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Saturation and Magnetization of Hexagonal Iron Oxide Compounds

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The value of the saturation magnetization at absolute zero of $BaO\cdot 6Fe_2O_3$ and related compounds can be explained as due to noncompensated antiferromagnetism.

The Bloch wall formation in small particles is discussed. One is led to the assumption that in these materials Bloch walls are nucleated at imperfections. In specimens containing randomly oriented large crystals, Bloch wall formation becomes appreciable at a positive field strength of the order of $4\pi I_s$.

By orienting the crystals in a magnetic field $(BH)_{max}$-values of 3×10^6 gauss oersted have been obtained.

The critical diameter for wall formation changes with temperature. An excess of walls formed at a different temperature from the temperature of measurement may persist in a metastable equilibrium.

I. SATURATION MAGNETIZATION

A CLASS of hexagonal iron-oxide compounds, of which $BaO\cdot 6Fe_2O_3$ is the prototype, has been dealt with in an earlier publication.[1] Figure 1 shows the saturation magnetization of $BaO\cdot 6Fe_2O_3$ as a function of temperature, as measured for single crystals along the hexagonal axis, which is the direction of easy magnetization. Figure 2(a) schematically shows the crystal structure.[2] In this hexagonal structure oxygen ions form a close packed lattice, some sites of which are occupied by Ba ions. The ferric ions are found on five nonequivalent sites in the interstices of the oxygen lattice.

The value of the saturation magnetization and the dependence of the paramagnetic susceptibility on temperature indicate that the magnetization of the materials under consideration is due to noncompensated antiferromagnetism. The value of the saturation magnetization at low temperatures could be estimated for this compound and related materials. In this estimation, based on Anderson's theory,[3] it is assumed that an angle $Me^{(1)}-O-Me^{(2)}$, where Me stands for two magnetic ions and O for the oxygen ion giving rise to superexchange between them, causes strong negative interaction if near 180°, while interactions between two magnetic ions can be neglected when this angle is near 90°. The dependence of the superexchange on distance is taken into account by neglecting all interactions which involve $Me-O$ distances in excess of 3A. Proceeding along these lines, one finds 40 Bohr magnetons as saturation moment of $BaO\cdot 6Fe_2O_3$ at absolute zero temperature, while an extrapolation of the measurements gives about 44 Bohr magnetons.

It has already[1] been shown that very slight alterations of the structure can change the noncompensated antiferromagnetism into compensated antiferromagnetism. The compound $K_2O\cdot 11Fe_2O_3$, the structure of which[2,4] is schematically represented in Fig. 2(b), is nonferromagnetic. This can be explained by the small change in ionic arrangement near the layer which contains the large Ba or K ion. The three O ions in the Ba layer are replaced by one O ion in the K layer so that again a strong interaction results. Because of this interaction the K layer now will be a mirror plane for the direction of the magnetic moments.

II. CRYSTAL ANISOTROPY AND COERCIVE FORCE

The energy of crystalline anisotropy K, which is shown as a function of temperature in Fig. 3, determines the coercive force. The strain energy can be neglected, since the magnetostriction constant measured normal to the direction of preferential magnetization is only about $2\cdot 10^{-5}$, at room temperature, while the shape anisotropy may be ignored because of the relatively low value of the saturation magnetization. In Fig. 4 the temperature dependence of $2K/I_s$ is compared with that of the coercive force for fine-grained material oriented at random. For pure rotation the coercive force ${}_IH_c$ should equal $0.96K/I_s$. The difference between the curves shown in Fig. 4 indicates that wall formation and wall movement must be taken into account.

The critical diameter for wall formation in isolated

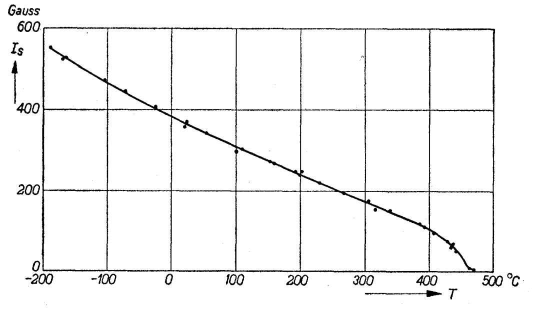

FIG. 1. The saturation magnetization of dense $BaO\cdot 6Fe_2O_3$ as a function of temperature.

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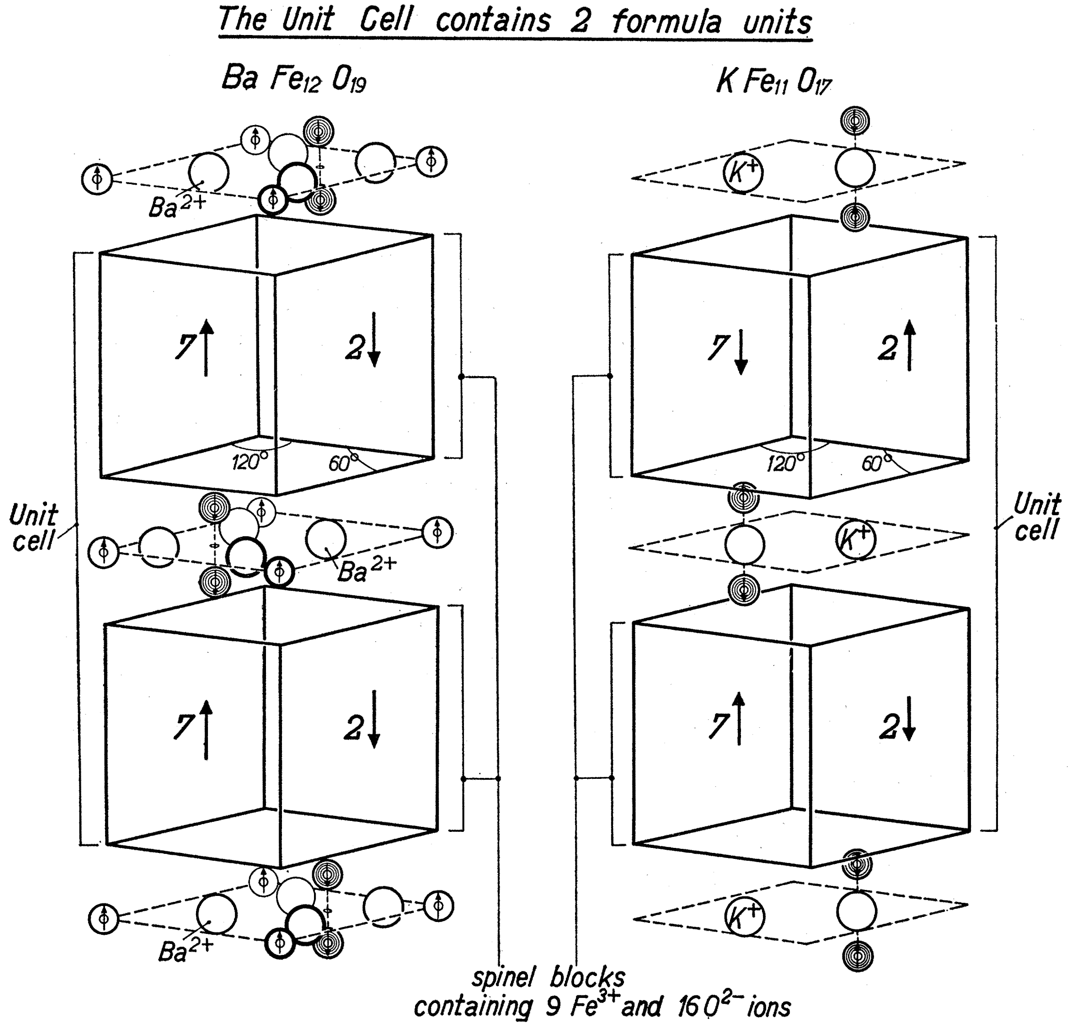
[1] Went, Rathenau, Gorter, and van Oosterhout, Philips Tech. Rev. **13**, 194 (1952).

[2] V. Adelsköld, Arkiv för Kemi, Mineralogi och Geologi **12A**, No. 29, 1 (1938).

[3] P. W. Anderson, Phys. Rev. **79**, 705 (1950).

[4] C. A. Beevers and M. A. S. Ross, Z. Krist. **97**, 57 (1937).



(a) (b)

FIG. 2. Comparison of the crystal structures of $BaO \cdot 6Fe_2O_3$, which shows noncompensated antiferromagnetism, and $K\ Fe_{11}O_{17}$, which shows compensated antiferromagnetism; schematic. Large circles represent oxygen (or Ba or K) ions. Small circles represent ferric ion in different crystallographic sites.

spheres of the material can be estimated to be as large as one micron. It varies with temperature as $K^{\frac{1}{2}}/I_s$, a quantity which is plotted in Fig. 5. For a given grain the number of walls can thus be expected to decrease with increasing temperature below 430°C. Especially those walls that are fixed at inclusions or regions of suitable strain, and therefore are least mobile, will persist at higher temperatures. On the other hand, the field strength necessary to move a particular wall decreases with temperature as $K^{\frac{1}{2}}$. It is believed that these two effects, the influence of which on the coercive force is opposed, cause the maximum in the ${}_IH_c$ curve of Fig. 4.

III. BLOCH WALL FORMATION IN SMALL PARTICLES

Kittel[5] has stated that Bloch walls will be created spontaneously if the crystal size surpasses a critical diameter, while for smaller dimensions an external field has to be applied which increases with decreasing particle size. On treating again[6] his model of a single domain sphere, we arrive at the conclusion that the field strength at which a wall is formed should be independent of particle size, in case the thickness of the wall is small compared with the crystal size. It has been found experimentally that the coercive force of large particles of $BaO \cdot 6Fe_2O_3$ is much smaller than that of small particles and also than the critical field strength which has been calculated, just as in the case of MnBi.[7] Thus we are forced to assume that walls are nucleated at imperfections of the crystals such as, e.g., grain boundaries.

The calculation runs as follows. The largest field is needed in the initial stages of wall formation; therefore

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[5] C. Kittel, Phys. Rev. 73, 810 (1948).

[6] Rathenau, Smit, and Stuyts, Z. Physik (to be published).

[7] C. Guillaud, thesis, Strasbourg, 1943.

only small angles θ have to be considered. If v is the disturbed region at the surface of the crystal and E_{ex} the increase in exchange energy, the energy balance reads

$$K\langle\theta^2\rangle_{\text{Av}}v+E_{\text{ex}}=[H_c+4\pi I_s/3]I_s\cdot\tfrac{1}{2}\langle\theta^2\rangle_{\text{Av}}v.$$

By taking the disturbed region sufficiently broad in the beginning, the exchange energy can be decreased. When it is neglected, one arrives at

$$H_c=2K/I_s-4\pi I_s/3.$$

The gain in demagnetization energy increases if the wall starts in the middle of the sphere. The coefficient of $4\pi I_s$ then becomes -0.86. In a thin plate magnetized along its normal, as is encountered in the hexagonal compounds, one arrives at the coefficients -1.01 and -2.02, respectively.

IV. THE MAGNETIZATION CURVE

While the stiffness with respect to rotation as given by $2K/I_s$ is very large, wall formation and wall displacement can be made difficult or easy at will by sintering the material at a low or a high temperature, respectively. The magnetization processes of rotation and wall displacement can therefore be separated.

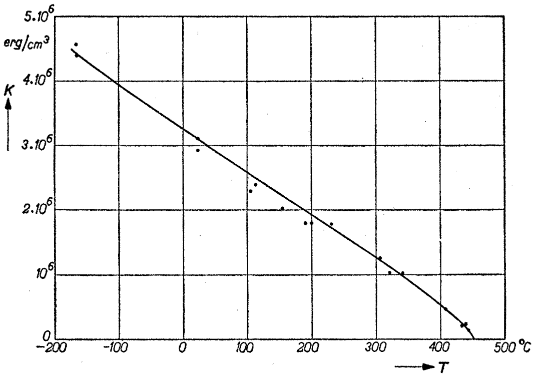

FIG. 3. Constant of crystal anisotropy K of $BaO\cdot 6Fe_2O_3$ as a function of temperature. (From $E_c=K\sin^2\theta+\cdots$.)

Let us consider the case that a wall can be created even in a small demagnetizing field, say zero. Owing to the random orientation of the crystals combined with a high resistance to rotation, large internal demagnetizing fields and, accordingly, wall displacements occur in positive external fields.

The problem can be approached[6] by ignoring rotations for the present, thus for $2K/I_s \gg H$. Let a crystal be represented as a small ellipsoid of revolution, with the easy direction along the axis. Let the demagnetization coefficient along the axis be n. The crystal is imbedded in a matrix which is thought to have the homogeneous magnetization I along a direction which makes an angle θ with the axis of the ellipsoid. The total internal field along the axis of the ellipsoid vanishes when an external field $H_0(\theta)$ parallel to the magnetization of the matrix is applied:

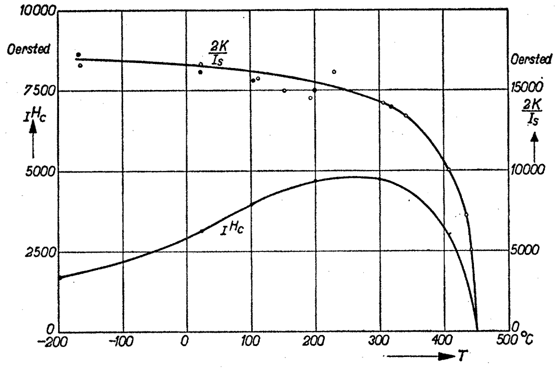

FIG. 4. The quantity $2K/I_s$ and the intrinsic coercive force $_IH_c$ as measured for fine-grained material as a function of temperature ($BaO\cdot 6Fe_2O_3$).

$$H_0(\theta)=(nI_s/\cos\theta)-nI.$$

If the external field exceeds $H_0(\theta)$, the ellipsoid is saturated, while for smaller external fields the magnetization of the ellipsoid decreases by wall formation so as to render the total internal field zero. By averaging over θ, Fig. 6 is obtained.

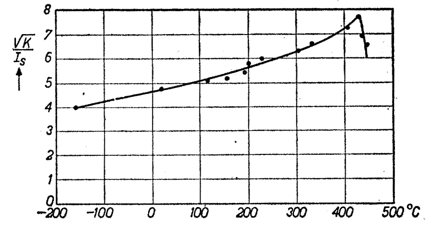

FIG. 5. The quantity $K^{\frac{1}{2}}/I_s$ as a function of temperature. ($BaO\cdot 6Fe_2O_3$.)

Figure 7 gives magnetization curves measured at a low and a high temperature. Figure 7(a) applies to small crystals and shows that at positive field strengths the upper branch of the loops can be represented by Stoner and Wohlfarth's[8] calculations for pure rotation.*

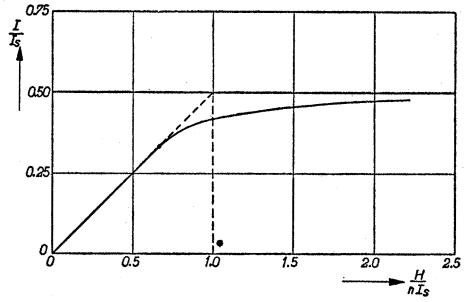

FIG. 6. Demagnetization by wall formation in positive fields as calculated for a model with $2K/I_s \gg nI_s$.

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[8] E. C. Stoner and E. P. Wohlfarth, Phil. Trans. Roy. Soc. (London) **240**, 599 (1948).

* The values for I_s and K used for the calculation of Stoner and Wohlfarth's curve were measured on single crystals.

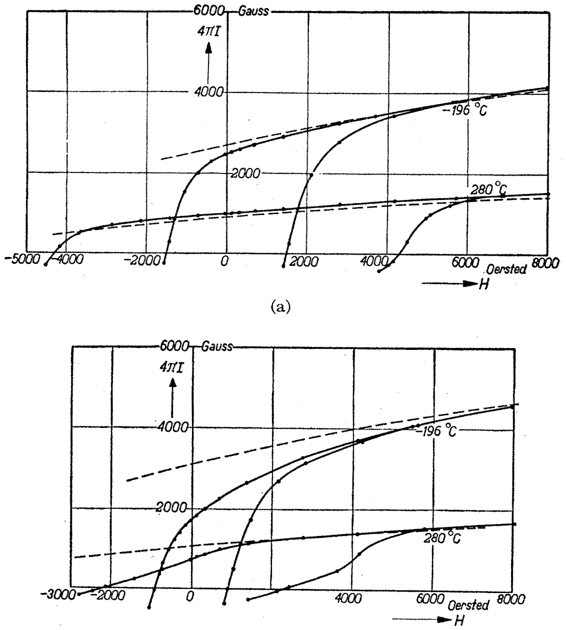

FIG. 7. Hysteresis loops for $BaO \cdot 6Fe_2O_3$ with random crystal orientation, measured at −196 and 280°C, respectively: (a) material with small crystals, obtained by sintering at a low temperature; (b) material with larger crystals.
Dashed: Demagnetization curves calculated for pure rotation.

Figure 7(b) for large crystals shows that appreciable wall formation occurs in positive fields of the order of $4\pi I_s$ (see Fig. 1), which is in accordance with Fig. 6 if one takes into account that the crystals are small plates with the hexagonal axis as normal.

In Figs. 8(a) and (b) the magnetization curves at room temperature are compared for coarse-grained material oriented, respectively, at random and in such a way that the easy direction of magnetization coincides with the direction of the external field. As is to be expected there is almost no demagnetization in positive fields in the oriented material.

In a forthcoming paper[6] it will be shown that the texture of the oriented material is improved by firing at high temperatures. This is explained by the absorption of misoriented crystals under the action of surface tensions. It suffices here to say that (BH)max-values of 3×10^6 gauss oersted have been obtained.

V. METASTABLE WALL CONFIGURATIONS

As was mentioned in Sec. II, the critical diameter for wall formation is proportional to $K^{\frac{1}{2}}/I_s$. Figures 5 and 9 show the increase of this quantity with temperature and its sudden decrease near the Curie point. It is an interesting question whether the wall configuration changes with a change in temperature in such a way that a stable equilibrium is maintained. The following experiment has been performed to answer this question.

The "initial" permeability in a "small" field of 500 oersteds has been measured at 15°C after establishing the equilibrium configuration of the walls at various temperatures T_d by demagnetization at these temperatures in an ac field. Figure 9 shows that the susceptibility after demagnetization either at low temperatures or at temperatures very near the Curie point, where $K^{\frac{1}{2}}/I_s$ is smaller than at room temperature, greatly exceeds the value obtained by demagnetization at room temperature. An excess of walls apparently remains in a metastable state within the material. On the other hand, demagnetization at temperatures where $K^{\frac{1}{2}}/I_s$ exceeds its room temperature value only leads to a slightly reduced susceptibility at room temperature, indicating that walls enter.

It is interesting to note that the minimum in the $(\mu_0 - 1)$-curve of Fig. 9 does not occur at 280°C, where ${}_IH_c$ is maximum, but near 400°C, where $K^{\frac{1}{2}}/I_s$ is maximum. For the fine-grained sample the permeability after demagnetization at elevated temperatures approaches the value calculated for rotation only.

Table I, in which $(\mu_0 - 1)$ after subtraction of the rotational part is given, reveals more clearly that an excess of walls is retained, while a deficiency is nearly supplied. If it is assumed that the stiffness of a wall is proportional to its energy and that after demagnetization at a certain temperature T_d the same wall con-

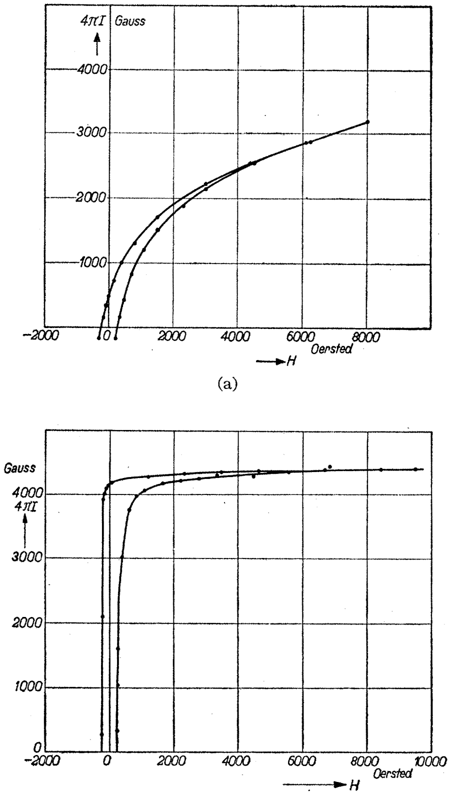

FIG. 8. Hysteresis loops for $BaO \cdot 6Fe_2O_3$ measured at room temperature for coarse grained material of small coercive force: (a) crystal orientation at random; (b) texture, the direction of easy magnetization being in the direction of the applied field.

figuration exists at different temperatures of measurement T_{m1}, T_{m2}, one expects

$$[(\mu_0-1)_{Td,\,Tm1}(K^{\frac{1}{2}}/I_s)_{Tm1}]/[(\mu_0-1)_{Td,\,Tm2}\cdot(K^{\frac{1}{2}}/I_s)_{Tm2}]=1.$$

Table I shows that this relation holds well if after demagnetization the change of temperature is such as to produce an excess of walls. The results are qualitatively summarized in the undermost part of Fig. 9.

The high degree of stability of an excess of walls might be due to some coupling of these walls during the demagnetization process by which they were formed. An additional experiment, in which no ac field was applied at the low temperature, points in this direction.

The specimens of Table I were demagnetized at 15° and, before being measured at 15°, cooled to −196°C. The (μ_0-1)-values obtained were 0.57 (specimen A) and 0.35 (specimen B). Comparison with (c) and (d) in Table I shows that an excess of walls is once more metastable. But not all walls formed at low temperatures are now retained.

TABLE I. Contribution of wall movement to (μ_0-1). T_m: temperature of measurement. T_d: temperature of demagnetization. Letters (a), (b), (c), and (d) as in the schematic representation of Fig. 9.

		T_m −196°	T_m 15°C	$\left[\frac{(\mu_0-1)_{-196}}{(\mu_0-1)_{15}}\cdot\frac{(K^{\frac{1}{2}}/I_s)_{-196}}{(K^{\frac{1}{2}}/I_s)_{15}}\right]_{T_d=\text{const}}$
		(A) large crystals		
T_d	−196°C	1.31 (a)	1.12 (b)	0.96
	15°C	0.97 (c)	0.41 (d)	1.94
		(B) small crystals		
T_d	−196°C	1.25 (a)	1.09 (b)	0.94
	15°C	0.72 (c)	0.21 (d)	2.8

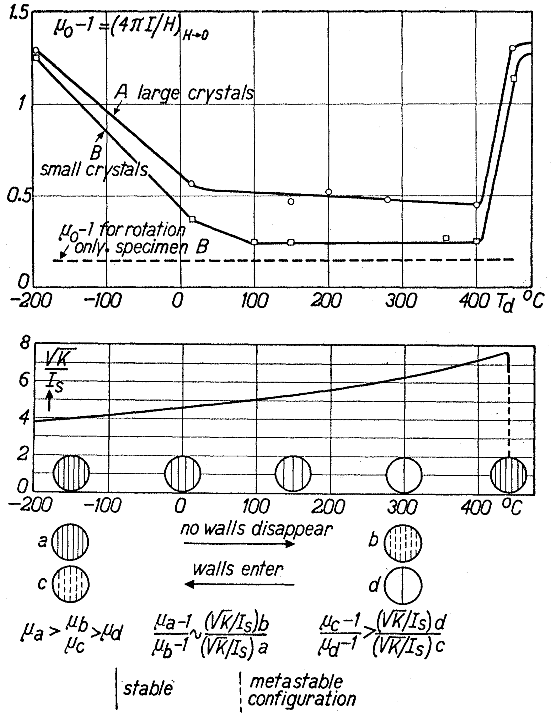

FIG. 9. Initial permeability μ_0 measured for $BaO\cdot 6Fe_2O_3$ with random crystal orientation at room temperature. Before the measurement the material was cooled down from above the Curie point in a field-free space, then demagnetized at the temperature T in an alternating-current field decreasing in amplitude from 4250 oersteds. It was then brought to 15°C and measured.

Curve A: large grains; curve B: small grains.

As is to be expected, demagnetization and measurement at −196°C, with an intermediate heating to 15°C, lead exactly to the values (a) of Table I.

The author wants to thank his colleagues Mr. J. Smit, Mr. E. W. Gorter, and Mr. A. L. Stuyts for help and discussions.

DISCUSSION

G. W. RATHENAU, *N. V. Philips Gloeilampen Fabrieken, The Netherlands* (in answer to questions): Near room temperature, magnetoelastic energy and shape energy are negligible compared with crystalline energy: λ (perpendicular to axis) $\cong 20\times10^{-6}$. The results are consistent with the idea that this is true also at higher and lower temperatures.

The texture can be made very perfect, as is shown by the curve for the low coercivity oriented sample.

Saturation of nonoriented material requires very high fields.

C. L. HOGAN, *Bell Telephone Laboratories, Murray Hill, New Jersey:* According to data recently taken at the Bell Telephone Laboratories, Ferroxdure at 9000 Mc induces a Faraday rotation of less than 0.1 degree/cm in a round wave guide, in applied magnetic fields up to 6000 oersteds. Compared with ferrites, it shows a very low loss at 9000 Mc, but high loss at 48 000 Mc.

M. T. WEISS, *Bell Telephone Laboratories, Murray Hill, New Jersey:* Have any ferromagnetic resonance experiments been made on these $BaO\cdot 6Fe_2O_3$ materials?

G. W. RATHENAU, *N. V. Philips Gloeilampen Fabrieken, The Netherlands:* Such experiments are being conducted, but no final results can yet be reported.