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Hall Mobility Measurements on Magnetite above and below the Electronic Ordering Temperature

Abstract: Hall effect measurements were made on a single crystal of magnetite in the temperature range 65 to 373°K. The Hall voltage was positive over the whole temperature range. The results can be explained by assuming that magnetite is a normal semiconductor below the transition point and a degenerate one above that temperature.

Introduction

When magnetite (Fe_3O_4) is cooled through the transition point at 119°K, electronic ordering of the Fe^{2+} and Fe^{3+} ions in the octahedral sites takes place.[1] This ordering is accompanied[2] by a factor of 10^2 reduction in electrical conductivity, supposedly due to Landau trapping of the carriers.[3] According to Heikes and Johnston[4] conductivity then takes place via a thermally activated diffusion process (hopping model). Friedman[5] has shown that in this model the Hall mobility also is activated. Fe_3O_4 is, therefore, a good candidate to check the existence of the hopping model.

So far no measurements have been reported of the temperature dependence of the Hall mobility in Fe_3O_4. Either the magnetic field was too low[6] or measurements were made only at room temperature.[7,8] The results reported here were obtained in the temperature range 65 to 373°K in magnetic fields up to 15 kOe.

Experiment

The sample* was a single crystal platelet, 0.5 mm thick, perpendicular to the (100) axis, with four indium line-contacts ultrasonically soldered to the circumference. Measurements were made in a dc magnetic field and an ac electric field with a frequency of 10 Hz. The Hall signal was amplified in a lock-in amplifier. Measurements were made either by reversing the direction of the magnetic field or by varying it between two values in the range from 9 to 14 kOe. The latter measurements greatly reduced the anomalous Hall voltage contribution to the total Hall voltage and gave, therefore, greater precision. Magnetoresistive effects and other spurious contributions were eliminated by reversing the magnetic field and interchanging the Hall and current contacts.

The ordinary Hall coefficient R_0 and the Hall mobility μ_H were calculated from the observed Hall angle ϕ via the equations[10]

$$R_0 = \rho_\perp \tan\phi / B_{eff} \text{ and } \mu_H = \tan\phi / B_{eff}$$

with

$$B_{eff} = \mu_0 H + \alpha 4\pi M,$$

where $\rho_\perp$ is the transverse resisistivity, μ_0 the permeability of free space, and $4\pi M$ the magnetization. The field parameter $\alpha = R_1/R_0$, where R_1 is the extraordinary Hall coefficient. It has been shown that α is independent of the magnetic field.[7]

Results

The temperature dependence of the dc conductivity is shown in Fig. 1. The solid line represents stoichiometric Fe_3O_4. It is derived from curves published by Verwey and Haayman[1] for sintered samples with varying Fe-O ratios. Comparison of the values at temperatures below the transition temperature with those reported by Calhoun[2] suggest that the c axis of the low temperature rhombohedral phase was parallel to the direction of the magnetic field.

The results of the Hall voltage measurements are summarized in Table 1. Magnetization measurements made by W. H. Cloud of the Central Research Department of the Du Pont Company are summarized in Table 2. The direction of the field was perpendicular to the plane of

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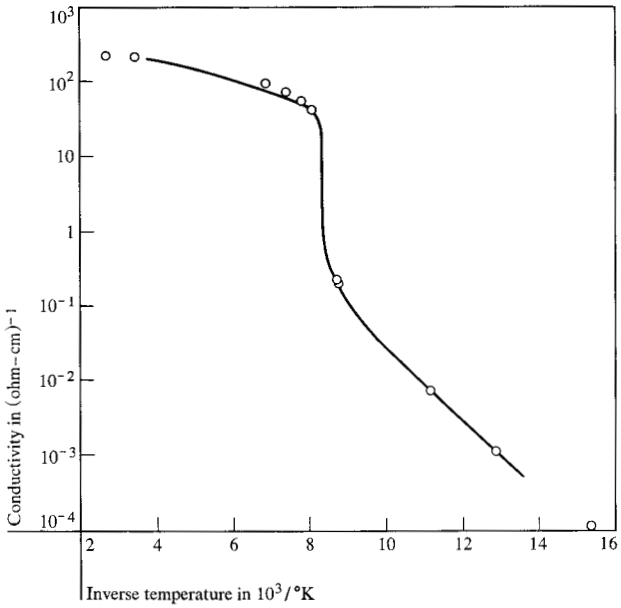

Figure 1 Conductivity vs temperature for a single crystal of Fe_3O_4.

Figure 2 Ordinary Hall coefficient and Hall mobility vs temperature.

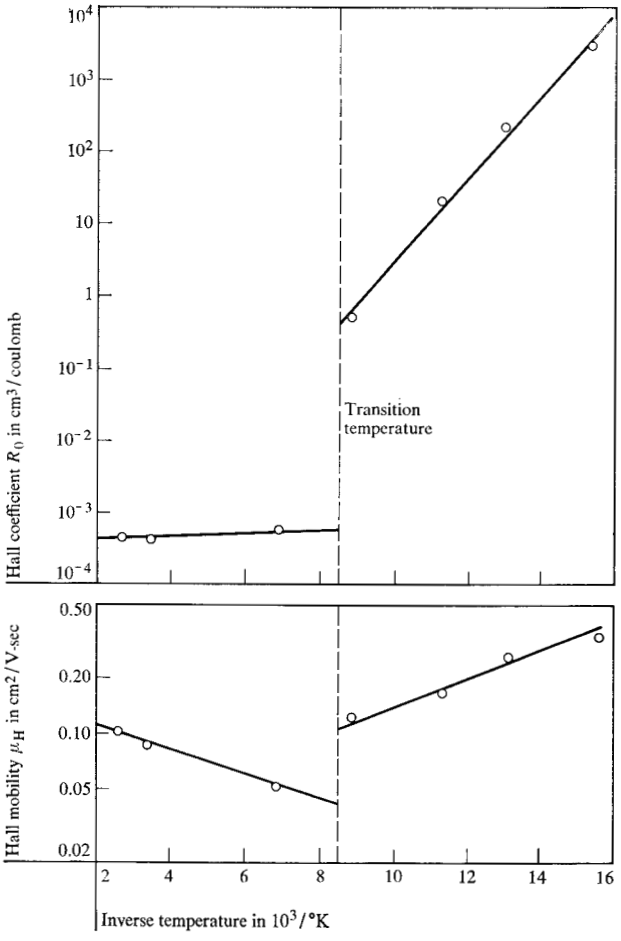

Table 1 Results of Hall angle measurements.

Temperature (°K)	*tan φ at 8.9 kOe* (10^{-3})	*Δtan φ/ΔH in range of 8.9 to 14.4 kOe* ($10^{-10}Oe^{-1}$)	*α*
373	−1.83	−(8.34 ± 1.00)	−297
292	−1.56	−(6.88 ± 0.34)	−288
145	−1.15	−(6.24 ± 0.81)	−356
114	−0.163	+(5.04 ± 2.26)	−23.7
89.3	−0.168	+(9.2 ± 2.3)	−17.5
77.4	−0.166	+(18.2 ± 1.6)	−11.6
65.0	−0.101	+(25.8 ± 3.6)	−6.36

Table 2 Field dependence of the magnetization.

Temperature (°K)	*Magnetization (kG) at 10 kOe*	*at 15 kOe*
373	5.980	6.011
292	6.237	6.260
145	6.280	6.311
114	6.29	6.41
89.3	6.266	6.394
77.4	6.254	6.386
65.0	6.239	6.412

the sample. These results were used to calculate the values of the Hall mobility and of the ordinary Hall coefficient shown in Fig. 2 and of the field parameter α given in Table 1.

Thermoelectric power measurements made at room temperature and at liquid nitrogen temperature gave a value of $-57\mu V/°C$ at both temperatures.

Discussion

The results of this work are typical of most work done on transition metal oxides in that no simple unequivocal explanation is yet available. The Hall constant found here corresponds to (1 ± 0.4) hole per molecule above the transition point in contrast to the results of Lavine[8] who found 0.257 electron per molecule. Comparison of the results in Tables 1 and 2 shows that above the transition point the rate of increase of magnetization is larger than the rate of increase of Hall angle. The sign of the calculated Hall values is thus determined by the field dependence of the magnetization. Errors in the latter are estimated to be 20 percent.

Below the transition point, the temperature dependence of the Hall mobility and of the Hall constant do not support the hypothesis of conductivity by carrier hopping. The features of a normal band model are present here.

The mobility decreases with increasing temperature, and the carrier density increases. The highest occupied band is the spin-down t_{2g} band. Since we have normal semiconductive behavior, we have to conclude that this band is split in the rhombohedral phase into three one-electron bands.[11] Conductivity takes place by the excitation of carriers from the lowest, filled, spin-down t_{2g} band to the next higher empty one. This can explain the observation of a positive ordinary Hall coefficient.

Above the transition point, the positive ordinary Hall coefficient can be explained by assuming that the band edges shift slightly and that the compound becomes nearly degenerate. This two-band model is supported by the fact that the Hall effect and the thermoelectric power have opposite signs. According to the theory of irreversible thermodynamics, the thermoelectric power Q is given by

$$Q = \frac{\sum_i (F - \epsilon_i)\mu_i}{eT\sum_i \mu_i},$$

where F is the Fermi energy, ϵ_i the energy associated with the motion of carrier i and μ_i the mobility of that carrier. The sign of the contribution of a carrier to the Hall signal, however, depends on the curvature of the $\epsilon(k)$ surface. In a case of narrower bands with complicated structure, it is thus possible for a carrier to be above the Fermi energy level and make a negative contribution to the thermoelectric power while making a positive contribution to the Hall effect. Whatever the case may be, we have to assume that some degree of compensation of the Hall voltage takes place, so that the actual number of carriers is smaller than the figure of one hole per molecule mentioned above, attractive though this figure may be.

A major difficulty that remains is to explain the difference between Lavine's results[8] and ours. Lavine's crystal was grown from the melt,[12] while Kershaw and Wold grew ours at 750°C by vapor phase transport. Lavine's crystal may have been slightly oxygen deficient and contained donor states. The electrons in the conduction band are in the spin-down state, and it is not possible to explain the high concentration of negative carriers that he observed by our model without reducing the saturation magnetization noticeably. It is unfortunate that he did not explicitly report the field dependence of the magnetization, since in our work that turned out to be the crucial parameter.

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