

Theory of Reversible Magnetization in Ferromagnetics

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In the statistical domain theory of Heisenberg and others it is assumed that the domains have constant volumes, but that their magnetic moments change from one direction to another as the field or stress is changed. This model is highly artificial, for the actual process is believed to be a growth of some domains at the expense of others by displacement of the boundary between them. In this article the equations of the statistical theory are derived without use of the simplified model, by an adaptation of Kondorsky's analysis of the boundary displacement process. The assumptions necessary for this derivation are discussed critically, and the effect of modifying them is investigated in several special cases.

§1. INTRODUCTION

IN AN endeavor to obtain theoretical expressions for the magnetostriction of iron crystals in weak fields, Heisenberg¹ introduced a simplified model of a ferromagnetic crystal that has been used with surprising success in calculating a number of properties of crystals and of polycrystalline specimens.²⁻⁶ In this model it is assumed that the domains are all of the same size; as the field is increased the domain volumes remain constant, but the magnetization of individual domains changes from one direction of easy magnetization to another, so that the magnetization of the specimen increases. The relative numbers of domains magnetized in the various possible directions are calculated by statistical methods. To justify such methods it is argued⁶ that the internal forces that really determine the microscopic state of affairs vary irregularly from point to point, and may therefore be considered random. But before the derivation can be completed it is necessary to become much more specific in the definition of "randomness;" and the definition that has to be adopted is difficult to interpret in terms of any physical picture of internal forces.

This model, despite its success, must be regarded as a makeshift. There is strong evi-

dence⁷⁻⁹ that changes in magnetization, whether reversible or irreversible, occur by a progressive reorientation of electron spins in the boundary region between domains, describable on a larger scale as a growth of favorably oriented domains at the expense of their less favorably oriented neighbors by displacement of the boundary between them. It is therefore the volumes that change and the domain magnetizations that remain constant. Heisenberg himself pointed this out in introducing the simplified model. His expectation that it might nevertheless lead to approximately correct results has been amply justified; its chief shortcoming is not any lack of agreement between theory and experiment, but rather that the artificiality of the model makes it difficult to interpret the assumptions of the theory in terms of a more realistic model, or to modify the theory by substituting less drastic assumptions in regard to the mode of behavior of the internal forces.

A mathematical analysis of the boundary displacement process was carried out by Bloch⁷ and by Becker¹⁰ in a few especially simple cases. It has recently been extended by Kondorsky,¹¹ who has obtained a formula for the re-

⁷ F. Bloch, *Zeits. f. Physik* **74**, 295 (1932).

⁸ K. J. Sixtus and L. Tonks, *Phys. Rev.* **37**, 930 (1931); **39**, 357 (1932); **42**, 419 (1932); **43**, 70 and 931 (1933); K. J. Sixtus, *Phys. Rev.* **48**, 425 (1935); W. Döring, *Zeits. f. Physik* **108**, 137 (1938).

⁹ F. Bitter, *Introduction to Ferromagnetism* (McGraw-Hill Book Co., 1937), p. 194 ff.; W. C. Elmore, *Phys. Rev.* **51**, 982 (1937); **53**, 757 (1938).

¹⁰ R. Becker, *Physik. Zeits.* **33**, 905 (1932).

¹¹ E. Kondorsky, *Physik. Zeits. Sowjetunion* **11**, 597 (1937); *Comptes rendus Acad. Sci. U.R.S.S.* **18**, 325 (1938); **19**, 397, 401 (1938); *Phys. Rev.* **53**, 319, 1022 (1938).

¹ W. Heisenberg, *Zeits. f. Physik* **69**, 287 (1931).

² R. Gans and J. v. Harlem, *Ann. d. Physik* **15**, 516 (1932); **16**, 162 (1933).

³ R. M. Bozorth, *Phys. Rev.* **42**, 882 (1932).

⁴ R. H. Fowler, *Statistical Mechanics*, second edition (Macmillan Co., 1936), p. 520.

⁵ N. Akulov and E. Kondorsky, *Zeits. f. Physik* **78**, 801 (1932); **85**, 661 (1933).

⁶ W. F. Brown, *Phys. Rev.* **52**, 325 (1937); **53**, 482 (1938); **54**, 279 (1938).

versible susceptibility of iron crystals. This formula involves the relative volumes v_i oriented in the various possible directions i ; when the field is in direction [111] or when only orientations nearest the axis of the specimen occur, the symmetry of the problem makes it possible to determine the v_i 's at once as functions of the magnetization, but in general this is not the case. Kondorsky therefore evaluates the v_i 's by the use of formulas borrowed from the statistical theory; these formulas give the relative numbers of domains, n_i , oriented in the various possible directions i in the simplified model of this theory.

Now the statistical theory itself, as has been shown by the writer,⁶ is capable of yielding formulas for the reversible susceptibility, and the formulas in some cases give excellent agreement with experiment. If, therefore, the formulas of this theory must be used in the end, it seems preferable to use them from the beginning, rather than mixing the two models. But if this final step can be avoided and Kondorsky's theory made complete in itself, his analysis is to be preferred because of its more realistic approach. This can be done: in fact it is possible, by introducing certain assumptions, to derive the equations of the "statistical" theory by an analysis similar to Kondorsky's, without any use of the simplified model or of statistical methods. The assumptions made in this derivation can be clearly stated in terms of the boundary motion process and the internal and external forces controlling it. By making slightly different assumptions, modified formulas may be derived in several simple cases. The two theories thus become one, and the Heisenberg model with its objectionable artificiality may be discarded without sacrifice of any of its essential results.

§2. BOUNDARY DISPLACEMENT THEORY: A REVIEW

In the boundary displacement theory it is assumed that the position of the boundary surface S_{ij} , between two domains whose magnetic moments are oriented in directions i and j , is determined by an equilibrium between external and internal forces. The external forces

(field components and stresses)* have a direct effect on the boundary position only insofar as they cause the external free energy density u_i on the i side of the boundary to differ from the value u_j on the j side. Thus if only fields are present, $u_i = -\mathbf{H} \cdot \mathbf{J}_i$ and $u_j = -\mathbf{H} \cdot \mathbf{J}_j$, where \mathbf{J}_i and \mathbf{J}_j are the vector magnetizations on the two sides; a change of field is effective in displacing the boundary only if it affects the difference $u_j - u_i = \mathbf{H} \cdot (\mathbf{J}_i - \mathbf{J}_j)$. If the boundary S_{ij} is supposed to undergo a virtual displacement, such that at each point P the surface is displaced normally through a distance $\delta x_{ij}(P)$ from side i toward side j , the increase in free energy due to external forces is

$$\int_{S_{ij}} (u_i - u_j) \delta x_{ij} dS;$$

so that the surface S_{ij} may be regarded as subject to a force $-u_i$ per unit area pushing on it from the i side, and a force $-u_j$ per unit area pushing on it from the j side. Since the effect on the boundary depends only on the values of the

* The "external" field \mathbf{H} and the "external" stresses are the field and stresses that would be produced by the same magnetizing currents and applied forces in a specimen macroscopically indistinguishable from the actual specimen, but homogeneous instead of being made up of domains. The actual field and stresses at an interior point P would not be affected appreciably if all the matter at a distance greater than r were to be replaced by homogeneous matter, provided r is large compared with the dimensions of the domains. The deviations of the actual field and stresses from the value for the homogeneous specimen are therefore determined by the state of affairs near P , and may appropriately be termed "internal" fields and stresses. The internal field and stresses as thus defined result from the inhomogeneous character of the material about P ; that is, from the domain structure itself, from inherent distortions, and from impurities. The field under discussion is one that is continuous throughout the interior of a domain: the atomic structure of the material and the nature of the elementary magnets are involved only indirectly, through such constants as J_s , λ_{100} , C . The internal field and induction therefore differ, and the question rises whether \mathbf{H} or \mathbf{B} , and whether stresses or strains, should be used as the independent variables. The answer depends on whether the simplifying assumptions to be made are a better approximation as applied to the one set of quantities or to the other. It is evident for example that, if the internal stresses are constant, the internal strains must vary as the domains change in size, because of magnetostriction. The use of field rather than induction as independent variable appears to lead to reasonable results, probably because the former is more nearly uniform for elongated domains, and the internal part is therefore a smaller part of the whole and more nearly continuous across the boundaries. The use of stresses and the use of strains as independent variables lead to slightly different results that usually lie on opposite sides of the correct one (see reference 6).

u_i 's and not on the way in which the fields and stresses are manipulated in order to attain these values, it is legitimate to regard the u_i 's as the independent variables, whether or not there are actually enough independently variable field and stress components to produce arbitrary variations in the u_i 's. (In iron crystals, with only six directions of easy magnetization, arbitrary variations of the u_i 's can actually be produced by varying the three field components and three components of tension.)

The internal forces include internal stresses and internal fields. To some extent these are inherent in the material and unaffected by the magnetization process. This is true for instance of internal stresses resulting from permanent distortion of local regions, and of magnetic forces due to small regions of permanent magnetic saturation in a definite direction, resulting from high local stresses. To a large extent, however, the internal forces acting at any point of a boundary may be expected to depend not only on the state of the material at that point when the boundary reaches it, but also on conditions at other points. For instance, magnetic forces on one boundary due to Poisson distributions of magnetic charge on other boundaries will vary with the positions of the other boundaries; again, the stresses at and near a boundary will be altered when a neighboring boundary is displaced, because of the magnetostrictive change in dimensions of the regions through which the second boundary has passed. Thus a boundary S_{ij} may be displaced even though u_i and u_j remain constant, because changes in other u_k 's may displace other boundaries and this in turn may alter the *internal* forces on S_{ij} .

These indirect effects seem too hopelessly complicated to analyze, and the usual procedure has been to avoid the difficulty by assuming that the permanent, local part of the internal forces is much larger. In many cases to which one would like to apply the theory, for instance in annealed specimens, this is certainly not true. On the other hand, the importance of magnetic forces between neighboring boundaries is decreased by the tendency of boundaries to assume shapes for which the Poisson densities vanish.^{7, 12}

¹² L. Landau and E. Lifshitz, *Physik. Zeits. Sowjetunion* **8**, 153 (1935).

Perhaps by arguments of this sort it would be possible to justify the neglect of indirect effects. At any rate, the results obtained by assuming them negligible seem to apply even in some cases (annealed polycrystalline nickel is an example⁶) in which the assumption is not strictly justified. In the remainder of the analysis, this assumption will be made.

The free energy associated with these local, permanent internal forces is of two kinds: (1) Energy associated with the region on each side of the boundary, but whose amount w per unit volume is different on the two sides, so that a displacement of the boundary S_{ij} produces a change in total energy of the form

$$\int_{S_{ij}} [w_i(x, y, z) - w_j(x, y, z)] \delta x_{ij} dS.$$

An example of this is the energy associated with permanent internal stresses, and arising from the fact that a reorientation of the magnetization vector is accompanied by a magnetostrictive change of dimensions of the affected region, and therefore involves work against the permanent internal stress in that region. In an iron crystal this energy, for a domain oriented along the positive or negative cubic axis Ox_i , is of amount $w_i = -\lambda_{100}\sigma_i(x, y, z)$ per unit volume, where λ_{100} is the magnetostriction of a crystal magnetized to saturation along such an axis, and the quantity written for brevity as σ_i is the local tension along the axis in question minus the mean tension along the other two axes.¹⁰ (2) Energy associated with the boundary layer between domains, but whose amount per unit area of the boundary varies with the position of the boundary, so that a displacement of the boundary S_{ij} produces a change in energy of the form

$$\delta \int_{S_{ij}} \epsilon(x, y, z) dS.$$

Here ϵ represents the boundary energy per unit area of the boundary, and depends on the local conditions (stresses, for instance) in the boundary layer. An example is the boundary energy discussed by Bloch,⁷ which results from the joint action of exchange forces and anisotropy

(spin-orbit) forces. This energy is given by

$$\epsilon \cong (J'C)^{1/2}/a^2, \quad (1)$$

where a is the lattice constant, J' is the exchange integral, and C is the anisotropy energy per atom. Internal stress distorts the lattice locally and therefore alters the values of these quantities. Kondorsky has added to C a magnetostrictive term, designed to take account of the fact that in the boundary region the magnetostriction has a value different from that corresponding to magnetic saturation. If the variation of ϵ with position of the boundary is due chiefly to variation of this magnetostrictive term, the magnitude of this variation is according to Kondorsky

$$\partial\epsilon/\partial x_{ij} = \frac{1}{2}\lambda'\delta\partial\sigma/\partial x_{ij}, \quad (2)$$

where λ' is the saturation magnetostriction minus the boundary value, δ is the thickness of the boundary layer, and σ is the internal stress.

In a virtual displacement of the boundary, the total change of free energy is

$$\delta W = \int_{S_{ij}} \{ (u_i - u_j) + (w_i - w_j) + \partial\epsilon/\partial x_{ij} + \epsilon[(1/r_1) + (1/r_2)] \} \delta x_{ij} dS. \quad (3)$$

The last term, in which r_1 and r_2 are the principal radii of curvature of the surface, takes account of the variation of the boundary area as the boundary progresses: $\delta dS = [(1/r_1) + (1/r_2)]\delta x_{ij} dS$. It may be regarded as a sort of surface tension, tending to contract the boundary. It plays a role in determining the size of the domains,¹²⁻¹⁴ but its inclusion in the present analysis would seriously complicate the equations. It can be safely omitted if the linear dimensions of the domains are large compared with the distances over which ϵ changes by large fractions of itself, that is if a domain contains many maxima and minima of ϵ , for then $\partial\epsilon/\partial x_{ij} \gg \epsilon/r_1$ or ϵ/r_2 . Even if this is not true, there is some justification for omitting the surface tension term in the fact that a boundary of type ij will be concave toward i in some parts and toward j in others, so that the average curvature should be small. This argument breaks down when domains of one type have become

so small as to be completely surrounded by others. Nevertheless this term will be omitted in the remainder of the analysis, on the assumption that it has been taken sufficiently into account by postulating the existence of domains of a certain average size.

The condition for equilibrium is that in a virtual displacement δW shall be zero, or

$$[w_i(x, y, z) - w_j(x, y, z)] + \partial\epsilon(x, y, z)/\partial x_{ij} = u_j - u_i. \quad (4)$$

The locus of points satisfying this equation defines an equilibrium position of the boundary for given values of the u 's. In order that the equilibrium be stable it is necessary in addition that

$$\partial[(w_i - w_j) + \partial\epsilon/\partial x_{ij}]/\partial x_{ij} > 0. \quad (5)$$

As long as this condition is satisfied the boundary proceeds reversibly as the u 's are varied. When the boundary reaches a point at which the left member of (5) changes sign, the equilibrium becomes unstable, and the boundary proceeds irreversibly until it either reaches a new position of stable equilibrium, or reaches another boundary and fuses with it (annulling it, if it is one of opposite type). Throughout the reversible part of this process, the change of position of the boundary produced by a change δu_i , δu_j in the external conditions is given by

$$\{ \partial[(w_i - w_j) + \partial\epsilon/\partial x_{ij}]/\partial x_{ij} \} \delta x_{ij} = \delta(u_j - u_i),$$

$$\text{or} \quad \delta x_{ij} = k_{ij} \delta(u_j - u_i), \quad (6)$$

where

$$k_{ij} = \{ \partial[(w_i - w_j) + \partial\epsilon/\partial x_{ij}]/\partial x_{ij} \}^{-1} > 0. \quad (7)$$

The total increase of volume of domains of type i at the expense of domains of type j , in unit total volume, is

$$\begin{aligned} \delta v_{ij} &= \int_{S_{ij}} k_{ij} \delta(u_j - u_i) dS \\ &= \bar{k}_{ij} S_{ij} \delta(u_j - u_i) = p_{ij} \delta(u_j - u_i), \end{aligned} \quad (8)$$

where S_{ij} is the total area of boundaries of type ij in unit volume of the specimen, and \bar{k}_{ij} is the mean value of k_{ij} .

To carry the analysis further it is necessary to make some assumption in regard to the mode of variation of \bar{k}_{ij} and of S_{ij} as the boundaries

¹³ J. Frenkel and J. Dorfman, *Nature* **126**, 274 (1930).

¹⁴ W. Döring, *Zeits. f. Physik* **108**, 137 (1938).

move. Kondorsky assumes: (1) that the quantities \bar{k}_{ij} remain constant; (2) that if there is no tendency for particular types of domain to be grouped together, S_{ij} is proportional to the product $v_i v_j$.

The constancy of the \bar{k}_{ij} 's is assured if there is negligible correlation between the mean reciprocals of the normal gradients of internal force, averaged over surfaces of equal force, and the corresponding values of the force. (By "internal force" is meant the quantity $(w_i - w_j) + \partial \epsilon / \partial x_{ij}$.) The assumption therefore is roughly equivalent to the assumption that the space rate of variation of internal force does not depend in any regular manner on the magnitude of the force itself. This is a reasonable assumption when the internal forces vary irregularly from point to point and force maxima occur in all ranges of force values. Irreversible displacements carry the boundaries to positions where the force gradients are different, and therefore should make the assumption more rather than less justifiable.

For the assumption $S_{ij} \propto v_i v_j$ Kondorsky offers no justification. It can be defended to some extent by the following argument. It must be assumed first that the S_{ij} 's are single-valued functions of the v_i 's. The total surface area S_i , bounding domains of type i in unit volume, is made up of portions S_{ij} ($j \neq i$) in contact with domains of the various types j . If there is no tendency for domains of one type to be grouped with domains of a particular other type,¹⁵ it is

¹⁵ The "grouping" excluded here (but to be investigated in § 4) means a situation in which some parts of the crystal contain only domains of two particular types, other parts no domains of these two types. Thus an iron crystal may consist of three types of region, in each of which the magnetization is parallel or antiparallel to a single one of the positive cubic axes; such a region in turn then consists of parallel and antiparallel domains. Even if grouping does not occur in this extreme form, there is probably a tendency toward it because of the fact (already noted) that the boundaries tend to assume shapes for which the Poisson densities vanish. This requires that the domains be elongated in the direction of their magnetizations; the areas between oppositely oriented domains must then exceed the areas between domains oriented at right angles to each other. For this reason it may seem more reasonable to assume not that $S_{ij} : S_{ik} = v_j : v_k$, but that $S_{ij} : S_{ik} = c_{ij} v_j : c_{ik} v_k$, where the c_{ij} 's are constant weighting factors. The further assumption that S_{ij} depends only on v_i and v_j leads to Kondorsky's equation $S_{ij} = a_{ij} v_i v_j$, with different proportionality constants for different types of boundary. Eq. (9) is unaffected except that the A_{ij} 's have a slightly different meaning, and the physical interpretation of Eq. (13) is no longer contained in as simple a statement as (10a).

reasonable to suppose that these portions S_{ij} are proportional to the corresponding volumes v_j ; then $S_{ij}/v_i v_j$ is the same for all j 's. By a similar argument it is the same for all i 's. Let $S_{ij}/v_i v_j = a$: then

$$S_i = \sum_{j \neq i} S_{ij} = a v_i \sum_{j \neq i} v_j = a v_i (1 - v_i).$$

If it is now assumed that the surface bounding domains of a particular type remains unchanged if the corresponding volume remains unchanged, it follows that a is a constant. This assumption is somewhat arbitrary, but may be partially defended if the internal forces and hence the shapes of the boundaries are irregular; for then a change in which some domains of type i grow larger and others smaller, so that the changes in volume compensate, may be expected to produce no significant systematic change in the shape of the aggregate of domains of type i , and hence in the bounding area.

If the assumptions just stated are made, Eq. (8) becomes

$$\delta v_{ij} = a \bar{k}_{ij} v_i v_j \delta(u_j - u_i) = A_{ij} v_i v_j \delta(u_j - u_i), \quad (9)$$

where the A_{ij} 's are constants; and hence

$$\delta v_i = \sum_{j \neq i} \delta v_{ij} = \sum_{j \neq i} A_{ij} v_i v_j \delta(u_j - u_i). \quad (10)$$

This equation is implied, though not explicitly stated, in Kondorsky's work. The assumptions on which it is based may be summarized as follows.

(1) The position of the boundary between domains of two types is determined by an equilibrium between external and internal forces.

(2) External forces are directly effective only insofar as they alter the free energy per unit volume in one or the other of the two regions separated by the boundary.

(3) The internal forces are preponderantly ones that depend only on conditions in or near the boundary; interactions over distances of the order of magnitude of the domain dimensions may be disregarded.

(4) The tendency of boundary forces to decrease the boundary area, having once been taken into account by postulating the existence of domains, may be neglected in studying the detailed motion of domain boundaries.

(5) There is no correlation between the mean reciprocals of the internal force gradients normal to surfaces of equal force, and the corresponding force values.

(6) The total area of all the boundaries of a given type in unit volume is a single-valued function of the relative volumes occupied by the various types of domain.

(7) There is no tendency of domains of one type to become grouped with domains of any particular other type. (The alternative assumption will be considered in §4.)

(8) When (7) is true, domains of any given type are in contact with domains of the other types over areas proportional to the relative volumes occupied by the various types.

(9) In a change in which the volume occupied by domains of a given type is unaltered, the combined surface area of these domains is also unaltered.

Stated this fully, the assumptions that must be made are dismayingly many. The last seven, however, are merely more precise expressions of the general assumption that the internal forces governing the boundary displacement process are local in origin, permanent in nature, and irregular in their spatial variation.

Kondorsky actually considers only the effect of a magnetic field ($u_i = -\mathbf{H} \cdot \mathbf{J}_i$) and writes not Eq. (10), but the equation for the reversible susceptibility derivable from it ($\delta J = \sum_i J_i \delta v_i$). He also supposes that there are only two values of the A_{ij} 's, one for boundaries between oppositely oriented domains and one for all other boundaries. Moreover he considers chiefly the case in which oppositely oriented domains are grouped together, so that Eq. (10) has to be modified somewhat. Nevertheless Eq. (10) is essentially due to Kondorsky.

§3. COMPLETION OF THE THEORY

The derivation of the equations of the "statistical" theory from Eq. (10) requires only one additional assumption; this will be stated first in a form that seems, but is not, trivial:

(10a) The reversible properties of a specimen are properties that it would be possible for a reversible specimen to have.

This means that a reversible specimen could have the properties described by Eq. (10), with

the same A_{ij} 's, without violating thermodynamics. But for such a specimen the v_i 's would be single-valued functions of the u_j 's and the δv_i 's would be their differentials, hence $\delta v_i/v_i = \delta(\log v_i)$ would be a perfect differential, and

$$\partial(A_{ij}v_j)/\partial u_k = \partial(A_{ik}v_k)/\partial u_j; \quad (11)$$

whence, since

$$\partial v_j/\partial u_k = A_{jk}v_j v_k = \partial v_k/\partial u_j, \quad (12)$$

$$A_{ij} = A_{ik} = \dots = A. \quad (13)$$

Thus assumption (10a) implies that:

(10b) The mean reciprocals of the gradients of internal force normal to the boundary are the same for all types of boundary.

If it is preferred, (10b) may be taken as the assumption and (10a) regarded as a corollary. There seems no doubt, if Kondorsky's description of internal forces is correct, that (10b) is an oversimplification. Nevertheless it leads to interesting results.

If condition (13) is satisfied, Eq. (12) shows that there is a function $\phi(u_1, u_2, \dots)$ such that $v_i = \partial\phi/\partial u_i$, and satisfying

$$\partial^2\phi/\partial u_i\partial u_j = A(\partial\phi/\partial u_i)(\partial\phi/\partial u_j) \quad (14)$$

for every $i, j \neq i$. The solution of this is

$$e^{-A\phi} = \sum_i f_i(u_i). \quad (15)$$

The functions f_i are determined by the condition $\sum_i \partial\phi/\partial u_i = 1$, whence $f_i = \exp[-A(u_i - c_i)]$, where the c_i 's are arbitrary constants, and

$$\phi = -(1/A) \log \sum_i e^{-A(u_i - c_i)}, \quad (16)$$

$$v_i = e^{-A(u_i - c_i)} / \sum_j e^{-A(u_j - c_j)}. \quad (17)$$

For a reversible specimen in which no directions are especially favored by the shape of the specimen, the v_i 's are equal when all the u_i 's are zero; the c_i 's may then be set equal to zero, and (17) becomes the formula for the n_i 's of the statistical theory. In the present theory, therefore, this formula corresponds to complete reversibility and implies equivalence of the different types of boundary.

For a specimen capable of irreversible changes, the integrated Eq. (17) still describes the behavior in reversible changes. The c_i 's will be zero only in the initial reversible change from

the demagnetized, unstressed state. In a reversible change from any other state, the c_i 's will have values determined by the initial state. An irreversible change takes the specimen from one set of c_i 's to another.

This may be illustrated by considering a specimen subject to a field H of variable magnitude but fixed direction; in this case $u_i = -J_s h_i H$, where J_s is the saturation magnetization and h_i is the cosine of the angle between magnetization and field for domains of type i . It will be assumed (this is admittedly an oversimplification) that the v_i 's are single-valued functions of the magnetization J , and that these functions are the same as if the specimen were reversible. For a reversible specimen the functional relations may be written parametrically in the form $v_i = z^{h_i} / \sum_i z^{h_i}$, $J/J_s = \sum_i h_i z^{h_i} / \sum_i z^{h_i}$ ($z = \exp(AJ_s H)$). If the more general equations are to give the same relations, the c_i 's must be given by $c_i = ch_i$, where c is a constant in reversible changes and varies in irreversible changes; then for the actual specimen $z = \exp(AJ_s H - c)$. Thus

$$J/J_s = \sum_i h_i e^{\eta h_i} / \sum_i e^{\eta h_i} = f(\eta), \quad (18)$$

where $\eta = AJ_s H - c. \quad (19)$

The curve for a completely reversible specimen ($c=0$) is that given by the statistical theory, and passes through the origin (Fig. 1, curve 1). The initial reversible change of magnetization follows this curve from the origin; thus the initial susceptibility is the same as in the statistical theory. A reversible change from any initial point P, P' follows a curve obtained by displacing 1 to the left or right until it passes through the point in question (Fig. 1, curves 2 and 3). The reversible susceptibility is the slope of this curve; it evidently depends only on J , and is given as in the statistical theory by the parametric equations $J = J_s f(\eta)$, $\chi_r = AJ_s^2 f'(\eta)$. Irreversible changes take the specimen from one such curve to another (Fig. 1, curve 4).

If the v_i 's are not assumed to be single-valued functions of the magnetization, it no longer follows that the reversible susceptibility is determined by the magnetization alone. Experimentally, it appears that such a functional relation between reversible susceptibility and

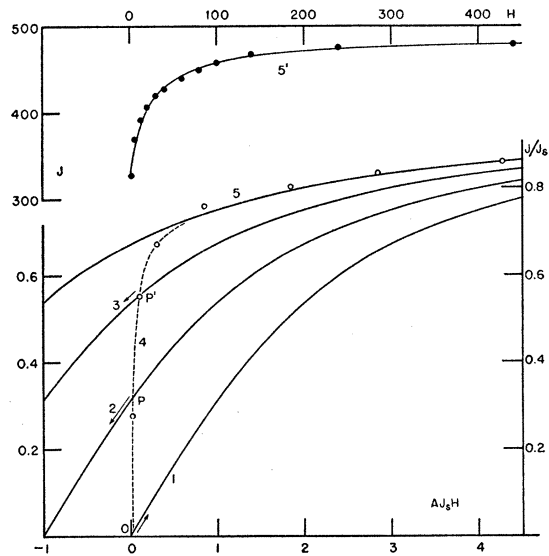


FIG. 1. Magnetization curves of specimen with polycrystalline domains. 1, theoretical curve of reversible specimen ($H_0=0$). 2 and 3, theoretical curves for reversible changes from initial states P and P' ($AJ_s H_0=1$ and 2 , respectively). Small reversible changes occur as indicated by the arrows at O, P and P' . 4, qualitative representation of the irreversible ascending magnetization curve. 5, a possible theoretical curve for high fields. 5', theoretical J vs. H curve calculated with values of H_0, J_s and A given in the text; solid circles are experimental values on the normal magnetization curve of a nickel ellipsoid at room temperature. The solid circles and curve 5' of the upper figure, plotted on a different scale and extended to lower fields, give the open circles and curve 5 ($AJ_s H_0=3.00$) of the lower figure.

magnetization holds approximately, but not exactly.¹⁶

For a polycrystalline specimen in which the domains are larger than the crystals, the direction of magnetization of each domain is a direction that minimizes its total free energy. This energy is due partly to the external field, partly to crystalline anisotropy forces (which cancel to some extent but not completely if the crystal axes are oriented at random), and partly to internal fields and stresses. All but the first of these are taken account of as internal forces, and therefore in the statistical theory such domains were treated as "isotropic," in the sense that every direction is a direction of easy magnetization, and the sums over directions of easy magnetization were replaced by integrals over the unit sphere. The corresponding limiting case in the present

¹⁶ R. Gans, *Physik. Zeits.* **12**, .1053 (1911); *Ann. d. Physik* **61**, 379 (1920).

theory would be one in which a domain may be magnetized in any direction, and may absorb a portion of an adjacent domain without undergoing any change of its direction of magnetization. The first of these conditions is satisfied if the domains are polycrystalline, but the second is not; for if the boundary moves, the crystalline forces and internal stresses in the absorbed region may be expected to change the direction of magnetization of the absorbing domain. Rotation of the magnetization vector should occur simultaneously with boundary displacement. The "isotropic domain" formulas are therefore a trifle difficult to justify in the present theory, although some of the best agreement between theory and experiment has been obtained with these very formulas, applied to polycrystalline nickel.⁶ It is clear, however, that these formulas result from either of two simplified theories: one in which boundary displacement is allowed, without change in the directions of domain magnetizations, and one in which changes in these directions are allowed, without displacement of the boundaries. If the actual process is a combination of these, the formulas that follow equally well from either alone should hold at least approximately when they are combined.

In this limiting case, Eq. (18) becomes

$$J = J_s(\coth \eta - 1/\eta) = J_s L(\eta), \quad (18')$$

where $\eta = AJ_s(H + H_0)$. (19')

Here c has been written $-AJ_s H_0$. The initial susceptibility is

$$\chi_0 = AJ_s^2 L'(0) = \frac{1}{3} AJ_s^2, \quad (20)$$

and the reversible susceptibility is $AJ_s^2 L'(\eta)$. The experimental verification of the formula for the reversible susceptibility (originally proposed by Gans),¹⁶ and of its dependence on J alone, has already been discussed.⁶ Additional confirmation of the theory may be obtained from the magnetization curve at high fields, where the magnetization process is practically reversible and should therefore follow a curve like 5, given by Eq. (18') with a positive value of H_0 and with $A = 3\chi_0/J_s^2$. The points in the upper part of Fig. 1 are experimental values obtained at 19.4°C by Kirkham¹⁷ on the ellipsoid he used for

magnetostriction measurements.¹⁸ The theoretical curve 5' has been calculated with $J_s = 487$ gauss, obtained by extrapolation of the J vs. $1/H$ curve at high fields ($L(\eta) \doteq 1 - 1/\eta$, $H \gg H_0$), and with the following values of the other constants, chosen to fit the curve to the data as well as possible: $H_0 = 21.1$ oersteds, and $\chi_0 = 23.2$ or $1/A = 3.52 \times 10^3$ erg cm⁻³.

A physical interpretation of H_0 must await a more complete analysis of irreversible processes. The initial susceptibility is not known for this specimen, but a rough check of $1/A$, which should be of the order of magnitude of the free energy density associated with the internal forces, may be made if these are assumed to be chiefly internal stresses of magnetostrictive origin. The energy density should then be of the order of magnitude of $\lambda_\infty^2 E_\infty$, where λ_∞ is the saturation magnetostriction and E_∞ the saturation value of Young's modulus.¹⁹ Since^{18, 20} $\lambda_\infty = 3.99 \times 10^{-5}$ and $E_\infty = 2.22 \times 10^{12}$ dynes/cm², this gives $1/A = 3.54 \times 10^3$. The numerical agreement is, of course, fortuitous; the agreement in order of magnitude, however, is significant. An experimental determination of the initial and reversible susceptibility of this specimen is being undertaken in this laboratory.

§4. MODIFICATIONS OF THE THEORY

The assumptions on which the formulas of the statistical theory are based have now been stated clearly. If any of these assumptions are modified, the theory must be modified accordingly. Several such modifications will now be considered.

(a) Inequality of the A_{ij} 's; grouping of domains

If the condition (13) is not satisfied, the reversible properties of the specimen are not ones that a reversible specimen could possess, and the equations describing these properties are not integrable. Nevertheless they are still useful. The case that will be considered is the one treated by Kondorsky: an iron crystal with two values of the A_{ij} 's, a value A for oppositely magnetized domains and a value B for domains magnetized at right angles to each other. Let u_i, v_i refer to the positive cubic axes and \bar{u}_i, \bar{v}_i to the corresponding

¹⁸ D. Kirkham, Phys. Rev. **52**, 1162 (1937).

¹⁹ M. Kersten, Zeits. f. Physik **12**, 665 (1931).

²⁰ S. Siegel and S. L. Quimby, Phys. Rev. **50**, 1165 (1936).

¹⁷ Unpublished data.

negative axes. If the crystal is subjected to a field of variable magnitude H in a fixed direction (l_1, l_2, l_3) , u_i and \bar{u}_i becomes $-HJ_{sl_i}$ and $+HJ_{sl_i}$, respectively, and Eq. (10) becomes

$$\delta x_i / \delta H = \beta (l_i y_i \sum_{j \neq i} x_j - x_i \sum_{j \neq i} l_j y_j), \quad (21)$$

$$\delta y_i / \delta H = \alpha l_i (x_i^2 - y_i^2) + \beta (l_i x_i \sum_{j \neq i} x_j - y_i \sum_{j \neq i} l_j y_j), \quad (22)$$

where $x_i = v_i + \bar{v}_i$, $y_i = v_i - \bar{v}_i$, $\alpha = AJ_s$, $\beta = BJ_s$. From (22), if j is the ratio of the magnetization J in the field direction to its saturation value J_s ,

$$\begin{aligned} \delta j / \delta H &= \sum_i l_i \delta y_i / \delta H \\ &= \alpha \sum_i l_i^2 (x_i^2 - y_i^2) \\ &\quad + \beta \sum_i \sum_{j > i} \{ (l_i^2 + l_j^2) x_i x_j - 2l_i l_j y_i y_j \}. \end{aligned} \quad (23)$$

If, as is supposed by Kondorsky, oppositely oriented domains are grouped together in the crystal, the relation $S_{ij} = av_i v_j$ must be replaced by the relations²¹

$$S_{i, i-} = av_i \bar{v}_i / (v_i + \bar{v}_i), \quad (24)$$

$$S_{i, j} = bv_i v_j, \quad S_{i, j-} = bv_i \bar{v}_j, \text{ etc.} \quad (25)$$

The α -term in (22) must therefore be divided by x_i ; (23) then becomes Kondorsky's formula for reversible susceptibility.

To complete the calculation in the more complicated cases, Kondorsky substituted in this formula the values of the v_i 's and \bar{v}_i 's (as functions of j) given by the statistical theory. It is clear from §3 that this is inconsistent with the assumption $A \neq B$. This inconsistency may be avoided by assuming merely that the v_i 's and \bar{v}_i 's are single-valued functions of j , and that these functions are the same as if the specimen behaved reversibly for changes of H alone. The x_i 's and y_i 's are then to be obtained as functions of j by eliminating δH from (21), (22) and (23) and integrating. For H along [100] or [110], the

²¹ Equation (24) follows from the fact that the previous analysis holds throughout the region $v_i + \bar{v}_i$, in which boundaries of type $i, i-$ exist, if S_{ij} is replaced by $S_{i, i-} / (v_i + \bar{v}_i)$ and if v_i, v_j are replaced by $v_i / (v_i + \bar{v}_i)$, $\bar{v}_j / (v_j + \bar{v}_j)$. To obtain Eq. (25), it must be assumed that the total area S_{ij}' separating domains of types i and $i-$ from domains of types j and $j-$ is made up of portions $S_{i, i}, S_{i, i-}, S_{i-, i}, S_{i-, i-}$ whose ratios are given by $S_{i, i} / S_{i, i-} = v_i / \bar{v}_j$, etc. Then $S_{i, j} = S_{ij}' v_i v_j / [(v_i + \bar{v}_i)(v_j + \bar{v}_j)]$, $S_{i, j-} = S_{ij}' v_i \bar{v}_j / [(v_i + \bar{v}_i)(v_j + \bar{v}_j)]$, etc. By the previous analysis, $S_{ij}' = b(v_i + \bar{v}_i)(v_j + \bar{v}_j)$; (25) follows at once.

integration leads to the following results: Without grouping,

$$\begin{aligned} [100] \quad j^2 &= x^2 - (1/9)[\frac{3}{2}(1-x)]^{2\alpha/\beta}, \\ \delta j / \delta H &= (\alpha/9)[\frac{3}{2}(1-x)]^{2\alpha/\beta} + \beta x(1-x); \\ [110] \quad j^2 &= 2x^2 - (2/9)[3(1-2x)]^{(\alpha+\beta)/\beta}, \\ \delta j / \delta H &= (\alpha/9)[3(1-2x)]^{(\alpha+\beta)/\beta} \\ &\quad + \beta \{ x(1-2x) \\ &\quad + (1/9)[3(1-2x)]^{(\alpha+\beta)/\beta} \}. \end{aligned} \quad (26)$$

With grouping,

$$\begin{aligned} [100] \quad j^2 &= x^2 - (1/9)[(1-x)/2x]^{2\alpha/\beta}, \\ \delta j / \delta H &= (\alpha/9x)[(1-x)/2x]^{2\alpha/\beta} \\ &\quad + \beta x(1-x); \\ [110] \quad j^2 &= 2x^2 - \frac{2}{3}(1-2x)[(1-2x)/x]^{2\alpha/\beta}, \\ \delta j / \delta H &= \frac{1}{3}\alpha[(1-2x)/x]^{2\alpha/\beta+1} \\ &\quad + \beta(1-2x)\{ x + \frac{1}{3}[(1-2x)/x]^{2\alpha/\beta} \}. \end{aligned} \quad (27)$$

The parameter $x = v_1 + \bar{v}_1$ runs from $\frac{1}{3}$ to 1 in case [100], from $\frac{1}{3}$ to $\frac{1}{2}$ in case [110]. The case $\mathbf{H} \parallel [111]$ was solved by Kondorsky without use of the statistical theory.

Kondorsky gives reasons for supposing that $\alpha \ll \beta$. In this case, both (26) and (27) become

$$\begin{aligned} [100] \quad j^2 &= x^2 - \frac{1}{9}, \quad \delta j / \delta H = \beta x(1-x); \\ [110] \quad j^2 &= 2x^2 - \frac{2}{3}(1-2x), \\ \delta j / \delta H &= \beta(x + \frac{1}{3})(1-2x). \end{aligned} \quad (28)$$

The statement that $\alpha \ll \beta$ implies not that boundaries between oppositely oriented domains do not move, but that they move irreversibly. Since this irreversible process proceeds rapidly, it may be a better approximation to evaluate the v_i 's by assuming that the 180° reversals are completed before the volume oriented perpendicular to the field has changed appreciably.²² This gives

$$\begin{aligned} [100] \quad \delta j / \delta H &= 2\beta/9, \quad (0 \leq j \leq \frac{1}{3}), \\ &= \beta j(1-j), \quad (\frac{1}{3} \leq j \leq 1); \\ [110] \quad \delta j / \delta H &= (2\beta/9)(1-9j^2/4), \\ &= \beta j(1/\sqrt{2} - j), \quad (\frac{1}{3}\sqrt{2} \leq j \leq 1/\sqrt{2}). \end{aligned} \quad (29)$$

²² N. Akulov, Zeits. f. Physik 69, 78 (1931).

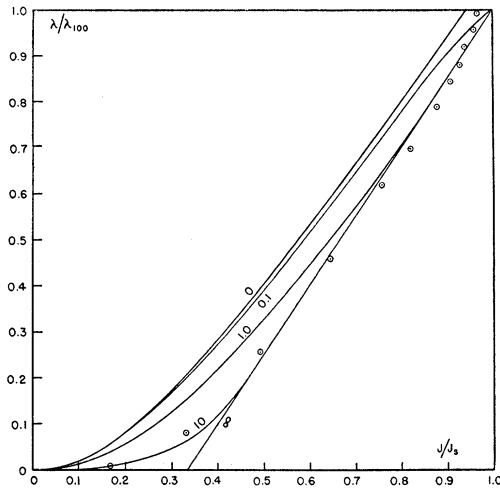


FIG. 2. Magnetostriction of iron crystal magnetized in [100] direction. Curves have been calculated theoretically by formulas (26) and (30); the number next to each curve is the corresponding value of α/β . Curve 1 coincides with Heisenberg's, curve ∞ with Akulov's. Circles are Webster's experimental values.

The curves obtained by either method agree with Kondorsky's and differ from those of the statistical theory ($\alpha=\beta$ in (26)) in that the [100] curve rises initially to a maximum equal to $9/8$ the value for $j=0$. Measurements of the reversible susceptibility of crystals should therefore show whether the relation $\alpha \ll \beta$ holds.

None of these formulas are applicable to the specimens measured by Williams.²³ The initial susceptibilities in directions [100], [110], [111] for these specimens were in the ratios 6 : 3 : 2, a fact that can be explained only by assuming that every domain is magnetized along one of the [100] directions nearest the specimen axis. If this assumption is made, the observed ratios can be explained by assuming either no grouping and $\alpha=\beta$ (statistical theory)⁶ or grouping and $\alpha \gg \beta$.¹¹ Kondorsky, accepting the grouping hypothesis, explains the large α in this case as measuring an *irreversible* initial susceptibility. Until measurements of the reversible susceptibility have been made, no conclusion seems possible. The two sets of assumptions give identical curves for reversible susceptibility as a function of j .

The magnetostriction may be calculated as a function of magnetization for the [100] and [110] cases considered before, from the equations

for j as a function of x together with^{1, 22}

$$\lambda/\lambda_{100} = \frac{3}{2}x - \frac{1}{2}. \quad (30)$$

For $\alpha=\beta$, with no grouping, this gives Heisenberg's¹ curves; for $\alpha \gg \beta$ it gives Akulov's,²² which are also obtained if the 180° inversions are assumed to be completed first by an irreversible process. These and several other cases are plotted in Fig. 2, together with Webster's²⁴ experimental values (with $J_s=1750$, $\lambda_{100}=19.5 \times 10^{-6}$, the values used by Heisenberg). The curve $\alpha=10\beta$ follows the experimental data more closely than either Heisenberg's or Akulov's, but the data are not sufficiently precise to make this of much significance.

Data on reversible susceptibility, taken if possible on crystals with a large enough demagnetizing factor to insure distribution of the domain magnetizations among all possible directions, are highly desirable. The reversible susceptibility curves for $\alpha \ll \beta$, $\alpha=\beta$, and $\alpha \gg \beta$ differ much more than the magnetostriction curves.

(b) More general relations

Assumption (10a) seems a thoroughly reasonable one, even if (10b) does not hold. The fact that one of these necessitates the other is a result of the previous assumptions, some of which are much more arbitrary than (10a). In particular, assumptions (5) to (9), leading to the relation $p_{ij}=A_i v_i v_j$, are open to question. If these are abandoned and (10a) is retained, (10b) no longer follows, but Eq. (8) now gives

$$\delta v_i = \sum_{j \neq i} p_{ij} \delta(u_j - u_i), \quad (31)$$

where the p_{ij} 's are functions of the u_i 's, with $p_{ji}=p_{ij}$. Hence $\partial v_i / \partial u_j = \partial v_j / \partial u_i$, and there is a function ϕ such that $\partial \phi / \partial u_i = v_i$. This function is arbitrary except for the one condition $\sum_i \partial \phi / \partial u_i = 1$. If $\phi = -(1/A) \log \psi$ and $u_i = -(1/A) \log \xi_i$, where A is any convenient constant of the proper dimensions, this becomes $\sum_i \xi_i \partial \psi / \partial \xi_i = \psi$, showing that ψ is a homogeneous function of degree 1 in the ξ_i 's. Thus

$$v_i = -(1/A \psi) \partial \psi / \partial u_i, \quad (32)$$

²³ H. J. Williams, Phys. Rev. **52**, 1004 (1937).

²⁴ W. L. Webster, Proc. Roy. Soc. **A109**, 570 (1925).

where ψ is a homogeneous function of degree 1 in the quantities e^{-Au_i} . The result obtained in §3 corresponds, with proper choice of A , to the case of a *linear* function.

These examples illustrate the greater flexibility of the present theory as compared with the statistical model.

§5. CONCLUSION

It has been shown that the equations previously obtained by means of an artificial model may also be obtained by a detailed analysis of the process of reversible boundary displacement. The necessary assumptions have been stated explicitly, and it is now possible to investigate the effect of modifications in these assumptions. The agreement with experiment is surprisingly good in view of the large number of assumptions that must be made in order to make the mathematics manageable.

Although more theoretical work will be necessary in the future, it may be fairly asserted that the immediate need is for more and better

experimental data rather than for further refinements of the theory.²⁵ Measurements of the reversible susceptibility of crystals are particularly desirable.

The writer wishes to express his appreciation to Professor E. P. Wigner for a number of very helpful discussions.

Note added in proof: Preliminary measurements have now been made on the specimen of Fig. 1. The specimen has become slightly harder magnetically; analysis of the magnetization curve at high fields now gives $\chi_0 = 19.7$, and the value determined by measurements at very low fields is 20.3. The difference is well within the precision of the high field value. The writer is indebted to Mr. J. L. Fowler and Mr. W. M. Woodward for assistance in these measurements, and to Professor S. L. Quimby of Columbia University for the loan of the specimen.

²⁵ There is need, however, for further theoretical study of *irreversible* boundary displacement. Some progress in this direction has been made by W. Döring, reference 14, and by E. Kondorsky, *Physik. Zeits. Sowjetunion* **11**, 597 (1937); *Comptes rendus Acad. Sci. U.R.S.S.* **20**, 117 (1938).

The Noncubic Growth of Single Crystals of Silver by Condensation from Vapor

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The condensation of silver vapor upon solidified, spherical drops of silver has been found to produce straight, thin, single-crystal needles of silver under certain conditions. The formation of the drops and the subsequent growth of the needles was a continuous process accomplished by condensing the vapor in vacuum upon an iron surface as that surface was cooling from above the melting point of silver to an equilibrium temperature just below the melting point. The shape and crystalline orientation of the needles indicate that they are the result of a nucleus growing by condensation much more rapidly in a certain $\langle 110 \rangle$ direction than in other directions, including other $\langle 110 \rangle$ directions.

IT is known that certain metals such as copper sometimes crystallize in the form of filaments or dendrites although the solid form of the metal possesses cubic symmetry.¹ The growth of small

single-crystal silver needles or spikes by condensation in vacuum as here described is of interest because it furnishes an additional test for any theory that may be advanced to explain the filamentary growth of cubic crystals.

The procedure by which the crystals here described were grown may be made clear by reference to Fig. 1 which shows a part of the

* The work here reported was done at Sloane Physics Laboratory, Yale University, New Haven, Connecticut.

¹ A photograph showing evidence of dendritic growth in a single crystal of copper is given by A. B. Greninger, *Am. Inst. Min. and Met. Eng., Tech. Pub.* 596 (1935).