the Morin temperature was found to decrease by about 10°C. In this range the transition of the antiferromagnetic (AF) axis from the trigonal direction [111] to the basal plane was found to be abrupt.

I. INTRODUCTION

HEMATITE, α-Fe$_2$O$_3$, is a rhombohedral crystal which is magnetically ordered below 960°K, and is essentially antiferromagnetic. Below the Morin transition point[1] ($T_M \cong 262°$K), it has been found[2] to be in an antiferromagnetic (AF) phase with the AF axis parallel to the trigonal [111] axis. Above T_M it is in the weak ferromagnetic (WF) phase, where the antiparallel spins are slightly canted and lie in the basal (111) plane. This transition was found to be field-dependent. An applied magnetic field parallel to the trigonal axis below T_M, will induce the well-known spin-flop transition, as was predicted by Néel[3] and experimentally verified[4–6] in the entire temperature range below T_M. Recently, Kaczér and Shalnikova[7] found the AF–WF transition to be induced also by an applied field perpendicular to the trigonal axis, below T_M. It was studied[7,8] only in a narrow temperature range below T_M because of the limited available magnetic field strength, namely $H<10$ kOe. In these experiments, abrupt phase transitions were noticed for applied fields making any angle with the trigonal axis. Using the notation $H_\perp$, $H_{||}$ for the perpendicular and parallel components of the critical field with respect to the trigonal axis, Kaczér and Shalnikova obtained an hyperbolic relation between these components while Flanders and Shtrikman found a parabolic relation. In order to get their relation, Kaczér and Shalnikova have assumed that the fourth-order mixed term $\frac{1}{2}Jm_X{}^2\cos^2\theta$ which appears in the phenomenological thermodynamical potential of Dzyaloshinsky[9] is appreciable. Here m_X is the component of the net magnetization in the basal plane, H is the applied field in the XZ plane, Z is parallel to the trigonal axis, θ is the angle between the AF axis and the trigonal axis. Kaczér and Shalnikova also predict a reverse WF→AF transition for a greater applied field corresponding to the second branch of their hyperbola, this being due to the additional fourth-order mixed term which favors the trigonal direction for high fields in the basal plane. Neither Kaczér and Shalnikova nor Flanders and Shtrikman have experimentally observed such a transition up to 10 kOe. Flanders and Shtrikman were able to account for their results by comparing the energies of the AF state with the spins perpendicular to the basal plane to that of the WF state with the spins in the basal plane, assuming a Hamiltonian of the form

$$\begin{aligned}E&=E_{\mathrm{ex}}+E_{DM}+E_{\mathrm{an}}+E_H\\&=\lambda\mathbf{M}_1\cdot\mathbf{M}_2-\mathbf{D}\cdot\mathbf{M}_1\times\mathbf{M}_2-(K_1/2M_0{}^2)(M_{1Z}{}^2+M_{2Z}{}^2)\\&\qquad-\mathbf{H}\cdot(\mathbf{M}_1+\mathbf{M}_2),\end{aligned} \tag{1}$$

which is identical to the thermodynamical potential used by Kaczér and Shalnikova for applied fields in the basal plane, if the fourth-order mixed term of Kaczér and Shalnikova is neglected. Here λ is the molecular-field constant, $\mathbf{D}$ is the antisymmetric exchanger tensor, K_1 is the uniaxial magnetocrystalline energy, H the applied field, $\mathbf{M}_1$, $\mathbf{M}_2$ are the sublattice magnetization vectors, and $M_0=|\mathbf{M}_1|=|\mathbf{M}_2|$. This

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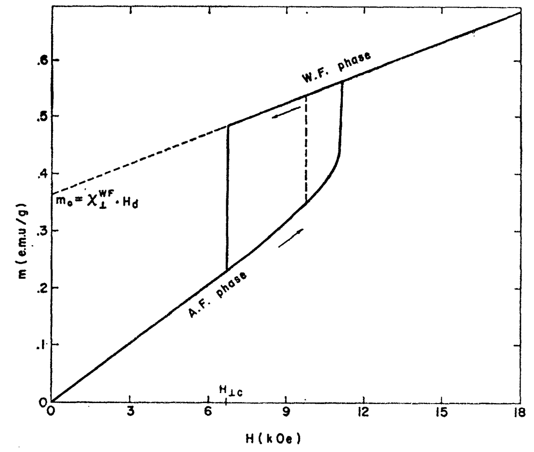

FIG. 1. Theoretical magnetization curve as a function of an applied field in the basal plane below the Morin transition temperature, assuming a spin Hamiltonian of the form (1) with an additional uniaxial anisotropy of the form $-K_2 \cos^4\theta$, calculated for the case: $\chi_\perp^{WF} = 18\times10^{-6}$ emu/gOe, $H_d = 2\times10^4$ Oe, $M_0 = 160$ emu/g, $K_1 = 4800$ erg/g, $K_2 = 1600$ erg/g. The dashed line connects equal energy states of the two phases.

gives the parabolic relation

$$H_\perp = (K_1/\sigma - \tfrac{1}{2}\sigma/\chi_\perp) - \tfrac{1}{2}(\chi_\perp - \chi_\parallel)/\sigma H_\parallel^2 = a(T) - bH_\parallel^2 \tag{2}$$

for the boundary between the AF and WF phases in the $H_\perp$, $H_\parallel$ plane. Here σ is the spontaneous magnetization in the WF phase, $\sigma \cong 0.4$ emu/g, $\chi_\perp$, $\chi_\parallel$, are the susceptibilities perpendicular and parallel, respectively, to the AF axis, $\chi_\perp = 20\times10^{-6}$ emu/g Oe, and $\chi_\parallel = 2\times10^{-6}$ emu/g Oe; hence $b = 2.3\times10^{-5}$ Oe^{-1}. This picture predicts also the relations $\chi_\perp^{AF} = \chi_\perp^{WF} = 1/\lambda$ that are consistent with their experimental results but inconsistent with other reported data.[10–12] The equilibrium equation derived from (1) predicts a gradual rotation of the AF axis.[13] This discrepancy can be removed, at least qualitatively, by assuming that $(K_1 - \frac{1}{2}\chi_\perp^{WF} H_d^2) \to 0$ as $T \to T_M$, where H_d is the Dzyaloshinsky-Moriya field, $H_d = DM_0$, and therefore, in the vicinity of T_M, the higher terms in the expansion of the magnetocrystalline anisotropy in the cosine directions become more important. Adding to (1) a term of the form $-K_2 \cos^4\theta$, one can explain the increase of $\chi_\perp^{AF}$ below T_M, and the abrupt change in the magnetization curves as shown in Fig. 1. The vertical dotted line shown in Fig. 1 connects two positions of equal energy in the AF and WF phases. The observed hysteresis is expected to be smaller than the theoretical one because usually there are defects in the crystals which reduce the potential barrier between the two phases. According to this picture the abrupt nature of the transition has to vanish gradually for decreasing temperature. The purpose of this work was to get more information about the character of the induced transition. It can supply indirect information about the form of the magnetocrystalline anisotropy and its temperature dependence. We looked also for the predicted WF→AF transition.

II. EXPERIMENTAL

We have used two different techniques for studying the phase transition, namely the rotating-sample-magnetometer (RSM) technique,[14] and the Mössbauer effect, which gives a more direct picture of the rotation of the AF axis. The magnetic field intensity was extended up to 20 kOe.

Appreciable signals were seen with the RSM technique for fields making an angle $0° < \varphi < 50°$, with the trigonal axis, at temperature up to about 10.5 degrees below T_M. The experimental results were found to lie on a set of parallel straight lines in the $H_\perp$, $H_\parallel^2$ plane, corresponding to a set of different temperatures as shown in Fig. 2, therefore fulfilling relation (2). Using the notation $H_{\perp c}$, $H_{\parallel c}$ for the critical fields perpendicular and parallel to the trigonal axis, respectively, one has the relation $H_{\perp c}(T)/H_{\parallel c}^2(T) = 2.3\times10^{-5}$ Oe^{-1}. Relation (2) agrees with the experimental results in the whole range studied, namely for $H \lesssim 20$ kOe, and is in good agreement with previous results obtained by

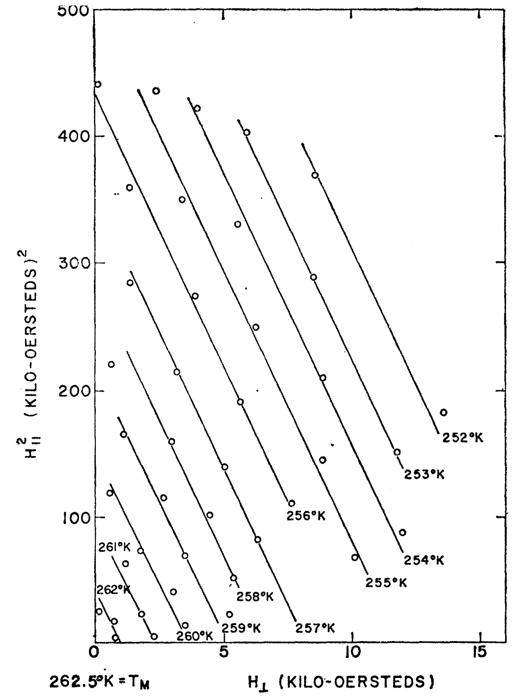

FIG. 2. RSM results of the critical field applied in different directions as a function of temperature, in the $H_\perp$, $H_\parallel^2$ plane.

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magnetic curve measurements.[8] The extrapolated results of $H_{\|c}(T)$, as obtained from Fig. 2, are in good agreement with those obtained by Besser and Morrish[4] with the pulse-field technique or those of Foner[5] who used pulse-field and resonance techniques (except for a small shift in T_M with respect to Foner's crystals). The RSM and Mössbauer measurements were both performed on K3220 series crystals, which were grown by J. P. Remeika of Bell Telephone Laboratories using the flux method.[12]

To observe the transition with an RSM, the crystal is rotated about an axis lying in the basal plane. A magnetic field is applied normal to this axis. A flat, circular sense coil is located close to the sample with coil and rotation axis coinciding. For a set of H and T values a sharp transition produces an output pulse as the crystal rotates through the critical angle. If the phase boundary in the $H_\perp$, $H_\|$ plane, designated by parabolic curves at constant temperature, has any breadth, the RSM signal will decrease as a function of increasing breadth. In the 0 to 20 kOe range, the output should also fall off as φ goes from 0 to $\pi/2$ coincident with increased angular broadening. This angular dependence is observed experimentally and could result from a small variation in K over the crystal volume. In fact, only in small, relatively pure crystals $\cong$1 mg, which presumably are less strained and more homogeneous, could signals be detected. This requirement of small size for the presence of a sharp transition was also observed by Kaczér and Shalnikova in their torque experiments.

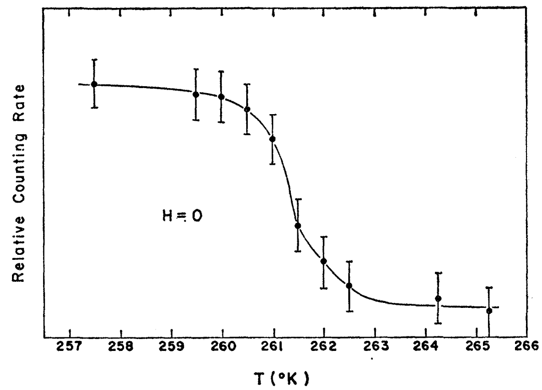

FIG. 3 Mössbauer results of the relative $\Delta m = 0$ absorption peak intensity as a function of temperature, with zero applied field and with the γ radiation parallel to the trigonal axis.

The observation of the change in the spin orientation 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 AF axis and the γ-ray direction. The measurements were performed on a constant-velocity spectrometer.[15,16] Keeping a steady external field, we could easily sweep the temperature slowly enough (about 0.5 deg during an affective 100-sec measurement time), by using a gas-cooled cryostat. Constant fields as high as 20 kOe were achieved by continuing the iron poles of the electromagnet into the cryostat up to a distance of 2 cm in between. An oriented single-crystal absorber was prepared from a large number of small single crystals of the K3220 series, of thickness of about 0.1 mm, to form a mosaic 15 mm in diameter. The trigonal direction was normal to the plane of the disc and parallel to the γ radiation. A ^{57}Co source of about 5 mCi was used. The Morin transition ($H = 0$) is shown in Fig. 3. By applying an external field of 20 kOe parallel to the basal plane, we have observed a

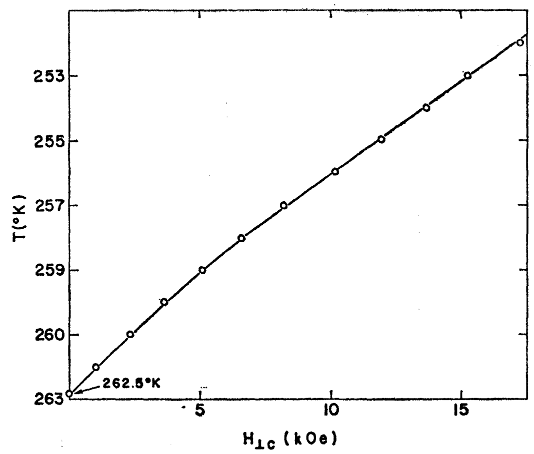

FIG. 4. Extrapolation of the RSM results giving the critical field $H_{\perp c}$ when applied in the basal plane, as a function of temperature.

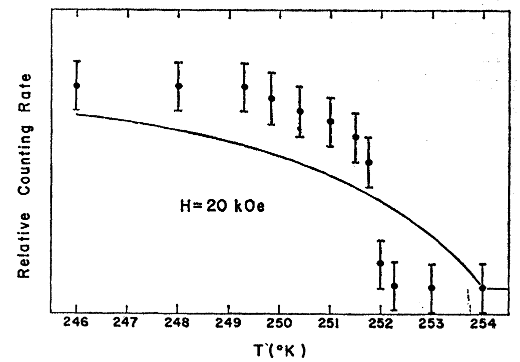

FIG. 5. Mössbauer results (points) of the relative $\Delta m = 0$ absorption peak intensity as a function of temperature, with an applied field of 20 kOe parallel to the basal plane and with the γ radiation parallel to the trigonal axis, with respect to a best-fit theoretical curve according to the gradual rotation picture.

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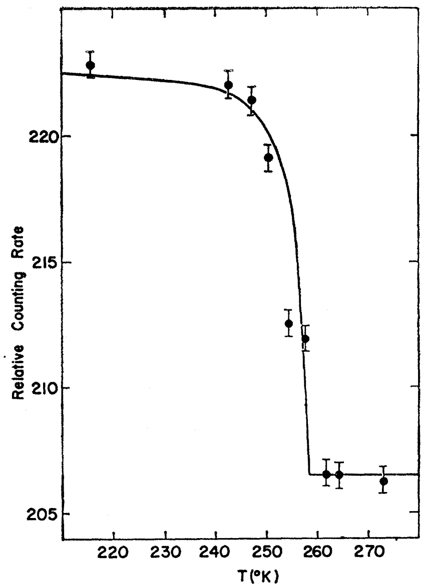

FIG. 6. Simkin and Bernheim's Mössbauer results (points) of the $\Delta m=0$ absorption peak relative intensity as a function of temperature, versus best theoretical curve, according to the gradual rotation picture, for $H=5$ kOe applied in the basal plane. Best fit was achieved for $T_M=263°\mathrm{K}$, $T_c=258°\mathrm{K}$.

quite abrupt transition at about 9.5 deg below T_M (see Fig. 5). The predicted critical temperature for this field, according to the RSM results, as is shown in Fig. 4 is about 1 deg lower.

We want to mention that care has to be taken in analyzing the transition results in those experiments where constant applied field and varying temperature are used. In this case, even a gradual transition near T_M seems to be abrupt. By expanding the first uniaxial anisotropic term K_1 around T_M, one can write, in first approximation, $K_1(T)=K_0+\alpha(T_M-T)$. In the gradual rotation picture, assuming a spin Hamiltonian of the form (1), one has $K_1(T_M)=K_0=\frac{1}{2}\chi_\perp{}^{\mathrm{WF}}H_d{}^2$. In this picture one obtains for a fixed field, applied in the basal plane, $\sin\theta(T)=H_d/H_{||c}{}^2(T)$. H and $H_0(T_c)=H_{||c}{}^2(T_c)/H_d$, where H_0 is the field for which the AF axis reaches the WF phase, and T_c is the corresponding temperature. Replacing H by $H_0(T_c)$ and using $H_{||c}{}^2(T)=2\lambda K_1(T)-H_d{}^2$, one gets

$$\sin\theta(T)=(T_M-T_c)/(T_M-T) \qquad \text{for} \qquad T\leq T_c. \quad (3)$$

In Fig. 5 we have compared our experimental Mössbauer results with the theoretical curve corresponds to the gradual rotation according to (3). Although it may have no significance we want to note that Simkin and Bernheim's results[17] seems to fit better to the gradual rotation picture than to the abrupt one, as is shown in Fig. 6. (The Morin transition of their crystals is rather wide.)

III. DISCUSSION

Our present RSM results are in good agreement with Flanders and Shtrikman's picture. The Mossbauer experiments also seem to show an abrupt transition. On the other hand, in Flanders and Shtrikman's picture it is difficult to explain the reported increase of $\chi_\perp$ below T_M. By adding to the spin Hamiltonian (1) the second term of the expansion of the magnetocrystalline anisotropy in the cosine directions, $-K_2\cos^4\theta$, we get magnetization curves of the form shown in Fig. 1. In this case the transition starts as a gradual one, but as the AF axis reaches a critical angle, which decreases with increasing temperature, the transition becomes abrupt. Such a transition can still take into account, in principle, all known experimental results. Moreover, it predicts an entirely gradual transition far enough below T_M. Mössbauer experiments at low temperatures, performed by Blum and Frankel,[18] seem to support this predicted behavior. The second transition (WF→AF), which is predicted by Kaczér and Shalnikova, was not seen even by applying fields as high as 20 kOe, although from their formula a much smaller field should have been sufficient as

$$H_{\perp c}\xrightarrow{\mathrm{WF}\to\mathrm{AF}}0 \quad \text{as} \quad T\to T_M.$$

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