The Electrical Conductivity of Magnetite

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Synopsis

The electrical conductivity of magnetite was measured in the temperature range including the transformation temperature. Measurements of single crystals showed a marked jump of conductivity at that temperature. The variation of conductivity with applied magnetic field is also measured and the amount of it was not so large as expected by the theory which assumes the transformation to be that of spontaneous magnetization. Previous theories are criticized on the basis of the experimental results obtained.

I. Introduction

It is well known that magnetite undergoes transformation at —160°*C* c.a., in which it shows a marked change in magnetization, a sharp maximum of specific heat and also some anomalies in other physical properties.(1) X ray powder patterns as well as Laue photograpgraphs(2) assure that no lattice change takes place at this transformation. So it is generally considered that this change is either due to the rearrangement of valence electron on cations among various lattice point or to some change in the electronic structure of the material. For the past several years, considerable discussions were made on this transformation. A crucial conclusion, however, is not obtained as yet, owing to the lack of experimental data. The purpose of this paper is to supplement these data with measurements on electrical conductivity and its dependence on magnetic field. For the present we have not found a satisfactory model to explain the transformation, but from our measurements it can safely be said that the transformation does not imply a change in spontaneous magnetization but that in magnetization characteristics.

II. Criticism to Previous Theories

We shall begin with a brief description of the mechanisms proposed in the past regarding this transformation, and poin out the deficiencies to corroborate these theories.

We can classify the previous theories into two types, namely, one based on the Hitler-London's picture and the other on the Bloch's picture. Theories of the first class

* The 550th Report of the Research Institute for Iron, Steel and Other Metals.

(1) P. Weiss and R. Forrer; Ann. d. Phys. **12** (1929), 276; T. Okamura; Sci. Rep. Tôhoku Univ. **21** (1932), 231.

(2) H. Shôji Sci, Rep. Tôhoku Univ. **24** (1935), 250.

were mainly developed by the members of the Nagoya and Osaka Universities [3]. They attributed the transformation to be an order-disorder transformation of electrons on cations, assuming different magneton numbers for divalent and trivalent Fe-ions. On the other hand the latter picture was adopted by S. Miyahara[4] and modified by one of the authors[5]. Both theories attempt to clarify the sudden change in spontaneous magnetization at the transformation temperature. But on analysing the experimental results carefully, one is confronted with the doubt of whether there is actually such a change.

The striking feature of this transformation is that the magnetization below the transformation temperature increases with an increase of magnetic field up to considerable high fields, so that saturation seems to take place above 20,000 Oe. The amount of jump of magnetization at the transformation temperature decreases with increasing field and may vanish though experiments have not been performed at such extremely high fields. If we interpret the observed magnetization in considerably high fields to be due to the spontaneous magnetization, we shall be compelled to consider that the spontaneous magnetization varies with fields. This point is difficult to explain by previous theories. We shall elucidate this more fully in the following.

The spontaneous magnetization is the result of the exchange interaction between electrons in the material. Exchange energy is of the order of 10^{-13} erg which is converted into temperature of about $1000°K$, and this in turn corresponds to a magnetic field of about 10^7 Oe. So if we wish to raise the spontaneous magnetization by an appreciable amount, it is generally necessary to apply such unattainable high fields except near the Curie temperature, where the spontaneous magntization itself is very low. This principle is violated in the first type of theories, since it assigns a definite spin quantum number to a given cation, so that, in order to explain the variation of magnetization with applied magnetic field it is necessary to assume that the cation arrangement is changed by the applied field for which occurrence we cannot find any legitimate reason. In the second type of theories, whose essential point lies in the excitation of electrons from the lower partly filled band to the upper band, the variation of spontaneous magnetization must be considered as the variation of hole number in the lower band. This in general will cause the variation of electrical conductivity. Since attainable magnetic field can reduce the amount of jump in magnetization at the transformation to below 1%, it is concluded that in this case the conduction electrons are almost the same as that at higher temperatures. We can no longer distinguish the material at the lower temperature side of the transformation in high magnetic field from that at the higher temperature side. Then the conductivity will also be nearly equal in these two cases, that is to say, the

(3) T. Nagamiya; Kagaku **14** (1944) 87 (in Japanese); K. Yoshida; Bussei-Ron Kenkyû **12** (1948), 14 (in Japanese); M. Shimizu; Read on April, 11, 1948 at the Meeting of the Phys. Soc. Jap.; H. Shimazu and K. Yoshida; Nippon Butsuri-Gakkai-shi **4** (1949), 74 (in Japanese).

(4) S. Miyahara; Proc. Phys. Soc. Jap. **24** (1942), 49.

(5) T. Hirone and N. Tsuya; Riken-Ihô **23** Butsuri 177 (1944) (in Japanese).

jump in conductivity observed without magnetic field will be cancelled by magnetic field. Great variation of conductivity with the applied magnetic field must be observed. Hence the measurement of this variation will serve as a powerful means to test the validity of the second type of theories.

III. Experimental Procedures

The samples used were natural magntite, some of which were obtained from Kamaishi, Iwate Prefecture and the others from Nagasaki Prefecture. Both polycrystals and single crystals were used. The apparatus for measuring conductivity is shown schematically in Fig. 1.

Most of the samples were cut in a size of 4 mm sq.× 22 mm, the sample a ([100]–Single crystal) in Fig. 3 etc. was 5 mm sq.×27.5 mm. Current terminals were connected to the edges of this rectangular bar. Potential terminals were 15 mm apart from each other; there were used at the same time as the thermojunctions with constantan wires. All contacts were pushed to the sample by small strong springs. The temperature was observed with both junctions and measurements were made only when the temperature differnce was sufficiency small so as to avoid the thermoelectromotive force. The sample was set in a metal case to make the temperature uniform and in order to control the temperature this metal case is wound by a constantan wire. This is again set in a glass tube and is evacuated. Liquid nitrogen was used to cool the glass tube.

The samples from Nagasaki Prefecture whose shape is illustrated in Fig. 8 were so small (edge length about 2 mm) that the apparatus could not be used and a special cartridge was prepared for them.

The result of the chemical analysis made on these samples are tabulated in Table 1.

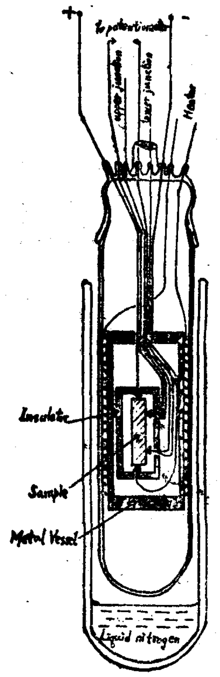

Fig. 1. Schematic Represntation of the Appratus for Measuring Electrical Conductivity.

Table 1

	FeO	Fe_2O_3	Si	Cu	S	atomic ratio of FeO; Fe_2O_3
Single crystal from Kamaishi	29.27	70.09	0.61	0.099	0.159	1.0773
Polycrystal from Kamaishi	29.81	67.88	0.82	0.062	0.018	1.0244
Single crystal from Nagasaki Pref.....	30.56	68.62				1.0101

The current was fixed throughout one series of measurements by inserting high resistance in series to the sample. Since the resistance of magnetite become very high at liquid nitrogen temperature, we were obliged to use very small currents, sometimes of the order of several μA. So it seemed necessary to test whether the Ohm's law is valid at such small currents. Some of the results are shown in Figs. 6a and 6b indicating that it is almost valid if we adopt the potentiometer method while the bridge method showed a remarkable deviation from it, especially at low temperatures. This will perhaps be due to the contact resistance at the terminals and for this reason we have used the potentiometer only.

Magnetization was measured by the usual ballistic method, simultaneously with the conductivity measurements, with constant magnetic field at various temperatures. Magnetic field was supplied by a de Bois type electromagnet. The results are shown in Figs.

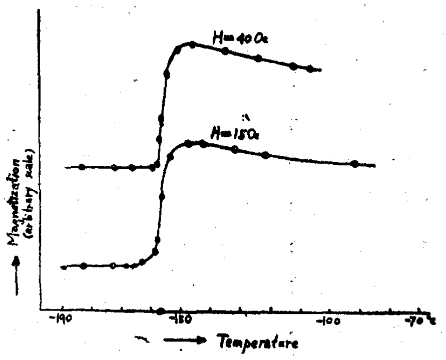

Fig. 2. Magnetization vs. Temperature (Polycrystal from Kamaishi)

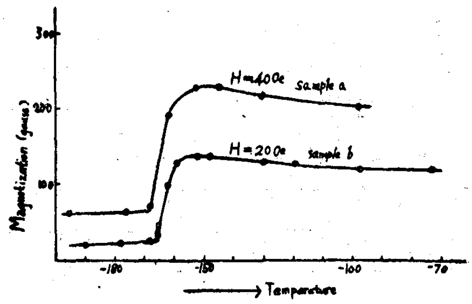

Fig. 3. Magnetization vs. Temperature Single crystals from Kamaishi

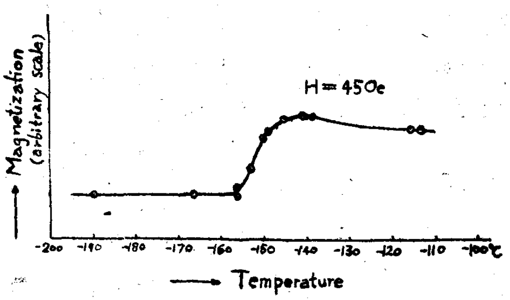

Fig. 4. Magnetization vs. Temperature (Single crystal from Nagasaki Prefecture)

2—4. Search coils (omitted in Fig. 1) wound on the specimen were of enameled wire whose diameter was 0.05 mm and their turn number was 100. Since the absolute value of magnetization is of little importance for us, the scale value of the ordinate is not so accurate. All the samples show magnetic transformation but its temperature and the amount of jump of magnetization seems to vary a little from sample to sample.

IV. Experimental Results

1. *Variation of conductivity with temperature.*

Figs. 5—8 show the results obtained for the variation of conductivity with temperature. It is difficult to determine the transformation temperature for poly-crystals from conductivity data, since the anomaly at the transformation is almost hidden from our observation by the contact resistance between grains. This effect is unavoidable. As stated in **III**, the contact resistance becomes very large, especially at low temperatures. The evidence of contact resistance between grains is also obtained by comparing the resistance of various samples with different grain size. Samples with large and few

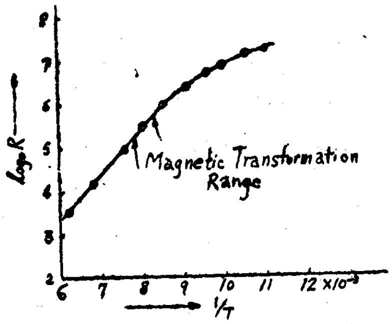

Fig. 5. Conductivity vs. Temperature (Polycrystal from Kamaishi)

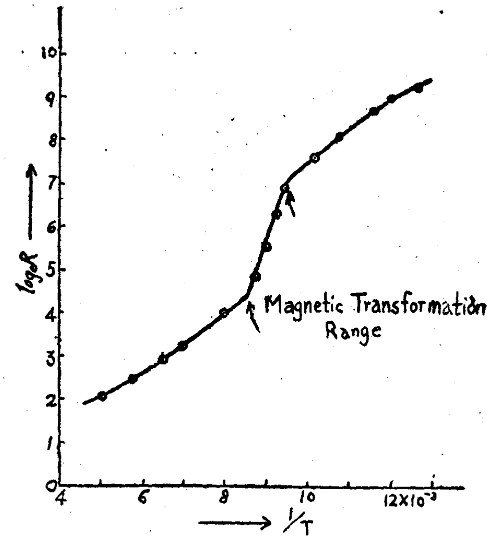

Fig. 6. Electrical Conductivity vs. Temperature. Single crystal from Kamaishi, Sample a.

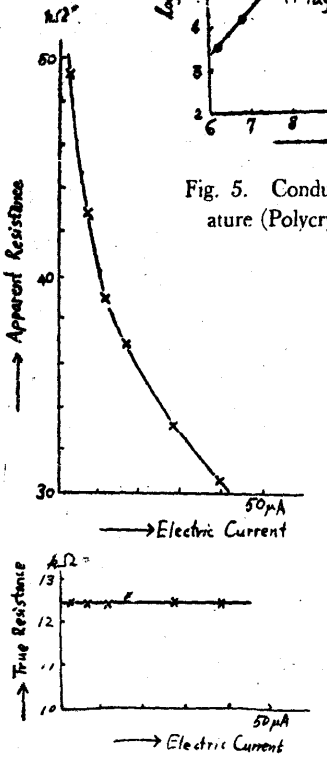

Fig. 6a. Validity of Ohm's law. The upper curve shows the result by bridge method, while the lower curve that by potentiometer method. (Resistance at liquid nitrogen temperature.)

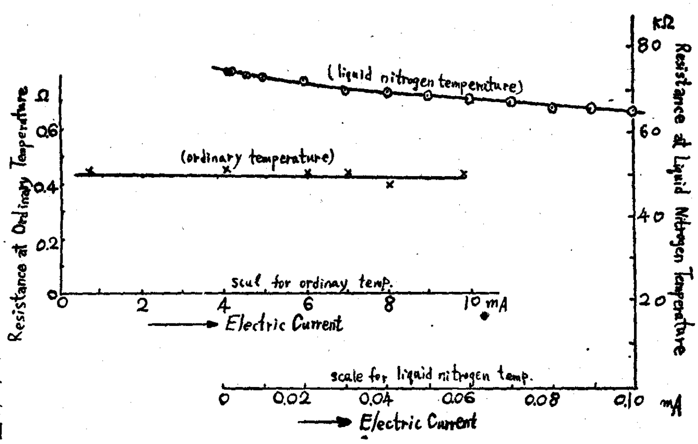

Fig. 6b. Validity of Ohm's Law, Sample b.

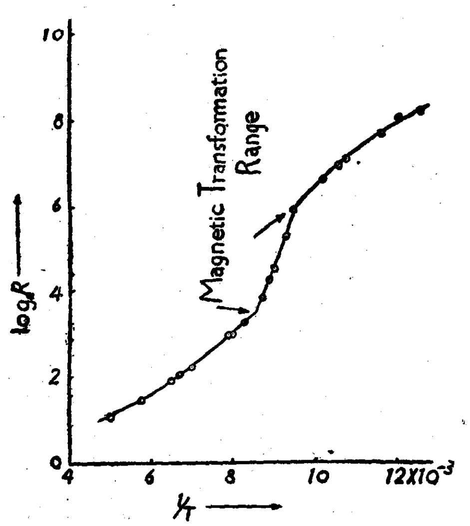

Fig. 7, Electical Conductivity vs. Temperature. Single crystal from Kamaishi, Sample b.

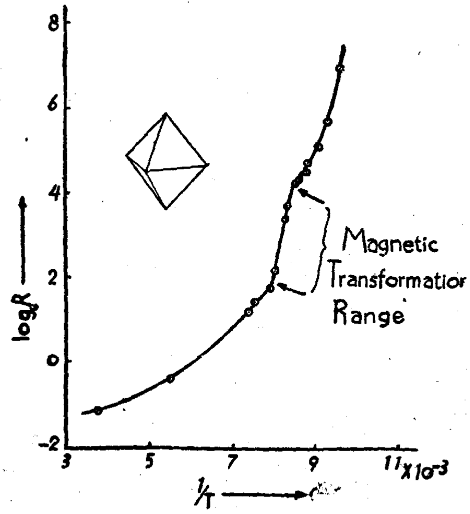

Fig. 8. Electrical Conductivity vs. Temperature. Single crystal from Nagasaki Prefecture, whose shape is shown in the figure.

grains show large conductivity. They are always about 10 to 100 times more resistive than single crystal samples. So we are likely to be misled if we deduce any conclusion regarding the transformation from the data on poly-crystals. Strictly speaking, even the single crystal has many visual cracks and an enormous number of microscopic striations, whose effect is actually observed by the sample in Fig. 6b. We believe that samples from Nagasaki Prefecture are the best ever obtained in this respect.

It has been an ambiguous point in the previous experiments on the behavior of the conductivity near the transformation temperature, whether there is actually a jump of conductivity value at that temperature or the conductivity curve merely change its slope or activation energy. According to our data on single crystals, some amount of jump at the transformation temperature is always found although it was necessary to take great care in the measurement. This is the expected result, if we assume that the transformation is of the first kind, obscured by the inhomogenity of substance or by some other reasons. As is obvious from the magnetization data, the transformation spreads over a certain range of temperature, this jump should also spread over the same range. Such jump has already been observed by Verwey for artificial $FeO(Fe_3O_2)_{1.025}$[(6)], while his jump is much sharper. The ratio of the conductivity corresponding to the beginning and finishing temperature of the transformation is about 10. The activation energies above and below the transformation temperature varies from sample to sample. Some of them are listed in Table 2. In general the difference between the magnitude of these two energies is comparably smaller for samples from Kamaishi than is reported by other authors.

Table 2. Electrical Conductivity of Single Crystals

Sample	Mean activation energies (ev) the transformation temperature: below	above	Resistivity at liquid nitrogen temperature	Resistivity at ordinary temperature
Specimen from Nagasaki Prefecture.......	0.16	0.069	3	0.1
Sample (a) from Kamasaki	0.071	0.052	1.54	0.058
Sample (b)	0.067	0.067	12.0	0.432

2) *Variation of conductivity with magnetic field*

This has already been measured by Y. Shirakawa[7)] at —196°,—95° and 0°C. Our results, shown in Fig. 9 are essentially the same as his, though the amounts of variation are somewhat higher in our case. Such difference may well be attributed to the difference of sample. The variation roughly parallels the magnetization and reaches the saturation value of 0, 8% above 1000 *Oe* at low temperatures. There seem to occur no significant phenomena below the transformation temperature.

From the discussions developed in 1, Miyahara's type of theories should no longer be valid and we must look for the origin of transformation in some other mechanism.

(6) E. J. W. Verwey; Nature **144** (1939), 327.
(7) Y. Shirakawa; Phys. Rev. **60** (1941), 835.

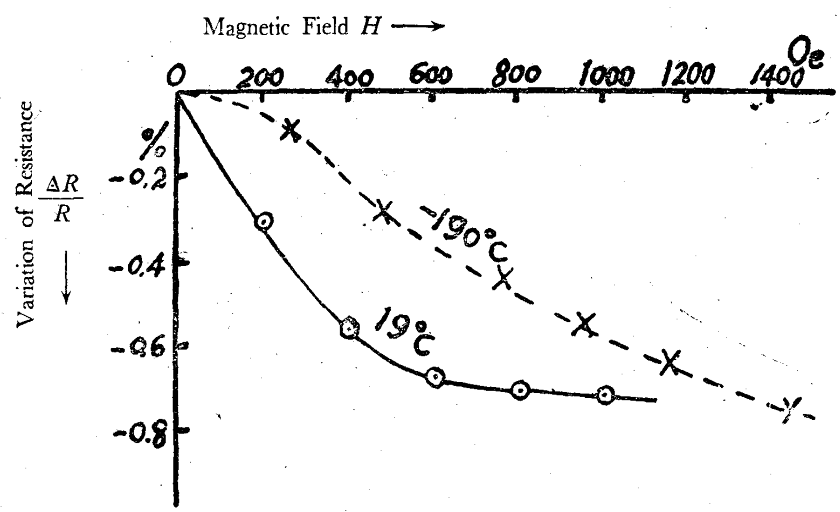

Fig. 9. Variation of Resistivity with Magnetic Field Single crystal from Kamaishi.

Summary

The conductivity data above stated assures that the low temperature transformation of magnetite is not be considered as that of the spontaneous magnetization. Magnetic field has no power of sweeping out this transformation. This will perhaps be corroborated by the measurements of the variation with magnetite field of other related physical properties such as thermoelectric power, specific heat, etc. It seems probable that the change of magnetization at the transformation is due to the change in anisotropy constant or stress energy which are the determining factors of magnetization characteristics.

Acknowledgments

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