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ELECTRIC TRANSPORT IN N-TYPE Fe_2O_3

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Synopsis

Resistivity, Seebeck-coefficient, Hall-coefficient and magneto-resistance of *n*-type single crystal ferric oxide (hematite), containing Sn^{4+} as an impurity, are reported. The resistivity does not show important anisotropy. The Hall- and magneto-resistance effects are probably related to the parasitic ferromagnetism present in this material, their magnitude depends strongly upon the orientation of the magnetic field with respect to the *c* axis. The magneto-resistance is probably a consequence of magnetostriction. Some information concerning the mobility of the electrons at higher temperatures ($T \geqslant 400°K$) is derived; at lower temperatures the conduction mechanism should be rather complicated, contributions from impurity conduction being also present.

A. *Introduction*. Several studies of the electrical transport in α–Fe_2O_3 have been made. Verwey *e.a.*[1]) demonstrated that ferric oxide, which is an insulator when pure and stoichiometric, can be made *n*-type semiconducting by substituting Ti^{4+} or Sn^{4+} for the ferric ions. Morin[2]) performed measurements of the resistivity and the Seebeck-coefficient on pure and titanium-doped ceramics. Hall data were also reported, but they appeared to be related to the parasitic ferromagnetism present in this material. Nakau[3]) reported on the anisotropy of the resistivity of natural single crystal hematite containing several per cents of impurities. His data indicate a remarkable anisotropy. In view of the impurities present the material investigated by Nakau should be *p*-type. Gardner, Sweett and Tanner performed measurements of resistivity and Seebeck coefficient of *n*-type and *p*-type ceramics and also published some resistivity data of single crystals[4]). These measurements were all taken at higher temperatures. Volger[6]) discovered relaxation losses in slightly reduced ceramics, which are probably due to electrons hopping around the defect centers produced by the reduction. The conduction mechanism is usually discussed in terms of charge carriers hopping between metal-ions sites[2]) [4]) [5]).

In this paper we want to report on the anisotropy of the resistivity, the magnetoresistance and the Hall effect, and also on the Seebeck coefficient of *n*-type natural single crystal hematite.

α–Fe_2O_3 crystallizes into the hexagonal corundum structure, in which the Fe^{3+} ions are situated in layers perpendicular to the *c* axis, the layers being separated by layers of O^{2-} ions. The material is antiferromagnetic below 950°K. Within each layer the magnetic moments of the Fe^{3+} ions are parallel, but the spins belonging to adjacent layers have antiparallel orientation. In pure material the spin directions are parallel to the *c* axis below 260°K and perpendicular to this axis at higher temperatures, with a slight parasitic ferromagnetism due to the fact that the magnetic sublattices have been canted with respect to each other[7) 8) 9)]. It has been found that quantities of about 0.1–1 at. % Sn^{4+} or Ti^{4+} may suppress the magnetic transition, the parasitic ferromagnetism then remains down to very low temperatures[7) 10) 11)].

B. *Experiments.* Investigations were made on a flake of natural single crystal hematite containing the impurities (mole %):

SnO_2: 1.2%; MgO: 0.4%; SiO_2: 0.2%; and MnO: 0.2%.

Since Sn^{4+} acts as a donor[1)] and Mg^{2+} and Mn^{2+} most likely as acceptors, we expect the material to be *n*-type, approximately one half of the donors being compensated by the acceptorlike impurities.

X-ray analysis indicated that the *c* axis was perpendicular to the plane of the flake. Etch pits could be produced by boiling HCl (diluted). These pits were found to exhibit a pronounced orientation which was used for checking the crystal orientation and quality of the material using the apparatus developed and described by Bouwknegt[12)] (see fig. 1). When the direction

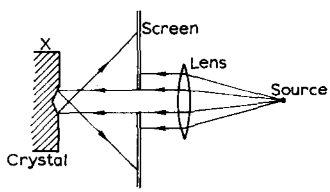

Fig. 1. Method used for checking the orientation of α–Fe_2O_3 after Bouwknegt[12)].

of the beam coincides with the *c*-axis, a figure of trigonal symmetry becomes visible upon the screen, from which also the position of the two-fold axes may be found. The etching also makes crystal boundaries clearly visible.

Rectangular platelets were cut with a diamond wheel with their plane perpendicular to the *c* axis and their longest dimension within $\approx 4°$ parallel to a two-fold axis.

Contacts were made by soldering indium onto the samples. Indium-gallium alloy also produced contacts of satisfactory quality.

1. *Resistivity and Seebeck-coefficient.* The resistivity $\perp c$ was measured by the four-terminal method. (fig. 2). The Seebeck coefficient with the

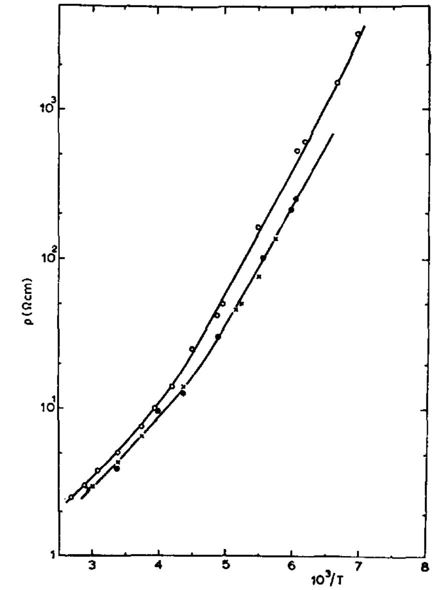

Fig. 2*a*. Resistivity $\perp c$ of α–Fe_2O_3($\simeq$ 1% Sn^{4+}) at low temperatures.

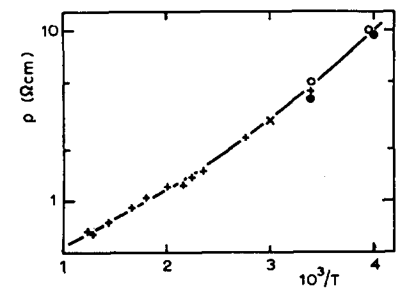

Fig. 2*b*. Resistivity $\perp c$ of α–Fe_2O_3($\simeq$ 1% Sn^{4+}) at high temperatures.

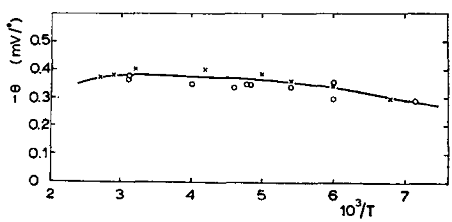

Fig. 3. Seebeck coefficient $\perp c$ of n-type Fe_2O_3($\simeq$ 1% Sn^{4+}).

temperature gradient perpendicular to the c axis was also obtained (fig. 3). The sign was negative, as expected. Two-probe resistivity measurements were performed with the electric field parallel to the c axis. The d.c. resistivity $//c$ exceeded the resistivity $\perp c$ by about a factor 2.5 at room temperature and about 1.5 at 140°K. Also a.c. measurements $//c$ were performed by means of a General Radio type 1605 A impedance comparator in combination with General Radio type 510, D, E, and F variable resistors. Measurements were made below 170°K between 100 Hz and 100 kHz. The resistivity was independent of frequency within a few per cents, consequently the anisotropy of the calculated resistivity is probably not much affected by resistance contributions from the contacts. The fact that the anisotropy of the resistivity is not important is of interest in view of the magnetic structure of Fe_2O_3.

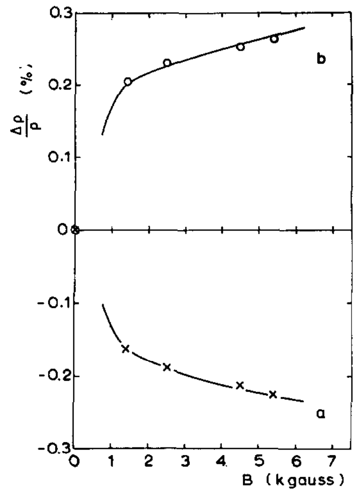

Fig. 4. Magnetoresistivity in *n*-type Fe_2O_3 ($\simeq$ 1% Sn^{4+}) at room temperature ($H \perp c$), *a*. transverse; *b*. longitudinal

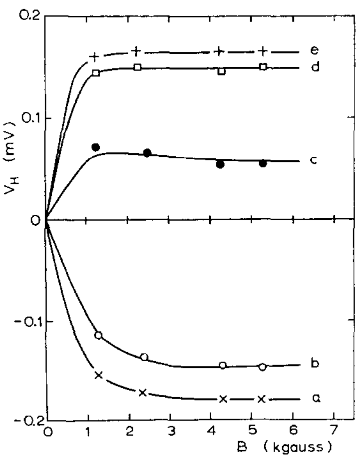

Fig. 5. Hall voltages *versus* magnetic field strength in *n*-type Fe_2O_3 ($\simeq$ 1% Sn^{4+}). Thickness of the sample 2.1 mm, $H \perp c$

a. $T = 293°K$ $I = 3.1$ mA
b. $T = 234°K$ $I = 2.2$ mA
c. $T = 193°K$ $I = 0.61$ mA
d. $T = 173°K$ $I = 0.28$ mA
e. $T = 150°K$ $I = 75$ μA

2. *Magnetoresistivity and Hall effect.* We found both longitudinal and transverse magnetoresistance. To the authors' knowledge such phenomena have not been reported for Fe_2O_3. The magnitude depends strongly upon the orientation of the sample with respect to the magnetic field. With $H \parallel c$ the effects nearly vanish ($\approx 10^{-2}\%$ at 5 kilogauss). Transverse and longitudinal magnetoresistivity with the magnetic field perpendicular to the c axis are given in fig. 4 as a function of the external magnetic field. Saturation is seen to take place, probably due to the parasitic ferromagnetism. The effects are nearly independent of temperature down to 120°K, so we conclude that the antiferromagnetic-ferromagnetic transition is suppressed by the large Sn^{4+} concentration [7] [10] [11]. The fact that the magnetoresistance vanishes for $H \parallel c$ is understandable, since the magnetization due to the parasitic ferromagnetism is always in the c plane. (It should be remarked that any shape anisotropy due to demagnetizing fields will be negligible, since the magnetization in this material is very small).

Also the Hall effect is very anisotropic. With $H \parallel c$ hardly any effect is present from which it was estimated

$$\mu_H < 4.10^{-2}\ \mathrm{cm^2/V \cdot s}] \quad [290°\mathrm{K} < T < 400°\mathrm{K}$$

With $H \perp c$ large Hall voltages were observed, showing saturation and remanence (fig. 5). Also these effects persisted down to 120°K, but a change of sign was found at about 200°K. It is seen that the saturation of the Hall voltages at high magnetic fields is rather complete, in fact much more complete than the effects reported by Morin in ceramic samples, so that also here no normal Hall effect can be detected. Possibly the theory by Abelskii and Irkhin[13] on the spontaneous Hall effect in ferromagnetic semiconductors could apply.

3. *Conductivity in high electric fields.* The current-voltage characteristics were measured with the electric field parallel to the c axis by means of a 10 kV pulse apparatus in which a condensor of 200 pF was discharged across the specimen through a Philips 5C 22 thyratron tube. The currents and voltages were made visible upon the screen of a Tektronix type 536 X–Y oscilloscope with type K pre-amplifier plug-in units. Measurements were made between 150°K and 100°K. The highest field strength obtained was 250 kV/cm. The conduction was found to be ohmic up to this field strength.

C. *Interpretation.* The slope of the log resistivity *vs.* reciprocal temperature graph changes at 250°K, which may be attributed to the onset of exhaustion of the uncompensated donor centers. The exhaustion will probably be complete at about 400°K. This is supported by the estimates of the Hall coefficient with $H \parallel c$ from which it is deduced:

$$n > 3.10^{19}\ \mathrm{cm^{-3}}\ (300°\mathrm{K}) \quad n > 5.10^{19}\ \mathrm{cm^{-3}}\ (400°\mathrm{K})$$

The number of uncompensated donors equals about 1.2×10^{20} cm^{-3}. It is then obtained

$$\mu \simeq 3.10^{-2}\ \mathrm{cm^2/V{\cdot}s} \quad (400°\mathrm{K}).$$

From the Seebeck-coefficient it follows that the density of states of the conduction levels (band) is between 2.10^{21} cm^{-3} and 1.5×10^{22} cm^{-3} dependent on the choice of the transport contribution to the Seebeck coefficient. The effective mass of the carriers is thus of the order of 50–100 m_e (m_e stands for the free electron mass). Above 400°K the resistivity continues to decrease, thus at these high temperatures the mobility should indeed be an increasing function of temperature. Since it is not certain that this behaviour persists below 400°K, the description of the mobility by an exponential law is not sure to hold, because of the temperature region being too limited.

At lower temperatures the situation becomes more complicated, as can be seen from the change of sign of the spontaneous Hall effect and the decrease of the Seebeck coefficient at lower temperatures. In view of the high defect concentrations the presence of a contribution due to impurity conduction[14]) seems very likely, for instance by impurity hopping. This is a thermally activated process, part of the activation energy being the energy of the charge vacancies in the donor levels in the fields of the ionized acceptors. On the average this energy is given by [15]):

$$E_a = 1.61 \frac{e^2}{\varepsilon} (N_D^{\frac{1}{3}} - 1.35\, N_A^{\frac{1}{3}})$$

ε stands for the dielectric constant, N_D for the donor density and N_A for the acceptor density (strictly speaking the formula is valid only if $N_A/N_D \lesssim 0.2$). It is easily verified that this contribution to the activation energy is very small, i.e. close to 10^{-2} eV, taking $N_D = 2.5 \times 10^{20}$ and $N_A = 1 \times 10^{20}$. Additional contributions to the activation energy may be due to deformation of the lattice around the charge carriers (impurity polaron conduction). The change of sign of the spontaneous Hall effect might be explained by contributions due to impurity hopping, since here the charge carriers are "holes" in the donor levels (cf. also the data by Ksendov *e.a.*[16]) on $Li_xNi_{1-x}O$).

The anisotropy and sign of the magnetoresistivity are similar to that produced by the magnetostriction arising from the parasitic ferromagnetism[17]). This strongly suggests that the magnetoresistance is the change of mobility upon deformation of the lattice, this change of mobility being nearly independent of temperature (if we assume the magnetostriction to remain the same towards lower temperatures if the transition is suppressed). This provides some evidence against the hopping picture, since a deformation of the lattice is expected to lead to a change of the activation energy and so to a relative change of mobility which would depend upon temperature.

Following the arguments of Heikes[18]) concerning the influence of the spin directions of initial and final ion sites on the electron hopping probability, one must expect the resistivity perpendicular to the c axis to be much lower than that in the *c* direction, since $\perp$ *c* the electrons may travel along layers of Fe^{3+} ions of the same spin direction, while on the other hand the movement of the electron in the *c* direction must proceed along ferric ions of either spin orientation. This expectation is at variance with our experimental finding that hardly any anisotropy occurs, which again provides some argument against the simple hopping picture.

In view of the high defect concentrations we may better state our conclusions in the following way. At higher temperatures the conduction takes place mainly along sites which are next to nearest neighbours to the donor ions. Because of the high donor concentration, paths composed of such sites, extending throughout the crystal will be present. At lower temperatures paths composed of sites which are nearest neighbours to the donors will contribute to the conduction, this corresponds to the aforementioned "impurity conduction", but these paths will usually not extend throughout the crystal, but will be locally interrupted. The contribution to the Hall effect from the latter paths may be positive, their contribution to the Seebeck coefficient will be nearly zero since the Fermi level nearly coincides with the donor levels in view of the large degree of compensation. It is thus understandable that the increasing importance of the impurity conduction at lower temperatures leads to the decrease of the Seebeck coefficient observed.

It is believed that the conclusions drawn have also some significance for the discussion of polycrystalline *n*-type Fe_2O_3 at similar doping levels, since it has been demonstrated[2]) that the resistivity of such ceramics is controlled by surface layers of higher resistivity caused by taking up of oxygen, which leads to partial compensation of the donors near the surface.

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