AUGUST 1, 9131 *PHYSICAL REVIEW* *VOLUME 38*

MAGNETIZATION AND THE MAGNETO-CALORIC EFFECT

By Francis Bitter
Westinghouse Research Laboratories, East Pittsburgh, Penn.

(Received June 17, 1931)

Abstract

Definition of the effect.—The magneto-caloric effect is defined as the reversible evolution of heat accompanying a change in the magnetization of a ferromagnetic substance, in contradistinction to the irreversible evolution of heat referred to as hysteresis.

Assumption regarding the mechanism of magnetization.—In two previous notes it was suggested that ferromagnetic substances are spontaneously magnetized in small regions containing roughly 10^5 atoms. Here the following points are briefly discussed: (1) the formation of these units, called blocks; (2) the interactions of these blocks to form clusters, which probably give rise to the Barkhausen effect; (3) the changes that take place in the neighborhood of the Curie point; (4) the changes that take place during magnetization.

The Magneto-caloric effect.—The essential result of the above discussion is that a sudden change in the applied field will produce changes in the energy of every block. The new energy distribution is not stable, and equilibrium is reached by means of an adiabatic diffusion process resulting from thermal agitation, which brings with it a reversible change in temperature. The mechanism is illustrated by means of a simple model.

The effect under certain simple conditions.—If the strains due to magnetostriction, stray internal fields, and the effect of crystal orientation are negligible, the magneto-caloric effect is amenable to calculation. It is pointed out under what experimental conditions such neglects are justifiable.

The interpretation of the experiments of Weiss and Forrer on Nickel.—A detailed comparison is undertaken between experimental observations of the magneto-caloric effect in nickel in high fields and the theoretical predictions based on the assumption that the effect is due to processes involving Weiss' molecular field. The agreement is satisfactory at temperatures not too near the Curie point. Too little is known about the nature of the magnetic transformation to permit a quanitative analysis to be made there.

Magnetization and the magneto-caloric effect in single crystals.—Akulov's static theory of the magnetization curve of single crystals predicts the absence of a magneto-caloric effect due to rotation of the regions of spontaneous magnetization, i.e., the work done in rotating the magnetization of such a region is equal to its change in potential energy, and therefore there can be no change in heat content. Experimentally this relation is approximately satisfied for iron and nickel, and less well for cobalt. If, in the case of cobalt, the discrepancy is real, a magneto-caloric effect of the order of 0.03°C is to be expected. The magnetization curves for crystals of nickel and cobalt on the basis of Akulov's theory are calculated. It is pointed out that experiments on the magneto-caloric effect of single crystals would be of great help in determining the mechanism of magnetization.

EVER since the introduction by Weiss of the molecular field to explain the spontaneous magnetization of ferro-magnetic substances, it has been difficult to understand how a substance in which such a field acts may be de-magnetized. Weiss himself suggested that the regions of spontaneous magnetization did not necessarily include the whole of a sample. It was suggested that crystal grains had natural boundaries at which to assume abrupt changes. This was not entirely satisfactory, as similar results had to be explained in single crystals. Recently Sizoo[1] has suggested that the "Lockerstellen," spontaneous imperfections in crystals, suggested by Smekal to explain chiefly mechanical and electrical properties, might somehow be connected with the breaking up of the regions of spontaneous magnetization. And more recently, the author has suggested[2] that the block theory of Zwicky might have considerable bearing on this problem. Whatever the cause, it seems very probable that ferromagnetic bodies are composed of permanently magnetized regions of some sort, and that the macroscopic effects observed are due to their interactions—thermal, mechanical, magnetic, etc. The problem is enormously complicated by the fact that besides having to account for the effect of one region on the next by means of its magnetization, magnetostriction, etc., accidental strains and impurities having a large influence on the magnetic properties must be taken into consideration. For instance, Yensen[3] has shown that the hysteresis loss of iron-silicon alloys can be halved by reducing the carbon content from 0.008 percent to 0.004 percent. Similarly some materials, permalloy for instance, may have a wide range of magnetic properties, depending on their previous thermal and mechanical treatment. It is quite evident, then, that the detail in the arrangement of ferromagnetic atoms is of great importance in determining some of the properties of the substance which they make up, and until such detail can be put into a theory, only a very rough agreement with experiment is to be expected. The best procedure for establishing a theory seems therefore to consist of showing that it contains mechanisms capable of describing a large number of phenomena, and that the order of magnitude of the various calculated effects is reasonable. Once such evidence for some group of initial assumptions is amassed, it may be possible to work out the detail of a more quantitative procedure. The following article is part of a preliminary program to discover whether a block theory is capable of describing ferromagnetic phenomena in general, and if so, to discover as many of the properties of such blocks as possible.

DEFINITION OF THE MAGNETO-CALORIC EFFECT

When a ferromagnetic substance is subjected to a cyclic magnetization process, the temperature gradually rises due to the existence of hysteresis. In other words, the work done on the sample in taking it through a cycle appears as heat. If, however, the change is not cyclic, so that the magnetic as well as the thermal energy may have changed, no statement can be made relating the change of temperature to the work done without a knowledge of the detail of the magnetization process. This evolution of heat in a part of a magnetic cycle was first observed by Weiss and Piccard[4] and later investigated

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[1] G. J. Sizoo, Physica **10**, 1 (1930) (in Dutch).

[2] F. Bitter, Phys. Rev. **37**, 91 (1931).

[3] T. D. Yensen, Trans. A.I.E.E. **43**, 145 (1924).

[4] P. Weiss and A. Piccard, Journal de Physique **7**, 103 (1917). C. R. **166**, 352 (1928).

more fully by Weiss and Forrer.[5] They discovered that in addition to the gradual increase in temperature due to hysteresis, there exists a *reversible* change in temperature. Thus they found that magnetizing a piece of nickel raised its temperature, but that demagnetizing it *lowered* its temperature. This reversible effect they called the magneto-caloric effect, and in this article the name will be used in this sense, rather than to designate any change in temperature accompanying magnetization. Subsequent experimenters working on the change of temperature with magnetization observed only hysteresis losses, and the magneto-caloric effect was not further studied until 1929 when Ellwood[6] investigated its detail with much more sensitive apparatus than that used in previous experiments. Both the results of Weiss and Forrer, and of Ellwood will be discussed further on.

ASSUMPTIONS REGARDING THE MECHANISM OF MAGNETIZATION

If we are to discuss the magneto-caloric effect, we must first have some notion of what goes on within a piece of iron, for instance, while it is being magnetized. In accordance with the introductory remarks, we will assume our sample, which may be called iron for the sake of definiteness, to be permanently magnetized in small regions. The magnetization of each region is a function of the temperature as given by the Weiss-Heisenberg theory,[7] and the energy is a function of the orientation of the magnetization with respect to the field and the crystal axes as given by Powell.[8]

The only reasonable estimate it has so far been possible to make of the size of these regions at room temperatures is by means of the law of approach to saturation. In an extended investigation Weiss and Forrer[9] found that the intensity per unit mass at a temperature T and in a field H is given in terms of the saturation intensity by the expression

$$\sigma_{H,T} = \sigma_{\infty,T}\left(1 - \frac{a}{H}\right) \tag{1}$$

where a is a constant. Now the potential energy of a block may be written in the form: (1) a term depending on the crystal orientation, (2) a term depending on the irregular field produced by the neighboring blocks, (3) a term depending on the mechanical distortion, and (4) on the external field. For sufficiently large fields the first three terms may be neglected, and we have for the potential energy of a block simply $\mu H \cos\theta$, where μ is the magnetic moment, and θ is the angle between μ and H. But it is known that the magnetization of a group of dipoles having such a potential energy function is given by

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[5] P. Weiss and R. Forrer, Ann. d. Physique **5**, 153 (1926).

[6] W. B. Ellwood, Nature **123**, 797 (1929); Phys. Rev. **36**, 1066 (1930).

[7] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928). Probleme der Modernen Physik, edited by P. Debye, p. 114, Hirzel, 1928. F. Bloch, Zeits. f. Physik **57**, 545 (1929), **61**, 206 (1930). Or for a more simple treatment see: E. C. Stoner, Proc. Leeds Phil. Soc. **2**, 56 (1930).

[8] F. C. Powell, Proc. Roy. Soc. **A130**, 167 (1930).

[9] P. Weiss and R. Forrer, Ann. d. Physique **12**, 279 (1929).

$$\sigma_{H,T} = \sigma_{\infty,T}\left(\coth x - \frac{1}{x}\right)$$
$$x = \mu H/KT \tag{2}$$

which reduces, for large values of x, to

$$\sigma_{H,T} = \sigma_{\infty,T}\left(1 - \frac{1}{x}\right) = \sigma_{\infty,T}\left(1 - \frac{KT/\mu}{H}\right) \tag{3}$$

or comparing (1) and (3), we see that $a = KT/\mu$. But $\mu = \sigma_{\infty,T}m$ where m is the mass of a block. Or, introducing N, the number of particles per block, we have $N = m/M$ (M = atomic weight) and consequently $a = KT/\sigma_{\infty,T}NM$ or

$$N = \frac{KT}{aM\sigma_{\infty,T}}\cdot \tag{4}$$

With the help of Eq. (4) it is possible to estimate the number of particles per block, but it is necessary to emphasize that this is only an estimate, and may be a very poor one in cases where there happen to be large local internal fields, or blocks having special shapes rendering the internal fields particularly effective, or perhaps impurities and strains that would invalidate the simple expression $\mu H \cos\theta$ for the energy. In fact, Weiss himself found that two samples of nickel did not follow Eq. (1), but in view of the many substances (including some samples of nickel) that did, and in view of Kapitza's experiments[10] on iron and nickel which are quite compatible with Eq. (1), it seems reasonable to assume that Eq. (1) is experimentally true and may provisionally be interpreted by Eq. (2). From Weiss' data, the block sizes given in Table I are obtained. The general indication of this calculation is that the magnetized units contain in the neighborhood of 100,000 atoms. These estimates are probably significant only as to order of magnitude.

TABLE I. *Estimate of the number of atoms cooperating to form a spontaneously magnetized region. Weiss' experimental data on the approach to saturation are used in Eq. (4). The values chosen for "a" are the average of Weiss' actual observations for each substance.*

Substance	a	$\sigma_{\infty 2T}$	M	N
Iron	6	217	56	350,000
Nickel	8.5	56	59	900,000
Magnetite $FeO \cdot Fe_2O_3$	17	920	33	48,000
Iron Sesquioxide Fe_2O_3	132	76	34	70,000
Fe_2B	255	160	40	15,000
Cementite Fe_3C	460	135	44	9,000
Fe+Co in all proportions	8	210	57	280,000

Before going on to a discussion of the magnetic properties of blocks of this size, it may be well to say a few words about their physical significance, and the factors which determine their existence. Consider, to begin with, a geometrically perfect ferromagnetic lattice near the absolute zero, and con-

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[10] P. Kapitza, Proc. Roy. Soc. **A131,** 243 (1931).

sider two possible configurations; in one it is uniformly magnetized; and in the second its two halves are uniformly magnetized in opposite directions. In the first case let the energy be E. In the second case it will be $E+\sigma S-\int f dv$ where σS represents the increase in energy due to the formation of a surface, and $-\int f dv$ represents the decrease in magnetic energy due to changes in the magnetic field. It may happen that the second state represents a lower energy than the first, in which case it may be expected to occur. In calculating the probability of its occurrence, it is of course necessary to take into consideration the entropy, or the number of ways in which a given final state can be produced. So it is easy to see that even a perfect crystal may break up into smaller regions of spontaneous magnetization. If the magnetic energy plays a large part in determining this breaking up, one will expect the size and shape of the regions to depend markedly on the external field.[11] In contradistinction to this model, consider now the same metal bereft of its ferromagnetism. Zwicky[12] has shown that the perfect crystal need not represent the most stable grouping of atoms, but that a secondary structure may appear. This secondary structure manifests itself by the contraction of certain planes at more or less regular intervals. Although it is not possible at present to state definitely that any given ferromagnetic substance has this or that block structure, still it must be borne in mind that quite independently of the tendency to form blocks resulting from magnetic considerations, certain prescribed blocks may already be there to determine the extent of the regions of spontaneous magnetization. In the latter case the size and shape of the blocks may be quite independent of the state of magnetization and more or less independent of the temperature. It is interesting to note that blocks of the order of magnitude of those deduced in Table I are distinctly comparable to those with which Zwicky's work is concerned. Because blocks of the order of magnitude of those deduced in Table I seem to be of the right size to account for magnetic phenomena over a wide range of temperatures and magnetizations, and would therefore seem to be very stable, we shall here assume the second hypothesis, that the block sizes and shapes are determined by energies other than magnetic. If this is true, it follows that a group of such blocks can change its resulting magnetization only by a rotation of the direction of magnetization of the individual blocks, rather than by the growth of one block at the expense of another through atomic jumps or rotations along an interface.

Assuming, then, that a piece of iron consists of spontaneously magnetized blocks approximately cubic in shape and containing roughly 10^5 atoms, we proceed to enumerate some of the expected properties of iron. Let us assume for simplicity that the internal magnetic fields are negligible. Later on we shall drop this assumption, and show the consequences that follow. Such conditions would exist only just below the Curie point where the spontaneous magnetization (and hence the magnetic moment of each block) is small. Under these circumstances each block will resemble a saturated piece of iron, and we

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[11] Concerning this type of block, see J. Frenkel and J. Dorfman, Nature **126**, 274 (1930).

[12] F. Zwicky, Helvetica Physica Acta **3**, 269 (1930).

may write its energy as a function of the direction of magnetization just as we would for a magnetically saturated macroscopic sample. Akulov[13] writes for the energy E_p of a cubic crystal

$$E_p = K_0 + 2K(s_1^2 s_2^2 + s_2^2 s_3^2 + s_3^2 s_1^2) \tag{5}$$

where s is a unit vector in the direction of magnetization having components s_1, s_2, s_3 along the rectangular axes perpendicular to the (100), (010), and (001) planes. Or, introducing polar coordinates for which $s_1 = \sin\theta\sin\phi$, $s_2 = \sin\theta\cos\phi$, $s_3 = \cos\theta$, the above expression reduces to

$$E_p = K_0 + \frac{K}{4}\{\tfrac{1}{2}(\tfrac{3}{4} - \cos 2\theta + \tfrac{1}{4}\cos 4\theta)(1 - \cos 4\phi) + (1 - \cos 4\theta)\} \tag{6}$$

K is a constant which Akulov interprets as being due to a quadrupole moment. More recently Powell[8] has shown that equivalent espressions can be obtained without assuming quadrupole moments by taking into consideration the interaction between "the effective electrons and the atoms to which they belong." In practice K must be evaluated by comparison with experiment. If a magnetic field is present, a term $-I_W H\cos\psi$ where ψ is the angle between I_W and H, must be added. I_W is the magnetization of a block as given by the Weiss-Heisenberg theory. By way of illustration a few curves have been plotted. If H is in a (100) plane, parallel to a (100) direction, the energy as a function of the direction of magnetization in this plane is given by

$$E_p(100) - I_W H\cos\theta$$

or, putting $h = 4I_W H/K$, we have for the energy per cm^3

$$E_p = [-\cos 4\theta - h\cos\theta]\frac{K}{4} + \text{const.} \tag{7}$$

Similarly, if H is in a (100) plane parallel to a (110) direction, the corresponding expression becomes

$$E_p(100) - I_W H\cos(\theta + \pi/4)$$

or

$$E_p = [-\cos 4\theta - h\cos(\theta + \pi/4)]\frac{K}{4} + \text{const.} \tag{8}$$

In Figs. 1 and 2 are plotted Eqs. (7) and (8) for $h = 0, 2, 5, 10$. It is assumed that $K > 0$. If $K < 0$, Eq. (7) represents magnetization in a (110) and Eq. (8) in a (100) direction. The full expressions for any directions of magnetization in any field are somewhat more complicated than (7) and (8), chiefly because of the simultaneous occurrence of both θ and ϕ. Knowing the function E_p, or potential energy of a block for any direction of magnetization in any field, we may write for the probability f of finding a block magnetized in the direction θ, ϕ in the prescence of any external field exp $(-E_p/KT)$ *provided we have an equilibrium distribution.* Knowing this distribution function, the mag-

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[13] N. S. Akulov, Zeits. f. Physik **54,** 582 (1929). See also G. S. Mahajani, reference (18).

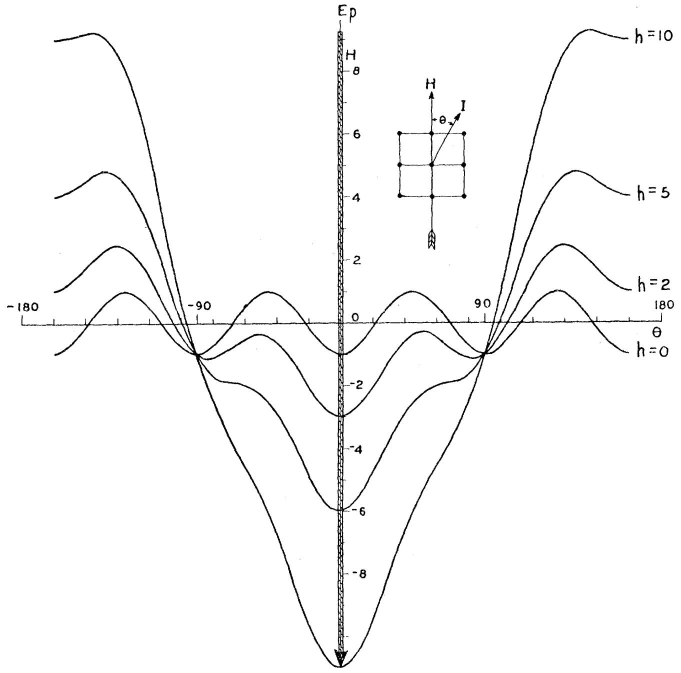

Fig. 1. The potential energy of a cubic crystal as a function of direction of magnetization in a (100) plane for various values of the external field which is proportional to *h* and is applied in a direction of easy magnetization (along a cube edge in iron).

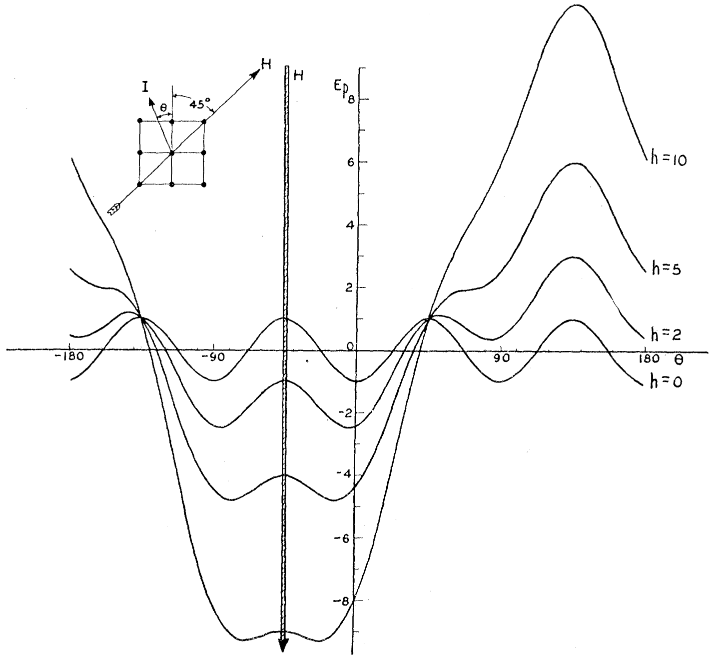

Fig. 2. The same as in Fig. 1, except that the field is applied in a direction of difficult magnetization. If the substance is iron, the figure represents conditons for *H* parallel to a (110) direction.

netization I and energy U of a macroscopic sample follow directly. The integrals will in general have to be evaluated by graphical methods. The chief point of interest, however, lies in the degree of approach to equilibrium in any special case. It is clear that the above expressions for E_p, and consequently also for I and U are single-valued functions of H. In other words, the material will not show hysteresis as long as equilibrium conditions are maintained. Just when equilibrium conditions are to be expected is determined by the following conditions. Suppose we apply a very large field to a substance, so that the potential energy curve becomes similar to that shown in Fig. 1 for $h=10$. If h is sufficiently large, most of the blocks will be magnetized in the direction $\theta=0$, and the distribution function will have a sharp maximum at this point. Suppose now the field is reduced so that the potential energy curve is that corresponding to $h=5$ in Fig. 1. A new distribution must set in. This new distribution must be created by a process of thermal diffusion. A closer inspection shows that the diffusion process is probably governed by a diffusion equation of the type

$$a\nabla\cdot(f\nabla E_p) + b\nabla^2 f = \frac{\partial f}{\partial t} \tag{9}$$

where a and b are constants. Physically this equation states that diffusion is determined by the concentration gradient and the potential forces, and that for equilibrium these two factors must just cancel each other. Without attempting even an approximate solution of Eq. (9) we may predict certain properties of its solutions in view of its physical content as described in the previous sentence. Suppose that for $t=0$ we have $h=5$, (see Fig. 1) and that the minimum is still deep enough so that most of the blocks are magnetized in the direction $\theta=0$. At the time $t=0$, h is changed from 5 to 0. Evidently the particles must diffuse to the right and left, at first rapidly, and then more slowly as the distribution becomes more uniform. Whether any appreciable number will get over the maxima at $\theta=\pm 45°$ will depend on the height of these maxima with respect to KT. If $E_p/KT \gg 1$ f will always be almost zero here. Hence there can be no gradient to speak of, and so very few particles will go from one minimum to the next. But E_p is directly proportional to the volume of a block. Thus we may say that if the blocks are large we would expect most of them to stay in the minimum $\theta=0$ even when $h=0$, whereas if they are small, we would expect a rapid distribution among the four minima at $\theta=0, \pm 45°$, and $180°$. In the first case there would be a large remanence, and in the latter none. A more detailed discussion of this aspect of the problem will appear elsewhere. Emphasis is desired here only on the nature of the physical processes that are assumed to take place during magnetization. It should be pointed out that the presence of strains will greatly modify the potential function E_p, and consequently the detail of the magnetization process. Becker[14] discussed the effect of uniform strains on E_p for a saturated crystallite, but beside these, the strains due to the magneto-striction of each block must eventually be taken into consideration. The fact that unstrained single crystals show very little if any hysteresis would indicate that the blocks are small. Rough estimates[15] of how small they must be in order to account for this lead to sizes comparable with those deduced in Table I.

In order to approximate actual conditions more closely we must now consider the effect of the internal magnetic field. A detailed discussion of this subject would take up too much space to be considered in this article, and we shall therefore confine ourselves to a qualitative discussion. The field inside a spherical cavity in a magnetized medium is $4\pi I/3$. Hence we may write approximately for the magnetic energy of a block $\boldsymbol{\mu}\cdot(\boldsymbol{H}+4\pi \boldsymbol{I}/3)$, and neglecting the term depending on crystal structure (see Eq. (6)), and neglecting strains, the magnetization of a group of blocks is given by

$$I = I_W\left(\coth x - \frac{1}{x}\right) \tag{10}$$

$$x = \frac{\mu}{KT}\left(H + \frac{4\pi}{3}\, I\right). \tag{11}$$

Spontaneous magnetization will occur, according to this equation, if $dI/dx < I_W/3$ or from Eq. (11) if

$$\frac{dI}{dx} = \frac{3KT}{4\pi\mu} < \frac{I_w}{3}$$

or in other words if

$$T < \theta_f = \frac{4\pi\mu I_w}{9K}\,\cdot \tag{12}$$

Now if $\mu = I_W v$ where $v \sim 10^{-18}$ cm^3 this gives $\theta_f \sim (4\pi \times 10^{-18}/9 \times 1.37 \times 10^{-16})(I_W)^2 \sim 0.01(I_W)^2$ so that even if I_W is only about 500, θ_f is a high temperature. Actually, for most ferromagnetic substances at room temperature, I_W is greater than 500, so that we may conclude that the blocks are magnetically coupled to one another and the magnetization of each tends to be more or less parallel to that of its neighbors. The presence of homogeneous strains, and the energy due to crystal structure, both of which factors were neglected above, would have served chiefly to determine the direction of spontaneous magnetization of such a group of blocks.

We saw that the Curie point of a group of blocks, θ_f, was proportional to $(I_W)^2$, the square of the intensity of magnetization of each block. Let θ_p be the Curie temperature of a spontaneously magnetized block as given by the formulae

$$\frac{I_W}{I_0} = \tanh \frac{\mu_B N_W I_W}{KT}$$

$$\theta_p = \frac{\mu_B N_W I_0}{K}$$

where $I_0 = I_W\,]_{T=0}$ and N_W is the Weiss molecular field constant.

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[14] R. Becker and M. Kersten, Zeits. f. Physik **64,** 660 (1930); R. Becker, Zeits. f. Physik **62,** 253 (1930).

[15] F. Bitter, Phys. Rev. **37,** 1176 (1931).

As we approach the Curie temperature from below we have at every temperature T a value of I_W determining θ_f. In other words

$$\theta_f\Big]_T = \frac{4\pi v}{9K} I_W^2\Big]_T$$

and the group of blocks will break up when $T=\theta_f$ or

$$\theta_f = \frac{4\pi v}{9K} I_W^2\Big]_{T=\theta_f}$$

Experimentally the magnetic transformation takes place in two stages. At a temperature θ_f the magnetic properties undergo a marked change, and at the tmperature θ_p there is a change in energy content corresponding to the change in energy of spontaneous magnetization of each block $-\frac{1}{2}N_W I_W^2$. In general these temperatures are only a few degrees apart. We shall assume that the experimentally observed temperatures θ_f and θ_p correspond to the theoretical temperatures deduced above. In order to determine the order of magnitude of the blocks that would give small values for $\theta_p-\theta_f$, we may write

$$\frac{\theta_f}{\theta_p} = \frac{4\pi\mu_W I]_{T=\theta_f}/9K}{N_W\mu_B I_0/K}$$

or

$$\frac{\mu}{\mu_B} = \frac{9N_W}{4\pi}\,\frac{\theta_f}{\theta_p}\,\frac{I_0}{I_W]_{T=\theta_f}}$$

where μ_B is a Bohr magneton, and μ is the magnetic moment of a block. μ/μ_B is of the same order of magnitude as the number of atoms per block. It is not desired at this point to attempt accurate estimates of block sizes, but rather to discover whether ferromagnetic phenomena in general are explicable in terms of blocks containing roughly 10^5 atoms, or in other words that the assumption of such blocks leads to no obvious inconsistences. With this in mind we may put

$$N_W \sim 10^4;\ \frac{\theta_f}{\theta_p} \sim 1;\ \frac{I_0}{I_W]_{T=\theta_f}} \sim 10$$

and find that $\mu/\mu_B=10^5$ in satisfactory agreement with the numbers in Table I. The phenomena near the Curie point will be discussed more fully elsewhere, but it may be stated in advance that there seems to be some hope of describing, with the help of this block model, the changes that take place.

Evidently this spontaneous coupling of the blocks will not cover an entire sample, for by breaking it up it is possible to reduce the total magnetic energy, and such a breaking up process may be expected to go on until clusters of blocks, or Barkhausen units, as they might be called, of a given size are formed. Just as there is an optimum size, so there will be an optimum shape, probably one that is more or less elongated in the direction of magnetization. When an external field is applied to a sample, the total field acting on a group will be approximately $(H+cI)$ where c depends on the shape of the group and is very small for elongated shapes, so that we may conclude that practically only the external field acts on the Barkhausen units.

In an unmagnetized sample these Barkhausen units will be magnetized in the various directions of easy magnetization (see the last section for further details), for instance in iron in the directions (± 100), (0 ± 10), (00 ± 1). Because of their size, they will be very little influenced by temperature. (We saw[15] that the energy of the blocks as their direction of magnetization changes, varies by an amount of the same order of magnitude as KT. Since the Barkhausen units contain thousands or millions of blocks, the above statement seems amply justified.) That is, temperature agitation will not be able to boost them out of the directions of easy magnetization, though it will, in general, determine the relative concentrations in the various directions of easy magnetization. If, now, we apply a small field to the above iron crystal in the (100) direction, a Barkhausen unit magnetized in the (-100) direction will no longer be stable, but will jump into the (100) direction. The relative numbers in these directions will be given (in the absence of hysteresis) by the usual exponential function $e^{\pm \mu_{BU} H/KT}$. μ_{BU} is the magnetic moment of a Barkhausen unit. From the initial slope of the ideal magnetization curve the size of μ_{BU} may be estimated, and it turns out to be of the same order of magnitude as actually observed Barkhausen units. As Akulov[16] has shown, once this initial process is complete, the rotation of the magnetization of the Barkhausen units sets in. This is further discussed in the last section. From the preceding it is clear why Akulov is able to develop so satisfactory a theory without considering internal fields or temperature.

According to what has been said, the magnetization process may be conceived as follows:

1. Small blocks containing approximately 10^5 atoms are permanently magnetized in accordance with the Weiss-Heisenberg theory, the energy as a function of direction of magnetization being determined by Powell's crystalline field, by the presence of strains, and by the internal and external magnetic field.

2. At room temperature these blocks become spontaneously magnetized in clusters, which probably give rise to the Barkhausen effect, and are here called Barkhausen units.

3. Magnetization consists of two processes, a rotation of the magnetization of the Barkhausen units as a whole, and the rotation of magnetization of individual blocks separately. The Barkhausen units will occupy only positions of minimum potential energy; one might say they are too large to execute Brownian movements. The blocks, on the other hand, are small, and so capable of picking up enough thermal energy to "push" them into regions other than minima of potential energy.

4. A change in field will produce two principal changes—a change in the position of the potential energy minima, and a consequent change in the direction of magnetization of each Barkhausen unit, and secondly a tendency to redistribute the number of Barkhausen units in the various minima. This

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[16] N. S. Akulov, Zeits. f. Physik **67,** 794 (1931).

latter process, called by Akulov[16] "Schrumpfprozess" is possible if the potential walls between minima are low enough to let blocks pass. If they are very high, as in strained material, the blocks cannot pass, there is no "Schrumpfprozess," and so the material exhibits hysteresis. Akulov[16] has shown that these two mechanisms suffice to give an approximate theory of the magnetization of single crystals of iron. In the last section of this paper his theory is applied to nickel and cobalt. The block theory gives an explanation of his Schrumpfprozess, and the elongated shape of the Barkhausen units explains why he was able to neglect the internal fields.

5. The final approach to saturation is due to the final alignment of the blocks composing the Barkhausen units.

6. As the temperature approaches the Curie point the Barkhausen units become smaller, and break up at $T=\theta_f$. At $T=\theta_p$ the magnetization of each block disappears.

7. Three arguments are adduced in favor of assuming blocks containing about 10^5 atoms, (a) an argument based on the law of approach to saturation, (b) an argument based on the absence of remanence in single crystals, and (c) an argument based on the small observed values of $\theta_p-\theta_f$.

THE MECHANISM OF THE MAGNETO-CALORIC EFFECT

The magneto caloric effect is of course, governed by thermodynamic principles. If a certain amount of work dW is done in changing the total energy of a system by dU, and if this change occurs adiabatically, then $dU=dW$. If the total energy of the system is of two kinds, potential, and thermal, we can write $dU=dE_p+dQ$ and solving for dQ, obtain

$$dQ = dW - dE_p. \tag{13}$$

Consequently, in order to calculate dQ, it is necessary and sufficient that we know the work done and the change in the potential energy. But Eq. (13) can of course throw no light on the detail of such a process, and it is the purpose of this section to illustrate, on the basis of what might be called a kinetic theory as opposed to a thermodynamic theory, how such a change takes place.

To study the mechanism of the magneto-caloric effect, let us consider first a very simple mechanical system which will later be shown to possess certain similarities to a ferromagnetic substance. This system consists of a large number of particles in thermal equilibrium, having one degree of freedom each, namely x. They are contained between the limits $x=0$ and $x=1$. $f(x)dx$ is the probability of finding a particle between x and $x+dx$. The particles are subjected to a force such that their potential energy at a point x is $\phi(x)$. Then it follows that when equilibrium has set in

$$f(x) = Ae^{-\phi(x)/KT}$$

where A is determined by the equation

$$\int_0^1 f(x)dx = 1$$

At some particular instant let $\phi_1(x) = x$. This function, and the corresponding distribution function f_1 are drawn in solid lines in Fig. 3. KT was chosen equal to unity. The total potential energy in this state is E_1

$$E_1 = N \int_0^1 \phi_1(x) f_1(x) dx.$$

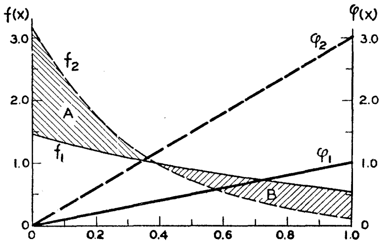

Fig. 3. If $f(x)dx$ represents the number of particles between x and $x+dx$, and $\phi(x)$ is the potential energy of a particle at the point x, then $f(x) = \text{const}\ e^{-\phi(x)/KT}$ at equilibrium and the figure shows $f(x)$ for two values of $\phi(x)$. If ϕ_1 is discontinuously changed to ϕ_2, the particles represented by region B will move to region A and so lose potential energy and gain thermal energy. If ϕ_2 changes to ϕ_1 the reverse processes take place. The reversible temperature changes are analogous to those occurring in the magneto-caloric effect.

N is the total number of particles. Now suppose the external field is suddenly changed so that the potential becomes $\phi_2(x) = 3x$. This change will result in the establishment of a new total potential energy $E_1{}^1$

$$E_1{}^1 = N \int_0^1 \phi_2(x) f_1(x) dx$$

and the amount of work done is obviously $E_1{}^1 - E_1$. The distribution f_1 is, however, no longer stable, and will change and gradually become f_2

$$f_2 = A_2 e^{-\phi_2(x)/KT}.$$

ϕ_2 and f_2 are drawn in dotted lines in Fig. 3. The energy in this state is

$$E_2 = N \int_0^1 \phi_2(x) f_2(x) dx.$$

If the change in potential energy from $E_1{}^1$ to E_2 proceeded adiabatically, this must have been compensated by a change in the thermal energy of the system.

$$-\Delta Q = E_2 - E_1{}^1.$$

In words, we can say that the number of particles represented by the area B in Fig. 4 have dropped from a region of higher potential to the area A which is at a lower potential, and have given up the energy of their "fall" in the form of heat. If now we change the field back again so that the potential becomes ϕ_1 again, the same processes will take place in the reverse order, only instead of "falling," the particles will be "lifted" by temperature agitation from the region A at low potential to the region B at high potential, and so convert a certain amount of thermal energy ΔQ into potential energy. It should be noted that the amount of heat evolved in going from state 1 to state 2 depends on the path taken. For, if we proceed first from ϕ_1 to some ϕ_0, and wait until equilibrium sets in,, and then to ϕ_2, the total heat evolved will be

$$N \int_0^1 \phi_0(f_1 - f_0)dx + N \int_0^1 \phi_2(f_0 - f_2)dx$$

instead of

$$N \int_0^1 \phi_2(f_1 - f_2)dx$$

which is the expression ΔQ above for the heat evolved in going from state 1 to state 2 in a single step. To see that these expressions are not equal, subtract the second from the first. The result is

$$N \int_0^1 \phi_0(f_1 - f_0)dx - N \int_0^1 \phi_2(f_1 - f_0)$$

which is obviously not zero. Similarly the heat evolved in the changes $\phi_1 \rightarrow \phi_0 \rightarrow \phi_2$ depends on whether or not the change $\phi_0 \rightarrow \phi_2$ was made after the equilibrium distribution f_0 had been established. Still again, the heat evolved in the change $\phi_1 \rightarrow \phi_2$ will depend on whether this change was instantaneous, and the diffusion actually took place in the field ϕ_2, or whether $\phi_1 \rightarrow \phi_2$ was gradual. Briefly the results are:

1. If the slope of the potential energy curve is suddenly increased, a rise in temperature follows.

2. If the slope of the potential energy curve is suddenly decreased, a drop in temperature follows.

3. The change in temperature accompanying a change in the applied field depends not only on the initial and final states, but also on the particular way in which the field is varied.

The Effect at High Temperatures in the Absence of Distortions

The analogy between the system discussed in the last section and a ferromagnetic body consists of the fact that in both cases a large number of particles strive toward an equilibrium distribution in a variable external field. In a piece of iron, the direction of magnetization of the atoms, the blocks, and the Barkhausen units are in thermal interaction, and the total magnetic energy is determined by the distribution of their angular coordinates. Here the problem is complicted by the fact that in addition to the potential in the external field the interaction of the various particles has to be considered. In accordance with what has been said in a previous section, the factors that have to be taken into account are: the crystal structure, the permanent distortions of the lattice, the distortions due to the varying magnetostriction in adjacent parts of the lattice magnetized in different directions, the stray magnetic fields, the externally applied magnetic field, and of course the degree of magnetization of each block if the applied fields are sufficiently strong to affect this. An accurate description of these various factors is not possible, and we shall consider under what conditions sufficient simplifications may be made to allow a more or less quantitative treatment. To begin with by assuming large crystal grains in a well-annealed material possessing no magnetostriction the complications due to strains are avoided. And further, by limiting the discussion to large fields, or to temperatures so high that KT is large compared to the variations in potential due to crystal structure (see Fig. 1, $h=0$), the complications arising from expressions similar to Eq. (5) are avoided. And if this high temperature is also near the Curie point where the intrinsic magnetization of each block is small, there will be no internal stray fields to consider. Internal fields will also be negligible if the regions of permanent magnetization are elongated, as is the case at low temperatures, where Barkhausen units of this form predominate, as pointed out in a previous section. Under this conditions, the energy of a block may be written simply*

$$-\mu H\cos\theta-\tfrac{1}{2}n\sigma_W{}^2m$$

where σ_W is the intensity of magnetization per unit mass of a block as accounted for by the Weiss-Heisenberg theory. The distribution of orientations of block moments is then given by the Langevin theory, and the energy per unit mass is

$$-\sum\mu H\ \cos\theta Nf(\theta)-\tfrac{1}{2}n\sigma_W{}^2.$$

where the summation extends over all the blocks and Nf is the number of blocks per unit mass of substance having a given orientation. But $\Sigma\mu\cos\theta Nf(\theta)=\sigma$, the observed intensity of magnetization, so that the energy becomes

$$-\sigma H-\tfrac{1}{2}n\sigma_W{}^2.$$

In changing the field to $H+dH$ the intensity changes to $\sigma+d\sigma$ and $\sigma_W+d\sigma_W$, and substituting in the above expression we have for the change in magnetic energy

$$-\sigma dH-Hd\sigma-N\sigma_Wd\sigma_W.$$

This estimate has neglected the possibility of a loss of energy, due, for instance, to the presence of a conductor in which currents are induced by the change in σ. We will assume that such conductors are not present. If they are, corrections must be applied.

The work done by outside forces in changing the field is

$$-\sigma dH.$$

Equating the work done to the change in magnetic energy and in heat content, we have

$$-\sigma dH=cdT-\sigma dH-Hd\sigma-n\sigma_Wd\sigma_W$$

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* n is the molecular field constant N_W expressed per unit mass instead of per unit volume.

c being the specific heat, or

$$dT = \frac{Hd\sigma + n\sigma_W d\sigma_W}{c} \cdot \tag{14}$$

This is the formula given by Weiss and Forrer[17] except that in Eq. (14) a distinction is made between $d\sigma$, the change in the apparent magnetization, and $d\sigma_W$, the change in the "Weiss" magnetization, and that here the special conditions are pointed out under which the formula may be expected to hold.

THE EXPERIMENTS OF WEISS AND FORRER

In this section the experiments of Weiss and Forrer[17] on nickel are discussed in such a way as to bring out in how far the molecular field theory of Weiss can describe the magneto-caloric effect in high fields quantitatively, and what the nature of the discrepancies between theory and experiment is. In their paper the authors describe an exhaustive series of experiments on the magnetization of nickel. The range of fields used was up to about 20,000 gauss. The particular aspect of their work to be discussed here concerns the change in temperature accompanying a change in the applied field from some value H to zero. In fields of this order of magnitude the chief contribution to the magnetization is still the alignment of the blocks, and only for much higher fields would the increase in σ_W, the magnetization of each block, come in. This does not imply, however, that the change in energy or heat content may not be due primarily to the small increase in intrinsic magnetization. Indeed, it is easily seen that a very small change in σ_W will have much more effect on the energy because of the presence of the molecular field constant n in $n\sigma_W^2/2$, than a much larger change in the apparent magnetization due to the alignment of the blocks.

Writing $d\sigma = d\sigma_{bl} + d\sigma_W$, (the total observed change is due to the change in orientation of the blocks plus the change in magnetization of each block) and considering here only the part due to $d\sigma_W$, we have from Eq. (14). Let us calculate the temperature change due to a given change in σ_W.

$$dT = \left(\frac{H + n\sigma_W}{c}\right) d\sigma_W . \tag{15}$$

This equation is not well suited to a comparison with experiment because σ_W is not a directly observable quantity. We may, however, write

$$d\sigma_W = \frac{\partial\sigma_W}{\partial H} dH + \frac{\partial\sigma_W}{\partial T} dT \tag{16}$$

and substituting in Eq. (15) obtain

$$dT = \frac{\partial\sigma_W/\partial H}{(c/H + n\sigma_W) - (\partial\sigma_W/\partial T)} dH \tag{17}$$

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[17] P. Weiss and R. Forrer, Ann. d. Physique 5, 199 (1926).

where

$$\sigma_W = \sigma_0 \tanh \frac{\mu_B}{KT}(H + n\sigma_W). \tag{18}$$

In using this relationship it is tacitly assumed that H is parallel to σ_W. According to a previous section, this will hold approximately for temperatures not too near the Curie point, because even before $H=1000$ gauss the Barkhausen units are all sensibly parallel to H, and the magnetization has reached the final lining up of the blocks where $\sigma=\sigma_W(1-a/H)$. But near the Curie point where the Barkhausen units are broken up and the blocks are not lined up even in fields of the order of 20,000 gauss, only a part of the blocks will be magnetized parallel to H—some even in the opposite direction. In other words, near the Curie point H will not be as effective in increasing σ_W as at lower temperatures. This prediction we will proceed to verify. Limiting ourselves to temperatures below 570°K we may regard the coefficients of Eq. (17) as constant. This may be seen as follows. For nickel $\theta=630°\mathrm{C}$, the saturation magnetization at $T=0$ is $\sigma_0=58$, and from the relation $\theta=\mu_B n\sigma_0/K$ we find $n=150{,}000$. From the magnetization diagram it is found that for $T<570°$, $\sigma_W>30$, and hence $n\sigma_W>4.5\times10^6$. Hence in Eq. (18) a change of H from 0 to 20,000 will change the argument $(H+n\sigma_W)$ of tanh by less than 2 parts in 450 or $\frac{1}{2}$ percent. From the nature of the function it follows that σ_W and its derivative will change by even less. This means that

$$\Delta T = \text{const}\,\Delta H \tag{19}$$

as Weiss and Forrer showed both theoretically and experimentally. They did not, however, evaluate the constant in Eq. (19), and this we proceed to do. From Eq. (18) it follows that

$$\frac{\sigma_W}{\sigma_0} = \tanh\frac{\theta}{T}\frac{\sigma_W}{\sigma_0}$$

$$n\frac{\partial\sigma_W}{\partial H} = \left[\operatorname{sech}^2\frac{\theta}{T}\frac{\sigma_W}{\sigma_0}\right]\Big/\left[\frac{T}{\theta} - \operatorname{sech}^2\frac{\theta}{T}\frac{\sigma_W}{\sigma_0}\right]$$

$$\frac{T^2}{\theta\sigma_w}\frac{\partial\sigma_w}{\partial T} = -\operatorname{sech}^2\frac{\theta}{T}\frac{\sigma_W}{\sigma_0}\cdot$$

These equations are easily solved numerically, and the results, substituted in Eq. (17) for three values of the temperature, are shwon in Table II.

TABLE II. *The magneto-caloric effect in nickel.*

$t=100°\mathrm{C}$	$t=200°\mathrm{C}$	$t=300°\mathrm{C}$
	From Eq. (17)	
$dT=0.38\times10^{-5}\,dH$;	$.90\times10^{-5}\,dH$;	$2.4\times10^{-5}dH$
	For $\Delta H=17{,}775$	
$\Delta T=0.068°$;	$0.16°$;	$0.42°$
	Experimentally* observed values are	
$\Delta T=0.065°$;	$0.13°$;	$0.32°$

* The experimental values are taken from the figure on page 194 of Weiss and Forrer's paper.[17]

The agreement for $t=100°C$ is remarkably good, but as we approach the Curie point ($t=357°C$) the observed value falls below the theoretical one, and it is suggested that this is due to the fact that for higher temperatures H is not parallel to σ_W in every block, and hence only a gradually decreasing component is effective.

Calculations for $T=\theta$ will not be attempted at this point because of the complexity of the phenomena involved.

THE EXPERIMENTS OF ELLWOOD[6]

Perhaps the most interesting experiments on the magneto-caloric effect are those in Ellwood, because they concern themselves with fields of a few hundred gauss—just the region in which the readjustment between the various regions of spontaneous magnetization is taking place. It is in such fields that the detail of the potential energy curves (see Fig. 1) may be expected to make itself felt. There exists at all fields a magneto-caloric effect dependent on the change in spontaneous magnetization, called σ_W in the previous section, and this may be calculated with a considerable accuracy. Such a process however, cannot account for the results observed by Ellwood, and it would be desirable to attempt an analysis in the light of the foregoing. The fact that Ellwood's experiments were carried out on polycrystalline material makes such an analysis difficult, but the fact that this material consisted of two phases (ferrite+cementite) renders the situation quite hopeless. The experiments were of such a nature that there does not seem to be any reason why they might not be carried out on single crystals. Because of the fundamental importance of such experiments, certain results to be expected on single crystals will be pointed out in the following section.

One inference may be drawn, however, from the existence of a magneto-caloric effect at low fields, namely that in this region temperature agitation must be considered in calculating the magnetization of those substances which show an effect.

THE THEORY OF AKULOV

Based on the work of Mahajani,[18] Kornfeld[19] and Powell,[21] first Webster,[21] and then more in detail Akulov[22] developed a static theory of the magnetization curve. That is, given the potential energy E_p of a region as a function of the direction of magnetization, Akulov calculates the positions of the energy minima, and a sumes that the minima are the only points of the curve actually occupied. That this is a good approximation is shown by the correctness of the theoretical magnetization curve for iron crystals which he was able to construct. It can be shown quite generally that in such a static theory there can be no magneto-caloric effect. It follows that Akulov's theory can be accepted only so long as $dW-dE_p=dQ=0$ within the experimental error. The

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[18] G. S. Mahajani, Roy. Soc. Phil. Trans. **228,** 63 (1929).

[19] H. Kornfeld, Zeits. f. Physik **22,** 27 (1924).

[20] F. C. Powell, Roy. Soc. Proc. **A130,** 167 (1930).

[21] W. L. Webster, Proc. Phys. Soc. **42,** 431 (1930).

[22] N. S. Akulov, Zeits. f. Physik **67,** 794 (1931).

relation is satisfied for iron as Akulov has shown. Let us apply it to nickel and cobalt. For nickel we may write

$$E_p = 2K(s_1^2s_2^2 + s_2^2s_3^2 + s_3^2s_1^2) + \text{const.}$$

as in Eq. (5), from which it follows that

$$E_p(111) - E_p(110) = \frac{K}{6} \equiv \Delta E_p.$$

ΔE_p is the difference in energy of magnetization in the (111) and (110) direction. From a study of the component of I perpendicular to H, or deviation effect, Powell[8] has calculated $2K$ so as to fit the observations of Kaya[23] $2K = -94.8\ I = -94.8\times 500$ ($2K$ is γNI in Powell's notation). From this we find $\Delta E_p = -0.39\times 10^4$ ergs/cc. ΔW, the difference in the amount of work required to magnetize nickel in the (111) and (110) directions is the area enclosed between the corresponding magnetization curves. Using the curves published by Kaya, we find $\Delta W = -0.34\times 10^4$ ergs/cc, which may be considered in satisfactory agreement with ΔE_p above. An actual plot of the theoretical magnetization curves in the (110) and (100) directions is shown in Fig. 4. The discrepancy between experiment and theory for the (100) direction is probably due chiefly to a correction that must be applied to account for the slope of the initial part of the curve. In the (110) direction the agreement is only qualitative. The theoretical curve was obtained according to Akulov's prescription for iron. The numerical value of $2K$ was taken as -94.8×500.

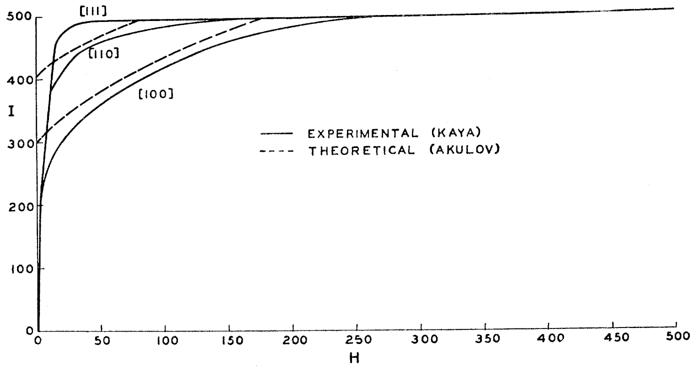

Fig. 4. The experimental magnetization curves of nickel in the principal directions as observed by Kaya, together with the corresponding theoretical curves as deduced by means of the static theory of Akulov.

For cobalt, Powell[8] has shown that E_p may be written in the form

$$E_p = -K_1I_x^2 - K_2(I_y^2 + I_z^2) \tag{20}$$

Powell found from the deviation effect that the difference in energy for a crystal magnetized in the direction of easy and difficult magnetization is

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[23] S. Kaya, Sci. Rep. Tohoku Univ. **17,** 639 (1928).

$$\begin{aligned} \Delta E_p &= -\, I^2(K_2 - K_1) \\ 2I(K_2 - K_1) &= 6.8 \times 10^3 \\ I &= 1.4 \times 10^3 \\ \Delta E_p &= -\, 4.85 \times 10^6 \text{ ergs/cc.} \end{aligned}$$

From the magnetization diagram given by Kaya[24] ΔW may be obtained by graphical integration and is found to be about -5.3×10^6. Whether or not this difference is an experimental error, it is hard to say. If it is not, we must assume that in cobalt there are changes in heat content for magnetization in the directions of difficult magnetization of the order of 10^6 ergs/cc which would correspond to temperature changes of the order of 0.03° C. Cobalt should be a very interesting substance for further experimentation. If the discrepancy between ΔE_p and ΔW is real, we must assume that a magneto-caloric effect is involved, and this in turn leads to the conclusion that a static theory such as Akulov's will not do. Instead of dealing with an equilibrium orientation, we must consider thermal agitation and the ensuing distribution of orientations as suggested in a previous section. Finally, it may be of some interest to see just what the above static theory predicts for the magnetization curve of cobalt in the direction of difficult magnetization. Using Eq. (20) above, it may readily be shown that up to saturation

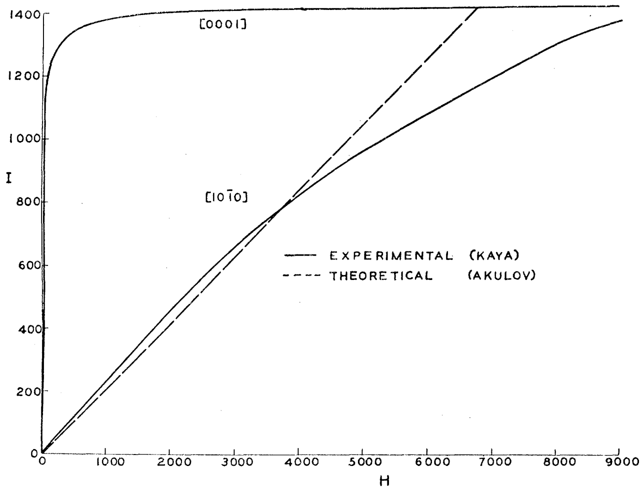

Fig. 5. The experimental magnetization curves of cobalt in its principal directions as observed by Kaya together with the corresponding theoretical curve as deduced by means of the static theory of Akulov.

$$I = \frac{H}{2(K_2 - K_1)} \tag{21}$$

In Fig. 5 the results of Kaya[23] are plotted together with Eq. (21), using $K_2 - K_1$ as found from the deviation effect, $2I(K_2 - K_1) = 6.8 \times 10^3$. The agreement is good except at high fields.

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[24] S. Kaya, Sci. Rep. Tohoku Univ. **17**, 1157 (1928).

As to the nature of the necessary corrections, little can be said at present. One possibility is the introduction of temperature, as has been suggested. Another is the introduction of the random internal fields. As long as the regions of spontaneous magnetization are elongated in the direction of resultant magnetization, this will be negligible. But if they are not, we must write for the energy of a block $\boldsymbol{\mu}(\boldsymbol{H}_e+\boldsymbol{H}_i)$, that is, take into account the internal as well as the external field. And finally there is the possibility that the crystals used in the experiments were not perfect, but locally distorted. This would necessitate the addition of an extra term in the potential energy function similar to that discussed by Becker,[14] and would involve a shifting of the positions at which E_p has a minimum. In how far each of these factors is actually important can be revealed only by further careful experimentation.

SUMMARY

A summary regarding the process of magnetization is to be found at the end of a previous section. About the magneto-caloric effect we might say that,

(1) At high external fields changes in spontaneous magnetization I_W are probably alone responsible for the observed results, but that block structure does play a minor role near the Curie point.

(2) On the basis of Akulov's theory one would expect no magneto-caloric effect after the first steep rise in the magnetization of single crystals, except, of course, insofar as I_W, the Weiss spontaneous magnetization, is altered.

(3) During the steep ascent of the magnetization curve near the origin an effect is to be expected.

(4) Discrepancies between the experimental and theoretical magnetization curves (calculated on the basis of Akulov's static theory) of nickel and cobalt may possibly be due to the presence of a magneto-caloric effect. This point could be tested by experiments on single crystals.

(5) Ellwood's experiments on carbon steel in fields of the order of 200 gauss indicate that temperature agitation must be considered, in this steel at any rate, in calculating its magnetization curve.