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FERROMAGNETIC PROPERTIES
OF HEXAGONAL IRON-OXIDE COMPOUNDS
WITH AND WITHOUT A PREFERRED ORIENTATION

BY

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**Ferromagnetic properties
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Mit 10 Figuren im Text.

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Besprechung der Magnetisierung von hexagonalen Eisenoxydverbindungen als Funktion der Feldstärke.

Bei der Bildung von Bloch-Wänden müssen Unregelmäßigkeiten im Kristallbau mitspielen (B). Bei regelloser Kristallverteilung und einer Kristallgröße oberhalb der kritischen kann Demagnetisierung durch Wandverschiebung schon bei positiven Feldstärken von ungefähr $4\pi I_s$ auftreten (C).

Durch Orientierung der Kristalle dieser Eisenoxydverbindungen Ferroxdure werden $(BH)_{\max}$ -Werte von $3 \cdot 10^6$ GB Oe erreicht. Durch Kornvergrößerung ergibt sich eine starke Verbesserung der Textur, die gedeutet wird (D).

A. Introduction.

A class of magnetic hexagonal iron-oxide compounds given the name of Ferroxdure has been dealt with in detail in an earlier publication¹. The prototype of these ceramic materials has the composition $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$.

We shall confine ourselves in this paper to material of about this composition.

The most important magnetic properties of this nonconducting permanent magnet material of high coercive force are represented in Figs. 1-3.

As is seen from Fig. 1, the saturation magnetization I_s at room temperature is about one fifth of that of metallic iron. The value of the magnetization at low temperatures can be explained, as was shown in¹, as being caused by non-compensated antiferromagnetism. Fig. 2 for the crystal anisotropy constant K shows that the forces binding the spins to the direction of the hexagonal axis are very strong. K is defined by the equation for the magnetic energy

$$E_c = K \sin^2 \theta + K' \sin^4 \theta + \dots, \quad (1)$$

where θ stands for the angle between the direction of the magnetization and the hexagonal axis of a single crystal. As is not unreasonable to

¹ WEST, J. J., G. W. RATHENAU, E. W. GORTER and G. W. VAN OOSTERHOUT: Philips Techn. Rev. 13, 194 (1952).

expect for a crystal of low symmetry, the difference of magnetization energy in different directions, given by K , is much greater than the equivalent quantity in cubic crystals, which, *e.g.*, for metallic iron is twenty times smaller at room temperature. In Fig. 3 the quantity $2K/I_s$ and the coercive force actually observed for fine-grained sintered material are plotted against temperature. The field strength $2K/I_s$ has the following significance. If a single crystal is magnetized to saturation along the easy direction of the hexagonal axis an antiparallel field must attain $2K/I_s$ to cause reversal of the magnetization by simultaneous rotation of the spins. For an assembly of crystals oriented at random the value $0.96K/I_s$ signifies the coercive force iH_c for which the magnetization vanishes, solely through simultaneous rotation of the spins¹. A comparison of the two curves in Fig. 3 immediately reveals that the reversal of magnetization in an actual specimen of the magnets under consideration cannot be solely due to rotational processes against the forces of crystal anisotropy. Firstly iH_c , though very large, is for the greater part of the curve

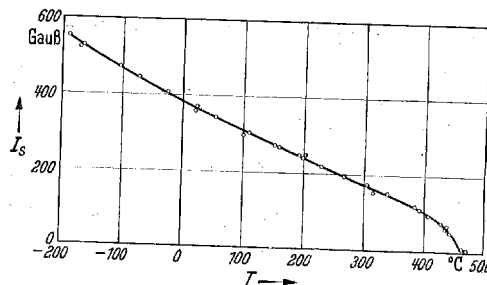


Fig. 1. Saturation magnetization of $\text{BaFe}_{12}\text{O}_{19}$ as a function of temperature.

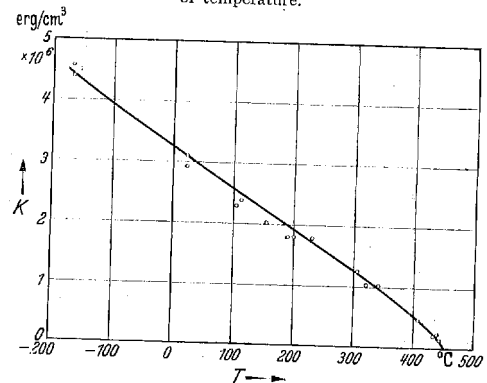


Fig. 2. Constant of crystal anisotropy K of $\text{BaFe}_{12}\text{O}_{19}$ as a function of temperature.

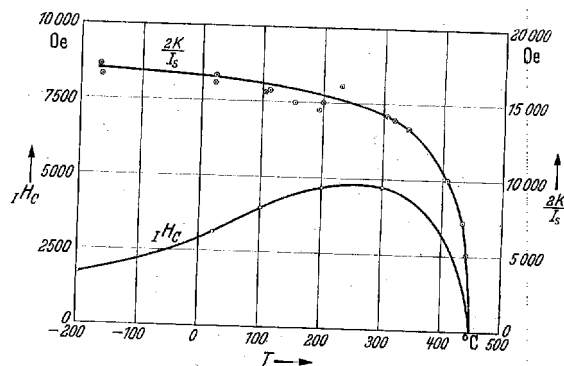


Fig. 3. The quantity $2K/I_s$ for $\text{BaFe}_{12}\text{O}_{19}$ and the coercive force iH_c of fine-grained sintered specimens as a function of temperature (particle size of the order of one micron).

¹ BOZORTH, R. M.: Ferromagnetism, p. 831. New York 1951.

much smaller than $0.96 K/I_s$ and, secondly, the dependence on temperature of both quantities is quite different¹.

It thus proves necessary to explain the coercive force of the fine-grained material and the hysteresis-loop, which will be treated more fully in section C, by assuming the formation and movement of Bloch walls in the small single crystals of which the material is composed. This assumption is by no means trivial in this special case, as will presently be shown.

B. Bloch-wall formation in small particles.

Let us for the sake of simplicity treat a small single crystal of diameter d containing a Bloch wall parallel to the hexagonal axis (Fig. 4b). The

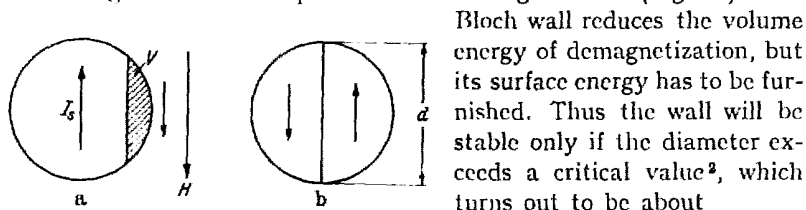


Fig. 4a and b. A spherical particle in which in a) a Bloch wall grows from the right-hand side, while in b) it separates two Weiss domains.

Bloch wall reduces the volume energy of demagnetization, but its surface energy has to be furnished. Thus the wall will be stable only if the diameter exceeds a critical value², which turns out to be about

$$d_c = \frac{9\sigma}{2\pi I_s^2}, \quad (2)$$

σ being the wall energy per cm^2 .

For Ferroxdure d_c is of the order of one micron at room temperature, a grain size which can be technically obtained by grinding and milling. It is the high crystal anisotropy K , which enters in the expression for σ , and the relatively low value of I_s that cause the large critical diameter d_c . For metallic iron d_c would be 50 times smaller.

It is a question of considerable interest how, after saturation and application of an external demagnetizing field, the wall enters the sphere of Fig. 4. An energy barrier has to be surmounted. It has been stated by KITTEL^{3,4} that above a certain size, exceeding d_c of equation (2), Bloch walls will be created spontaneously, but for smaller dimensions an external field has to be applied, the critical magnitude of which he has calculated. We believe that this calculation needs some revision, and that the correct critical field does not depend upon the particle size, this being very large compared with the thickness of a Bloch wall.

¹ The strain energy will not be considered in what follows, since the constant of magnetostriction on saturating along a direction of the basal plane proves to be only about $20 \cdot 10^{-6}$.

² KITTEL, C.: Rev. Mod. Phys. **21**, 541 (1949).

³ KITTEL, C.: Phys. Rev. **73**, 810 (1948).

⁴ BOZORTH, R. M.: Ferromagnetism, p. 831. New York 1951.

Our calculation, which very closely resembles that of KITTEL, runs as follows.

It is seen that the largest field H_c is needed in the very initial stage of the formation of the wall, so we have to consider only small angles of deviation θ of the spins. Therefore if the Bloch wall starts at the surface of the sphere (Fig. 4a) the energy balance reads

$$K \cdot \overline{\theta^2} \cdot v + E_{\text{ex.}} = (H_c + \frac{1}{3} \cdot 4\pi I_s) \cdot I_s \cdot \frac{1}{2} \overline{\theta^2} \cdot v. \quad (3)$$

Here v is the volume of the disturbed region, $\frac{1}{3} \cdot 4\pi I_s$ the demagnetizing field from the bulk acting in v , and $E_{\text{ex.}}$ the exchange energy, which can be made vanishingly small as compared with the anisotropy energy by taking the disturbed region sufficiently broad in the beginning. Ignoring it, one obtains for the critical field strength

$$H_c = 2K/I_s - 0.33 \cdot 4\pi I_s. \quad (4)$$

Thus H_c is independent of the particle size. It can be shown that the gain in demagnetizing energy is larger if the wall starts in the middle of the sphere. In that case the coefficient of $4\pi I_s$ is -0.86 . For a thin plate magnetized along its normal these values are -1.01 and -2.02 respectively.

So we arrive at the conclusion that Bloch walls will be created in pairs with opposite screw orientation (+ and - walls). If only the situation with one wall is stable, the other one will disappear, turning over the spins on its way.

For Ferroxdure the condition is satisfied that the wall thickness (about 10^{-6} cm) is small compared with the critical diameter (about 10^{-4} cm).

We expect from this analysis that large crystals should also retain a very high coercive force ($2K/I_s - 2.02 \cdot 4\pi I_s \approx 7000$ Oe at room temperature). Since this is contrary to the experiments we must assume that the Bloch walls are nucleated at places where the anisotropy energy is lower due to imperfections most probably occurring at the crystal boundaries.

C. The magnetization curve.

It has been shown in the preceding section that in specimens of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ containing crystals of the order of magnitude of one micron, single domain behaviour may be expected at room temperature near the remanence point. At large negative field strengths walls are probably introduced at places where the anisotropy is locally reduced.

When trying to understand the magnetization loop of fine-grained material we have to explain at first the course of the curve representing

H_c as a function of temperature (Fig. 3). It has been stressed in¹ that the critical diameter d_c of equation (2) increases with temperature as $K^{1/2}/I_s$. This means that for a given grain diameter at elevated temperatures below the region of the CURIE temperature fewer walls are to be expected than at a lower temperature, at which a higher saturation magnetization aids in forming them. Especially those walls which 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 $K^{1/2}$. It is believed that these two effects, the influence of which on the coercive force is opposed, cause the maximum in the curve H_c versus temperature.

The material under consideration is ideal for separating the magnetization processes of rotation and wall movement. While the stiffness with respect to rotation given by $2K/I_s$, is very large compared to $4\pi I_s$, the wall formation and wall movement can be made rather easy by firing the material at a high temperature and thus increasing the diameter of the grains to some thousand times the critical diameter d_c .

Considering this case, the walls will be formed already in very small demagnetizing fields, say zero. Due to the random orientations of the crystals large internal demagnetizing fields are present, which cause Bloch-wall formation already in positive external fields, leading to a low remanence. Because an appropriate analysis is very difficult, we shall try to approach the problem by using mean values throughout and ignoring the pure rotation for the present ($H \ll \frac{2K}{I_s}$). Without wall formation the $I-H$ curve coming from saturation should then be the straight line $I = \frac{1}{2} I_s$.

Let us consider a small ellipsoid of revolution in the matrix, which will be assumed to have a homogeneous magnetization I in the z direction. The easy direction is along the axis of revolution (ξ) and the demagnetization coefficient in that direction is n . The angle between z and ξ is θ . It is seen that the total internal field h_z in the ellipsoid will vanish for an external field parallel to I given by

$$H_0(\theta) = \frac{n I_s}{\cos \theta} - n I. \quad (5)$$

For $H > H_0(\theta)$ the ellipsoid is magnetized to saturation, but for lower fields wall formation occurs and the magnetization decreases in such a way that the internal field h_z remains zero. The total magnetization as a function of H can now be calculated by averaging over θ , and the

¹ WENT, J. J., G. W. RATHENAU, E. W. GORTER and G. W. VAN OOSTERHOUT: Philips Techn. Rev. 13, 194 (1952).

curve of Fig. 5 is found. For $H = \frac{2}{3} n I_s$ in all ellipsoids walls are created, and for decreasing field the slope of the curve for the dense material assumes the constant value $\frac{1}{2}$. It is seen that the field at which an appreciable decrease of the magnetization due to wall formation occurs is about $n I_s$. For Ferroxdure with its plate-like particles this should be about $4\pi I_s$. This is in agreement with the experiments. Fig. 6 shows curves of specimens fired at different temperatures and therefore having different grain sizes. In Fig. 7 the curves are plotted for two such materials, measured at a low and at a high temperature, one (a) with small crystals and the other (b) with large grains showing that the fall-off field varies with temperature approximately as $4\pi I_s$. Curves for pure rotation as calculated by STONER and WOHLFAHRT¹, on inserting the values of K and I_s as measured for single crystals, are dashed.

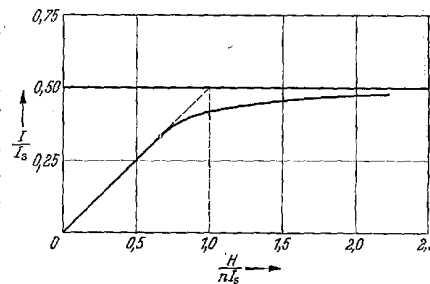


Fig. 5. Demagnetization curve calculated for an assembly of crystals which are oriented at random. Field strength for wall formation and displacement are assumed to be zero. $2K/I_s = \infty$.

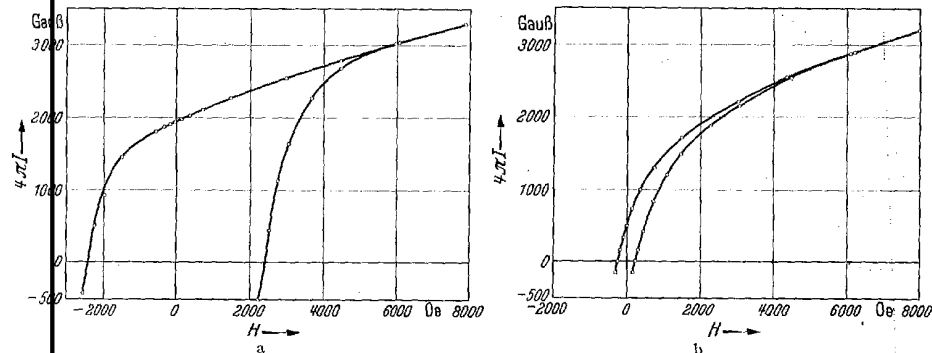


Fig. 6a and b. Hysteresis loops at room temperature of $\text{BaFe}_{12}\text{O}_{19}$ sintered at 1350 and 1400°C respectively.

In this connection it is also interesting to note that the remanence of hexagonal metallic Cobalt² is only 27% of the saturation value.

It is seen from Fig. 6b that the slope of the $I-H$ curve near $H=0$ is greater than the theoretical value $1/8\pi$. This may be due to some

¹ STONER, E. C., and E. P. WOHLFAHRT: Phil. Trans. Roy. Soc. Lond. **240**, 599 (1948).

² BOZORTH, R. M.: Ferromagnetism, p. 266. New York 1951.

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clustering of similarly oriented crystals, or to walls which pass through crystal boundaries, thus leading to smaller demagnetization.

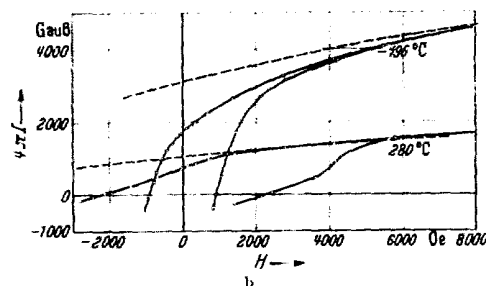
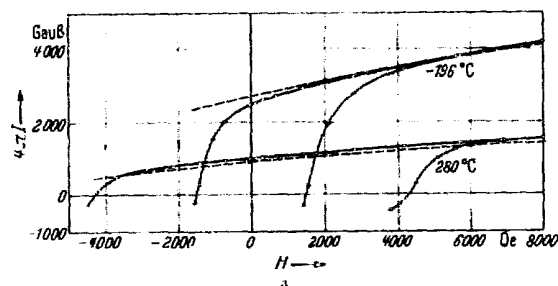


Fig. 7a and b. Hysteresis loops for $\text{BaFe}_{12}\text{O}_{19}$ oriented at random, measured at -196° and 280°C respectively. a) a material with small crystals, obtained by sintering at a low temperature, b) a material with larger crystals. Dashed: demagnetization curves calculated for pure rotation.

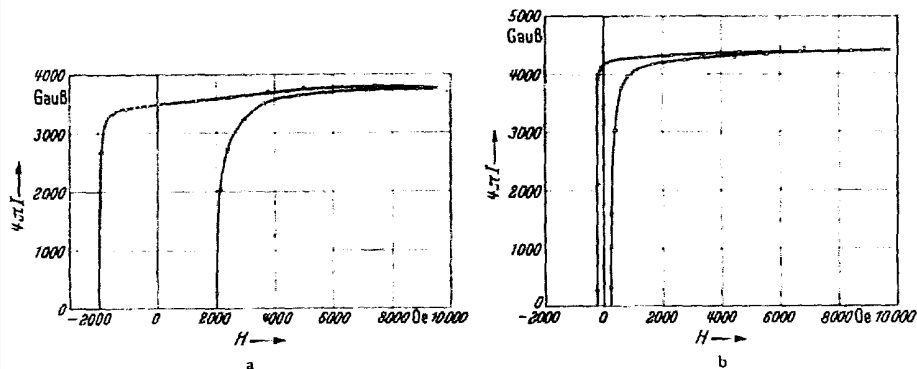


Fig. 8a and b. Hysteresis loops at room temperature measured for pseudo-unicrystalline material along the direction of preferred magnetization, to be compared with Fig. 5. a) small crystals, b) large crystals, higher density.

For the sake of comparison Figs. 8a and b show the magnetization curves of pseudo-unicrystalline specimens of the same material (section D), with small and large crystals respectively. As can be expected,

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for positive fields these curves do not show a decrease of magnetization through wall formation (due to the formation of internal poles) as strong as represented in Figs. 6 and 7.

In connection with the above considerations dealing with a material for which it was assumed that rotations were absent, while wall displacements could easily occur, one may ask how the magnetization curve will be if wall formations are strictly excluded while only rotations occur. This case can be realized by working with particle sizes much smaller than the critical one. Whereas in the first case considered the remanent induction for crystals with one direction of preferred magnetization proved to be much less than half of the saturation induction, it turns out that in the latter case it is larger. This can be understood as follows.

The remanence value of $2\pi I_s$ has been deduced by assuming that in each particle the magnetization points in the easy direction, giving a minimum of the energy of crystal anisotropy. The inner demagnetization energy, however, which has been dealt with above, may then be large. In reality the sum of both energies has to be minimized. Therefore the actual value of the remanence will exceed $2\pi I_s$ and corresponds to the magnetization in a positive field, smaller than $4\pi I_s$, in STONER and WOHLFAHRTS curve. Due to the large value of $2K/I_s$ the saturation magnetization was measured on a single crystal. Therefore we were not able to verify experimentally the above statements with certainty.

D. Preferred orientation in the polycrystalline ceramic material.

It has been stressed that, since it is due to non-compensated antiferromagnetism, the magnetic saturation of the hexagonal iron-oxide compounds is not very large. Except for corrections which are treated in section C the remanent magnetization of an assembly of crystals with uniaxial magnetic anisotropy, oriented at random, is equal to half the saturation value.

From a technical point of view the volume of permanent-magnet material needed to produce a given field in a given volume of air gap is about inversely proportional to the value $(BH)_{\max}$ in the part of the B - H diagram, where B is positive and H negative¹. From Fig. 9 it will be evident that the only way to raise the $(BH)_{\max}$ value of a material with very high coercive force H_c is to increase the remanence $4\pi I_r$, for if the coercive force for the magnetization were infinitely

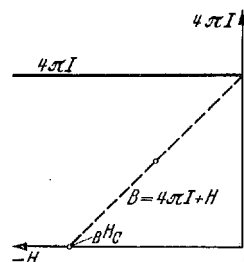


Fig. 9. Schematic $4\pi I$ and B curves at negative field strengths.

¹ BOZORTH, R. M.: Ferromagnetism, p. 348. New York 1951.

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large the coercive force for the induction B would be $H_c = 4\pi I_r$, and the $(BH)_{\max}$ value would amount to

$$\left(\frac{4\pi I_r}{2}\right)^2.$$

It has therefore been our aim to arrive at a preferred orientation of the hexagonal axes, which is the direction of easy magnetization of the small single crystals within the sintered permanent magnet bodies. We have succeeded in producing a preferred orientation of this kind by orientating small single crystals of the hexagonal compounds in a strong magnetic field and compacting them by pressing, preferably in a magnetic field. In the subsequent firing operation the preferred

orientation is not destroyed but on the contrary greatly improved. This can be shown by a comparison of the remanent magnetization of the specimen in the direction

Table I.

	B_r	$B_{r\perp}$	$B_r/B_{r\perp}$
before firing . . .	1500	870	1.72
after firing . . .	3100	420	7.4

in which the orienting field had been applied and normal to it, before and after firing. According to table 1 the ratio of the remanent magnetizations greatly increases on firing.

This improvement of the preferred orientation by firing will be discussed more fully below. Here it suffices to say that by orienting the crystals the $(BH)_{\max}$ value of Ferroxdure permanent magnets has been increased from 0.9 to 3.0 times 10^6 GB Oe. The curves in Figs. 8a and b give the magnetization for oriented Ferroxdure-samples which have been fired at lower and higher temperatures respectively.

The orientation of such sintered ceramics becomes apparent when the specimens are broken. Rupture occurs generally along the basal planes, which develop very perfectly. When the specimen is correctly tilted with respect to a light source a pronounced reflection of light by the basal planes can be observed. Specimens with a texture, in the form of a cube with two faces parallel to the hexagonal basal plane of the crystals, demonstrate--when overfired--the existence of the texture through the preferential growth of the crystals along the basal plane. In Figs. 10a and b micrographs of such a specimen are seen with the plane of the figure normal, respectively parallel, to the hexagonal axes. The large dimensions of the crystals in the basal plane and the small dimensions normal to it are evident.

In discussing the improvement of preferred orientation by firing, two explanations are possible. Firstly it might be thought that the crystals which are incorrectly oriented are generally those that have the

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smallest dimensions and therefore disappear under the action of the surface tension at the boundary of air and the crystals. However, since the disappearance of the incorrectly oriented material occurs mainly after the specimen has been sintered to about four-fifths of the X-ray density, it seems that the following explanation is more appropriate.

It has been shown for metals that a crystal cannot absorb another one which has about the same orientation or a twin orientation¹. The

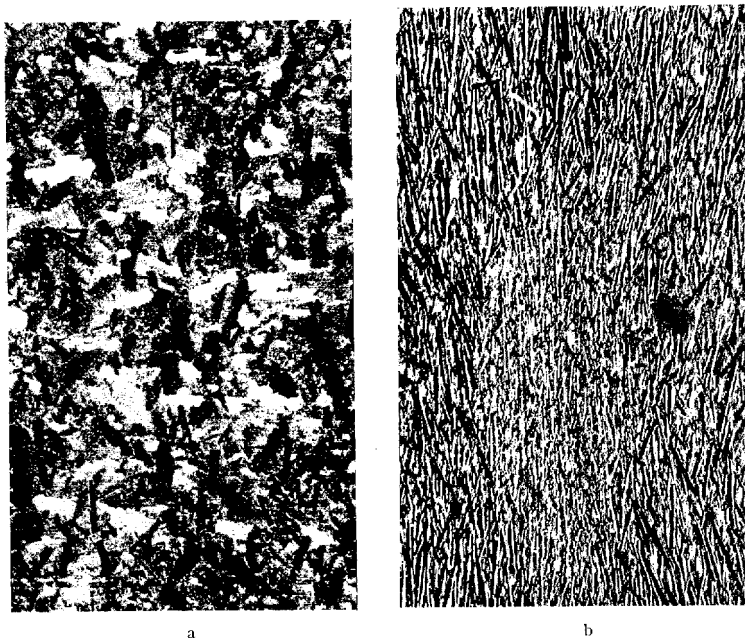


Fig. 10a and b. Microphotographs of a Ferroxidure cube with oriented crystals, a) the hexagonal basal planes being in the plane of the picture, b) the basal planes being normal to the plane of the picture. 10 \times .

improvement of a preferred orientation by grain growth has also been followed directly by electron-emission microscopy². It turns out that only those crystal boundaries move that have large interfacial energies due to different orientation of neighbouring grains. If an incorrectly oriented crystal is imbedded in a matrix of equally oriented crystals it grows only if it is large compared with the crystals of the matrix. Otherwise it will be absorbed.

The condition for growth is approximately³: $D/d > 2\gamma_{at}/\gamma_{tt}$, where γ_{at} is the interfacial energy of the boundary of the incorrectly oriented

¹ TIEDEMA, T. J., W. MAY and W. G. BURGERS: *Acta Crystallogr.* **2**, 151 (1949).
LACOMBE, P., and A. BERGHEZAN: *C. R. Acad. Sci., Paris* **228**, 93 (1949).

² RATHENAU, G.W., and G. BAAS: *Physica, Haag* **17**, 117 (1951).

³ SMITH, C. S.: *Trans. Amer. Soc. Met. Preprint* **37** (1951).

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large grain within the matrix of small grains, while γ_{ii} is the mean interfacial energy between similarly oriented grains. D and d are the diameters of the crystal under consideration and that of the adjacent particles respectively.

For the plate-like Ferroxdure particles the above-calculated inequality does not apply, but it is easily shown by energy considerations that a similar relation holds also in this case. Consider, therefore, a thin plate (thickness δ , diameter D) where θ is the angle of misfit with respect to the surrounding, perfectly oriented, crystals of mean thickness d . The misfitting particle will disappear if the total surface energy is reduced by the absorption. This leads for $D \gg \delta$ to the approximate relation $\delta/d \geq 2\gamma_{di}/\gamma_{ii}$ for growing, and if it is smaller then the particle will disappear. Here γ_{di} and γ_{ii} have the same significance as above. γ_{di} will strongly increase with θ .

In conclusion, it may thus be expected from this analysis that in the course of the sintering process misoriented crystals with about the same dimensions will be absorbed by the matrix.

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