val implied by (38) is then very much greater than that between the elementary processes.

process is on the average not much greater than the stochastic part. If α is too large this condition will fail; but in this case fluctuations are unimportant, and no stochastic justification is needed for the Onsager minimum principle.

ACKNOWLEDGMENTS

The author wishes to express his indebtedness to Professor Norbert Wiener, with whom he discussed this work continuously from its inception through its early growth. He also wishes to thank Mrs. Hanna Goldring and Mr. Alvin E. Fein for their interest in the work.

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Magnetization of a Magnetite Single Crystal Near the Curie Point*

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The isothermal M-H curves of magnetite in the principal crystallographic directions have been measured from room temperature to the Curie point. These curves give the anisotropy energy and spontaneous magnetization as a function of temperature. Near the Curie point the magnetizing field required to create a single domain is found to be <100 amp/m, giving an unambiguous experimental determination of the spontaneous magnetization in this critical region. Temperature increments of 0.1°C define the Curie point with an uncertainty of <0.05°C. In the neighborhood of the Curie point the M-H curves are very nonlinear; replotting the data in the form of H-T curves at constant magnetization shows that in this region the magnetic energy can be expressed as $U_M=-\mu_0 W M^2/2$, where W is a constant.

I. INTRODUCTION

FERROMAGNETIC materials are characterized by the existence of a spontaneous magnetic moment in the absence of an applied field. The observed magnetization is determined by the magnitude of the spontaneous magnetization of small regions called domains, and the relative sizes and orientations of the individual domains in the collection which forms the sample. The application of a magnetic field causes the observed magnetization to increase for two reasons: the domain structure tends to be eliminated, with favorably orientated domains growing at the expense of less favorably orientated ones, and finally all domains turn against crystalline anisotropy into the direction of the applied field; the magnetization within each domain increases, giving rise to what we will call an "induced" magnetization. The latter effect is negligible far from the Curie point, so that, when domain alignment is complete, the observed magnetization does not increase with increasing field; consequently, the spontaneous magnetization of the domains is easily studied by extrapolation to zero field from fields high enough to eliminate the domain structure. However, near the Curie point, the induced magnetization becomes appreciable, as is shown by the experimental fact that the observed magnetization continues to increase in fields high enough to have already aligned the domains. The resulting experimental problem of separating the two effects of domain alignment and induced magnetization within a domain has remained unsolved ever since the classic work of Weiss and Forrer[1] on nickel.

The data of Weiss and Forrer were presented in the

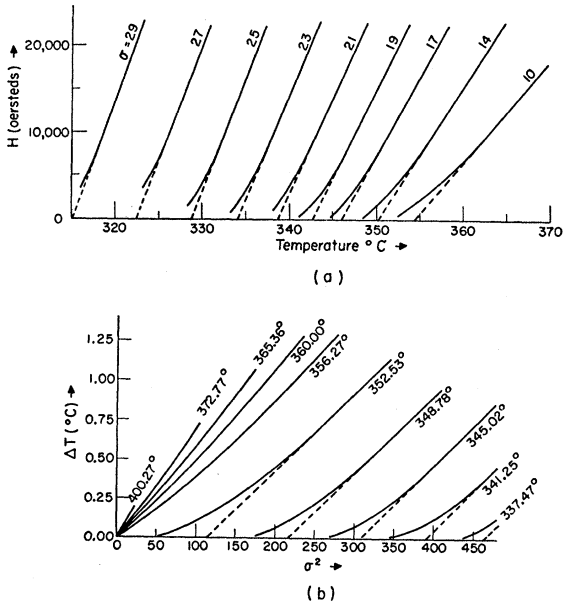

FIG. 1. Experimental data for nickel near the Curie point: (a) H-T curves, (b) magnetocaloric effect. σ, magnetization/g; ——, from measured M-H and ΔT-H curves; - - - -, extrapolated (after Weiss and Forrer[1]).

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[1] P. Weiss and R. Forrer, Ann. phys. [10] 5, 153 (1926).

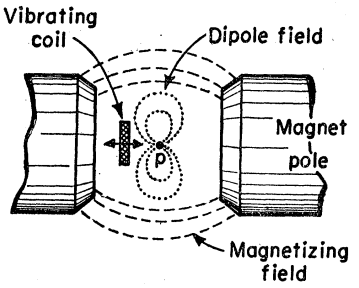

FIG. 2. Principle of the vibrating-coil magnetometer.

form of isothermal magnetization curves (M-H curves), and the increase in temperature ΔT in an adiabatic magnetization (ΔT-H curves). In order to separate domain alignment from induced magnetization, two courses were followed: transformation of the M-H curves at constant temperature into lines of H-T at constant magnetization; transformation of the ΔT-H curves into ΔT-M^2 curves, which requires a second use of the M-H curves. If the magnetic internal energy can be written as $U_M=-\mu_0 W M^2/2$, where W is a constant and M the observed magnetization, thermodynamics gives the following general results regarding the magnetic equation of state and the temperature rise ΔT during an adiabatic magnetization[2]:

$$H=(kT/\mu_0\beta)f(M/M_0)-WM, \quad (1)$$

$$\Delta T=(\mu_0/2C_L)W(M^2-M_s^2), \quad (2)$$

where β is an arbitrary constant, f an arbitrary function, C_L the lattice specific heat, and M_0 and M_s the observed spontaneous magnetization at absolute zero and temperature T, respectively. If we now interpret M, M_0, and M_s as referring to a single domain rather than to the total observed moment, and assume the magnetic energy of domain alignment to be different from $U_M=-\mu_0 W M^2/2$, then a means of separating domain alignment from induced magnetization is available from

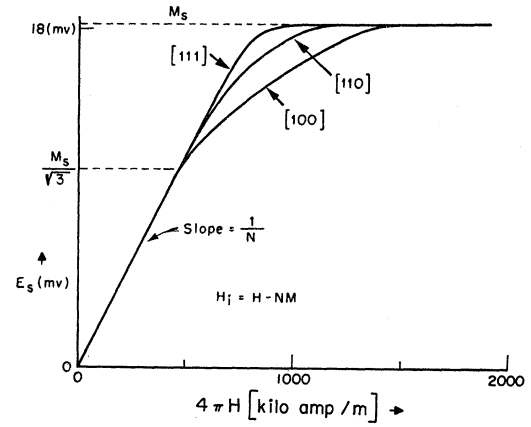

FIG. 3. Room-temperature M-H curves for single-crystal magnetite.

[2] R. Becker and W. Döring, *Ferromagnetismus* (Edwards Brothers, Inc., Ann Arbor, 1943), pp. 42 and 69.

Eq. (1) or Eq. (2). At constant M, Eq. (1) gives H as a linear function of T, with the T intercept giving the temperature of spontaneous magnetization M_s; according to Eq. (2), ΔT as a function of M^2 is a straight line with an intercept of M_s^2 at $\Delta T=0$.

When the data of Weiss and Forrer are replotted in this way, the results of Fig. 1 are obtained. The curves are linear for high fields (corresponding to large ΔT's); the curvature observed at low fields (small ΔT) was attributed to domain alignment effects. The indicated linear extrapolations give M_s-T according to Eqs. (1) or (2). It is often stated in the literature that the magnetocaloric effect provides a way of separating domain alignment from induced magnetization near the Curie point, as opposed to any such possibility using the isothermal magnetization curves. The above results show that both methods are arbitrary and equally unsatisfactory, since they are both based on the assumption $U_M=-\mu_0 W M^2/2$ within a domain. The object of the present paper is to describe an unambiguous experimental method of measuring the spontaneous and induced magnetization of a single domain in the critical region near the Curie point.

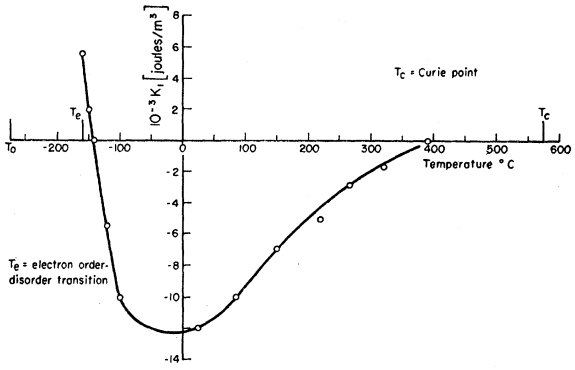

FIG. 4. Anisotropy constant K_1 *vs* temperature for magnetite (low-temperature data after Bickford[7]).

Domain alignment proceeds by two mechanisms: domain wall motion, and rotation against crystalline anisotropy of the magnetization within a domain. It is well known that wall motion in a single crystal is completed in very low fields, resulting in correspondingly low-field saturation in an easy direction of magnetization.[3] Furthermore, as the temperature is increased, the field required for wall motion becomes smaller. Theoretically, easier wall motion is expected because of decreasing magnetostriction, strain, and anisotropy; experimentally it is observed as a decrease of coercive force and disappearance of hysteresis with increasing temperature. Thus, by using a single crystal, the spontaneous and induced magnetization within a domain can be measured near the Curie point undisturbed by domain effects.

[3] K. Honda and S. Kaya, Sci. Repts. Tohôku Univ. **15**, 721 (1926).

II. EXPERIMENTAL

1. Procedure

The isothermal magnetization curves of a single crystal of magnetite were measured from room temperature to the Curie point. The measurements were made with a newly developed vibrating-coil magnetometer.[4] The principle of operation of this instrument is shown in Fig. 2. A small sample of magnetic material in an external magnetizing field becomes a magnetic dipole. The magnetic field of this dipole is converted into an ac electrical signal by means of a coil vibrating along the axis of the dipole and at a distance far enough away to allow room for temperature-generating apparatus around the sample. The signal is amplified and recorded by standard techniques.

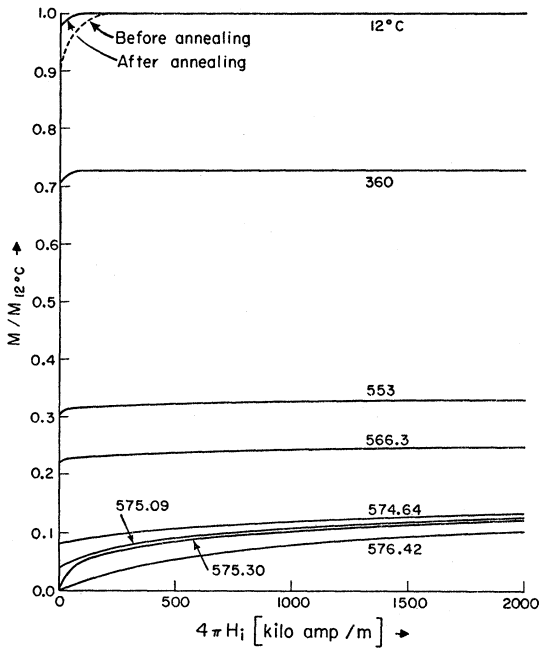

FIG. 5. M-H_i curves in the [111] direction from room temperature to the Curie point for single-crystal magnetite.

The major problem in making a practical instrument is elimination of the signal induced by the curvature of the magnetizing field. A complete description of the vibrating-coil magnetometer is given in reference 4.

The sample was an oblate spheroid cut from a synthetic single crystal of magnetite grown in this laboratory.[5] The minor axis of the spheroid pointed in the [110] direction; the ratio of major to minor axis was 4.77 and the calculated demagnetizing factor N was 0.129.

Magnetite is a brittle ceramic which has to be shaped by grinding. In order to make an accurate ellipsoid, a flat disk with its normal in the [110] direction was fastened with wax onto a rotating spindle and mounted

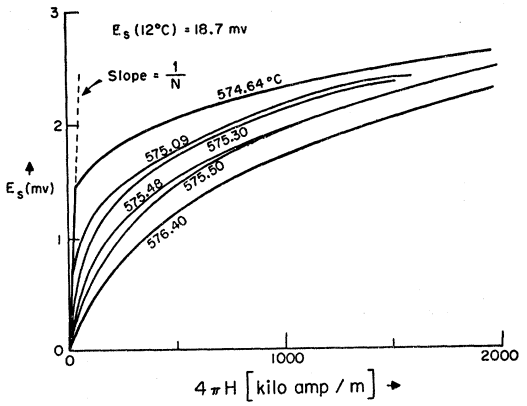

FIG. 6. M-H curves in the [111] direction near the Curie point for magnetite single crystal.

in a microprojector, which cast an enlarged shadow outline of the shape. The rotating sample was shaped by a small counter-rotating grinding wheel guided by hand. Grinding proceeded until the shadowgraph coincided with a calculated ellipsoidal curve. Special waxing and transfer techniques allowed both faces of the disk to be shaped in succession. At the high magnification used (30×), the final departure from ellipsoidal shape was nowhere greater than 0.0005 in.

During measurement, the sample was heated in a small water-cooled furnace; in order to eliminate temperature gradients in the sample, it was placed in a copper thimble within the furnace. Sample temperature was measured with a standard thermocouple and potentiometer. To prevent any change in the oxidation state of the sample, the equilibrium atmosphere of CO and CO_2 was provided at each temperature.[5]

2. Experimental Results

The magnetization curves in the three principal crystallographic directions were measured from room

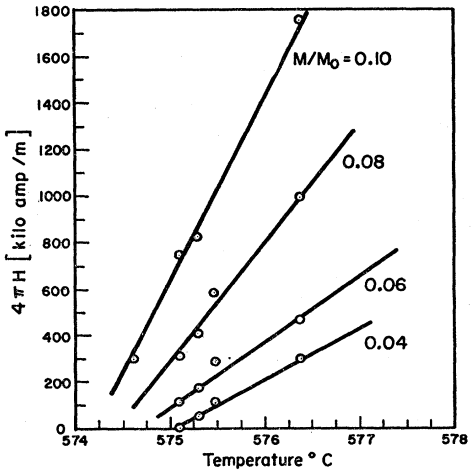

FIG. 7. H-T curves in the [111] direction for magnetite near the Curie point (from the experimental data of Fig. 6).

[4] D. O. Smith, Rev. Sci. Instr. (to be published).
[5] J. Smiltens, J. Chem. Phys. **20**, 990 (1952).

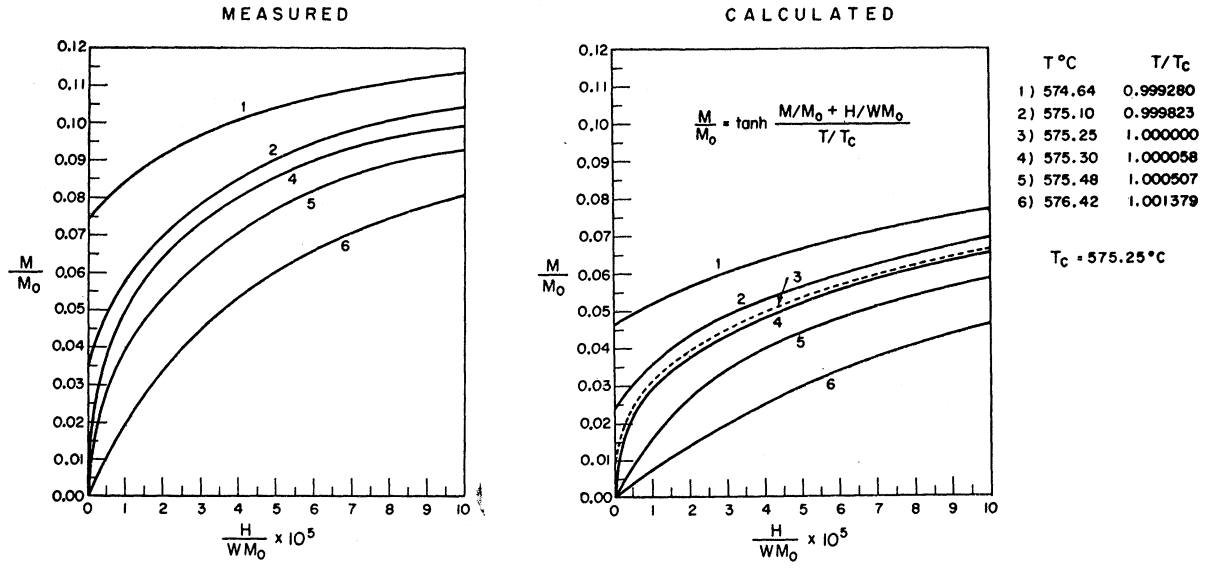

FIG. 8. Comparison of measured and calculated M-H curves in the [111] direction for magnetite near the Curie point.

temperature to the Curie point. Typical curves recorded by the vibrating-coil magnetometer are shown in Fig. 3.[6] The first-order anisotropy constant is found from the area between the curves for the [110] and [100] directions, and is shown in Fig. 4 as a function of temperature. The low-temperature data of Bickford[7] are included for completeness.

Representative results for the M-H_i curves in the [111] direction from room temperature to the Curie point are shown in Fig. 5 (internal field $H_i=H-NM$). M-H curves near the Curie point are shown in Fig. 6.

III. INTERPRETATION

First let us estimate the influence of domain alignment on the curves of Figs. 5 and 6. The sharp curvature in the magnetization curve at 12°C for fields of less than 20 ka/m is certainly due to domain alignment; annealing at 600°C reduces the internal strain so that subsequent magnetization at 12°C gives a single domain in a field of 10 ka/m. As the temperature is increased, the curvature in low fields becomes less sharp, and the induced magnetization begins to become apparent in the gradual slope of the M-H curves at higher fields (see $T=553$°C and 566.3°C). The magnetization curve at 574.64°C shows no trace of domain alignment on the scale of H used in Fig. 5, although the induced magnetization in low fields is becoming more important; a magnified H scale showed that the domains were removed in <100 amp/m. Thus, the data of Fig. 6 in the immediate neighborhood of the Curie point are to be interpreted as a direct measure of the spontaneous and induced magnetization of a single domain. The Curie point lies between the last experimental curve which has a spontaneous moment and the first one for which there is no spontaneous moment, i.e., between 575.09°C and 575.30°C. This defines the Curie point to <0.1°C; more data are available which reduce this uncertainty to <0.05°C. The Curie point has been taken as 575.25°C. Of course, the temperature was not determined to this degree of absolute accuracy but only relative to the particular thermocouple used.

In order to determine if the experimental data can be represented by $U_M=-\mu_0 WM^2/2$, the H-T curves obtained from Fig. 6 are shown in Fig. 7. The best representation of these data are straight lines, so that over the limited range of H and T for which data are available, W can be considered a constant.

The Weiss theory of ferromagnetism interprets the constant W in terms of an internal field proportional to WM and β as the dipole moment of a magnetic carrier (electron spin). The resultant equation of state is

$$\frac{M}{M_0}=\tanh\left(\frac{M/M_0+H/WM_0}{T/T_c}\right), \qquad (3)$$

with T_c=Curie temperature and $W=kT_c/\mu_0 M_0$. For magnetite $T_c=848$°K, $M_0=512$ ka/m, which gives $W=1.97\times10^3$. The magnetization curves calculated from Eq. (3) are compared with the experimental data of Fig. 6 in Fig. 8; the H scale is replotted in terms of $H/WM_0=9.90\times10^{-7}H$. It is seen that the general features of the two sets of curves are the same, although detailed correspondence is lacking; the experimental induced-magnetization is of the order of twice the theoretical value.

The spontaneous magnetization as a function of temperature in the immediate vicinity of the Curie point is shown in Fig. 9. It is seen that with temperature increments of 0.1°C the transition from the ferromagnetic to the paramagnetic state is completely sharp.

[6] mks units will be used here [1 oersted = (1000/4π) amp/m].
[7] L. R. Bickford, Jr., Phys. Rev. 78, 449 (1950).

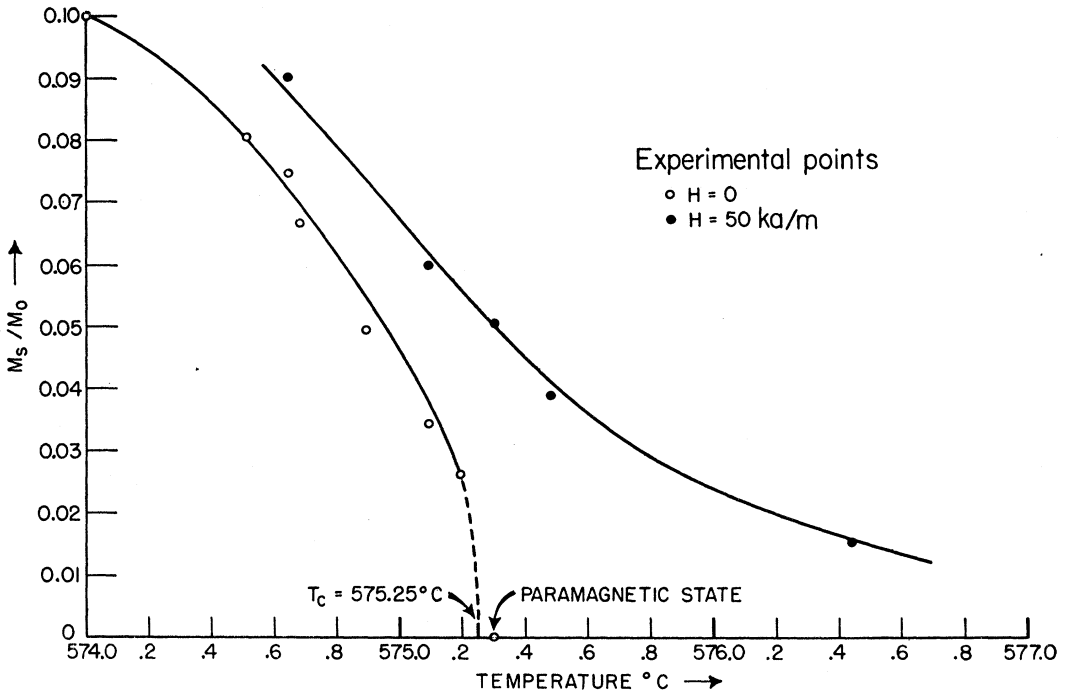

FIG. 9. M_s/M_0 *vs* T in the [111] direction near the Curie point for single-crystal magnetite.

The effect on the observed magnetization of a field of 50 ka/m is also shown.

IV. CONCLUSIONS

A single crystal of magnetite has been measured with the newly developed vibrating-coil magnetometer to yield an unambiguous determination of the spontaneous magnetization of magnetite near the Curie point. However, near the Curie point there is no observable anisotropy (see Fig. 4); hence, there are no longer any preferential domain directions, and alignment in weak fields would be expected to occur also for polycrystalline samples. This is substantiated by the measurements of Potter on iron near the Curie point.[8] Potter found the same magnetocaloric effect in single-crystal and polycrystalline iron. Deviations from the Weiss theory were attributed to domain alignment effects; however, if domains were important, we would expect different results for the two samples. If domains do not play a large role in the magnetization curves near the Curie point, then the data of Weiss and Forrer for nickel should be reinterpreted. Additional measurements on both polycrystalline and single-crystal magnetite and nickel are needed in order to resolve this question.

The transition from the ferromagnetic to the paramagnetic state in magnetite has been found to be sharper than is revealed by temperature increments of 0.1°C; these increments are an order of magnitude smaller than those used in any previous study of a ferromagnetic Curie point. The question arises as to the ultimate sharpness of the magnetic transition. One can imagine that between the ferromagnetic state, characterized by long-range order, and the paramagnetic state, which is to a first approximation completely disordered, there might be intermediate stages of short-range order which could have a spontaneous moment. This might be revealed by the lack of a sharp Curie temperature. Experiments are therefore planned to determine the precise nature of the magnetic Curie point by using temperature increments of 0.01°C.

V. ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor A. R. von Hippel for the use of the facilities of the Laboratory for Insulation Research, and for his advice and encouragement during the course of this research.

[8] H. H. Potter, Proc. Roy. Soc. (London) **A146**, 362 (1934).