Fig. 1. This is only roughly so. The reason for the discrepancy between them is not understood.

As remarked previously, one of the predictions of the hydrogen-like model of impurities is the existence of discrete excited levels. Such levels may be evidenced by the existence of relatively sharp absorption lines in the spectra of doped materials at low temperatures. Two such lines are found in indium-doped silicon (see Figs. 1 and 2). We have located them at 0.147 ev and 0.152 ev. Burstein has identified these lines respectively, with the $1s \rightarrow 3p$ and $1s \rightarrow 4p$ transitions.[2]

An interesting feature of these lines is their temperature dependence as illustrated in Fig. 2. Unfortunately our measurement of this dependence was hindered by an inferior resolving power ($\Delta\nu_R \sim 10^{-3}$ ev). It is, however, obvious from the figure that at about 74°K the line width is greater than 10^{-3} ev (i.e., resolving power), at about 50°K it is comparable to 10^{-3} ev and at about 20°K it is less than or equal to 10^{-3} ev. This type of temperature dependence has been previously observed in boron-doped silicon.[3] It has been treated theoretically by Lax and Burstein.[5] They indicate that the line broadening is due to a broadening of the ground state of the impurity due to an interaction with lattice vibrations. The temperature range over which the line width transition is observed in the present case is essentially that predicted by their theory.

ACKNOWLEDGMENTS

I should like to express my appreciation to W. W. Tyler for resistivity and Hall measurements and to J. H. McTaggart for his assistance.

[5] M. Lax and E. Burstein, Phys. Rev. **91**, 208 (1953).

PHYSICAL REVIEW VOLUME 99, NUMBER 2 JULY 15, 1955

Electrical Conductivity and Seebeck Effect in $Ni_{0.80}Fe_{2.20}O_4$

F. J. Morin and T. H. Geballe
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received March 25, 1955)

Electrical conductivity and Seebeck effect have been measured as functions of temperature on single-crystal samples of $Ni_{0.80}Fe_{2.20}O_4$. A thermal hysteresis has been observed in the conductivity but not in the Seebeck effect. This suggests that the hysteresis involves the charge carrier transfer process but not the production of carriers. The activation energy associated with the transfer process is estimated to be 0.10 ev in the high-temperature state and 0.06 ev in the low-temperature state.

1. INTRODUCTION

MAGNETIC losses in ferrites have been interpreted[1,2] as being due to an electron transfer of the type

$$Fe^{2+} + Fe^{3+} = Fe^{3+} + Fe^{2+},$$

with an activation energy required for the transfer process. It is generally believed that the process of electrical conduction in ferrites also involves such a transfer. We have therefore made measurements of electrical conductivity and Seebeck effect as functions of temperature in order to determine an independent value of the energy required for the electron transfer. This result is presented below. In the course of measurements, an unexpected thermal hysteresis was encountered for which we offer no explanation at the present time.

2. EXPERIMENT

The two crystals of nickel ferrite used were obtained from Linde Air Products Company. Chemical analysis indicated the composition to be $Ni_{0.80}Fe_{2.20}O_4$. The growth direction was within a few degrees of [111].

[1] J. K. Galt, Bell System Tech. J. **33**, 1023 (1954).
[2] H. P. J. Wijn and H. van der Heide, Revs. Modern Phys. **25**, 99 (1953).

A rectangular bar 0.608 in. long (in the growth direction), 0.206 in. wide, and 0.0600 in. thick was cut from the crystal. Electrical contacts were fired on in air at about 660°C for 5 minutes using a silver paste. The contacts were arranged so that 4-point electrical conductivity, Hall effect, and Seebeck effect measurements could be made. The contacts were nonrectifying. The Hall voltage was found to be too small to detect. The Seebeck voltage per degree, or thermoelectric power proved to be a smoothly varying function of temperature. The results are shown in Fig. 1 and interpreted in

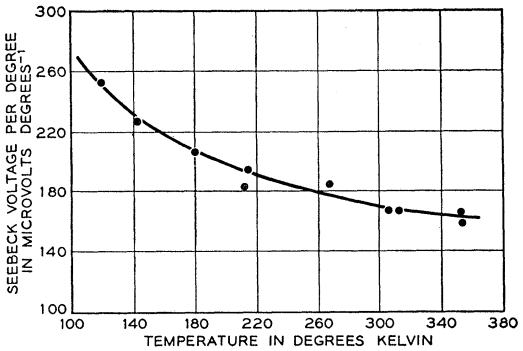

FIG. 1. Seebeck effect as a function of temperature.

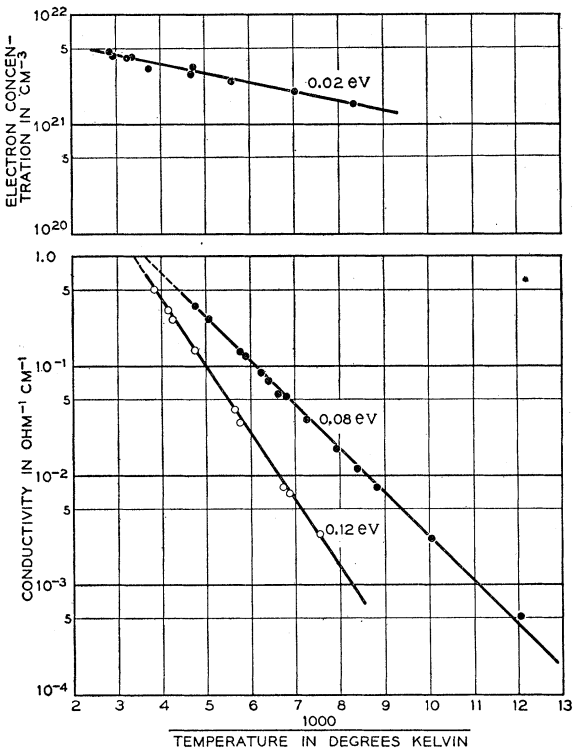

FIG. 2. Electron concentration and electrical conductivity as a function of reciprocal temperature.

the next section. The results of the electrical conductivity are shown in Fig. 2, where log conductivity is plotted against reciprocal absolute temperature. Between 130° and 210° the points fall on either of two straight lines. Below 130° the points fall on the upper line with the smaller negative slope. The points above 210° all fall on the lower line with the greater negative slope. Four times while cooling, the conductivity "jumped" from the lower curve to the upper curve; and four times while warming, the conductivity jumped from the upper curve to the lower curve. We were unable to effect a jump from one curve to the other by mechanical shock, magnetic field, or discharging a spark coil near the sample. However, there is some evidence that the magnetic field may have "conditioned" the sample to jump near the temperature at which the field was applied. The lower-curve to upper-curve jumps initially occurred around 120°K and the upper- to lower-curve jumps occurred as high as 200°K. After applying a magnetic field at 170°K, the upper- to lower-curve jump was actually observed to take place within the time constant (3 seconds) of the galvanometer at 176°K, while the sample was warming 0.3° per minute. The reverse jump was then observed to occur at 170°K while the sample was cooling 0.090° per minute. In the latter case, the cooling rate in a high vacuum was followed for over 90 minutes, with no observable change in rate occurring before, during or after the jump in conductivity. This indicates there is no latent heat associated with the jump and there is no sharp change in heat capacity near the jump.

A longitudinal section amounting to about one-third of the sample was cut off and new contacts fired on. The piezoresistance of this new sample was measured at room temperature using a stress of 5×10^7 dynes/cm². The effect was only that to be expected from dimensional change. The conductivity was measured several times over the critical temperature range and repeated the upper curve of Fig. 2, no jump was observed. A slice was cut from a second crystal and conductivity *vs* temperature was measured several times. The upper curve was repeated, no transition was found. Thus, the upper conductivity curve appears to be the one typical of these crystals.

3. ANALYSIS

The data of this experiment are interpreted in terms of a model[3] for conduction in a *d*-level semiconductor. Conductivity, as usual, is taken as the product of carrier concentration, carrier mobility, and electronic charge:

$$\sigma=n\mu e. \tag{1}$$

The relation between carrier concentration and Seebeck effect Q is assumed[4] to be

$$n=N\exp^{-Q/k}, \tag{2}$$

where N is the concentration of electronic levels involved in the conduction process. In this case, $N=2.8\times10^{22}$, the number of octahedral cation sites/cm³ of ferrite. The thermoelectric effect, which depends on carrier concentration, did not undergo a transition. The results therefore, in terms of the model, suggest that the conductivity transition involves only the charge transfer process. Carrier concentration computed from measured Q and Eq. (2) is shown in Fig. 2. The slope of this plot is 0.02 ev, the energy required for the production of carriers. The two conductivity slopes are 0.12 and 0.08 ev. Thus the energy involved in the mobility (transfer) process is 0.10 ev in the high-temperature state and 0.06 ev in the low-temperature state.

Chemical analysis indicated the first crystal to be 52.60 percent Fe and 20.05 percent Ni by weight. Assuming a complete oxygen lattice and electrical neutrality, the composition of the crystal is calculated to be

$$Ni_{0.80}{}^{2+}Fe_{0.21}{}^{2+}Fe_{1.99}{}^{3+}O_4{}^{2-}$$

Ten percent of the iron, or $\sim3\times10^{21}$ atoms/cm³, is Fe^{2+}. Since Fe^{2+} acts as a donor center with respect to Fe^{3+}, this result is in agreement with the carrier concentration determined from thermoelectric effect and thereby lends support to that calculation.

We wish to thank G. W. Hull for preparing the sample and his aid in making the measurements.

[3] F. J. Morin, Phys. Rev. **93**, 1195 (1954).

[4] However, the assumption about the Fermi level is doubtful here since the handling of the kT term is doubtful and QT is about the magnitude of kT.