Magnetic and Electric Properties of Natural and Synthetic Single Crystals of Magnetite*†

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When a crystal of magnetite has been cooled through the low temperature transition (near −164°C) in a demagnetized state, the magnetization undergoes a large and abrupt increase in the three principal crystallographic directions [100], [110], and [111] upon warming. The behavior of the magnetization upon cooling in a magnetic field is influenced by crystallographic orientation as well as by the strength of the applied field. The form of the magnetization curve at temperatures below the transition depends on the crystallographic direction and on the magnetic treatment of the specimen while cooling through the transition. Barkhausen experiments lead to tentative ideas concerning domain orientation. Significant information concerning the nature of the transition was also obtained from measurements of thermal expansion and saturation magnetostriction.

The magnetic effects in the low temperature transition region appear to be influenced by the establishment of internal stresses which cause a "freezing-in" of preferential domain directions below the transition region. The stress and domain pattern resulting appears to depend on the magnetic treatment of the crystal during its passage through the transition region.

The temperature dependence of the electrical resistivity is in agreement with the results of Verwey and de Boer for sintered magnetite. Some preliminary observations are reported on the effects of magnetic fields on the resistivity.

1. INTRODUCTION

MAGNETITE (Fe_3O_4) is a ferromagnetic semiconductor crystallizing in the so-called inverse spinel lattice.[1] In the vicinity of −160°C it exhibits a second-order transition at which its physical properties change rather abruptly.[2–8] A brief survey of early work on magnetite is given by Bickford.[9]

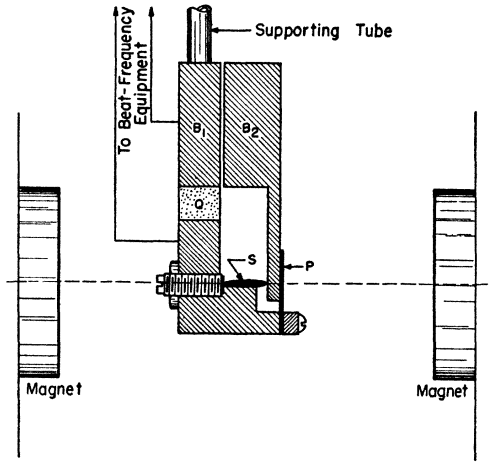

FIG. 1. Schematic diagram of the dilatometer.

The purpose of the present study was to investigate the magnetic and electric properties of magnetite single crystals in static fields, the dependence of these properties on temperature, and in particular the behavior in the vicinity of the low temperature transition. It became apparent during the work that helpful information might be obtained by also investigating the Barkhausen effect, the longitudinal saturation magnetostriction, and the thermal expansion of magnetite single crystals. Such measurements were therefore performed and are also reported.

2. SPECIMENS AND MEASUREMENTS TECHNIQUES

Measurements were made on both natural and synthetic single crystals of magnetite. The natural crystals were analyzed by J. Smiltens of this Laboratory; their composition appeared to be very nearly stoichiometric, although some ambiguity arises from the presence of impurities, mostly iron pyrite. The synthetic single crystals were grown by J. Smiltens[10] from a melt in the form of cylinders *ca.* 5 mm diam. and 20–40 mm long. Their chemical composition corresponded to the stoichiometric ratio within limits of error (Nos. 3 and 4). Some measurements were also made on a polycrystalline specimen (No. 5, composition, Fe_2O_3:FeO = 1.074).

In order to allow magnetic as well as electric measurements to be made on a single specimen, the shape chosen was that of an oblate spheroid (*ca.* 5 mm diam., 1 mm thickness). The specimens were cut with a diamond wheel and ground to shape with emery cloth. The only synthetic crystals available at the time of this investigation appeared to have rather large internal stresses, and to be cracked along the scratches drawn on the specimen for purposes of orientation (No. 3 cracked along [110], No. 4 along [100]). The magnetic measurements indicated greater hysteresis than for the natural single crystals, especially at temperatures below the transition. The crystallographic planes of the

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[9] L. R. Bickford, Tech. Rept. XXIII, ONR Contract N5ori-07801, Lab. Ins. Res., M.I.T. (October, 1949).
[10] J. Smiltens, Lab. Ins. Res., M.I.T. (to be published).

specimen disks No. 1, 2, and 3 were (110); No. 4, (100). The place of origin of the natural single crystals was Chester, Vermont.

The resistivity of the specimens was obtained in the usual manner by measuring the difference in potential between two probes in contact with the specimen for a known current traversing the specimen. No attempt was made to determine accurately the absolute value of the resistivity since the current density was not uniform throughout the specimen, and because the temperature coefficient of resistivity is in our case the parameter of interest.

The magnetization was measured with a new type of pendulum magnetometer[11] in which the specimen is surrounded by a "null-coil" through which a current is passed in such a sense as to cancel the magnetic moment of the specimen. In this manner one avoids the necessity of measuring directly the magnetic field gradient and the force acting on the specimen in the inhomogeneous field.

The Barkhausen effect in the spheroidal specimens was observed by means of a small search coil with *ca.* 150 turns of No. 42 enameled copper wire wound closely around the specimen on a thin paper form. The pick-up coil was connected to the input of a wide-band, high gain amplifier the output of which was connected to the vertical plates of an oscilloscope. The Barkhausen pips, on the average, were 5 to 10 times higher than the background noise.

The dilatometer for measuring the magnetostriction and thermal expansion of the spheroidal magnetite specimens is shown in schematic form in Fig. 1. The basic idea of the device is that, as the diameter of the specimen S changes, the inner faces of the brass blocks B_1 and B_2 alter their separation; if these two faces are used as condenser plates the corresponding variation in capacity can be used to calculate the change in dimensions of the specimen.[12] A positive pivot-action is furnished by the phosphor-bronze ribbon P; the Bakelite block Q isolates the two condenser plates electrically. The change in capacity was measured with a beat-frequency equipment developed in this Laboratory for the measurement of the dielectric constant of gases.[13] The instrument was calibrated with a fused quartz specimen.

Besides ease of construction, the holder showed very good stability as a result of the "pinching" action exerted by the phosphor-bronze ribbon. By placing the

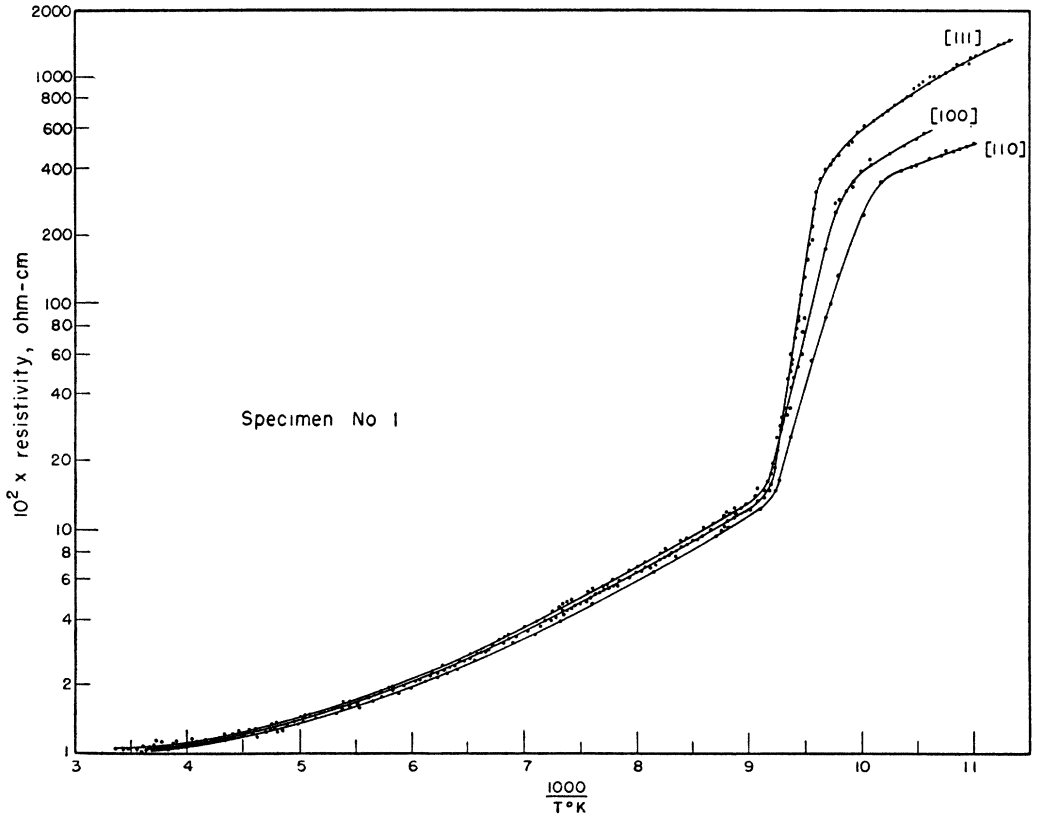

FIG. 2. Cooling curves, resistivity *vs.* $1000/T°K$; natural magnetite single crystal.

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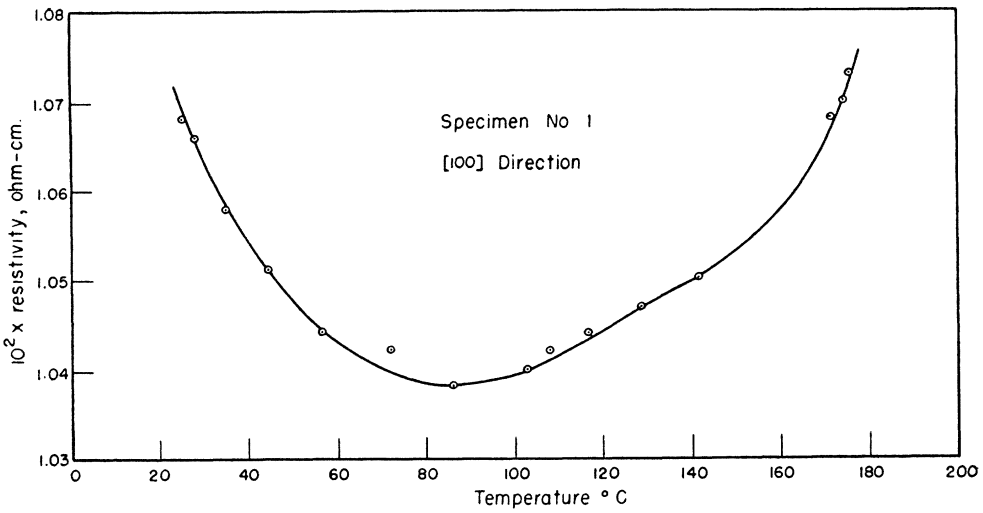

FIG. 3. Warming curve, resistivity *vs.* temperature, natural magnetite single crystal, showing maximum.

specimen horizontally the magnetostriction for a selected direction in the plane of the disk could be measured in magnetic fields applied parallel to this or to any other direction in the plane of the disk.

3. MAGNETIC AND ELECTRIC BEHAVIOR ABOVE THE TRANSITION

Above the transition temperature (*ca.* -164°C) magnetite behaves magnetically much like nickel; its saturation magnetization is 4.45×10^5 amp./m (445 c.g.s./cm^3) and its anisotropy constant $K=-10^4$ joule/m^3 (-10^5 erg/cm^3). Its Curie temperature lies at *ca.* 570°C, and in polycrystalline form at room temperature it has an initial permeability of approximately 17.

Barkhausen Effect

In the present investigation of the Barkhausen effect of natural magnetite it was found that the activity on the oscilloscope vanishes almost completely in the vicinity of -143°C. This is in accord with the recent work of Bickford,[14] who determined, from ferromagnetic resonance experiments, that the anisotropy constant K_1 of magnetite vanishes at this temperature but increases rapidly again in magnitude as the transition temperature is approached.

Electrical Properties

Magnetite exhibits interesting electrical properties above the low temperature transition as well as below. A discussion of the striking difference between the electrical behavior of Fe_3O_4 and that of the related lattices Mn_3O_4 and Co_3O_4 is given by Verwey and de Boer[8] based on experiments with sintered bars of these materials. In Fig. 2 are shown the results of our measurements of the resistivity of natural magnetite single crystals for the three principal crystallographic directions. These measurements were made while the crystal was cooled very slowly in a demagnetized state.

Of interest above the transition is the behavior of the resistivity in the vicinity of $+100$°C, as already pointed out by Verwey and de Boer; in order to bring out the situation more clearly we have plotted in Fig. 3 resistivity *vs.* temperature for the [100] direction of a specimen of natural magnetite. It appears that magnetite is another of the few investigated cases of substances for which the conductivity traverses a maximum value at a reasonably low temperature. Another interesting example of this type of behavior is silicon carbide, which has been thoroughly investigated by Busch and Labhart.[15]

Effects of Magnetic Field on Resistivity

The change in resistivity of magnetite at ordinary temperatures upon application of a strong magnetic field is quite small (*ca.* 0.1 percent). For example, it was found that the resistivity in the [110] direction *decreases* at temperatures above the transition by about 0.1 percent upon application of a strong magnetic field parallel to either [110] or [111]. On the other hand, if the strong magnetic field is applied parallel to [100] at these temperatures, the [110] resistivity *increases* a few tenths of one percent. These observations were made on specimen No. 1.

Thermal Expansion

The thermal expansion of natural single crystals of magnetite has apparently been investigated only by Okamura.[7] He gives the results of measurements on

[14] L. R. Bickford, Jr., Phys. Rev. **76**, 137 (1949); Tech. Rept. XXIII, ONR Contract N5ori-07801, Lab. Ins. Res., M.I.T. (October, 1949).

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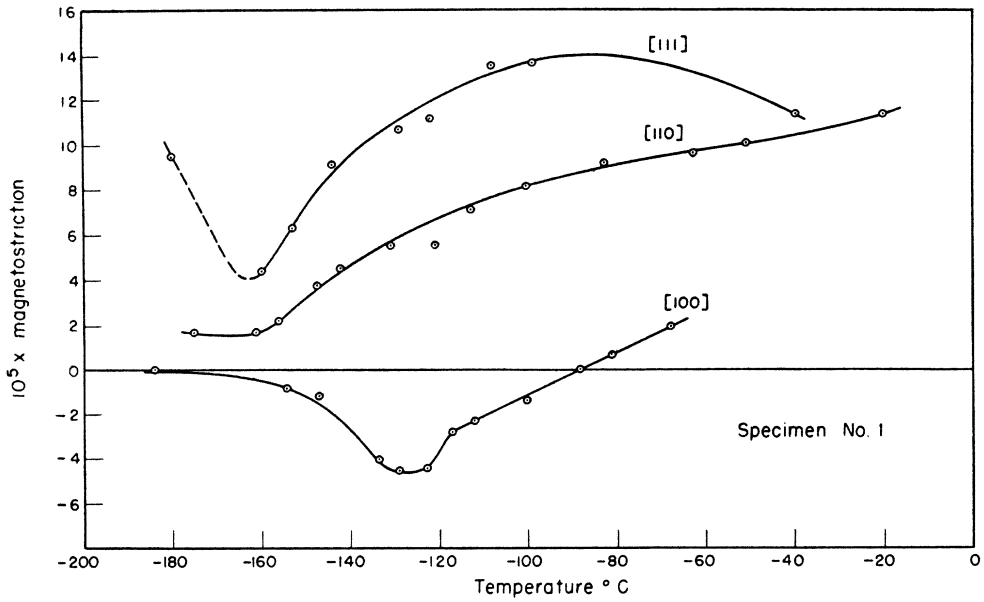

FIG. 4. Longitudinal saturation magnetostriction *vs.* temperature, natural magnetite single crystal.

one rod cut from a single crystal, but does not indicate the crystallographic orientation of the axis of the rod.

The present measurements were made on one of the oblate spheroids cut from a natural single crystal. For a temperature interval of 50°, i.e., from −150° to −100°C, the thermal expansion coefficients for the three principal crystallographic directions were found to be as follows: [100], 4.66×10^{-6}/°C; [110], 7.16×10^{-6}/°C; [111], 11.3×10^{-6}/°C±*ca.* 5 percent.

Magnetostriction

At temperatures above the transition, the longitudinal saturation magnetostriction ($\Delta L/L$ measured parallel to applied magnetic field) proved to be positive for the [110] and [111] directions; the [100] direction has a positive value at temperatures above −88°C and is negative below this temperature (Fig. 4). Because of the so-called "form effect" (specimen No. 1 is an oblate spheroid) the values of magnetostriction given in Fig. 4 are too large by possibly as much as a factor of 2. No accurate estimate of this factor can be made, since the elastic constants of magnetite are not known. By using long, thin rods the influence of the specific form of the specimen can be eliminated, but the present data are still useful in showing the temperature dependence of the magnetostriction and the relative values for the three principal crystallographic directions.

4. EFFECTS IN THE VICINITY OF THE TRANSITION

Magnetization

As the temperature of a magnetite specimen is lowered the magnetization, measured by the steady state method, increases in a manner depending not only on the applied magnetic field but also on the crystallographic direction along which the field is applied. This behavior as such is, of course, not unusual, but the effects occurring when the transition region of magnetite is reached are quite so.

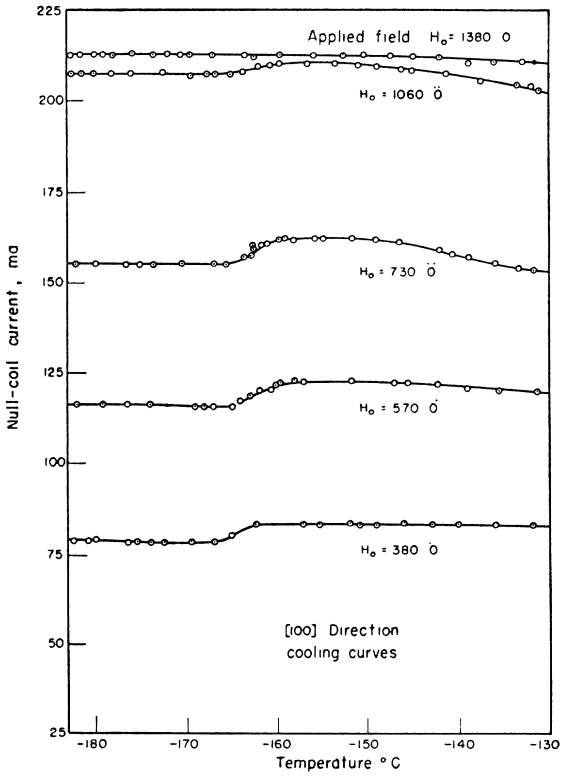

FIG. 5. Cooling curves, magnetization (arbitrary units) parallel to [100] *vs.* temperature, natural magnetite single crystal. Curves are for various values of fixed external magnetic field.

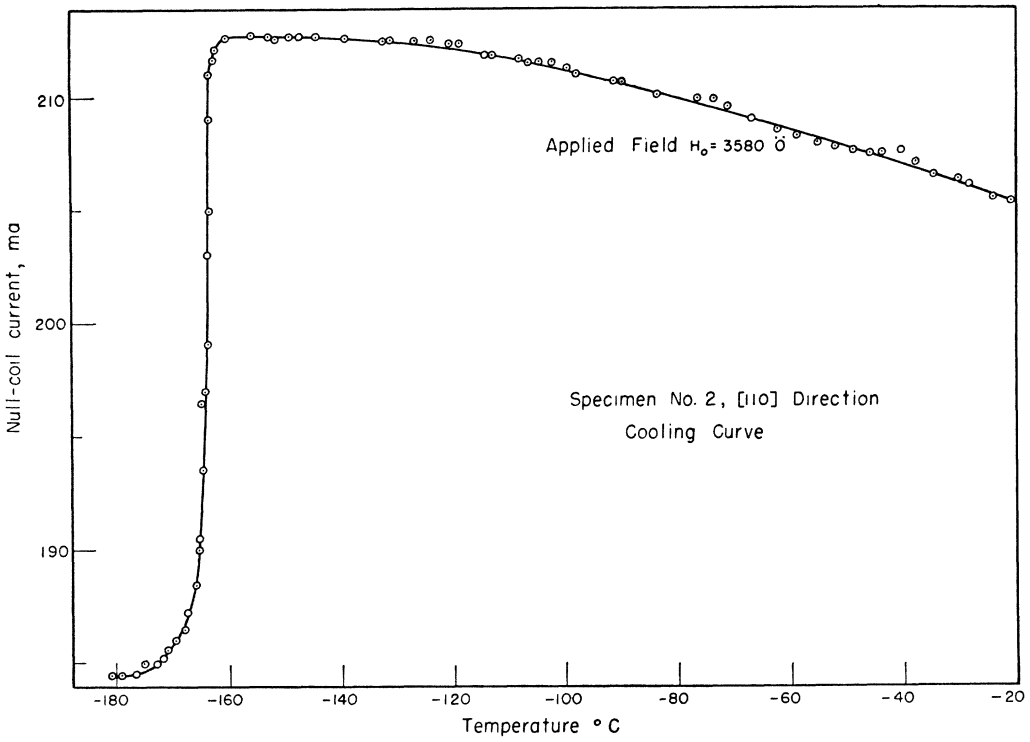

FIG. 6. Cooling curve, magnetization (arbitrary units) parallel to [110] *vs.* temperature, natural magnetite single crystal.

Figure 5 shows measurements on specimen No. 2; the ordinate gives the values of the magnetometer null-coil current, which is proportional to the magnetization of the specimen. The field was applied in this case along the [100] direction, and the various curves correspond to fixed values of the external magnetic field. If the field is applied along the [111] direction the results are very similar to those for the [100] direction. Repeated with the magnetic field along the [110] direction, the outcome of this experiment is quite different (Fig. 6). Even for large fields one observes in this orientation upon cooling a large and rapid decrease in magnetization. In the [100] and [111] directions on the other hand, only a slight diminution in magnetization occurs if weak fields are applied, while in strong fields one observes a slow monotonically increasing magnetization with falling temperature.

This behavior might be interpreted as indicating that the abrupt change in magnetization is primarily a characteristic of the [110] direction of magnetite. However, if one demagnetizes the specimen carefully while the temperature is still above the transition, cools then through the transition in zero field, and measures again in successive experiments the magnetization along the three principal crystallographic directions while the temperature rises through the transition, one finds the results shown in Fig. 7. These data refer to specimen No. 1, but the same situation was found to hold for No. 2, for several samples cut parallel to other

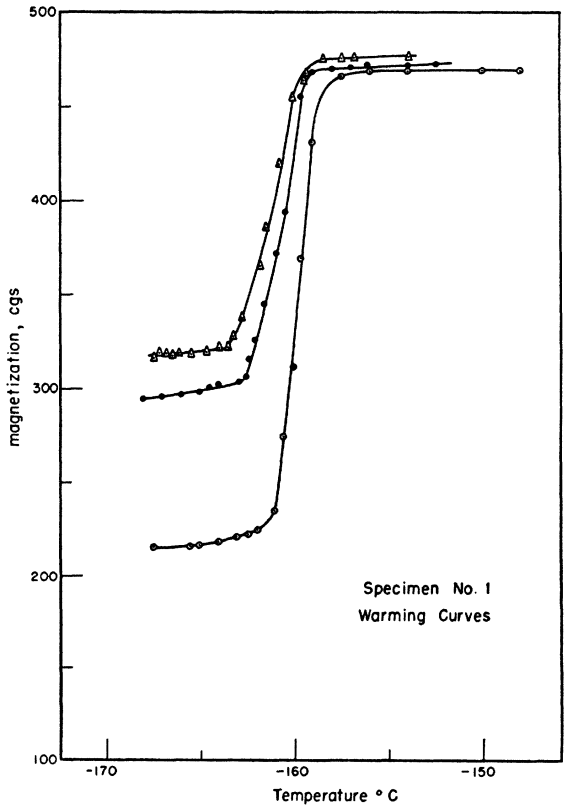

FIG. 7. Warming curves, magnetization (c.g.s.) *vs.* temperature, parallel to the three principal crystallographic directions, natural magnetite single crystal.

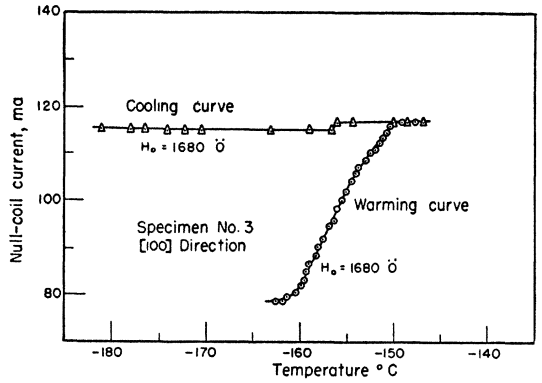

FIG. 8. Magnetization (arbitrary units) *vs.* temperature, synthetic magnetite single crystals. Specimen No. 3, [100] direction.

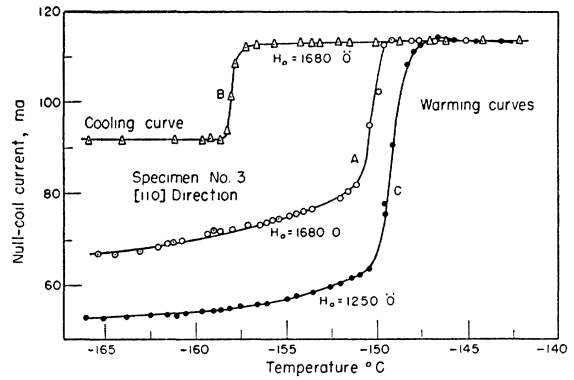

FIG. 9. Magnetization (arbitrary units) *vs.* temperature, synthetic magnetite single crystals. Specimen No. 3, [110] direction.

crystallographic planes, and also for synthetic single crystals.

Comparing Figs. 5, 6, and 7 we see that the temperature dependence of the magnetization is different for the three principal crystallographic directions, and is determined by the magnetic prehistory of the specimen. Cooled through the transition in zero field, the crystal upon warming undergoes a large abrupt increase in magnetization in all three crystallographic directions. During cooling through the transition in intermediate and large fields, the magnetization undergoes a large abrupt decrease for the [110] direction but not for the [100] nor [111] directions. In weak fields all three directions exhibit during cooling a complicated behavior, but always an over-all decrease in magnetization occurs as the temperature is lowered through the transition.

Although the same general behavior was found for the two synthetic single crystals,[16] these latter specimens showed several additional features of interest which were not found in the natural crystals. The warming curve (Fig. 8) of specimen No. 3, for example, shows that the magnetization in the [100] direction increases gradually over a 10° interval with an increase in magnetization of about 45 percent for an applied induction of 0.168 weber/sq. m (1680 oersteds). The center of this magnetic transition (for the [100] direction) is at a slightly higher temperature (−155°C) than that of the natural crystals (−161°C; see Fig. 6). On the other hand, the [110] direction of this specimen behaves quite differently (Fig. 9). The change in magnetization is rapid for both cooling and warming through the transition region, but the temperatures at which the abrupt changes in magnetization take place for the same external induction (0.168 weber/sq. m), differ in curves *A* and *B* by 8°C. Warming in a weaker field, after cooling through the transition region in zero external field, caused a rapid change in magnetization at an even higher temperature than −150°C (curve *C*, Fig. 9).

Specimen No. 4 gave similar results (Figs. 10 and 11), except that the temperature difference between the transitions for warming and cooling was even larger, namely 20°C. Furthermore, whereas for specimen No. 3 the warming curve in the region below the transition for the [110] direction (Fig. 9) shows a gradual increase in magnetization, specimen No. 4 in its corre-

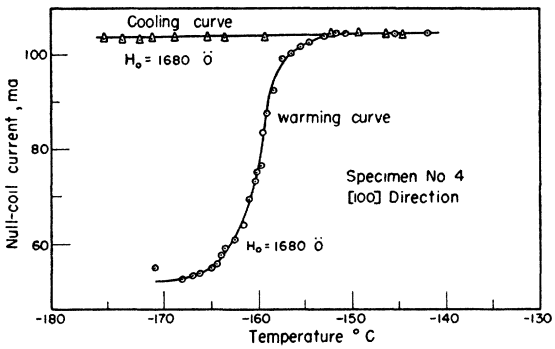

FIG. 10. Magnetization (arbitrary units) *vs.* temperature, synthetic magnetite single crystals. Specimen No. 4, [100] direction.

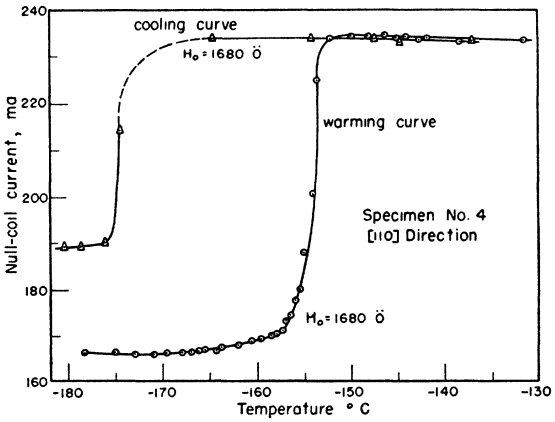

FIG. 11. Magnetization (arbitrary units) *vs.* tempeature, synthetic magnetite single crystals. Specimen No. 4, [110] direction.

[16] Specimen Nos. 3 and 4 cracked in the grinding process; measurements were nevertheless made on these specimens after cementing the pieces together, because no other synthetic single crystals were available at that time.

sponding temperature range shows (warming curve, Fig. 11) a constant value of magnetization in this same crystallographic direction. The center of the [100] warming curve (specimen No. 3) in Fig. 8 lies at a temperature (−155°C) between the [110] "warming transition" and "cooling transition" (−150° and −158°C) of Fig. 9; the same is true for specimen No. 4 (Figs. 10 and 11).

Specimen No. 5, the synthetic polycrystalline specimen of non-stoichiometric composition, was found to give in the transition region a small decrease in magnetization upon cooling in an applied induction of 0.168 weber/sq. m, but after cooling in zero field showed a large and rapid increase in the vicinity of −180°C upon warming (Fig. 12).

Next, the shape of the magnetization curves (M *vs.* H) for the three principal directions at temperatures just above and below the transition was investigated[17] (Fig. 13). The curves corresponding to −180°C were each taken after the specimen (No. 1) had been demagnetized above the transition and then cooled directly to −180°C in zero field. It is seen that below the transition, after cooling in zero field, the crystal is much more difficult to magnetize than at temperatures above this region.

If, on cooling through the transition, a "freezing in" of some unit occurs, either on an atomic or on a domain scale, the magnetization curves below the transition might differ after cooling in fields of various strengths. This is actually the case, as shown for the magnetization parallel to [100] in specimen No. 2 (Fig. 14). The specimen was demagnetized above the transition, the indicated field H_0 applied and held constant while cooling through the transition, and the specimen demagnetized again below the transition temperature before the corresponding magnetization curve was taken. Similar experiments for the [111] direction gave the same kind of curves, except that cooling in a given field H_0 parallel to [111] did not raise the magnetization curve quite as much as for cooling in a field of the same strength oriented parallel to [100]. In contrast, the [110] direction remained difficult to magnetize even after cooling through the transition region at applied inductions of several tenths of a weber/sq. m (several thousands of oersteds) oriented parallel to [110]. This difference between the three principal crystallographic directions makes less surprising the behavior of the magnetization upon cooling in the transition region as shown in Figs. 5 and 6.

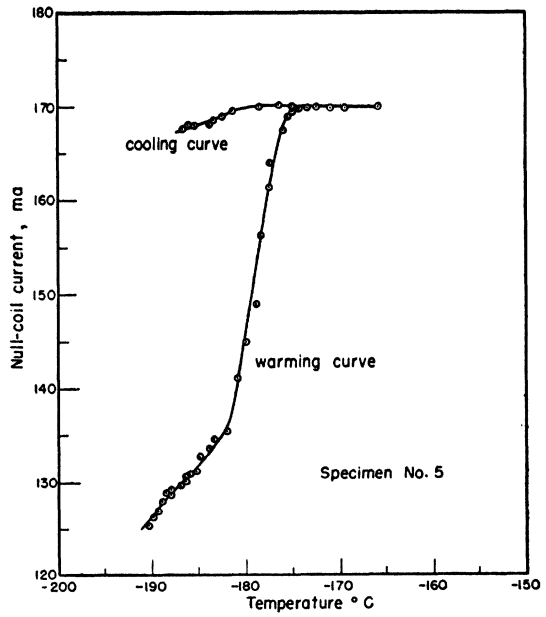

FIG. 12. Magnetization (arbitrary units) *vs.* temperature, synthetic polycrystalline non-stoichiometric magnetite.

[17] Okamura and Ogawa (reference 7) apparently failed to observe the important differences between the magnetization curves below the transition for cooling in finite and in zero fields.

Barkhausen Effect

The magnetic behavior of magnetite in the vicinity of the transition might be the result of oriented internal stresses resulting from a rapid change of the magnetostriction and the lattice dimensions in the transition region. If this results in a "freezing in" of ferromagnetic domains by the internal stresses, an investigation of the Barkhausen effect in the vicinity of the transition should give significant information. The following observations were made on specimen No. 2.

(a) After careful demagnetization and cooling through the transition in zero field, observation of the Barkhausen effect with slowly increasing applied field indicated that only about 75 to 85 percent of the magnetization results from irreversible wall displacements, as indicated by strong pips on the cathode-ray screen; the remainder, not visible on the screen, may be due to domain rotations. A similar experiment performed at

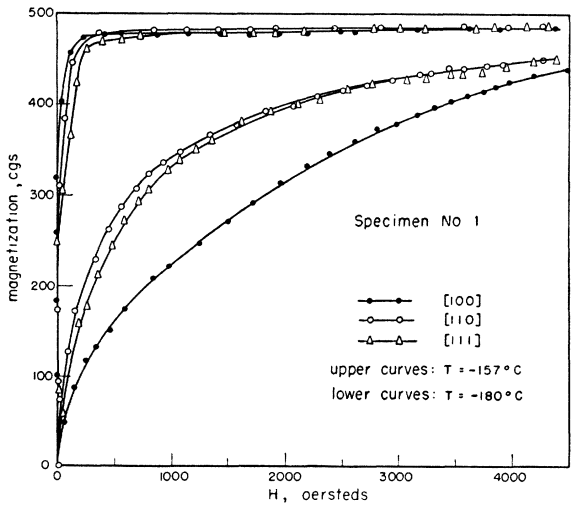

FIG. 13. Magnetization *vs.* H, natural magnetite single crystal. Upper curves for $T=-157$°C; lower curves for $T=-180$°C.

room temperature indicated that more than 95 percent of the technical saturation magnetization is the result of irreversible wall displacements; this observation is in accord with the well-known interpretation of the magnetization process in ferromagnetic single crystals.

(b) We have seen that the [100] direction is very easy to magnetize after cooling through the transition in a strong field parallel to [100] and careful demagnetization. After such treatment, the crystal showed during slow magnetization a Barkhausen noise over practically the whole extent of the [100] magnetization curve.

(c) When the crystal is cooled through the transition in a strong field parallel to [100] and subsequently carefully demagnetized, the domains might be expected to align themselves with their magnetization vectors parallel to that particular [100] axis along which the external field had been applied. If then a weak or medium field is applied parallel to this [100] edge and its direction made to oscillate slightly, the domains would rotate to follow the applied field and little or no Barkhausen noise should be observed. On the other hand, if the same demagnetized crystal, after cooling in a strong field parallel to [100], were exposed to a medium field, slowly changing in direction by a few degrees about [110] (that is, normal to the [100] direction in the (110) plane) the domain walls might be displaced irreversibly and in very great numbers since the sign of the [100] component of the bulk magnetization M tends to reverse. In this case one would expect to observe a strong Barkhausen noise. Such experiments were performed and this picture was verified. This interpretation might be the basis of an explanation of the "magnetic memory" first observed by Li.[2]

(d) A supposition that irreversible domain reorientations might occur upon simply cooling or warming the demagnetized crystal through the transition did not prove to be true. No Barkhausen noise was observed when the crystal was treated this way. However, when the specimen was warmed through the transition in a weak field, after having been cooled in a demagnetized condition, a very definite display of Barkhausen pips was seen on the oscilloscope screen during the passage through a temperature interval of approximately 5°C, beginning at about −166°C. This effect probably results from the decrease of the inner magnetic field, upon warming through the transition, which in turn results in an increase in the demagnetizing field.

(e) If a magnetic field is suddenly applied to a ferromagnetic crystal the magnetization will of course require some finite time to acquire the value corresponding to the applied field. A rough estimate of this time interval can be obtained by observing the duration of the Barkhausen noise immediately after the sudden application of a magnetic field. It was found that the time lag in the magnetization, by irreversible wall displacements, of magnetite at temperatures below the transition depends upon the magnetic treatment during cooling. After cooling in zero field, the lag is approximately one second for all three principal crystallographic directions. After cooling in a strong field parallel to [100], however, the lag corresponding to the same field is approximately 2 sec. for the field suddenly applied parallel to [110], but is less than $\frac{1}{4}$ sec. for the field applied parallel to either [100] or [111]. It would be of interest to investigate the low frequency complex permeability of magnetite at low temperatures and its dependence on magnetic treatment while cooling through the transition.

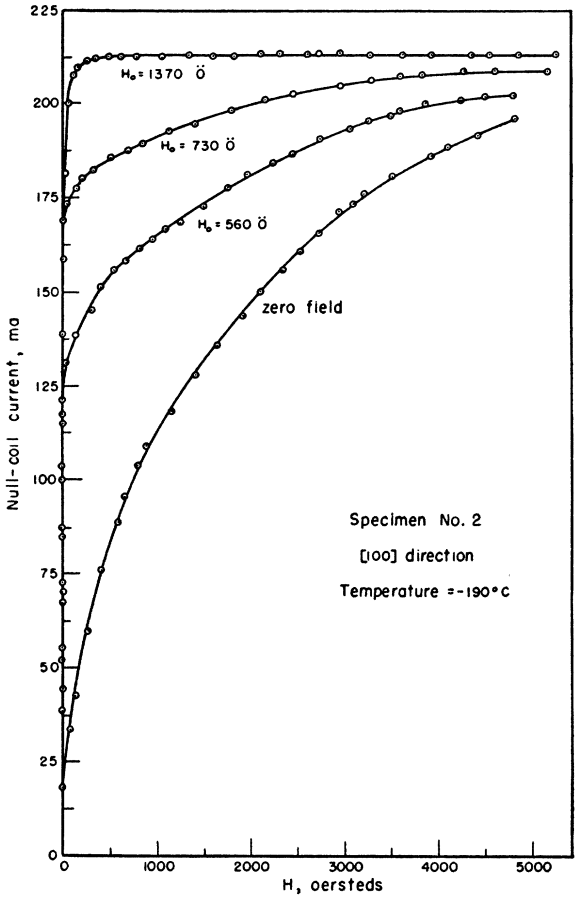

FIG. 14. Magnetization *vs.* H, natural magnetite single crystal. $T = -180$°C. Curves are for various values of external "annealing field" H_0 applied during passage through transition region.

Resistivity

In agreement with the results of Okamura[7] and of Verwey,[8] the single crystal specimens of magnetite showed a large and rapid increase in resistivity as the temperature was lowered through the transition region (Fig. 2). The resistivity at temperatures below the transition depends markedly upon crystallographic direction and the values of this parameter for the three principal directions are in the approximate ratios $(\rho)_{[111]}:(\rho)_{[100]}:(\rho)_{[110]} = 5:3:2$. Furthermore, although the magnitude of the rapid change in the transition interval is approximately the same for all three direc-

tions, the rate of change is seen to be greatest for [111] and smallest for [110]. According to Verwey and Haayman[18] the resistivity of stoichiometric magnetite changes approximately 100-fold in the transition region; specimen No. 1 (Fig. 2) gives an increase of about 30-fold. A chemical analysis of this sample indicated a ratio Fe_2O_3:FeO of 0.967, but this chemical analysis is probably somewhat meaningless because of the presence of a small amount of iron pyrite.

The polycrystalline specimen (No. 5), with a ratio Fe_2O_3:FeO=1.074, gave only a small change in resistivity at its transition, which occurred at a lower temperature than that of the natural crystals. These results are also in agreement with those of Verwey and Haayman.[18]

Influence of the Magnetic Field on Resistivity

In general, the fractional change in resistivity at temperatures below the transition upon application of a strong magnetic field is of the order of one percent, that is, somewhat larger than above the transition. As stated previously, for temperatures above the transition the application of a strong magnetic field parallel to either the [110] or [111] direction caused the [110] resistivity to *decrease ca.* 0.1 percent; for a field parallel to [100] the resistivity *increased* a few tenths of one percent. Below the transition the application of a strong magnetic field in any of the three principal crystallographic directions caused the [110] resistivity to *decrease* by a few percent.

Thermal Expansion

When warmed through its transition magnetite shows a rapid increase in dimensions in the transition region, as shown in Fig. 15. The [111] and [110] directions have positive expansion coefficients both above and below this region; [100] below the transition shows an anomalous contraction upon warming, and apparently undergoes a change in sign of the expansion coefficient at approximately −152°C, becoming normal or positive above this latter temperature. The coefficient of thermal expansion for the [111] direction within the transition region itself is very large, having approximately the value 150×10^{-6}/°C (see the slope of the [111] curve at −164°C in Fig. 15), or about ten times that of copper at ordinary temperatures. The rate of expansion of the crystal (No. 1) in the [110] direction appears from Fig. 15 to be even larger, but obviously the data within the transition region for this direction are too scanty to permit definite quantitative conclusions. On the other hand, the [100] curve indicates a less radical change of dimension parallel to this

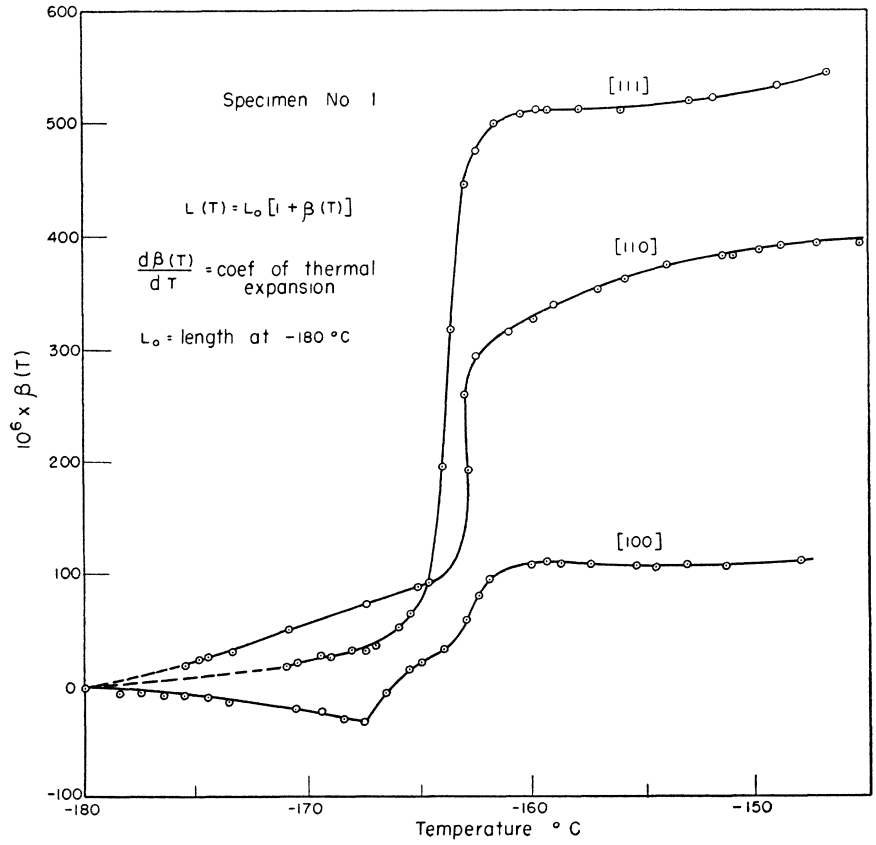

FIG. 15. Change of dimension *vs.* temperature, for the three principal crystallographic directions, natural magnetite single crystal. Coefficient of thermal expansion is slope of the curves shown.

[18] E. J. W. Verwey, Nature **144**, 327 (1939); E. J. W. Verwey and P. W. Haayman, Physica **8**, 979 (1941).

direction. The rapid changes in the [111] and [110] directions are seen to take place within a 1° or 2°C interval around −164°C, the same temperature at which the magnetization changes most rapidly (e.g., see Fig. 6).

Magnetostriction

The longitudinal saturation magnetostriction of specimen No. 1 is shown as a function of temperature in Fig. 4. The values were taken while the specimen was cooling; those at temperatures below the transition were found after cooling the crystal through the transition in a demagnetized state. As previously mentioned, the values given have not been corrected for the "form effect" which depends[19] on the demagnetization coefficient, the magnetization, and several unknown elasticity parameters. Nevertheless, the magnetostriction below the transition is seen to be negative and small in the [100] direction, positive and approximately five times larger parallel to [111] than [110].

5. CONCLUSIONS

We may summarize the principal electric and magnetic properties of magnetite single crystals as follows.

(1) The resistivity increases rapidly within the transition region upon cooling; the magnitude and the temperature of the "resistivity transition" depend on composition.

(2) The resistivity at temperatures below the transition is markedly influenced by the presence and orientation of a magnetic field applied during cooling through the transition.

(3) There is a minimum in the resistivity of magnetite at a temperature of approximately +100°C.

(4) The magnetic properties of magnetite below the transition temperature depend on its magnetic state while cooling through the transition region. The crystal is magnetically hard in all three principal crystallographic directions if cooled in a demagnetized state. Certain crystallographic directions can be made magnetically soft below the transition by a "magnetic annealing" process, that is, by cooling the crystal through the transition with a strong magnetic field applied in these directions.

(5) Barkhausen experiments seem to indicate that this magnetic annealling establishes preferred directions for domain alignment.

(6) In a narrow temperature region centered about 20°C above the low temperature transition, there is little or no Barkhausen activity.

(7) Upon warming through the transition region magnetite undergoes an abnormal expansion which is anisotropic.

(8) The longitudinal saturation magnetostriction at temperatures below the transition is strongly anisotropic, positive for the [111] and [110] directions, negative for the [100] direction. The magnetostriction in the [100] direction changes sign at −88°C, being negative below this temperature and positive above; the values for the [111] and [110] directions remain positive up to room temperature.

The behavior of the resistivity of magnetite in the vicinity of the low temperature transition has been attributed by Verwey and de Boer[8] to an ordering of the conduction electrons, and in a more recent paper Verwey, Haayman, and Romeijn[20] suggest a pattern of order. According to their model the tetragonal axis of of the "electron lattice" (at temperatures below the transition) can be established by the application of a magnetic field while the crystal is cooled through the transition; the tetragonal axis is that [100] axis of the high temperature crystal which makes the smallest angle with the applied magnetic field. This model of Verwey *et al.* has been used recently by Bickford[9] to explain the magnetic effects exhibited by magnetite in the low temperature transition region, and is discussed in the accompanying paper.[21] An alternative explanation is as follows. As the crystal is cooled through the transition, there occurs a rapid anisotropic contraction of the lattice which, together with the finite magnetostriction, gives rise to a peculiarly oriented stress pattern. This stress pattern, as might be expected from elementary ferromagnetic domain theory, could give rise to energetically preferred crystallographic directions parallel to which the domains would become aligned. One might expect that the nature of the low temperature stress pattern (and consequently of the domain pattern) would depend upon the orientation of the domains as the crystal cools through the transition region, and this orientation depends, of course, upon the magnitude and direction of the applied magnetic field. We have thus a tentative picture of the magnetic annealling process and of the magnetic memory of magnetite. It is clear, however, that a satisfactory detailed explanation of the low temperature transition of magnetite is not yet at hand.

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[20] Verwey, Haayman, and Romeijn, J. Chem. Phys. **15**, 181 (1947).

[21] L. R. Bickford, Jr., Phys. Rev. **78**, 449 (1950).