

Thermoelectric properties of magnetite at the Verwey transition

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Thermoelectric-power measurements were carried out in the temperature range 80–300 K on five synthetic single crystals of magnetite, Fe_3O_4 , differing in oxygen stoichiometry. The anomalous behavior of the Seebeck coefficient below the Verwey temperature was interpreted with a model of mixed conduction.

I. INTRODUCTION

Recently, there has been an increasing interest in the compound magnetite (Fe_3O_4) and, in particular, in the order-disorder transition occurring at the so-called Verwey temperature T_V . For a long time, the accepted model of this transition was one proposed by Verwey,¹ in which the extra electrons at the iron ions on the octahedral sites are ordered below the transition temperature in alternate (001) planes of Fe^{2+} and Fe^{3+} ions, resulting in an orthorhombic structure.² However, over the last few years several experimental results have shown that this simple scheme of charge ordering must be modified. Evidence of a more complicated structure was found in neutron-diffraction,³ electron-diffraction,⁴ Mössbauer,⁵ NMR,⁶ heat-capacity,⁷ and magnetic-disaccommodation experiments.⁸ Recent neutron diffraction experiments by Shirane *et al.*⁹ revealed that the structure must be rhombohedral; the intensity distribution suggested alternate layers of Fe^{2+} and Fe^{3+} ions in the ab plane, but substantial disagreement remains between experimental magnetic intensities and simple model calculations of the magnetic structure, and thus a more complex charge ordering is still not ruled out.

The electrical conduction mechanism in relation to the order-disorder transition has been studied by various authors, theoretically as well as experimentally. Several models have been proposed, i.e., double exchange,¹⁰ pair localization,¹¹ small polaron hopping,^{12,13} and band models.¹⁴ Lorenz and Ihle¹⁵ were successful in calculating the electrical conductivity above and below T_V . Their calculations are based on the Hamiltonian introduced by Cullen and Callen¹⁴; they attacked the problem beyond the Hartree approximation by means of the Green's-function cluster approximation. More recently, Klinger¹⁶ gave a semiquantitative polaron model to describe the conduction phenomena. The essential features of both models are equal in that the most important term in their Hamiltonians is the nearest-neighbor Coulomb repulsion term, which they assume to be responsible for the electron ordering below T_V . The experi-

mental data reported in the literature are not unanimous. Drabble *et al.*¹⁷ reported that the impurity content and the stoichiometry have little effect on the low-temperature electrical conductivity. However, Hall-effect measurements reported by different authors reveal that below the transition temperature the conduction can take place by negatively^{18,19} or positively²⁰ charged carriers. The same controversy was reported for the thermoelectric power^{20,21} at low temperatures.

In our opinion, the scattering in the data is caused by the impurities and the stoichiometry of the materials. To investigate this, we preferred to study the magnetite problem by means of the Seebeck effect, since the interpretation of the Hall effect in ferrimagnets is questionable. The results of this study are given in Sec. III.

II. EXPERIMENTAL

Synthetic single crystals were prepared from $\alpha\text{-Fe}_2\text{O}_3$ (99.9% purity) by means of a floating-zone technique in an optical furnace.²² After the crystallization, the crystals were annealed for 70 h at 1130°C in $\text{CO}_2\text{-H}_2$ mixtures, with partial oxygen pressures between 6×10^{-5} and 6×10^{-11} atm; during cooling to room temperature, the $\text{CO}_2\text{-H}_2$ ratio was changed in such a way that the slope of the $P_{\text{O}_2}\text{-}1/T$ curves was the same as that proposed by Smiltens²³ for growing stoichiometric magnetite crystals.

Thermoelectric measurements were carried out on single crystalline rods (3 cm, 0.5-cm diam, [110] direction parallel to the axis of the sample), which were sealed with Stycast 2850GT between two copper blocks and placed in a cryostat. The temperature of these blocks could be established independently of each other. In this way it was possible to increase the temperature difference between the blocks, while keeping constant the average temperature of the crystal. The temperature difference across the samples was measured with copper-constantan thermocouples (50- μm diam), ultrasonically soldered with indium on the surface of the crystal; the thermoelectric voltage was measured both via the copper and via the constantan wires. The temperature difference was

varied between 0.2 and 5 K, and from a plot of at least five measured voltages against the temperature difference the thermoelectric power was determined. These plots were always straight lines which did not intersect the abscissa in the origin. The slope of the curves revealed the values of the thermoelectric power excluding spurious voltages in the circuit. In the temperature region where the thermopower changed strongly, the temperature difference was limited to about 1.5 K. In addition to thermoelectric measurements, the electrical conductivity of the samples was measured with a four-probe method. No precautions were taken to prevent twinning of the crystals, so that all the measurements below the Verwey transition were carried out on twinned specimens.

III. RESULTS AND DISCUSSION

Thermoelectric power was measured on five samples, the only difference being the annealing atmosphere used in the preparation of the specimens: A: $\log_{10} P_{O_2} = -4.2$; B: $\log_{10} P_{O_2} = -9.0$; C: $\log_{10} P_{O_2} = -9.7$; D: $\log_{10} P_{O_2} = -9.9$; E: $\log_{10} P_{O_2} = -10.2$. Specimen A was annealed very close to the phase boundary $Fe_3O_4-Fe_2O_3$ (Ref. 24) and contained an excess of oxygen equivalent to about 1% cation vacancies. No phase segregation was observed in the specimens with x-ray diffraction, nor with microscopic investigation. All the other samples were very close to the stoichiometric

composition, and no essential differences could be detected with chemical analysis. The sample E was annealed very close to the Fe_3O_4-FeO phase boundary.²⁴ The lattice parameters of the samples varied between $a = 8.393 \text{ \AA}$ (sample A) and $a = 8.398 \text{ \AA}$ (sample E).

In Fig. 1(a) the absolute thermopower of the five samples is plotted against temperature. Corrections were made for the absolute thermopower of the copper and constantan wires.²⁵ The values of the Seebeck coefficient above the Verwey transition are in very good agreement with the data of Griffiths²⁶ and Lavine,¹⁸ but the values of 30–35 $\mu\text{V/K}$ reported by Constantin²¹ are rather in disagreement. Only a small difference was found between the oxidized sample A and the other samples, indicating that above the transition temperature the thermoelectric properties are hardly influenced by the oxygen stoichiometry. In the ordered state, however, the influence of the stoichiometry is remarkable. The oxidized sample A shows a large decrease of the Seebeck coefficient, indicating conduction by a strongly decreasing number of negatively charged carriers. For the more stoichiometric samples B to E, the decrease is even larger, but at lower temperatures the thermoelectric power increases again and becomes positive, pointing to positively charged carriers.

In order to interpret these data, we will assume that an energy gap exists between two kinds of electron states. In the case of ionic order, these

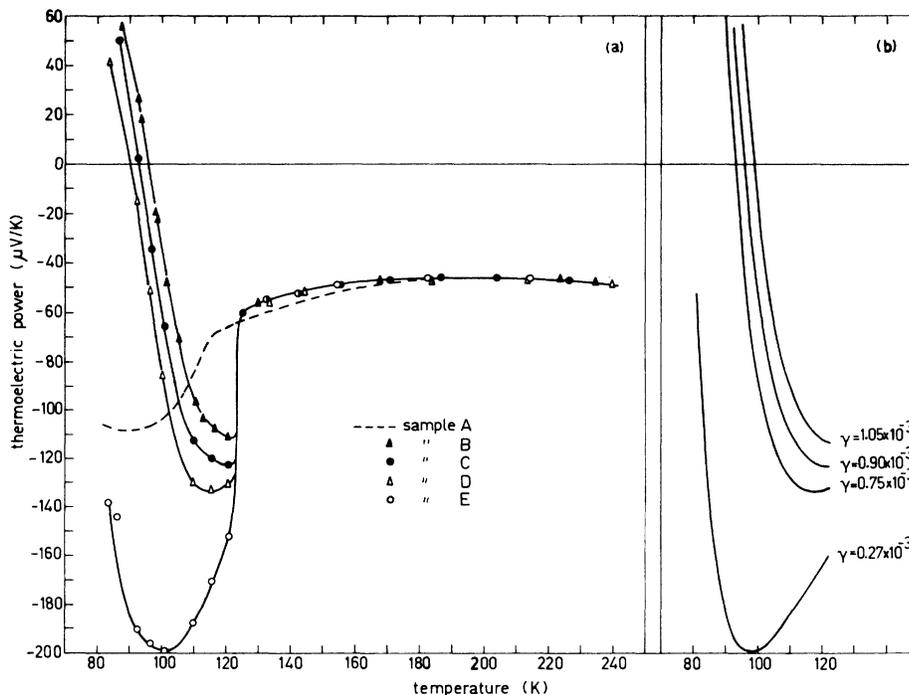


FIG. 1. Absolute thermopower vs temperature. (a) Experimental data of magnetite single crystals. The lines are only meant as a guide to the eye. For the characterization of the samples A to E, see text. (b) Calculated values according to Eq. (4) using $2\Delta = 0.106 \text{ eV}$ and $q_p - q_n = 0.009 \text{ eV}$.

states can be considered as localized on Fe^{2+} and Fe^{3+} ions, respectively. Thus one can distinguish two kinds of charge carriers resulting in a mixed conduction: holes in the Fe^{2+} levels and electrons in the Fe^{3+} levels. With this model the behavior of the thermopower of the stoichiometric samples B to E can be explained, as will be shown below. However, the thermopower of the most oxidized sample A is in disagreement with this model: oxidation introduces Fe^{3+} ions, which implies that the Seebeck coefficient should become positive. But in addition to the excess of Fe^{3+} ions, an equivalent number of octahedral cation vacancies must be present which are defects in the regular rows of iron ions. From the work of Constantin²¹ it can be seen that a concentration of impurities of about 1% changes the nature of the charge carriers below the transition from p to n . This might be related to the interference of the relatively large number of impurities with the ordering phenomenon. The large number of vacancies in specimen A may have the same influence upon the crystallographic order and the thermopower as ionic impurities. This view is supported by the electrical conductivity measurements (Fig. 2). The transition temperature of the stoichiometric specimens B to E is the same for all: 122 K. For the nonstoichiometric compound a temperature of 116 K was found. Moreover, the transition in this sample was diffuse compared with the other samples, where the jump in the conductivity occurred in a region of 0.5 K.

The excess of oxygen in the specimens B to E is very small, within the experimental error of wet chemical analysis ($\pm 0.1\%$), and the number of vacancies will not affect the ordering. Charge carriers are, within the proposed model, created by excitation of an electron across an energy gap. If the gap width is denoted as 2Δ , the distribution of the electrons over the two kinds of states is given by

$$\begin{aligned} n_1 &= N_1 / \{1 + \exp[-(\Delta + \epsilon)/kT]\}, \\ n_2 &= N_2 / \{1 + \exp[(\Delta - \epsilon)/kT]\}. \end{aligned} \quad (1)$$

In these equations, n_1 and n_2 are the numbers of electrons below and above the energy gap, respectively, while N_1 and N_2 are the total numbers of available levels, which are both taken as equal to half the number of octahedral sites occupied by an iron ion. Then the number of negative charge carriers is $n = n_2$ and the number of positive charge carriers is $p = N_1 - n_1$. The Fermi level ϵ is measured from the middle of the gap and can be calculated from the equation:

$$n_1 + n_2 = n_t, \quad (2)$$

in which the total number of electrons (n_t) is re-

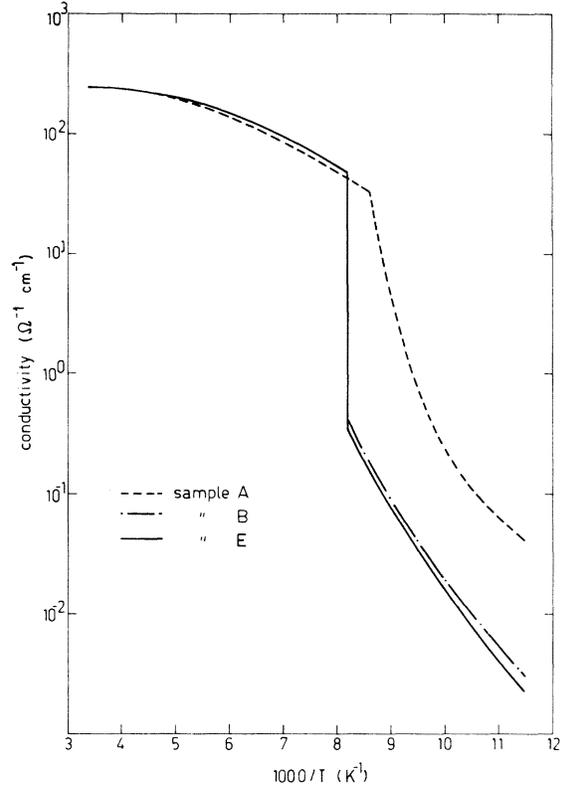


FIG. 2. Electrical conductivity of the samples A, B, and E. Above T_V the conductivity data of the samples B-E are identical within experimental error. Below T_V the data of the samples C and D are between the values of the samples B and E.

lated to the degree of oxidation by

$$n_t = N(1 - 3\gamma). \quad (3)$$

As a measure for the degree of oxidation we have introduced the cation vacancy concentration γ , defined by $\text{Fe}_{2+2\gamma}^{3+}\text{Fe}_{1-3\gamma}^{2+}\text{V}_\gamma\text{O}_4$. N is the number of formula units per cm^3 . Ignoring the kinetic term,²⁷ the Seebeck coefficient can be expressed as

$$S = \frac{1}{eT} \frac{-n(\Delta - \epsilon) + p(\Delta + \epsilon) \times \mu_p / \mu_n}{n + p \times \mu_p / \mu_n}. \quad (4)$$

In this equation, μ_p and μ_n are the mobilities of the p - and n -type charge carriers, respectively, which are assumed to be thermally activated¹⁶

$$\begin{aligned} \mu_p &= C \exp(-q_p/kT), \\ \mu_n &= C \exp(-q_n/kT). \end{aligned} \quad (5)$$

The Seebeck coefficient has been calculated as a function of T , using Δ , $q_p - q_n$, and γ as parameters. We get a good agreement with experiment by taking $2\Delta \approx 0.10-0.11$ eV, $q_p - q_n \approx 0.01$ eV, and values of γ in the order of magnitude of 0.001, which is in

the range expected from chemical analysis. As an example, the curves with $2\Delta=0.106$ eV and $q_p - q_n=0.009$ eV are shown in Fig. 1(b). The jump in the thermopower at T_V is obviously not found in the calculated curves, because the gap 2Δ disappears at the Verwey transition as a consequence of the disappearance of the ordering; the calculation holds only for the low-temperature phase.

Fitting this model to the electrical conductivity data, one has to assume that the activation energy in the mobility of the n -type carriers is about 0.11 eV at T_V , and decreases to 0.04 eV at 80 K (q_p should be 0.01 eV higher according to our calculations). The total conductivity $\sigma = ne\mu_n + pe\mu_p$ can be calculated with these values, and one finds $\log_{10}\sigma - 1/T$ curves which nearly coincide for various values of γ in the temperature range $90 \text{ K} < T < T_V$, and spread slightly below 90 K; the conductivity shifts gradually to lower values with decreasing values of γ . Because of the uncertainty in the experimental results, it was not possible to verify these features rigorously, although the same trend was found. However, the model certainly explains the small changes in the conductivity in comparison with the large variations of the thermopower as a function of the stoichiometry.

From the above-mentioned results it is clear that the thermoelectric power is very sensitive for the oxygen stoichiometry, and especially for the excess of Fe^{3+} ions. This implies that monovalent impurities will also influence these properties to a great extent; the total number of elec-

trons (n_t) cannot be considered as being determined by the oxygen content only. Preliminary spectrochemical analysis of some samples indicated, for instance, that sodium was present in the order of 50 ppm, which will introduce an equal number of Fe^{3+} ions. A detailed investigation of the influence of doping upon the electrical properties of magnetite below the Verwey transition is still in progress in our laboratory. However, from the results given in this paper, we may conclude that the electrical conduction in this compound is of a mixed type. The thermopower measurements can be explained with a relatively simple model of charge transport on two levels. The results also indicate that the main part of the activation energy in the conductivity must be due to a thermal activated mobility which is a strong indication of polaronic conduction.¹⁶ It is obvious that the oxygen stoichiometry and monovalent impurities have a decisive influence whether p - or n -type conduction is observed in the ordered state. The controversy about the sign of the charge carriers, which is reported in literature,¹⁸⁻²¹ is not real.

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