Magnetic Properties of Magnetite Crystals at Low Temperature

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(Received April 11, 1932)

Thin circular disks cut parallel to the 100, 110 and 111 planes of magnetite crystals were prepared. The components of the intensity of magnetization normal and parallel to the magnetic field at temperatures down to that of liquid air were investigated by the method of torsion. It was found that the magnetic properties of the crystal abruptly changed at about $-160°C$. This temperature corresponds exactly to the temperature at which the specific heat of magnetite increases suddenly to a maximum as was found by Millar two years ago. X-ray photographs taken at room temperature and at liquid air temperature show no difference indicating that there is no change in the distribution of the points of diffraction. The intensity of the two patterns requires further measurements. Weiss' theory of the molecular field cannot be applied as $-160°C$ is not a Curie point.

Introduction

In his investigation on the heat capacities of ferrous oxides at low temperatures Russell W. Millar[1] found that the specific heat of magnetite (Fe_3O_4) rises suddenly to a maximum at 114.15°K. He assumed that this maximum is due to a change in the magnetic properties.

P. Weiss and P. N. Beck[2] have measured the specific heat of iron, nickel, and magnetite at various temperatures, and found an increase of specific heat of these substances near their critical points. Weiss explained this change as due to the change of magnetic energy. He showed that the magnetic energy per cubic centimeter of a ferromagnetic substance is:

$$E = -\tfrac{1}{2}H_m I = -\tfrac{1}{2}NI^2$$

where I is the magnetic moment per unit volume, H_m the molecular field and N is a constant depending on the substance. The negative sign indicates that it is necessary to supply heat to demagnetize the substance. Therefore

$$\frac{dE}{dT} = -\frac{N}{2}\frac{d(I^2)}{dT}$$

where T is the temperature. The increase of specific heat is

$$C_m = \frac{1}{\rho J}\frac{dE}{dT} = -\frac{1}{2}\frac{N}{\rho J}\frac{d(I^2)}{dT}$$

where ρ is the density of the substance and J is the mechanical equivalent of heat. With this formula Weiss found a very good agreement between the theory and the experiment.

[1] Russell W. Millar, Jour. Amer. Chem. Soc. **51**, 215 (1929).
[2] Weiss and Beck, Journ. de Physique [4] **7**, 249 (1908).

Therefore it is of interest to investigate the magnetic properties of magnetite at low temperatures to see whether there are any changes at the point where the specific heat increases and to see whether these changes can be explained by Weiss' theory. It is the purpose of the present work to investigate this point. The magnetic properties of magnetite crystals at ordinary temperatures have already been investigated by V. Quittner,[3] so the present investigation is limited to low temperatures and especially to temperatures from $-150°C$ to $-170C$.

Method of Investigation

Magnetite crystals from West Lessetsk, Ural, with an octahedral habit, were obtained from Ward's Natural Science Establishment at Rochester, New York. They were found to have a great homogeneity. Three circular disks parallel to the planes 100, 110 and 111 were carefully prepared by grinding a crystal (one for each disk) on the grinding machine to suitable dimensions for the investigation. The dimensions of the disks are as shown in Table I.

Table I.

Plane of disk	Diameter in cm	Thickness in cm	Volume in cc
100	0.95	0.096	0.0674
110	1.08	0.079	0.0723
111	0.83	0.083	0.0449

The volumes of the disks were calculated from their weight and density the latter having been determined from a large crystal.

The investigation was divided into two parts: (1) The determination of the component of intensity of magnetization normal to the magnetic field at temperatures between $-150°C$ and $-170°C$; (2) The determination of the parallel component between the same temperatures.

The methods used in determining these components are essentially the same as those used by P. Weiss[4] in his experiments on pyrrhotite crystals. The crystal disk is suspended between the pole pieces of an electromagnet and the couple exerted on the crystal by the magnetic field is determined by balancing it against the couple of the suspending wire.

In measuring the normal component, the crystal disk is suspended with its plane horizontal in a horizontal magnetic field. Suppose the intensity of magnetization I makes an angle ϕ with field H, then the couple exerted by the field on the crystal of volume V is

$$N = VHI \sin \phi .$$

Now $I \sin \phi$ is the component of intensity of magnetization perpendicular to the field H. Therefore

$$I_{\perp} = \frac{N}{VH} = \frac{k\theta}{VH}$$

[3] V. Quittner, Arch. des Sci. [4] **26**, 358, 455, 585 (1908); also Ann. d. Physik [4] **30**, 289 (1909).

[4] P. Weiss, Jour. de Physique [4] **4**, 469 (1905).

where k is the torsion constant of the suspension and θ is the angle of deflection of the crystal. Thus the normal component, $I_{\perp}$, for different directions in the crystal in a constant field can be measured by rotating the crystal in the magnetic field.

The parallel component of magnetization is determined by suspending the disk in a vertical position in a horizontal magnetic field with its plane making a small angle α with the direction of the field. Then, under the action of the field, the disk is rotated about a vertical axis through a small angle ρ. Let R (Fig. 1) be the disk and H the direction of the field. Then the torque exerted on the disk by the field is

$$N = I \cos \phi HV \sin (\alpha - \rho)$$
$$= I_{\parallel} HV \sin (\alpha - \rho)$$
$$I_{\parallel} = N/[HV \sin (\alpha - \rho)] = K\rho/[HV \sin (\alpha - \rho)].$$

By orientating the disk in the field the parallel component in different directions in the crystal can be obtained.

The apparatus employed was essentially a rotating electromagnet with a system of suspension similar to that used by Weiss.

The thermocouple, used to measure the temperature at which the crystal is maintained, is made with No. 40 copper and constantan wires. One of its junctions is maintained in melting ice and the other is placed close to the disk. The thermocouple was calibrated both before and after the experiment against the fixed freezing points of the following substances and liquid air temperature, determined by means of an oxygen vapor pressure thermometer:

Mercury	−39°C	Toluene	−95.1°C
Chlorobenzene	−45.2°C	Carbon disulfide	−111.6°C
Ethyl acetate	−83.6°C	Liquid air	−190.7°C

The cooling system consists of a Dewar flask and a copper tube. The copper tube has an inner diameter of about 3 cm and a total length of about 18 cm. The tube is capable of adjustment to different heights thus exposing part of its surface to the air outside of the Dewar flask. The temperature inside the tube depends on the area which is exposed to the air and on the depth to which the tube is immersed in the liquid air. By experimenting and adjusting the height of the copper tube any desired temperature can be maintained constant inside providing liquid air is added to the flask from time to time.

Procedure

After the magnetic field and the thermocouple have been calibrated and the torsion constant of the suspension determined, the magnetite crystal is set in position. The suspension is adjusted until the crystal is in the middle of the field and the zero position in the absence of the magnetic field is noted.

In measuring the component of magnetization normal to the field the crystal disk is put in the horizontal position. A field is applied to the disk and the magnet is rotated around its axis several times before any measurement is taken in order that the crystal may be uniformly magnetized. After the crystal is magnetized the magnet is set in a definite position and the deflection of the disk noted. The magnet is then turned through 10 degrees and the deflection again noted. This process is continued until the magnet has been rotated 360 degrees. The direction of rotation of the magnet is then

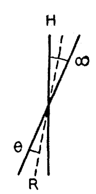

Fig. 1.

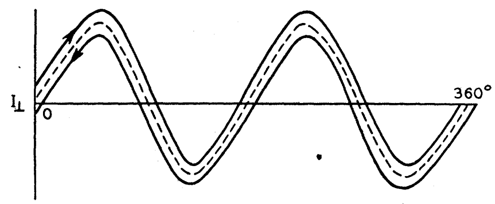

Fig. 2.

reversed and readings taken every 10 degrees until it reaches its initial position.

The normal component of magnetization is calculated from the equation $I_{\perp} = K\theta/VH$. Plotting the results with the angles of rotation of the magnetic field as abscissas and $I_{\perp}$ as ordinates, two curves are obtained as shown in Fig. 2. One of the curves is obtained when the field is rotated from 0° to

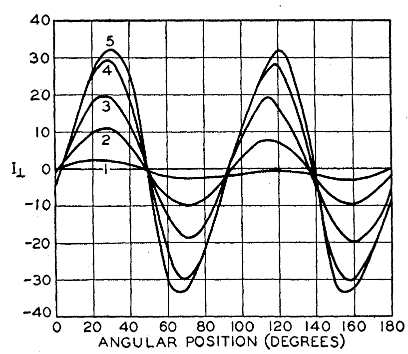

Fig. 3. Normal component of intensity of magnetization in plane (100). At temperature −155°C. 1, H=282.75 gauss; 2, H=435.00 gauus; 3, H=489.37 gauss; 4, H=598.12 gauss; 5, H=696.00.

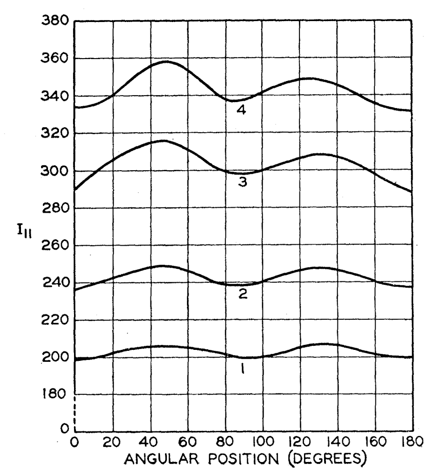

Fig. 4. Parallel component of intensity of magnetization in plane (100). At temperature −155°C. 1, H=282.75 gauss; 2, H=369.75 gauss; 3, H=435.00 gauss; 4, H=489.37 gauss.

360° and the other is obtained when it rotated back from 360° to 0°. The area between the two curves increases with increase in the hysteresis loss due to rotation.

By taking the average of the ordinates of these two curves as the ordinate of the third, we obtain a curve of I corrected for hysteresis. That this is true has been proved experimentally by V. Quittner.[5] All the curves of the normal components of magnetization which are shown in the next section are plotted this way.

In determining the parallel component of magnetization the crystal is set in the vertical position and the zero position noted in the absence of the magnetic field. The field is applied and before taking any reading the crystal is rotated several times about a horizontal axis. The direction of the magnetic field is then adjusted by rotating the magnet until there is no deflection of the crystal. In this position the direction of the field is in the same plane as the direction of the intensity of magnetization. The magnet is then turned to the right or left through an angle of 5 degrees and the deflection of the crystal noted.

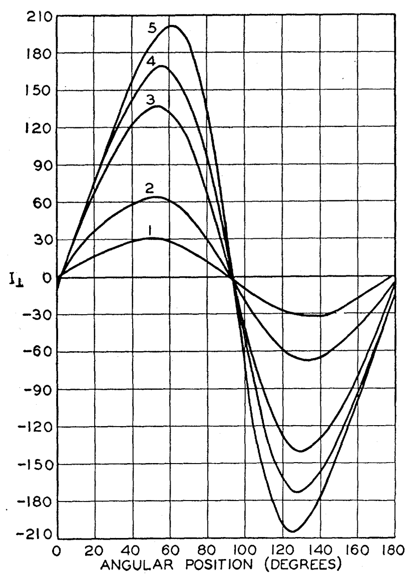

Fig. 5. Normal component of intensity of magnetization in plane (100). At temperature $-166°$C. 1, $H=184.87$ gauss; 2, $H=282.75$ gauss; 3, $H=435.00$ gauss; 4, $H=489.37$ gauss; 5, $H=598.12$ gauss.

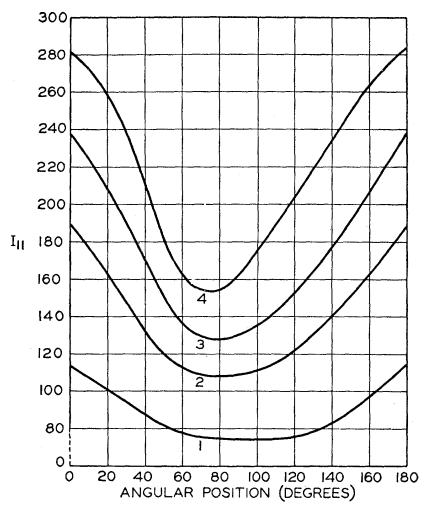

Fig. 6. The parallel component of magnetization in plane (100). At temperature $-166°$C. 1, $H=184.87$ gauss; 2, $H=282.75$ gauss; 3, $H=369.75$ gauss; 4, $H=489.37$ gauss.

The field is removed, the crystal rotated 10 degrees about the normal passing through its center, and the measurements repeated in this position. By this process the disk is rotated in steps of 10 degrees until 360° is reached. $I_\parallel$ is then calculated from the equation

$$I_\parallel = K\rho/[VH \sin(\alpha - \rho)].$$

The Experimental Results

Figs. 3 and 4 show respectively the variation of the normal and parallel components of magnetization in the disk parallel to the 100 plane at tem-

[5] V. Quittner, Arch. des Sci., [4] **26,** 456 (1908).

perature $-155°C$. Both of these components have two maxima and two minima in 180 degrees. The two maxima and also the minima differ a little from each other. The parallel component has maximum and minimum values when the field is in the directions of the tetragonal and diagonal axes respectively, while the normal component has its maximum and minimum values when the field has directions between these axes. The amplitude of these curves increases as the field strength increases. It would probably reach a maximum and then decrease to zero when the field is increased to a point where the crystal is saturated.

Figs. 5 and 6 also show these two components of magnetization in the 100 plane, but at a temperature $-166°C$. It can be seen that both of these components have now a period of 180° and the amplitude of the curves become far greater than before.

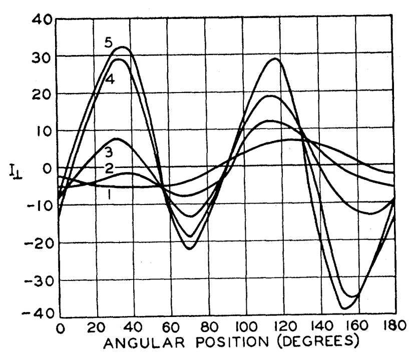

Fig. 7. Normal component of intensity of magnetization in plane (110). At temperature $-155°C$. 1, $H=184.87$ gauss; 2, $H=282.75$ gauss; 3, $H=369.75$ gauss; 4, $H=489.37$ gauss; 5, $H=598.12$ gauss.

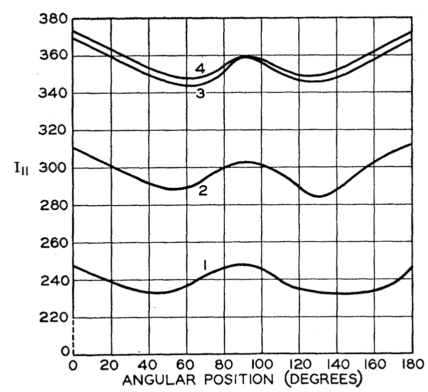

Fig. 8. The parallel component of intensity of magnetization in plane (110). At temperature $-155°C$. 1, $H=282.75$ gauss; 2, $H=369.75$ gauss; 3, $H=489.37$ gauss; 4, $H=598.12$ gauss.

Figs. 7 and 8 show these two components in the disk cut parallel to the 110 plane and at temperature $-155°C$. At the field of 184.9 gauss the curve for the normal component has only one maximum and minimum in 180 degrees and the amplitude is rather small. As the field increases the number of maxima and minima increases to two instead of one. And the two maxima and also the minima are different from each other. Both the curves of the two components show apparently a period of 180 degrees. For the parallel component the maxima and the minima are in the directions of the tetragonal, digonal and trigonal axes, while the normal component has its maximum and minimum between these three axes.

Figs. 9 and 10 show these two components in the same 110 plane, but at the temperature $-166°C$. The curves show again a great change as in the 100 plane and the form of the curves of the two components are somewhat similar to those obtained in 100 plane at the same temperature, $-166°C$.

Figs. 11 and 12 show the two components in the 111 plane at temperature

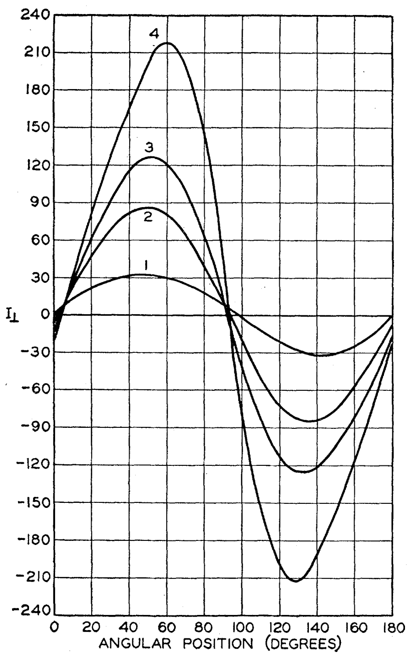

Fig. 9. Normal component of intensity of magnetization in plane (100). At temperature −166°C. 1, H=184.87 gauss; 2, H=282.75 gauss; 3, H=369.75 gauss; 4, H=489.37 gauss.

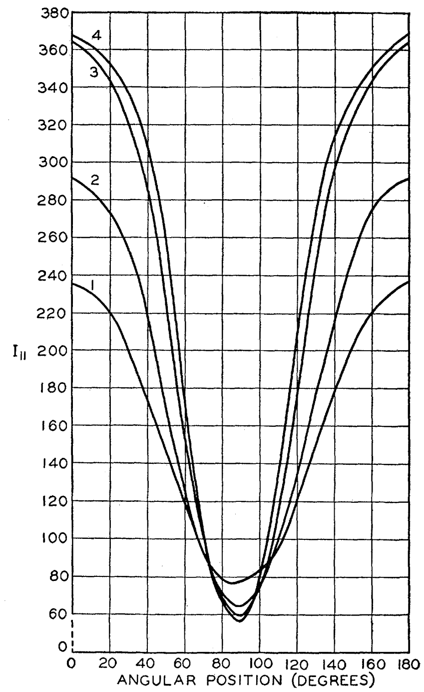

Fig. 10. Parallel component of magnetization in plane (110). At temperature −166°C. 1, H=282.75 gauss; 2, H=369.75 gauss; 3, H=489.37 gauss; 4, H=598.12 gauss.

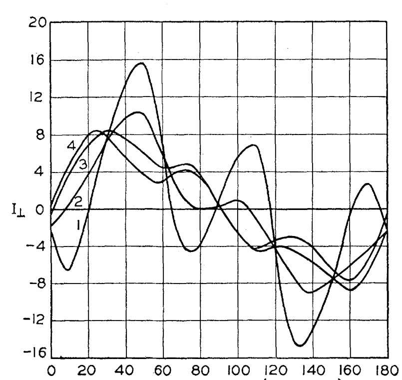

Fig. 11. Normal component of intensity of magnetization in plane (111). At temperature (111). At temperature −155°C. 1, H=435.00 gauss; 2, H=543.75 gauss; 3, H=435.00 gauss; 4, 783.00 gauss.

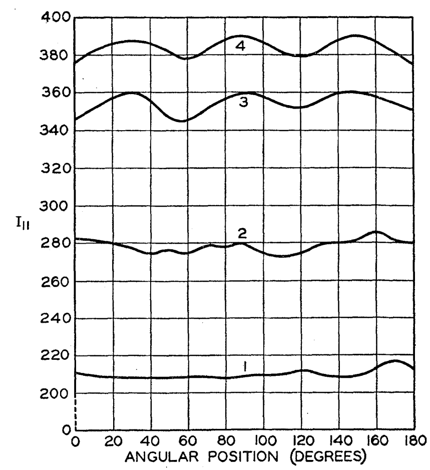

Fig. 12. The parallel component of intensity of magnetization in plane (111) At temperature −155°C. 1, H=184.87 gauss; 2, H=282.75 gauss; 3, H=435.00 gauss; 4, H=598.12 gauss.

$-155°C$. The forms of the curves of these two components vary as the field varies. For the normal component it has three maxima and minima in 180 degrees with amplitudes all different. As the field changes, the maximum and minimum points shift and show a phenomenon which is very complicated. For the parallel components there are three maxima and minima in 180° when the field is large but the curves become irregular when the field is small.

Figs. 13 and 14 show the two components in the same plane, 111, but at temperature $-166°C$. The curves again are greatly changed and they have forms somewhat similar to that obtained in 100 and 110 planes. Instead of three maxima and three minima in 180 degrees as at temperature $-155°C$ there is now only one maximum and one minimum.

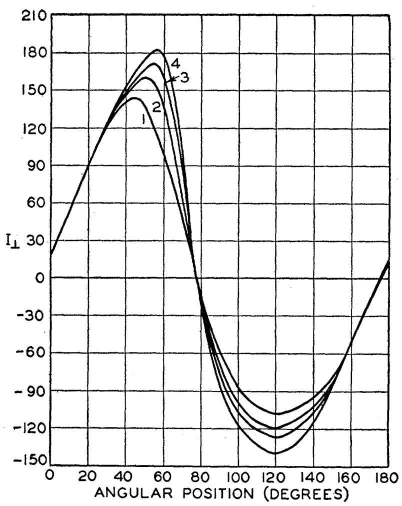

Fig. 13. Normal component of intensity of magnetization in plane (111). At temperature $-166°C$. 1, $H=435$ gauss; 2, $H=543.75$ gauss; 3, $H=619.87$ gauss; 4, $H=783.00$.

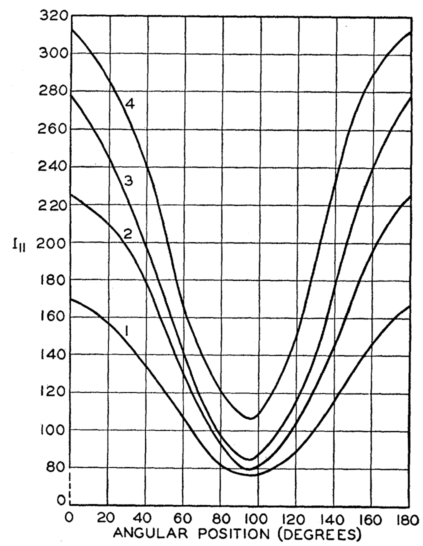

Fig. 14. Parallel component of intensity of magnetization in plane (111). At temperature $-166°C$. 1, $H=184.87$ gauss; 2, $H=282.75$ gauss; 3, $H=435.00$ gauss; 4, $H=696.00$ gauss.

From the above data we can see plainly that there is a great change in magnetic properties when the magnetite crystal is cooled through the range of temperature from $-155°C$ to $-166°C$.

In order to show definitely at what temperature this change takes place the normal component in a definite direction in the disk is determined by applying a given field and, at the same time, varying the temperature. Fig. 15 shows the variation of the normal component in a certain direction in the 111 plane when the applied field is 696 gauss. The temperatures are plotted as abscissas and the deflections, which are proportional to $I_\perp$, are plotted as ordinates. The curve shows clearly that the change takes place at about $-160°C$. In the other directions in the disk the variation is not so large but one can always find such a variation at about −160°C. Thus we see that a change takes place at that temperature which is just the temperature at

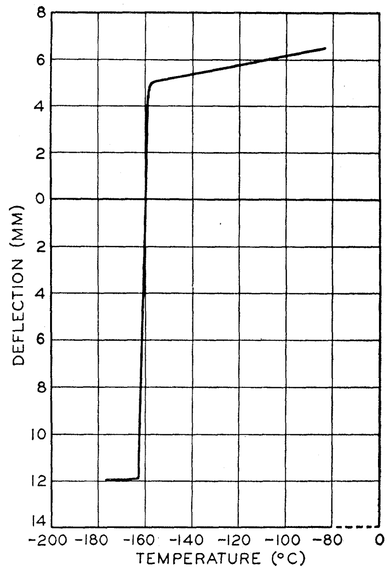

Fig. 15.

which the specific heat of magnetite increases to a maximum as has been mentioned in the introduction.

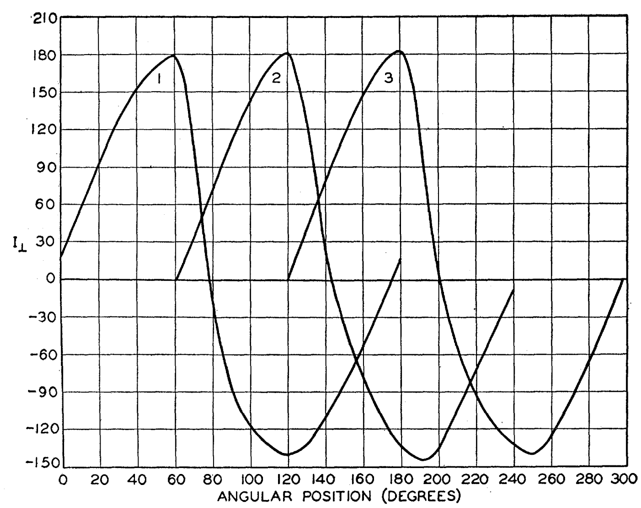

Fig. 16.

Furthermore the position of the maximum and the minimum of the curves of the two components obtained at temperatures lower than −160°C depends upon the direction in which the magnetic field is applied during the process of cooling. Fig. 16 shows this effect for $I_{\perp}$. Curve 1 is obtained after the disk 111 is cooled through the temperature $-160°C$ with the direction of the field applied along the direction marked zero. Curve 2 is obtained when the field is applied in a direction 60 degrees from the previous position during the process of cooling and curve 3 is obtained similarly when the field is applied in a position 120 degrees from the first position.

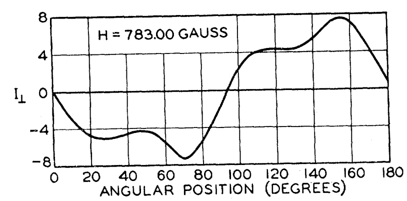

Fig. 17. Normal component of magnetization in 111 plane at temperature $-166°C$. When the crystal is cooled in the absence of the field.

This phenomenon of the shifting of the position of maxima and minima of the normal component was found in all three disks. A similar shifting was also found for the parallel component. It seems as if we can locate the position of maxima and minima of the curves of these two components in any position that we please, depending on the position of the crystal in the field when it is cooling.

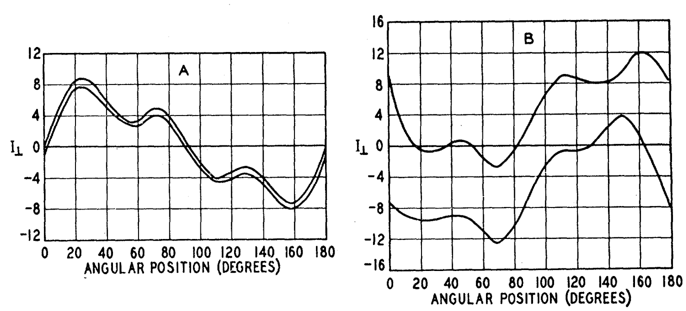

Fig. 18. *A*, Rotating hysteresis-loop in 111 plane at temperature $-155°C$. *B*, Rotating hysteresis-loop in 111 plane at temperature $-166°C$ after the crystal is cooled in the absence of the field.

On the other hand, if the crystal was cooled through the range of temperature from $-155°C$ to $-166°C$ in the absence of the magnetic field, then the change will be different. Fig. 17 shows the normal component of magnetization in 111 plane taken at temperature $-166°C$ after it has been cooled to that temperature in the absence of an external field. This curve still has three maxima and three minima in 180 degrees, but they are shifted 90° as we see if we compare it with curve 4, Fig. 11. The hysteresis of rotation in this case is about ten times as large as compared with that which was obtained at $-155°C$ (Fig. 18).

Discussion of Results

From previous investigations made on magnetic crystals at room temperatures, V. Quittner has shown that magnetite, so far as its magnetic properties are concerned, possesses the symmetry of the orthorhombic system. According to that symmetry, the normal component of the intensity of magnetization in the 111 plane should have, between 0° and 180°, three different waves with the possibility that one or even two of these waves may disappear completely. This is what has been found in the present investigation at the temperature −155°C. The curves obtained at −155°C in all the disks have similar forms to those found by Quittner at room temperature. Thus we can conclude that the magnetic symmetry of the magnetite has not been changed when cooled down to the temperature −155°C. But the forms of the curves are completely changed when the crystal is cooled in the magnetic field below −160°C. Therefore, the magnetic symmetry of magnetite must be changed from the magnetic point of view at least.

Weiss' theory of the Curie point cannot be applied to the phenomenon discovered because −160° is not a curie point. We might of course consider a double change, a sudden loss of magnetism and an increase of magnetism is the neighborhood of −160°C. We would have to introduce a second constant of another internal magnetic field N_3 which would be equal to 33800 approximately. But this attempt is unsatisfactory and the theory of the phenomenon requires further experiments.

X-ray photographs both at room temperature and at liquid temperature were taken. The distribution of the points in both pictures is the same, but the question of the intensities remains open.

Acknowledgment

The writer wishes to express his sincere appreciation to Professor J. Kunz for his suggestion of the problem and to him and to Professor E. H. Williams for their constant encouragement and suggestions during the investigation. Thanks are also due to Professor F. W. Loomis for his permission to use the laboratory, to Mr. N. P. Goss for his help in taking the x-ray photographs, and to the Rockefeller Foundation which provided him with a fellowship.