tition function of this paper and that of Onsager and Kaufman differ in order n^{-2} at most for all values of T.

Because of the smallness of the discrepancy between the two calculations for $n \gg 1$, a detailed study of these differences would seem of little value. The thermodynamic properties and investigations of order in the lattice have been studied in some detail by Onsager and Kaufman.

A two-dimensional system in which the jth point interacts with the $j+m-1$th in addition to the $j+1$th and $j+n$th can also be treated by the methods given here. In such a model each point interacts with six neighbors. The thermodynamic properties of such a system are now being studied.

The author is indebted to Professor A. Nordsieck for suggesting the problem and giving helpful advice. Thanks are also due to the AEC for a predoctoral fellowship grant.

PHYSICAL REVIEW VOLUME 78, NUMBER 4 MAY 15, 1950

Ferromagnetic Resonance Absorption in Magnetite Single Crystals*†

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(Received December 16, 1949)

The microwave resonance absorption technique, at both 1.25 and 3.3 cm wave-lengths, was used to study the ferromagnetic crystalline anisotropy characteristics and g-factor of magnetite Fe_3O_4. The experiments were performed on single crystals, both synthetic and natural, from room temperature to −195°C. Depending upon the temperature, magnetite single crystals were found to have magnetic anisotropy characteristics similar to those of single crystals of the three ferromagnetic elements. From room temperature to −143°C, they behave like nickel; between −143° and the transition which magnetite is known to undergo at *ca.* −160°C, like iron; and below the transition, somewhat like cobalt. At room temperature, values of $g=2.12$ and K_1 (first-order anisotropy constant) $= -1.10\times10^4$ joule/m^3 (-1.10×10^5 erg/cm^3) were obtained. It was found that below about −90°C the absolute value of K_1 decreases with decreasing temperature, reaching zero at *ca.* −143°C. Between −143° and the transition K_1 is positive and increases with decreasing temperature. The vanishing of crystalline anisotropy at −143°C accounts for the peak in initial permeability found near this temperature. The g-value was found to decrease gradually and monotonically with decreasing temperature. The behavior of magnetite in the resonance experiments below the transition seems to indicate that the magnetic symmetry is uniaxial in this temperature region. This conclusion is consistent with the findings of other investigators. Below the transition the magnetic axis is that [100] direction most nearly parallel to a strong magnetic field applied to the crystal as it is cooled through the transition. At temperatures not far below the transition it is possible to change the magnetic axis from one [100] direction to another by means of a strong magnetic field.

I. INTRODUCTION

THE investigation reported here was part of a program initiated at the Laboratory for Insulation Research to study the fundamental properties of magnetite, as the first step in a longer-range plan to investigate the properties of ferromagnetic semiconductors. Its object was to study magnetite by the microwave resonance technique from room temperature to liquid nitrogen temperature. As will be seen, the microwave resonance absorption experiment is capable of yielding information concerning ferromagnetic crystalline anisotropy. Specifically, it provides one with sufficient information to calculate the anisotropy constants appearing in the energy expression of a feromagnetic crystal. In addition, it gives a value of the spectroscopic splitting factor, or g-factor, for the material.

II. PROPERTIES OF MAGNETITE

It has been established by Verwey and co-workers[1-3] that magnetite possesses the cubic inverse spinel structure. The explanation proposed[1] for the high electrical conductivity of magnetite at room temperature (10^{-2} ohm cm) is that the distribution of ferrous and ferric ions among the octahedral cation lattice sites is random and fluctuating. That is, one can think of all 16 of these positions as being occupied by ferric ions, with 8 electrons continually changing their position from one site to another.

In a wide range around room temperature, the magnetic properties of magnetite are quite similar to those of nickel. Its saturation magnetization (4.6×10^5 amp/m or 460 c.g.s/cm^3) is about the same as for nickel, and, like nickel, its direction of easy magnetization is the body diagonal [111].

Millar[4] determined the specific heat as a function of temperature, and found an anomalous peak *ca.* 10° wide

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[*] This work was sponsored jointly by the ONR, the Army Signal Corps, and the Air Force under ONR Contract N5ori-07801.

[†] From a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at the Massachusetts Institute of Technology.

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[1] E. J. W. Verwey and J. H. de Boer, Rec. trav. chim. **55**, 531 (1936).

[2] E. J. W. Verwey and P. W. Haayman, Physica **8**, 979 (1941).

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

[4] R. W. Millar, J. Am. Chem. Soc. **51**, 215 (1929).

centered at *ca.* −160°C. Although the magnetization in weak fields drops sharply, the saturation magnetization does not change in cooling through this temperature region, in which magnetite undergoes a transition of some sort.[5] Li[6] showed by the results of torque measurements that the magnetic symmetry changes from cubic above the transition to some form of uniaxial below. He reported that if a single crystal had been cooled through the transition in a strong magnetic field, the direction along which this field had been applied became the direction of easy magnetization, or symmetry axis, below the transition. It is interesting to note that the torque curves made at −155°C (just above the transition) show that the crystal is most easily magnetized along the [100] direction. Li apparently failed to notice this fact.

Okamura[7] showed that the electrical resistivity increases abruptly upon cooling through the transition region. In studying this effect, Verwey and Haayman[2] made extensive measurements on a series of sintered samples of varying composition. They discovered that both the transition temperature and the magnitude of the discontinuity in resistivity varied uniformly with the ratio Fe_2O_3/FeO. From this behavior of the electrical resistivity Verwey concluded that the distribution of ferrous and ferric ions among the octahedral lattice sites became ordered at the transition. Such an ordering implies that electronic interchange becomes more difficult, and the resistivity, together with its activation energy, would be expected to increase. According to this picture the transition is an electronic order-disorder phenomen. Verwey[3] further pointed out that the ordered structure could no longer have cubic symmetry, and suggested that the most probable structure was a tetragonal** arrangement of the cations in their normal positions. Referring to Li's experiments[6] with cooling magnetite through the transition in a magnetic field, Verwey suggested that the tetragonal axis of his ordered structure would be the cube edge most nearly parallel to the applied magnetic field.

An anomalous peak in initial permeability found by Weiss and Renger[8] at −138°C and by Snoek[9] at −130°C seems to have been regarded as another direct manifestation of the transition, even though it occurs 20° or so higher than the transition.

III. THEORY OF THE RESONANCE EXPERIMENT

The resonance process can be pictured as a "coupling in" of a microwave field with the Larmor precession of electron spins. As a result, energy is absorbed from the microwave field by the spins. The Larmor precession frequency ν_L of free electron spins in an external magnetic field is given by the relation††

$$\nu_L = g(e/4\pi m)B, \tag{1}$$

where B is the applied magnetic induction, g the spectroscopic splitting factor, e the electron charge, and m the electron mass. For free electrons, $g=2.00$, and the Larmor frequency is 2.80 megacycles per 10^{-4} weber/m², or one gauss, of magnetic induction.

In a ferromagnetic material, the electrons participating in the resonance process are the *3d*-shell electrons which are responsible for the ferromagnetism. Because of the influence of demagnetizing effects and effects of ferromagnetic crystalline anisotropy, the magnetic induction governing the spin precession is not the externally applied induction.

As a consequence of ferromagnetic crystalline anisotropy, the energy of a crystal depends upon the relative orientation of the magnetization. For magnetite, as for other cubic ferromagnetic crystals, the anisotropy energy can be written

$$E = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2) + \cdots, \tag{2}$$

where K_1 and K_2 are the first- and second-order anisotropy constants, and α_1, α_2, α_3 are the direction cosines of the magnetization with respect to the crystallographic axes. For most purposes only the first term of this expression need be used, and the crystalline anisotropy is characterized by a single constant K_1.

Kittel[10] has derived equations governing the resonance condition for ferromagnetic materials by solving classically the equations of motion of the bulk magnetization. For an ellipsoid with principal axes parallel to the x, y, z co-ordinate axes, and demagnetizing factors designated by N_x, N_y, and N_z, the resonance condition is

$$\nu_0 = \frac{\gamma}{2\pi}\mu_0\{[H_z + (N_y + N_y^e - N_z)M_z] \times [H_z + (N_x + N_x^e - N_z)M_z]\}^{\frac{1}{2}}, \tag{3}$$

where ν_0 is the microwave frequency, γ is the gyromagnetic ratio equal to $ge/2m$, μ_0 is the magnetic permittivity of free space, H_z is the static magnetic field, and M_z is the z-component of the magnetization. The microwave magnetic field is along the x-direction.

The dependence of the resonance condition upon crystal orientation is contained in the factors N_x^e and N_y^e, which express the effect of crystalline anisotropy, and must be calculated for individual cases. The general expressions for N_x^e and N_y^e, in case the *xy*-plane (containing both the static and r-f magnetic field) is the (100) plane of a cubic crystal, have been given by Kittel. In corrected form[11] they are, considering only the first-order anisotropy term,

$$\mu_0 N_x^e = (2K_1/M_z^2)\cos 4\theta, \tag{4}$$

$$\mu_0 N_y^e = (\tfrac{3}{2} + \tfrac{1}{2}\cos 4\theta)K_1/M_z^2, \tag{5}$$

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[5] P. Weiss and R. Forrer, Ann. de physique [10] 12, 279 (1929).

[6] C. H. Li, Phys. Rev. 40, 1002 (1932).

[7] T. Okamura, Science Repts. Tôhoku Imp. Univ. [1] 21, 231 (1932).

** The proposed structure, which Verwey calls tetragonal, is actually orthorhombic, belonging to the Imm crystal class.

[8] P. Weiss and K. Renger, Archiv f. Elektrotechnik 2, 406 (1914).

[9] J. L. Snoek, *New Developments in Ferromagnetic Materials* (Elsevier Publishing Company, Inc., New York, 1947).

†† Rationalized MKS units are used in this presentation.

[10] C. Kittel, Phys. Rev. 73, 155 (1948).

[11] C. Kittel, Phys. Rev. 76, 743 (1949).

where θ is the angle between the manetization and a [100] crystal direction.

Corresponding expressions for the (110) plane of a cubic crystal are[12]

$$\mu_0 N_x{}^e = (2-\sin^2\theta - 3\sin^2 2\theta)K_1/M_z{}^2, \tag{6}$$

$$\mu_0 N_y{}^e = 2(1-2\sin^2\theta - \tfrac{3}{8}\sin^2 2\theta)K_1/M_z{}^2, \tag{7}$$

where θ is the angle between the static magnetization and a [100] crystal direction.

Equation (3), together with expressions for $N_x{}^e$ and $N_y{}^e$ in terms of crystalline anisotropy, specifies the resonance condition in ferromagnetic single crystals. It was assumed in the derivations that the crystal is magnetized to saturation and the static magnetization is along the z-direction. Accordingly, M_z can be replaced by M_s, the saturation magnetization. It has been verified[13] by resonance experiments on an iron single crystal that Eq. (3) correctly describes the effect of crystal anisotropy on the resonance process.

IV. EXPERIMENTAL PROCEDURE

The procedure employed in measuring the resonance absorption is essentially that described by Arnold and Kip.[14] The sample is mounted in a rectangular resonant cavity, driven in the TE_{102} mode; this cavity forms one arm of a wave guide magic T bridge. The opposite arm of the bridge is terminated by a matched load. In the other two arms are a klystron oscillator and a crystal detector. To a good approximation, the power reflected from the cavity on resonance, P_r, is related to the unloaded Q of the cavity Q_0 by

$$P_r/P_i = \left\{\frac{Q_e/Q_0 - 1}{Q_e/Q_0 + 1}\right\}^2, \tag{8}$$

where Q_e is the external Q of the cavity, which is unaffected by the magnetostatic field, and P_i is the power incident on the cavity, maintained constant during the experiment. The magnetic loss in the cavity is proportional to $1/Q_0$, since the sample is located in a region of maximum magnetic and minimum electric field. Therefore, by measuring P_r/P_i as H_z increases, and applying Eq. (8), one obtains the relative magnetic absorption as a function of H_z.

Two microwave frequencies were used in these experiments; one in the X band (*ca.* 9000 mc/sec.), and the other in the K band (*ca.* 24,000 mc/sec.). The same type of experimental arrangement was used at both frequencies. An electromagnet provided the static field, which was applied normal to the wide face of the wave guide, orthogonal to the r-f magnetic field.

Figure 1 shows a detailed view of the cavity. In order to allow a change in its orientation with respect to the magnetic field, the sample, in the form of a thin circular disk, is mounted on a rotatable cylinder which forms a section of the cavity end-wall. At the other end of the cylinder is a pointer to indicate the orientation of the crystal relative to a graduated arc on the cavity body. By means of a screw, the cylinder is forced into close contact with a tapered phosphor-bronze "iris" in the cavity end-wall, thus providing good electrical contact and a continuous flat end-wall. The disk, on one side of which a thin layer of copper has been electroplated, is soft-soldered to the cylinder.

The cavity is thermally insulated from the rest of the wave guide system in order that measurements can be carried out continuously from room temperature to liquid nitrogen temperature. This insulation is provided by a short section of wave guide made of Bakelite, on the inside walls of which has been evaporated a thin layer of silver. The cavity, located below the Bakelite thermal junction, is surrounded by a cylindrical copper container. A nichrome resistance wire heater, wound around a mica form, surrounds the cavity inside the copper container. The container is immersed in liquid nitrogen in a Dewar flask between the magnet poles. By controlling the heater current, the sample temperature can be maintained constant within ±0.5°C during the experiment, from *ca.* −100° to −195°C.

Resonance absorption experiments were made on both natural and synthetic magnetite crystals. To permit measurements to be made along all principal crystallographic directions, disks were cut in two different crystal planes, (100) and (110). Each experiment was made on at least two different samples.

The disk thickness is about 0.005 to 0.008 cm, and the diameter ranges from about 0.28 cm for X band to about 0.18 cm for K band. The ratio of diameter to thickness averages about 25, so the demagnetizing factors in the plane of the sample are small. Formulas given by Osborn[15] were used for the calculation of N_x, N_y, and N_z, with the disks considered as oblate spheroids.

The natural single crystals were from Chester, Vermont. Their Fe_2O_3/FeO ratio could not be determined by chemical analysis because of the presence of small inclusions of pyrite and other foreign materials. Comparison of the transition temperature (−163°C) for these materials with the transition temperatures of a series of samples of varying oxygen content published by Verwey and Haayman[2] indicates that the ratio Fe_2O_3/FeO must be about 1.05.

The synthetic crystals were grown by Smiltens and Fryklund[16] of this Laboratory. They were grown from a melt into the form of cylinders 0.6 cm in diameter and *ca.* 5 cm long. Since the orientation of the crystal axis with respect to the cylinder axis was random, it was necessary to orient the crystal, for cutting, by means of x-rays. The probable error in cutting the disks to the proper plane was ±1.0 degrees of arc. Smiltens has found

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[12] L. R. Bickford, Jr., Tech. Rept. XXIII, ONR contract N5ori-07801, Lab. Ins. Res., M.I.T., (October, 1949).

[13] A. F. Kip and R. D. Arnold, Phys. Rev. **75**, 1556 (1949).

[14] R. D. Arnold and A. F. Kip, Phys. Rev. **75**, 1199 (1949).

[15] J. A. Osborn, Phys. Rev. **67**, 351 (1945).

[16] J. Smiltens and D. H. Fryklund, Lab. Ins. Res., M.I.T. (to be published in the near future).

the synthetic crystals to be essentially stoichiometric with respect to the ratio of iron oxides (Fe_2O_3/FeO) $=0.998$). This is consistent with the fact that the transition temperature is about −155°C. Domenicali's[17] values of saturation magnetization, obtained from pendulum magnetometer measurements, were used for M_s.

V. RESULTS

The results obtained from the resonance experiments and subsequent discussion thereof will be presented in three sections, corresponding to different temperature ranges: (A) Above the transition (from room temperature to −153°C for synthetic crystals and to −160°C for natural crystals); (B) in the transition region (−154° to −157°C for synthetic, −163° to −168°C for natural crystals); and (C) below the transition (−158° to −195°C for synthetic crystals). No detailed experiments were made below the transition with natural crystals.

A. Above the Transition

Figure 2 shows a typical room temperature resonance at 1.25 cm wave-length. The line is very broad, as is the case for most ferromagnetic materials. A minimum of absorption can be seen at about 0.3 weber/m^2 (3000 gauss). This minimum is predicted by theory if a relaxation term is introduced into the equations of motion as has been shown by Yager.[18]

Equation (3), together with expressions for N_x^e and N_y^e in terms of crystal orientation and anisotropy, contains two unknowns: g and K_1. Therefore, results obtained from two different crystal orientations are sufficient to determine these quantities. In the case of samples cut from the (100) crystal plane, measurements made with the [100] and [110] directions parallel to the static field were used for this purpose. For (110) plane samples, [100] and [111] direction measurements were used.

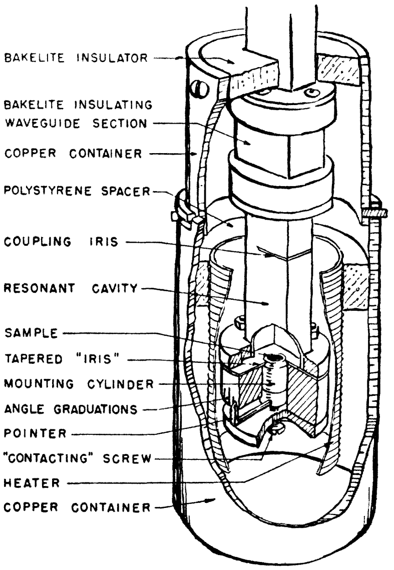

FIG. 1. Details of resonant cavity.

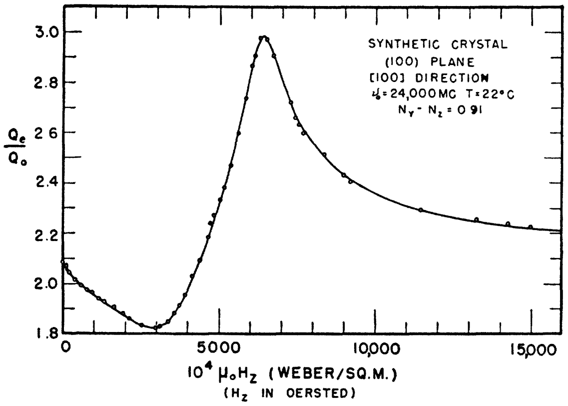

FIG. 2. Typical K-band absorption curve.

Table I gives average values of g and K_1 obtained at room temperature. The number of different samples used, including both (100) and (110) planes, is indicated.

An additional uncertainty is introduced because the values of M_s have a probable error of ±2 percent.

Figure 3 shows theoretical and experimental values of resonance induction (applied magnetic induction corresponding to the maximum of absorption) as a function of crystal orientation. It represents experiments made at 1.25 cm with a (100) plane sample of a synthetic crystal. The theoretical curve, given by the solid line, was obtained in the following manner. From experimental data for [100] and [110] parallel to the static field ($\theta=0$, 45°), g and K_1 were calculated. These values of g and K_1 were introduced into (4) and (5) to obtain $\mu_0 N_x^e$ and $\mu_0 N_y^e$ as a function of θ. Finally, these effective demagnetizing factors were used in Eq. (3) to obtain $\mu_0 H_z$ as a function of crystal orientation. The circles represent the experimentally observed values of $\mu_0 H_z$.

Figure 4 shows resonance induction *vs.* crystal orientation for the (110) plane of a synthetic crystal, at room temperature and 1.25 cm wave-length. The theoretical curve was calculated using Eqs. (6) and (7).

From Figs. 3 and 4 it can be seen that the crystal orientation with respect to the static field direction can be accurately obtained by the resonance experiment,

TABLE I. Room temperature values of g and K_1.

Wave-length	3.3 cm		1.25 cm
Type of crystal	natural	synthetic	synthetic
No. of samples	2	4	7
$10^{-4} K_1$ (joule/m^3) $10^{-5} K_1$ (erg/cm^3)	-1.15 ± 0.04	-1.10 ± 0.08	-1.12 ± 0.10
g	2.13 ± 0.04	2.12 ± 0.04	2.09 ± 0.04

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[17] C. A. Domenicali, Tech. Rept. XXV, ONR contract N5ori-07801, Lab. Ins. Res., M.I.T. (October, 1949); Phys. Rev. **78**, 458 (1950).

[18] W. A. Yager, Phys. Rev. **75**, 316 (1949).

once the crystal plane has been established. It is to be noted that the resonance induction is lowest in any crystal plane when the static field is near the direction of easy magnetization, and is highest near the direction of most difficult magnetization.

Essentially the same information as that given in Figs. 3 and 4 is plotted as a function of temperature in Fig. 5. Here the resonance induction at 3.3 cm is plotted for three directions in a (100) plane synthetic crystal from room temperature to the transition. Corresponding curves for (110) plane samples have a similar appearance. All the curves cross at -143°C, indicating that at this temperature the resonance field is independent of crystal orientation. In other words the crystal is magnetically isotropic at this temperature, the anisotropy constant K_1 vanishing. It is interesting to note that this "isotropy point," or temperature at which the anisotropy vanishes, is the same for both natural and synthetic crystals, whereas the transition temperature is different for the two types of crystal. Below $-143°$, the minimum resonance induction is along [100], indicating that this is the direction of easy magnetization.

Values of K_1 and g obtained from data such as that plotted in Fig. 5 are given in Table II. K_1 is plotted as a function of temperature in Fig. 6. It is seen that K_1 changes rapidly below -90°C, changing sign at -143°C. The g-factor decreases monotonically with temperature.

The absorption line width decreases with decreasing temperature, with a corresponding increase in intensity at the maximum. Very roughly, the line-width is halved and the maximum absorption intensity is doubled between room temperature and the transition.

B. In the Transition Region

In the original experiments at X band the surprising discovery was made that the resonance absorption dropped off rapidly and completely disappeared in the transition region without any significant change in resonance induction. This disappearance was especially disturbing since it was found that the line-width did not change during the process, thus ruling out the most likely explanation for the phenomenon, namely, that some frictional forces present during the transition caused the line to broaden to such an extent that it was no longer observable.

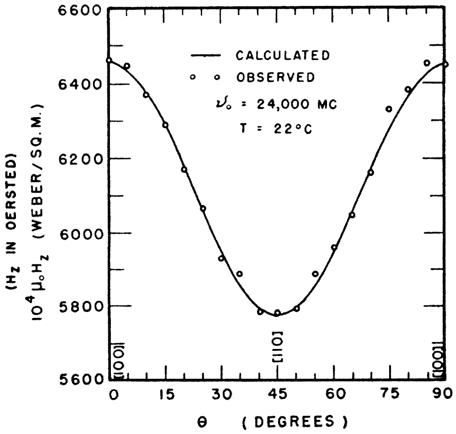

FIG. 3. Resonance induction *vs.* crystal orientation in (100) plane of synthetic crystal at K band. Solid line is theoretical curve for $g=2.07$; $K_1=-1.10\times10^4$ joule/m³; $M=4.72\times10^5$ amp./m; and $N_y-N_z=0.91$.

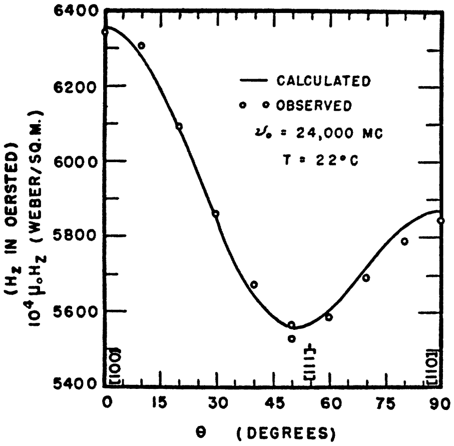

FIG. 4. Resonance induction *vs.* crystal orientation in (110) plane of synthetic crystal at K band. Solid line is theoretical curve for $g=2.10$; $K_1=-1.12\times10^4$ joule/m³; $M=4.72\times10^5$ amp./m; and $N_y-N_z=0.91$.

The initial experiments were performed with oblate ellipsoids having a thickness exceeding the skin depth of the microwave field. With these samples it was observed that the disappearance of resonant absorption was accompanied by a large increase in non-resonant absorption, that is, by absorption which was more or less independent of magnetic field strength. This was interpreted as being due to a large increase in eddy current skin depth in the sample as the electrical resistivity increased by a large factor in the transition region. Thus a greater volume of the sample was exposed to the microwave field, leading to an increased absorption not necessarily of magnetic origin. This effect was not observed in samples whose thickness was roughly equal to the microwave skin depth at room temperature.

When the resonance experiments were repeated at K band, it was found that as the absorption line disappeared in passing through the transition, an additional double peak appeared at low values of magnetic induction. Figure 7 shows this effect. There was no gradual shift in resonance induction. Above the transition (curve A) one line was present, while below the transition (curve C) the other was present. In the transition region (curve B), one line grew as the other diminished in such a manner that the total absorption remained more or less constant.

The duration of the transition region, as reflected in the resonance experiments, is *ca.* 5°C for the natural crystals and *ca.* 3°C for the synthetic crystals. This fact was determined by observing the absorption at

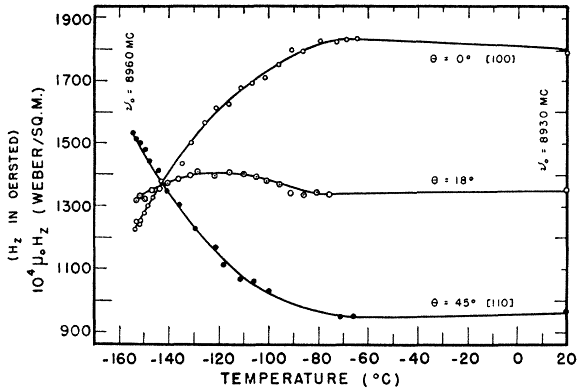

FIG. 5. Resonance induction *vs.* temperature in (100) plane of synthetic crystal at X band. $N_y - N_z = 0.935$.

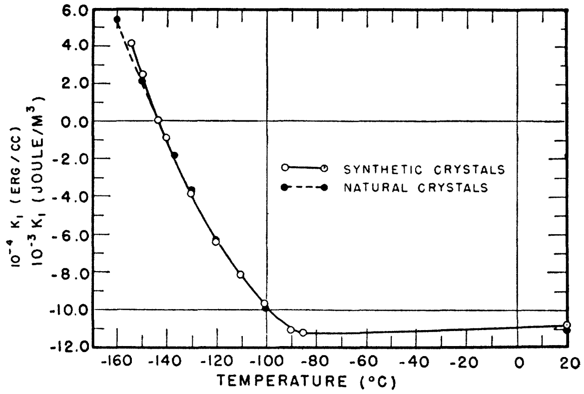

FIG. 6. Anisotropy constant K_1 as a function of temperature (from X-band data).

zero applied induction as the temperature slowly changed through the transition region. As can be seen from Fig. 7, at K band there is an increased absorption below the transition at zero static field.

C. Below the Transition

Experiments were made below the transition in both (100) and (110) planes along the principal crystallographic directions [100], [110], and [111]. The results obtained support the interpretation that the magnetic symmetry below the transition is tetragonal (or some other uniaxial symmetry in which the crystal is difficult to magnetize in the plane orthogonal to the axis), and that the magnetic axis can be selected from among the equivalent [100] directions of the original cubic crystal by cooling the magnetite through its transition in a strong magnetic field. In particular, it seems that the axis, or direction of easy magnetization, becomes the [100] direction most nearly parallel to the biasing magnetic field.*

For example, one of two different absorption curves can be obtained along the [100] direction of a (100) plane sample, depending upon magnetic treatment through the transition, as is shown in Fig. 8. Both curves of Fig. 8 were obtained with the measuring field along the same [100] direction of the crystal at −190°C. For curve A the biasing and measuring fields were parallel, and for curve B they were orthogonal.** In the former case the measuring field is along the direction of easy magnetization, and the resonance induction is low; whereas in the latter case the measuring field is along a [100] direction in the plane perpendicular to the magnetic axis, hence along a direction of difficult magnetization, and the resonance induction is high. Curve A results if the biasing field is applied within 45° of the [100] direction of the measuring field, and curve B, if the biasing field is applied within 45° of the perpendicular [100]. Similar results were obtained for other combinations of measuring and biasing field orientations, consistent with the picture of uniaxial magnetic symmetry below the transition.

Resonance absorption was observed at 3.3 cm wavelength for the three combinations of biasing and measuring field orientation which led to K band resonance at high induction; namely, along the [100] direction in (100) plane, and along both [100] and [110] directions in the (110) plane when the biasing field had established the magnetic axis orthogonal to these directions. Otherwise, resonance absorption was not detectable below the transition at X band.

In those cases where the resonance occurred at high applied induction at 1.25 cm, it was found that the position of the maximum changed quite rapidly with temperature. An even more interesting effect which depends upon the temperature is the following. At temperatures less than 20° or so below the transition, the application of a strong magnetic field (1.5 weber/m² or 15,000 gauss) appeared to change the direction of the magnetic axis. For example, suppose that in a (100) plane crystal the biasing field had established the mag-

TABLE II. g and K_1 as a function of temperature.

Temperature	10^{-3} M_s†	Synthetic crystal		Natural crystal	
		g	10^{-4} K_1*	g	10^{-4} K_1*
(°C)	(amp/m)		(joule/m³)		(joule/m³)
22	472	2.12	−1.08	2.17	−1.10
−100	491	2.08	−0.97	2.13	−0.98
−120	494	2.08	−0.64	2.12	−0.63
−130	496	2.07	−0.39	2.10	−0.37
−140	497	2.05	−0.08	2.08	−0.08
−143	497	2.05	0.00	2.08	0.00
−150	499	2.03	0.26	2.06	0.22
−153	499	2.03	0.42		
−160	500			2.06	0.54

* 10^{-5} K_1 (erg/cm³). † M_s (c.g.s.).

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* In order to simplify the discussion we shall denote by ***biasing field*** that magnetic field, applied to the crystal as it cools through the transition, which establishes the direction of the magnetic axis. In general, the biasing field is removed and the crystal demagnetized before it is rotated into position for making the absorption measurement. The field which is used in the resonance experiment we shall call the ***measuring field***.

** Experimentally this is easily accomplished by rotating the entire cavity about its axis for cooling through the transition, then rotating it back to the normal position for making the measurement. In this way the biasing field can be applied along any crystal direction *in the plane of the sample*.

netic axis along the same [100] direction as the measuring field. Suppose further that at −170°C the cavity was rotated 90° about its axis and an induction of 1.5 weber/m^2 applied for a short time along the perpendicular [100] direction. If the cavity were then returned to its normal position and the resonance experiment performed rapidly, the resulting absorption curve would be the same as one which would be obtained after the biasing field had been applied along the perpendicular [100]. In other words, the magnetic axis had been rotated by the strong magnetic field. It can be seen from this behavior that the measuring field itself acts as a biasing field at temperatures close to the transition, making it difficult to observe the resonance at these temperatures along crystal directions normal to the magnetic axis.

Figure 9 shows the biasing effect of a measuring field along the [100] direction of a (100) plane sample. Curve *A* was made after the biasing field had established the magnetic axis along the perpendicular [100] direction. Continued application of 1.5 weber/m^2 along the measuring field direction at temperatures below *ca.* −187°C did not change the appearance of this curve. Curves *B*, *C*, and *D* were made in succession as the crystal warmed from −186° to −180°C. It can be seen that the measuring field for each curve produced a change in the succeeding curve. At temperatures between −155° and −170°C a curve like curve *A* of Fig. 9 could be observed only if the experiment were performed rapidly, and could not be reproduced unless the crystal were again subjected to a perpendicular biasing field. The shifting of the axis takes place gradually, as though in intermediate curves (*B* and *C*) the axes were along different [100] directions in different domains, or regions of the crystal. Figure 9 also shows the dependence of resonance induction upon temperature for the high field peak.

For the very low field peak of curve *D* of Fig. 9, and for similar peaks occurring in other crystal orientations, it was found that the absorption as a function of applied induction increased discontinuously. This effect was strongly suggestive of the Barkhausen effect which can be observed during the magnetization of ferromagnetic materials.

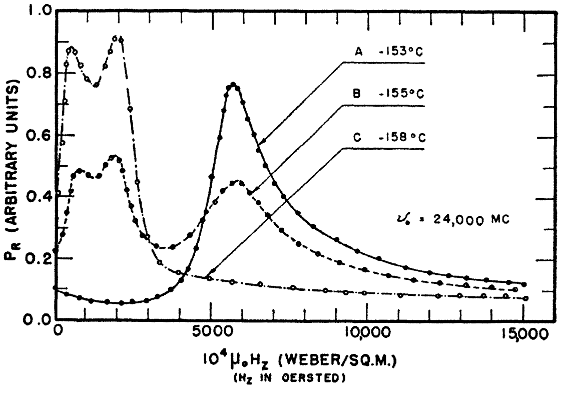

FIG. 7. Absorption curves in the transition region at *K* band. (100) plane; [100] direction; $N_y - N_z = 0.905$.

VI. DISCUSSION OF RESULTS

Above the Transition

The values of first-order anisotropy constant obtained from our resonance experiments are in agreement with the small amount of information about magnetite's crystalline anisotropy given in the literature. Our value of $K_1 = -1.10 \times 10^4$ joule/m^3 at room temperature agrees with -1.07×10^4 joule/m^3 calculated from the results of Quittner's torque experiments.[19] Similar calculations from Li's results[6] at −155°C give $K_1 = 0.43 \times 10^4$ joule/m^3, which should be compared with our value of 0.40×10^4 joule/m^3 at the same temperature.

The vanishing of crystalline anisotropy at −143°C explains the maximum in initial permeability which was reported by various observers[8, 9] to occur 20° or 30° above the transition. The two parameters of major importance in determining initial permeability are crystalline anisotropy and magnetostrictive energy. According to elementary domain theory,[20] the surface energy of domains varies as the square root of these quantities, and the initial permeability is large when this surface energy is small. The development of mixed ferrites of high initial permeability is accomplished by reducing both the crystalline anisotropy and the magnetostriction to very low values.[9] Domenicali's[17] curves of magnetostriction *vs.* temperature for a magnetite single crystal show no anomalous behavior in the vicinity of −145°C. Therefore the initial permeability should be affected by variations in the absolute magnitude of the crystalline anisotropy in such a way that it increases as this quantity decreases with temperature, and *vice versa*. Accordingly, a peak in initial permeability is to be expected near the temperature at which the crystalline anisotropy vanishes.

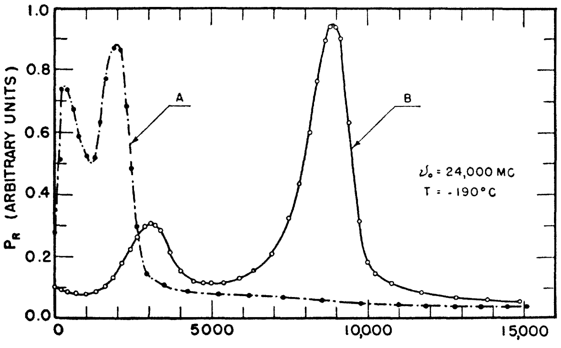

FIG. 8. Absorption curves below the transition in [100] direction of (100) plane, showing effect of magnetic prehistory. For curve *A*, biasing and measuring fields were parallel; for *B*, they were perpendicular. $N_y - N_z = 0.910$.

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[19] V. Quittner, Ann. d. Physik [4] **30**, 289 (1909).

[20] See, for example, R. Becker and W. Döring, *Ferromagnetismus* (Verlag. Julius Springer, Berlin, 1939).

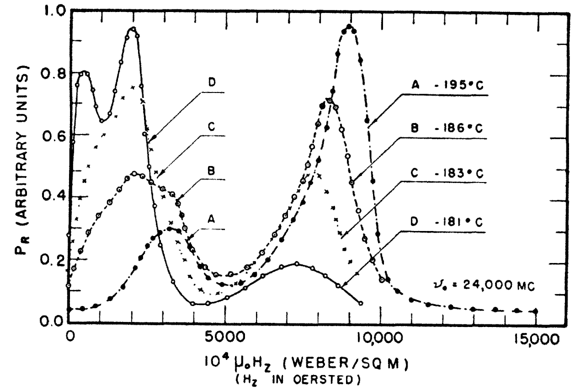

FIG. 9. Absorption curves below the transition, showing effect of temperature and strong magnetic field. (100) plane; [100] direction; $N_y - N_z = 0.910$.

Figure 10 shows the behavior of initial permeability κ_i as a function of temperature for the same natural single crystals of magnetite used in the resonance experiments. It can be seen that the maximum of this curve lies within a few degrees of the isotropy point, −143°C. Figure 10 also shows that κ_i drops off sharply in the transition region. The previous interpretation[9] of the initial permeability peak as a direct manifestation of the transition appears to be incorrect.

In the Transition Region

The complete disappearance of resonance absorption in the transition region in the initial *X* band experiments can be explained by the following considerations. Equation (3) shows that resonance absorption is to be expected for a particular microwave frequency even at zero static magnetic field. Using tentative values of anisotropy constants for magnetite below the transition (obtained from the resonance experiments) it was calculated that, at zero applied induction, resonance absorption would be observed at about 16,000 mc/sec. if the magnetization were along the direction of easy magnetization. In other words, the Larmor precession frequency of the electron spins even in the absence of an applied static magnetic field is 16,000 mc/sec., which exceeds the frequency of 3.3 cm microwaves. Addition of a static field increases the precession frequency. Consequently, resonance absorption below the transition is undetectable at 9000 mc/sec. unless the magnetization is along a direction of difficult magnetization, that is, in the plane perpendicular to the magnetic axis.

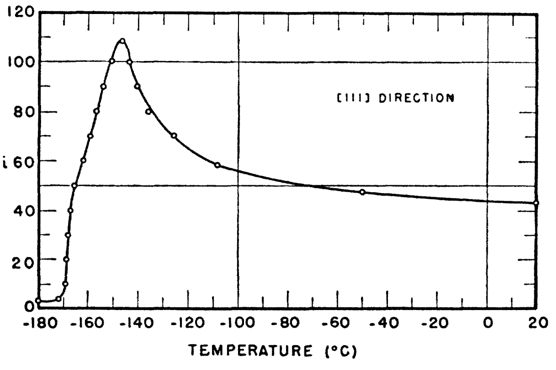

FIG. 10. Initial permeability of natural single crystal of magnetite.

The simultaneous existence in the transition region of absorption peaks characteristic of both cubic and uniaxial magnetic symmetry indicates that the transition of the entire crystal from one type of symmetry to the other does not occur simultaneously. On the other hand, the absence of a gradual shift in resonance induction with decreasing temperature shows that the transition does not produce a gradual distortion of magnetic symmetry, with the uniaxial anisotropy increasing continuously to its value below the transition. Rather, it is concluded that in a given small region of the crystal the symmetry changes discontinuously from cubic to uniaxial, and that as the temperature decreases through the transition region more and more of these small regions of the crystal change to the lower form of magnetic symmetry. The temperature range over which this process occurs is narrower for the synthetic crystals (3°C) than for the natural (5°C).

Below the Transition

From the results of some of our resonance experiments, anisotropy constants were calculated[12] for magnetite below the transition, assuming tetragonal magnetic symmetry. Predictions concerning resonance induction in other experiments, using these constants, were verified only qualitatively. It was not felt that sufficient experimental data were obtained in this investigation to warrant a distinction between the different types of uniaxial symmetry. For this purpose, it would be especially informative to investigate in detail the dependence of resonance induction upon orientation in the plane perpendicular to the magnetic axis. Such an investigation would require that the biasing magnetic field be applied normal to the plane of a (100) plane sample. This condition could not be fulfilled with our experimental arrangement.

Domenicali[17] has investigated the magnetization *vs.* applied magnetic field characteristics for magnetite after it had been subjected to different kinds of magnetic treatment while cooling through the transition. The area between magnetization curves for two different directions of a single crystal represents the difference in energy of magnetization for the two directions, and can be expressed in terms of the crystalline anisotropy constants. Using the tentative values of anisotropy constants for magnetite below the transition calculated from our experiments, we made predictions concerning areas between magnetization curves for different crystal directions after various orientations of biasing field. The agreement between our predicted areas and those measured from Domenicali's curves is within about 30 percent. Domenicali has offered an alternative interpretation of magnetic effects at the transition in terms of a freezing-in of the domain pattern by internal stresses as the crystal cools through the transition.

We can only speculate as to the cause of the change in magnetic symmetry at the transition. Verwey's picture[1–3] of an ordering of the electronic structure at the transition, leading to a tetragonal (or orthorhombic) lattice symmetry, seems to give a reasonable explanation for the observed electrical effects. Domenicali's[17] results of thermal expansion measurements with magnetite single crystals would seem to indicate that the crystal structure is no longer cubic below the transition, although the change in structure is so small that it cannot be detected readily by x-rays. It is probable that the magnetic symmetry follows the crystal symmetry. In determining the magnetic axis, the biasing magnetic field may act through magnetostrictive effects which lead to a condition of minimum energy with the axis along the [100] direction most nearly parallel to the biasing field.

The ability of a strong magnetic field to change the direction of the magnetic axis below the transition calls to mind an analogous effect in ferroelectric barium titanate reported by Matthias and von Hippel.[21] Above its Curie point (120°C) barium titanate is cubic; below it, tetragonal, the tetragonality increasing with decreasing temperature. One of the [100] crystal directions is the tetragonal axis. If an electric field is applied to the crystal, the axis becomes the [100] direction most nearly parallel to the field. Thus it is possible to establish the direction of the axis by cooling the crystal through its Curie point in an electric field, or to change the direction of the axis below the Curie point by the application of a field.

Finally, a few remarks will be made concerning the double resonance peaks observed below the transition. Double peaks were observed in X band experiments with iron single crystals by Kip and Arnold,[13] and also in our early experiments with magnetite above the transition. The explanation offered by Kip and Arnold is that in weak fields the magnetization is not completely aligned by the field. When this fact was accounted for in the resonance equation, it was found that a second and very broad peak was predicted at low field strengths. According to this explanation no double peak would be expected along the direction of easy magnetization. Experimentally, only single peaks were observed at K band, where the resonance induction was much larger than that required to saturate the material magnetically.

Figure 8 shows two very well-defined peaks in a resonance curve obtained below the transition with the measuring field along the magnetic axis, or direction of easy magnetization. In some cases, the low field peak was sharper and stronger than the high field peak. Both of these observations are difficult to explain on the basis of incomplete magnetic saturation.

A critical experiment would be to repeat the measurements at a higher microwave frequency ($K/2$ band), where the resonance would occur at higher values of applied induction. If the double peaks should still appear in these experiments, an explanation for them would have to be found on grounds other than lack of magnetic saturation.

The author is grateful to Professor A. von Hippel for making the facilities of the Laboratory for Insulation Research available to him, and also for continued encouragement and helpful advice during the course of this work. Thanks are also due many members of the Laboratory for their cooperation, in particular C. A. Domenicali and S. Lawrence. In addition, the author wishes to thank Dr. C. Kittel, of the Bell Telephone Laboratories, for some illuminating discussions of his results.

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[21] B. Matthias and A. von Hippel, Phys. Rev. **73**, 1378 (1948).