tion experiments with polarized neutrons become practicable.

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# Domain Walls in Antiferromagnets and the Weak Ferromagnetism of $\alpha$-$Fe_2O_3$†

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At the Néel temperature local nucleations of the antiferromagnetic order and their subsequent growth lead to the formation of domain walls. The domains in an antiferromagnet are thermodynamically stable only when the anisotropy force opposing the gradual switch of spins in the Bloch zone is small such that the wall energy is offset by the gain in entropy. However, in most cases the domain wall would owe its stability to the presence of lattice imperfections, such as interstitial atoms or dislocations. A typical magnetization curve of an antiferromagnet with ferromagnetic domain walls is depicted.

The weak ferromagnetism observed in the (111) plane of $\alpha$-$Fe_2O_3$ (hematite) is identified with the magnetization in domain walls pinned down by lattice imperfections. An assumption that the linear dimension of domains is, on the average, $10^4$ atomic spaces gives the observed strength of the weak ferromagnetism. The disappearance of this ferromagnetism at *ca* $-20$°C when the magnetic axis switches from a $[11\bar{2}]$ direction to the [111] direction is due to the extreme difference in the anisotropy force in the (111) plane and that in a plane containing the [111] axis. The following experimental findings on $\alpha$-$Fe_2O_3$ are interpreted: (a) The variation of the ferromagnetism as the temperature increases shows the general feature of the decrease of long-range order in cooperative phenomena, being very gradual at lower temperatures and growing sharper and sharper as the temperature approaches the Néel point. (b) In the transition region of the two antiferromagnetic states of $\alpha$-$Fe_2O_3$ an applied field in the (111) plane causes a decrease of the temperature at which the ferromagnetic effect and the large magnetostriction effect disappear but produces no change in the neutron diffraction intensity of the (111) line.

## I. DOMAIN WALLS IN ANTIFERROMAGNETS

### 1. General Considerations

THE existence of domains in antiferromagnets was proposed by Néel to explain the increase of susceptibility of antiferromagnets with field intensity.[1] More recently, Néel[2] suggested that the weak magnetic remanence observed in the chlorides of the iron group[3] should be attributed to the magnetization of the net moments of the domain walls. Furthermore, the sharp decrease of Young's modulus in NiO and CoO at the Néel point observed by Street and Lewis[4] and in CoO by Fine[5] may be caused by the effect of change of domain structure under external stress.

In general there are two types of domain boundaries in antiferromagnets, the change-step boundary and the change-axis boundary. The former is analogous to the 180° boundary in ferromagnets. In the latter the magnetic axis at one side of the boundary is in a different direction from that at the other side; this is geometrically conceivable, when there are several crystallographically equivalent easy directions of sublattice magnetization. The crystallographic twins observed in crystals of NiO are probably change-axis domains.[6] The distribution of such domains is very much subjected to the influence of internal strain, applied stress, etc., besides the thermal factor.

The formation of domains in ferromagnets is promoted by the reduction of magnetostatic energy, while this is not so in antiferromagnets in the absence of an external field. However, the stability of domains in antiferromagnets is warranted at finite temperatures, if the wall energy is counterbalanced by the gain in entropy. When the formation of the spin lattice begins to take place at the Néel temperature, local nucleations of the antiferromagnetic order and their subsequent growth must lead to the formation of domains, no matter whether the latter is thermodynamically favored or not. Consequently, the existence of domain boundaries should be found to accompany an antiferromagnetic transition, even though their existence might be transient. A number of domain walls are likely to be pinned down by lattice imperfections, such as dislocations and interstitial atoms, and continue their existence.

† Work supported by the U. S. Army Signal Corps and the Office of Naval Research under contracts with the Laboratory for Magnetics Research, Carnegie Institute of Technology.

[1] L. Néel, Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, September, 1953 (Science Council of Japan, Tokyo, 1954), p. 701.

[2] L. Néel, Brussels Conference, September, 1954 (unpublished).

[3] W. J. Haas and B. H. Schultz, J. phys. radium **10**, 7 (1939). References to earlier theories are listed in this article.

[4] R. Street and B. Lewis, Nature **168**, 1036 (1951).

[5] M. E. Fine, Revs. Modern Phys. **25**, 158 (1953).

[6] Y. Y. Li, Phys. Rev. **100**, 627 (1955).

Similarly to the ferromagnetic case, an antiferromagnetic domain boundary must spread over a finite transition layer, the so-called Bloch zone. Figure 1 shows an idealized one-dimensional model of a 180° boundary. The difference of 180° phase angle between the two neighboring domains is made up by the gradual changes in the phase angles from one spin to a neighboring one. In this figure the spins in the Bloch zone are parallel to the boundary. Geometrically they may be parallel to any plane containing the antiferromagnetic axis. However, in a real antiferromagnet the formation of a domain wall increases the anisotropy energy and so the spins of the wall region would be kept parallel to a plane in which the least anisotropy is involved. The following discussions of this section given in terms of a 180° domain boundary apply equally well to the change-axis domain boundaries.

## 2. Energy and Entropy

In a domain wall the increase of exchange energy is kept down by a gradual switch of the orientation of moments. The situation may be expressed in an idealized manner[2] by the following scheme:

$$0\ \pi\ 0\quad \pi\quad 0\ \cdots\ 0\ \pi\ \cdots\ 0\quad \pi\quad 0\ \pi, \tag{A}$$

$$0\ \pi\ 0\quad \pi\quad 0\ \cdots\ 0\,\vdots\,0\ \cdots\ \pi\quad 0\quad \pi\ 0, \tag{B}$$

$$0\ \pi\ 0\,\vdots\,\left(1+\frac{1}{N}\right)\pi\quad \frac{2}{N}\pi\ \cdots\ \cdots\ \cdots\ \frac{N-2}{N}\pi\quad \left(1+\frac{N-1}{N}\right)\pi\,\vdots\,\pi\ 0. \tag{C}$$

In (A) the antiparallel order is continued from one end to the other. (B) shows two domains with a sharp boundary at the middle. In both cases the phase angle is either 0 or $\pi$. In (C) the Bloch zone spreads over $N-1$ spins between the two dotted vertical lines. The phase angle of the $k$th spin in the Bloch zone is increased by $k\pi/N$ in comparison with that in (A). The increase of energy,[7]

$$w_{\text{ex}}\approx\pi^2|J|s^2/Na^2, \tag{1}$$

per unit area, where $J$ is the exchange integral, $s$ the spin quantum number and $1/a^2$ is the number of lines of magnetic ions across a unit area of the wall. For simplicity $a$ is taken as the cubic root of a unit cell volume. Equation (1) is obtained by using the approximate expression $|J|s^2\varphi^2$ for the increase of exchange energy. $\varphi$ is $\pi/N$ in the boundary region. On the other hand, the thickness of the Bloch wall is restricted by the anisotropy force; the increase of anisotropy energy is

$$w_{\text{anis}}\approx KNa/10, \tag{2}$$

per area of the wall, where $K$ is the anisotropy constant referred to a unit volume of the material. The factor $\frac{1}{10}$ is added there for approximating the fact that most of the spins are not exactly along the hard direction. The third contribution to the increase of energy is the magnetostatic energy of the net moments in the boundary region. This energy is extremely small because the ferromagnetic moment of the Bloch zone is indeed small. By minimizing the total increase of energy [the sum of Eqs. (1) and (2)], we find the wall thickness

$$N\approx(10\pi^2|J|s^2/Ka^3)^{\frac{1}{2}}, \tag{3}$$

and

$$w_{\text{wall}}\approx(\pi^2|J|s^2K/10a)^{\frac{1}{2}}. \tag{4}$$

[7] Our estimate of wall energy follows the same method as used by Kittel for a ferromagnetic domain wall. See C. Kittel, Revs. Modern Phys. **21**, 541 (1949).

The main contribution to the entropy of a domain wall comes from its flexibility. Unlike its counterpart in ferromagnets, the locality and topographic details of an antiferromagnetic wall are not determined by the demagnetization factor. A part of the wall surface may shift one or several atomic spaces to the left or to the right with respect to its neighboring parts. Instead of a straight plane, the wall would look like a patchwork on whose seams the shifts of the wall position take place. Let the total area of the wall be $Aa^2$, and in the average a shift of position occurs $n$ units of $a$ apart. The entropy

$$\begin{aligned} S&\approx k\ln(p^{A/n2})\\ &=kA(\ln p)/n^2, \end{aligned} \tag{5}$$

where $p$ is the number of ways in which the boundary may change its position at any point. Whether this shift leads to an appreciable increase of energy depends on the strength of the exchange interaction among the spins in the plane of the domain boundary. Assuming this increase in energy is negligible we have from

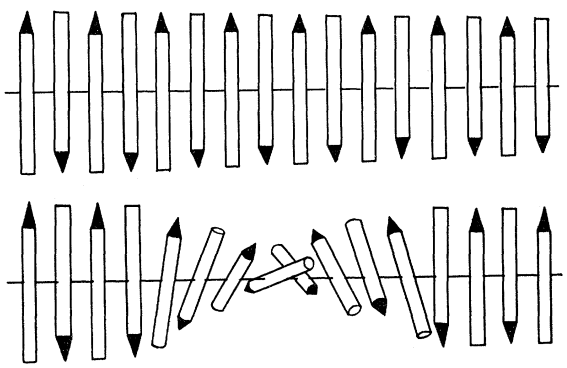

FIG. 1. An idealized one-dimensional model of a 180° domain wall. Upper: a single domain. Lower: a Bloch zone and the neighboring domains.

Eqs. (4) and (5) the free energy of a domain wall

$$\Delta F \approx \pi s(|J|k/10a)^{\frac{1}{2}} - kT(\ln p)/n^2a^2 \qquad (6)$$

per unit area. Evidently $p \gtrsim 3$. (For too large a shift an appreciable increase of energy may be induced.) The domain wall is thermodynamically demanded if its formation leads to a decrease in the free energy, i.e., $\Delta F < 0$. To satisfy this condition, the anisotropy constant involved in the gradual switch of the spins must be small. Since $n$ can never be smaller than 1, we deduce from Eq. (6) that when $K > 10^6 T^2/T_c$ erg/cm$^3$ a domain wall is thermodynamically unstable. Since a high anisotropy is quite common in antiferromagnets, domain walls cannot always hold their own without the intervening of lattice imperfections. Furthermore, the increase in energy caused by a zigzag of the boundary would not be negligible. In fact, we are inclined to believe that in most cases domain walls actually owe their existence to the stabilizing effect of imperfection centers.

### 3. Magnetization of Domain Walls

The Bloch zone has a noncompensated moment. Its orientation is in the plane containing the easy direction of sublattice magnetization and the least anisotropy. Néel[2] found that this moment is negligibly small, unless the Bloch zone extends over only a very small number of atomic spaces, i.e., in case that $|J|/K$ is extremely small [see Eq. (3)]. However, a domain wall held down by lattice imperfections, such as interstitial atoms and dislocations, must have its Bloch zone compatible with the dimension of the imperfection center, i.e., at most, several atomic spaces. The net moment in such cases is of the order of one ionic moment per line of ions across the wall. This moment can reverse its direction by turning $\varphi$ $(=\pi/N)$ into $-\varphi$. (The changes of the phase angle through 180° can be achieved in either a right-hand screw fashion or a left-hand screw fashion.) In the absence of an external field, there is equal probability for the moment being in one direction or the opposite. This balance can be upset by an applied field $H_d$ barely strong enough to overcome the potential barrier which hinders the free rotation of ionic moments. Unless the temperature is very near to the Néel point, the applied field, which has a sufficient strength to bring the net moment of the Bloch zone into alignment, could not break up the antiferromagnetic coupling of spins in the domains but cause a partial inclination of spins toward the field direction. Therefore, after the saturation of the ferromagnetic moment, the magnetization should continue to increase at a constant rate which represents the susceptibility of the antiferromagnetic lattice itself. The susceptibility after the saturation should be almost the same as that just below $H_d$. Any possible difference between these two readings would be only of the order of magnitude of $\chi_\perp - \chi_{II}$ or less, where $\chi_{II}$ and $\chi_\perp$ are respectively the susceptibilities when the applied field is parallel and perpendicular to the preferred axis. A hysteresis with a weak remanence should be observed in such an antiferromagnet. We can only expect a remanence at most $10^{-3}$ times that of the ordinary ferromagnets, and probably much less than that, for the ferromagnetic moments involved here are indeed very small. The magnetization curve and a part of the hysteresis loop of an antiferromagnet with ferromagnetic domain walls (Fig. 2) is constructed according to the ideas presented above. Magnetization curves of this kind are actually observed in $FeCl_2$ and in other compounds,[3,8] as well as $\alpha$-Mn.[9]

### II. DOMAIN WALL FERROMAGNETISM IN $\alpha$-$Fe_2O_3$ (HEMATITE)

The magnetism of $\alpha$-$Fe_2O_3$ has been studied in detail. Among those who measured the susceptibilities and magnetization, Smith,[10] Guillaud,[11] Chevallier,[12] Morin,[13] Pauthenet,[14] and Bizette *et al.*[15] have made definite contributions. Anderson *et al.*[16] have observed in $\alpha$-$Fe_2O_3$ a ferromagnetic resonance from which the anisotropy force may be estimated. Its magnetostric-

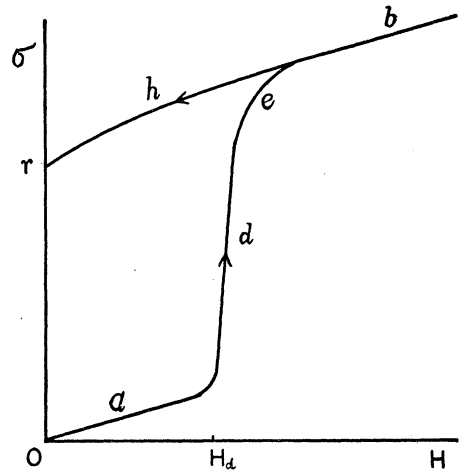


FIG. 2. A typical magnetization curve of an antiferromagnet with ferromagnetic domain walls. *a* and *b* are the straight lines of the paramagnetic magnetization of the antiferromagnetic lattice. The sharp rise in the part *d* is due to the reversal of the domain-wall moments whose direction is not favored under the applied field. $H_d$ is the field strength required to overcome the potential barrier which hinders this reversal. The part *e* represents the gradual switch of the domain-wall moments to the field direction. *h* is a part of the hysteresis loop. The remanence is registered on the ordinate at *r*.

[8] Starr, Bitter, and Kauffmann, Phys. Rev. **58**, 977 (1940).
[9] Arrott, Coles, and Goldman, Phys. Rev. **98**, 1864 (1955); A. Arrott (private communication).
[10] T. T. Smith, Phys. Rev. **8**, 721 (1916). References to earlier magnetic measurements on $\alpha$-$Fe_2O_3$ may be found in this article.
[11] C. Guillaud, J. phys. radium **12**, 489 (1951).
[12] R. Chevallier and S. Mathieu, Ann. phys. **18**, 258 (1943); R. Chevallier, J. phys. radium **12**, 172 (1951).
[13] F. J. Morin, Phys. Rev. **78**, 819 (1950).
[14] L. Néel and R. Pauthenet, Compt. rend. **234**, 2172 (1952).
[15] Bizette, Chevallier, and Tsai, Compt. rend. **236**, 2043 (1953).
[16] P. W. Anderson *et al.*, Phys. Rev. **93**, 717 (1954).

tion has been studied by Urquhart and Goldman.[17] The neutron diffraction experiment of Shull *et al.*[18] confirms an earlier finding that below *ca* 950°K this crystal has two antiferromagnetic states. Figure 3 shows the spin arrangements as revealed by neutron diffraction. The magnetic lattice is the same for these states; the spin axis is in the [111] direction below *ca* 250°K while it is in a $[11\bar{2}]$ direction between 250°K and 950°K. We propose to call them respectively the *A*II and *A*I states of $\alpha$-$Fe_2O_3$. Besides these complications a weak ferromagnetism in the (111) plane with a saturation magnetization about 0.4 emu per $cm^3$ was first noticed by Smith[10] and confirmed by later experimenters. It is always found in coexistence with the *A*I state. Both Smith and Pauthenet[14] found that a weak isotropic ferromagnetism, besides the anisotropic one is observed in the temperature ranges of both *A*I and *A*II states in natural crystals from the island of Elba. However, it is not found by Smith[10] and Chevallier *et al.*[12] in natural crystals from sources other than Elba, nor by Guillaud[11] working with laboratory-prepared specimens of highest purity. Also, it is observed by Anderson *et al.*[16] that the ferromagnetic resonance in laboratory-grown crystals disappears when the temperature is cooled down below the temperature of transition between the two antiferromagnetic states. We notice that the isotropic ferromagnetism is absent in most specimens and varies in intensity from one specimen to another when it occurs, while the anisotropic ferromagnetism is constantly observed. The magnetization curve[10,13,15] is of the type depicted in Fig. 2 with a small critical field $H_d$. We shall show that the anisotropic ferromagnetism in $\alpha$-$Fe_2O_3$ may be explained on the basis of domain-wall magnetization. Several tentative explanations of the origin of the parasitic ferromagnetism in $\alpha$-$Fe_2O_3$ have been previously discussed by Néel,[19] Snoek,[20] and Forrer[21] respectively. Among them, Snoek's idea of attributing the effect to incoherent regions in antiferromagnets reads like a forerunner of the present theory. Néel's assumption of the existence of $Fe^{+2}$ ions and the resultant ferromagnetism similar to that in $Fe_3O_4$ might be correct in explaining the isotropic magnetization of some natural crystals. None of the previous work has furnished an acceptable explanation of the following magnetic behavior of $\alpha$-$Fe_2O_3$:

(a) A permanent moment of 0.4 emu per $cm^3$ means only 0.02% of the total magnetic moment of $Fe^{+3}$ ions per $cm^3$; i.e., only 200 out of one million contribute to the noncompensated alignment of moments.

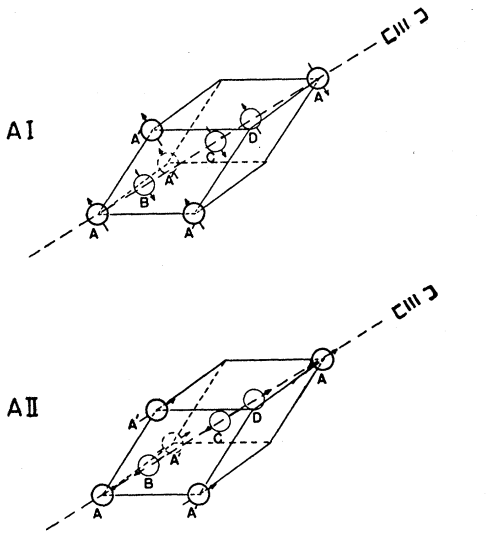


FIG. 3. The antiferromagnetic states of $\alpha$-$Fe_2O_3$. The five cations along the [111] diagonal and those at three corners of a rhombohedral unit cell are shown.

(b) This ferromagnetism disappears when the spins are disordered at the higher transition point and also when the antiferromagnetic axis flops through 90° to the [111] direction at the lower transition point.

(c) The magnetization is found in the (111) plane when the antiferromagnetic axis lies in that plane.

Our explanation is based on the idea of domain walls in antiferromagnets presented in Sec. I with the following assumptions:

(i) The domain wall in hematite at the *A*I state does not owe its existence to the condition of thermodynamical equilibrium but rather to the stabilizing effect of lattice imperfections. As a result, the net moment in the narrow Bloch zone is of the order of 1 ionic moment per line of ions across the wall.

(ii) At room temperature, the domain walls are, on the average, about $10^4$ atomic distance apart.

(iii) In hematite at the *A*II state the domain wall cannot be retained even with the intervening of lattice imperfections.

The resonance experiment of Anderson *et al.*[16] indicates that within the (111) plane there is an anisotropy force equivalent to 60 gauss, while in a plane containing the [111] direction the anisotropy is equivalent to 30 000 gauss. Therefore, in the *A*I state the spins within the Bloch zone are oriented parallel to the (111) plane and the net moment is also in this plane. The observed strength of the weak ferromagnetism in the (111) plane is accounted for by the assumption (ii). The domain size of $10^4$ atomic spaces should not cause a line broadening of the magnetic diffraction of neutrons. From the third assumption (iii), the magnetization observed in the *A*I state should disappear in the *A*II state. This must not be regarded as an *ad hoc* assumption for the following reason: In the *A*II state the easy direction of

[17] H. M. A. Urquhart, thesis, Carnegie Institute of Technology, 1954 (unpublished); H. M. A. Urquhart and J. E. Goldman, preceding paper [Phys. Rev. **101**, 1443 (1956)].
[18] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).
[19] L. Néel, Ann. phys. **4**, 249 (1949); Compt. rend. **228**, 64 (1949); Revs. Modern Phys. **25**, 58 (1953).
[20] J. L. Snoek, Physica **16**, 333 (1950); J. phys. radium **12**, 188 (1951).
[21] R. Forrer, J. phys. radium **12**, 188 (1951).

sublattice magnetization is along the [111] axis. To rotate a moment away from this direction involves a large increase of anisotropy energy. The anisotropy force in a plane containing the [111] direction is not exactly known for the $A$II state. Presumably its magnitude is of the order of $10^5$ gauss as in the $A$I state. The wall energy is proportional to $\sqrt{K}$ if the domain boundary exists on its own accord, or increases proportional to $K$ if its Bloch zone is confined to the dimensions of the imperfection center which holds the wall in place. Since in $\alpha$-$Fe_2O_3$, the latter is the case, the increase in energy due to a domain wall in the $A$II state is 100 to 1000 times larger than in the $A$I state. We suggest that the imperfection center, which, in the $A$I state stabilizes the domain walls, cannot do the same in the $A$II state against such a large increase of energy. Therefore, as the temperature decreases through the transition point of the two states the domain walls must disappear through mutual annihilation and migration to the surface. As the temperature increases again through the transition point, domain walls are recreated by nucleation and then stabilized by the imperfection centers. It is extremely improbable that the moments of the antiferromagnetic lattice would turn 90° *en masse* at the transition.

It is interesting to note the following.

### A. Temperature Dependence of the Weak Ferromagnetism of the *A*I State

As the temperature approaches the Néel point (*ca* 950°K) the long-range order of antiparallel coupling of spins diminishes rapidly, and so the majority of local disorders can no longer be described as boundaries of domains. Therefore, we may expect that the decrease of ferromagnetic magnetization with temperature assumes the same course as the decrease of antiferromagnetic order and vanishes above the Néel point. The curve of observed thermal variation of this ferromagnetism[14] actually shows the general feature of the decrease of long-range order in cooperative phenomena, being very gradual at lower temperatures and growing sharper and sharper as the temperatures approach the order-disorder transition point.

### B. Transition between *A*I and *A*II States

The magnetostriction measurements taken by Urquhart and Goldman[17] lead to several results of interest. Before the present theory of domain-wall ferromagnetism was available, the data could not be satisfactorily interpreted. It is found that the temperature, at which the magnetostriction first goes through zero and the large magnetostrictive effect disappears lies in the neighborhood of the transition point between the two states and decreases linearly with increasing applied field at the rate of about 1°C per 1000 gauss. This cannot be taken as an indication that the temperature of the $A$I–$A$II transition depends on the applied field, for it finds no confirmation in the neutron diffraction experiment of Corliss, Hastings, and Goldman,[22] in which the intensity of the (111) reflection is recorded with applied field in the (111) plane. When the antiparallel-coupled spins switch into the [111] direction this line must disappear. Corliss *et al.* have found no difference in the variation of intensity with zero and 6000 gauss applied. We find that these two experimental findings taken together are very informative and lend further evidence to the theory of domain wall ferromagnetism. While the bulk of the crystal is not affected by the applied field used in the two experiments, the existence of the domain wall in the $A$II state is given a slight advantage under the applied field until a lower temperature is reached. This not only puts the magnetostrictive effect into harmony with the neutron diffraction observations but also agrees with the conclusion of Urquhart and Goldman from the bulk of the magnetostrictive data that the ferromagnetic component of the spin system is mainly responsible for the magnetic strain under external field. Also, we believe that Chevallier's observation of the dependence on applied field of the temperature at which the parasitic ferromagnetism disappears indicates the dependence of the stability of domain walls in $A$II when a field is applied. The interpretation of the magnetostriction at room temperature is given in an article by Urquhart and Goldman[17] from the present viewpoint.

### C. $Cr_2O_3$

Parasitic ferromagnetism has not been observed in $Cr_2O_3$ which is isomorphous in crystal structure. The only antiferromagnetic state reported in $Cr_2O_3$ has the magnetic axis in the [111] direction,[23] similarly to the $A$II state of $\alpha$-$Fe_2O_3$. The anisotropy force in $Cr_2O_3$ in a plane containing the [111] axis is probably of the same order of magnitude as that in $\alpha$-$Fe_2O_3$.

#### ACKNOWLEDGMENTS

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[22] Corliss, Hastings, and Goldman, Phys. Rev. **93**, 893 (1945).
[23] T. R. McGuire *et al.*, Phys. Rev. **98**, 1962 (1955).