Ordinary Hall Effect in Fe_3O_4 and $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ at Room Temperature*†

JEROME M. LAVINE‡

Division of Applied Science, Harvard University, Cambridge, Massachusetts

(Received November 24, 1958)

Room temperature Hall measurements on a synthetic crystal of Fe_3O_4 and on a synthetic single crystal of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ are reported. The thermoelectric power of the sample of Fe_3O_4 was also measured and verified that the sign of the charge carrier was negative. The ordinary Hall measurement of Fe_3O_4 suggests that the number of conduction electrons at room temperature is of the order of $3 \times 10^{21}/cm^3$, in rough agreement with Verwey's model. The ordinary Hall coefficient of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ also suggests a large carrier concentration, of the order of $5 \times 10^{20}/cm^3$ at room temperature. The Hall mobility of Fe_3O_4 is of the order of 0.5 cm^2/volt-sec and the Hall mobility of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ is of the order of 0.05 cm^2/volt-sec. The conductivities of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ and of a synthetic single crystal of $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$ have been measured and compared with the conductivity of Fe_3O_4 employing a simple model for the mobility and associating the activation energy obtained from resistivity data with the number of conduction electrons. The observed data are in good agreement with the simple model.

INTRODUCTION

THE ferrites are a class of metal oxides which display a negative temperature coefficient of resistivity. Fe_3O_4 has the highest room temperature conductivity, of the order of 10^2 ohm-cm^{-1} and a behavior not characteristic of the other ferrites. At $-153.8°C$, Fe_3O_4 goes through a transition causing marked changes in its physical characteristics. In the case of stoichiometric Fe_3O_4, the conductivity increases by a factor of 100 as the temperature is increased through the narrow transition region. Verwey[1] has suggested that the high conductivity of Fe_3O_4 above the transition is due to the free exchange of electrons between equivalent ions with different valence in the octahedral sites. The inverted spinel structure of Fe_3O_4 has one Fe^{2+} and one Fe^{3+} ion per Fe_3O_4 group located in octahedral sites. This may be alternatively described as two Fe^{3+} ions plus one electron. Since all occupied octahedral sites are equivalent in the absence of any order, Verwey has proposed that these extra electrons are distributed at random on the Fe^{3+} ions in the octahedral sites. This random distribution is then connected with a continuous interchange of the extra electrons on the Fe^{2+} ions. Verwey has also proposed that the low-temperature transition in Fe_3O_4 is due to the ordering of ferrous and ferric ions in the octahedral sites, resulting in a reduction of the free exchange of electrons and a reduction of the conductivity below the transition temperature. The effect of ordering would be a change of the crystal symmetry and an anisotropy in the conductivity. The anisotropy in the conductivity has been observed by Calhoun[2] and the change of crystal symmetry has been observed by Abrahams and Calhoun.[3]

It was the purpose of this investigation to measure the number of electrons contributing to the conductivity of Fe_3O_4 above the transition by measuring the ordinary Hall coefficient on a synthetic crystal of Fe_3O_4.[4] The Hall measurement was also made on a sample[5] of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ at room temperature in order to determine the effect of diluting the number of Fe^{2+} ions with Ni^{2+} ions in the octahedral sites. The conductivities of the sample of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ and of a sample[5] of $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$ were measured as a function of temperature.

THE MEASUREMENT

It has been well established[6-11] that the Hall voltage in ferromagnetics is given by

$$V_H = (R_0 H + R_1 M)I/t, \tag{1}$$

where V_H = the Hall voltage in volts, R_0 = the ordinary Hall coefficient in volt-cm/amp-oersted, R_1 = the extra-ordinary Hall coefficient in volt-cm/amp-gauss, H = the magnetic field inside the sample in oersteds, M = the magnetization of the sample in gauss, I = the current through the sample in amperes, and t = the sample dimension parallel to the applied field, for a rectangular sample, in cm.

The ordinary Hall coefficient, R_0, is customarily determined by measuring the slope of the curve of the

[1] E. J. W. Verwey and P. W. Haayman, Physica 8, 979 (1941).
[2] B. P. Calhoun, Phys. Rev. 94, 1577 (1954).
[3] S. C. Abrahams and B. A. Calhoun, Acta Cryst. 6, 105 (1953).
[4] This sample was generously provided by Professor A. R. Von Hippel of the Laboratory for Insulation Research, Massachusetts Institute of Technology.
[5] The single crystals of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ and $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$ were generously supplied by Dr. W. Clarke of the Linde Air Products Company.
[6] A. Kundt, Wied. Ann. 49, 257 (1893).
[7] A. W. Smith, Phys. Rev. 30, 1 (1910).
[8] A. W. Smith and R. W. Sears, Phys. Rev. 34, 166 (1929).
[9] E. M. Pugh, Phys. Rev. 36, 1503 (1930).
[10] E. M. Pugh, and T. W. Lippert, Phys. Rev. 42, 709 (1932).
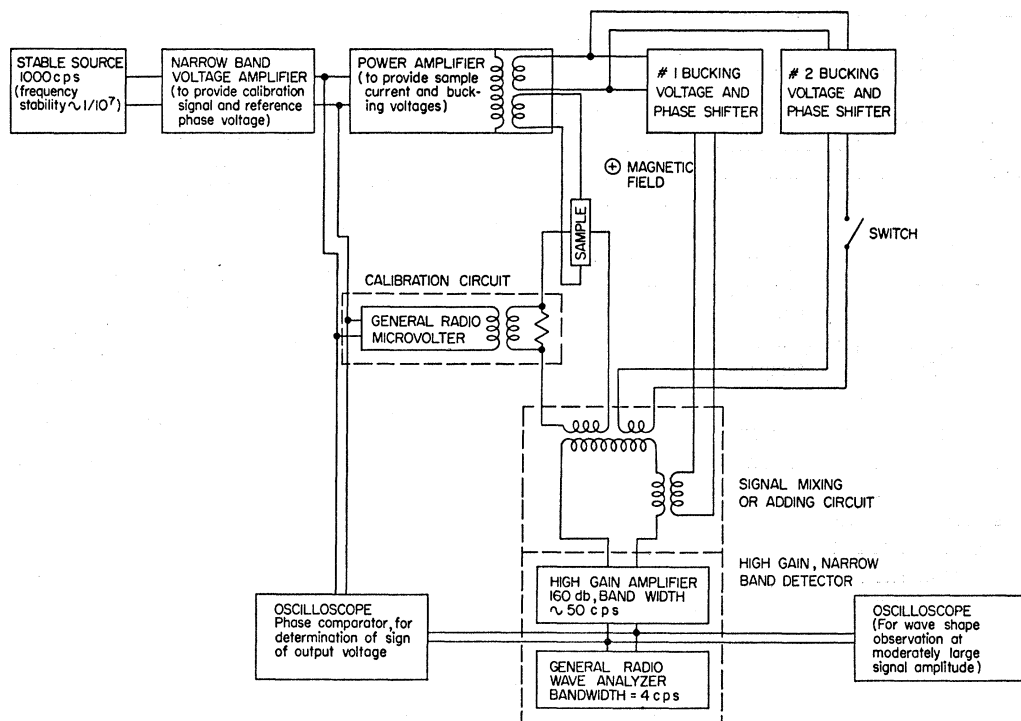[11] Pugh, Rostoker, and Schindler, Phys. Rev. 80, 688 (1950).

FIG. 1. A block diagram of the equipment.

Hall voltage as a function of applied magnetic field above technical saturation where M is essentially constant. In the case of Fe_3O_4, the extraordinary Hall voltage (R_1MI/t) is about 100 times larger than the ordinary Hall voltage (R_0HI/t) requiring high resolution measurement techniques. Due to the unavoidable asymmetry in positioning the Hall probes, there exists an IR drop between the probes which is both magnetic field and temperature dependent. The voltage due to the magnetoresistance is about 3 times larger than the ordinary Hall voltage, but the two can be separated electrically by reversing the magnetic field. In order to prevent temperature changes in the IR drop from masking the desired ordinary Hall voltage, temperature stability of the order of 10^{-3}°C was necessary. This requirement prevented measurements at temperatures different from room temperature, and demanded that the sample current be held to low values. Thus, although the ordinary Hall coefficient of Fe_3O_4 was substantially larger than that of a metal, the product R_0HI/t was considerably smaller than for a metal, for typical laboratory fields. The available Hall power required a system capable of detecting about 10^{-18} watt with a noise level near 10^{-9} volt. Moreover, although small currents were used, the IR drop was of such magnitude that the current was required to be stable to about one part in 10^5. This stability was also required of the voltage used to buck out the IR drop. In making Hall measurements, the presence of other transverse voltages can

only be excluded by using an ac technique. For this measurement, a 1000-cps current and a dc magnetic field was used with a field-reversing technique. Figure 1 shows a block diagram of the system used. The No. 1 bucking unit bucked out the IR drop and other voltages present, while the No. 2 bucking unit was used to obtain fine resolution in the Hall voltage. The system and the measurement technique have been described in detail elsewhere.[12,13]

A detailed analysis of the errors[14] involved in these measurements yields about 10% uncertainty in the measurement of the Hall voltage of Fe_3O_4 and about 6% uncertainty in the Hall voltage of $(NiO)_{0.75}(FeO)_{0.25}$ (Fe_2O_3). However, the largest uncertainty arises because it was not possible to ensure that M was constant over the region of the measurement. The approach to saturation[15] is given by

$$M = M_s(1 - a/H - b/H^2 \cdots) + K_0H. \qquad (2)$$

The term in a/H has been explained by Néel[16] as due to nonmagnetic cavities or inclusions in the material. The term in b/H^2 depends upon the magnetic anisotropy

[12] J. M. Lavine, Technical Report No. 225, Cruft Laboratory, Harvard University, March 10, 1956 (unpublished).

[13] J. M. Lavine, Rev. Sci. Instr. 29, 970 (1958).

[14] J. M. Lavine, thesis, Harvard University, May, 1955 (unpublished), Appendix A.

[15] R. M. Bozorth, Ferromagnetism (D. Van Nostrand Company, Inc., New York, 1951), p. 486.

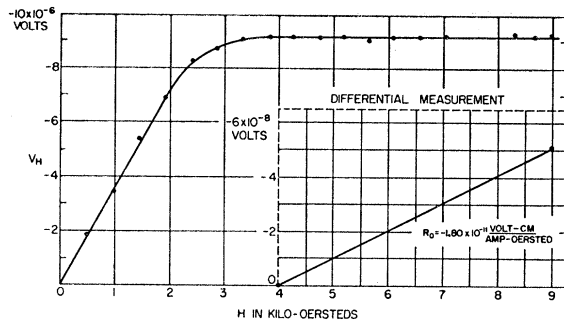[16] L. Néel, J. phys. radium 9, 184 (1948).

FIG. 2. The Hall voltage as a function of applied magnetic field for Fe_3O_4 at room temperature.

and the elastic state of the crystal and is strongly dependent upon crystal orientation with respect to the magnetic field. The K_0 term which may be crudely described as the field alignment of temperature disoriented spins has been calculated by Holstein and Primakoff.[17] Measurements[18] were made on the Fe_3O_4 sample to try to determine the change in M above saturation, and thus calculate the uncertainty in the ordinary Hall voltage. However, it could only be concluded that these effects did not alter the measured voltage more than percentage-wise. Because of this uncertainty in the Fe_3O_4 measurement, it is desirable that the value of R_0 determined from the ordinary Hall voltage be considered as an upper limit. In the case of $(NiO)_{0.75}$ $(FeO)_{0.25}(Fe_2O_3)$ this effect introduces about 10% uncertainty in the determination of R_0.

Because of the temperature stability requirements in the case of Fe_3O_4, the sample holder was enclosed in a Dewar thus restricting the magnet gap to two inches, and the maximum field to 9000 oersteds. In the case of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ the sample was measured outside of the Dewar, in a one-inch gap, with a maximum field of 12 000 oersteds.

RESULTS

(A) Fe_3O_4

The sample of Fe_3O_4 used in this measurement was grown by Smiltens[19] and was one of the first large synthetic ferrite crystals grown. With respect to stoichiometry and impurities, it was substantially better than natural crystals. It was not, however, a single crystal, but was composed of several large grains. The multi-grain structure of the sample did not alter the Hall voltage, which is isotropic, but probably did introduce noise which hindered the measurement somewhat. The sample was cylindrical with 0.25-inch diameter, and 0.50 inch long.

Figure 2 shows a plot of the Hall voltage of the Fe_3O_4 sample as a function of the applied magnetic field.

[17] T. Holstein and N. Primakoff, Phys. Rev. **58**, 1098 (1940).
[18] Reference 12, Appendix B.
[19] J. Smiltens, J. Chem. Phys. **20**, 990 (1952).

The lower portion of the figure shows the result of the differential measurement used to resolve the slope of the curve above technical saturation. Because of the small signal-to-noise ratio, probably due to noise generated at the contacts, in the bulk, and at the grain boundaries, and also due to temperature fluctuations, no resolution of the Hall voltage between 4000 and 9000 oersteds was obtained. However, 31 independent measurements were made between the two values of applied field so that the uncertainty in the measured voltage was no greater than 10%. The change in the Hall voltage between 5000 and 9000 oersteds was 5.04×10^{-8} volt for a sample current of 300 ma. Taking into account the correction[20] for a length-to-width ratio less than 4, the value of R_0 deduced from this voltage is $R_0 = -1.8 \times 10^{-11}$ volt-cm/ amp-oersted. The value of N^*, the effective number of conduction electrons/cm^3, obtained from the relation

$$R_0 = 10^{-8}/N^*e, \qquad (3)$$

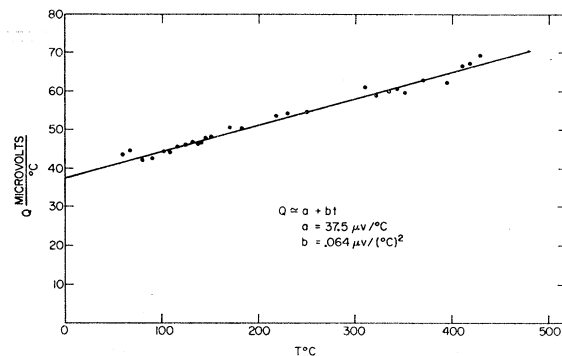where $e = -1.60 \times 10^{-19}$ coulomb, is $N^* = 3.47 \times 10^{21}$

FIG. 3. The thermoelectric power of Fe_3O_4 against Cu as a function of temperature.

electrons/cm^3. Because of the uncertainty of R_0, the value of N^* is a lower limit on the charge carrier density. Thermoelectric power measurements of the Fe_3O_4 sample against copper, shown in Fig. 3, also indicate that the sign of the carrier is negative.

The upper limit of the room temperature Hall mobility, μ_H, obtained from the relation

$$\mu_H = R_0\sigma 10^8, \qquad (4)$$

where $\sigma = 250$ ohm-cm^{-1}, is $\mu_H = 0.450$ cm^2/volt-sec.

Measurements of the conductivity as a function of temperature were also made, but since measurements on Smiltens' crystals have been reported by Calhoun[2] they are not included here.

In Table I are listed some of the physical properties of Fe_3O_4 sample No. 18. All temperature dependent values are room temperature (300°K) values unless otherwise stated.

[20] Isenberg, Russell, and Greene, Rev. Sci. Instr. **19**, 685 (1948).

(B) $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$

The sample of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ obtained from the Linde Air Products Company was a single crystal. The measurements on this sample were subject to less uncertainty than in the case of Fe_3O_4 because the signal-to-noise ratio was larger. Figure 4 shows the curve of the Hall voltage as a function of applied magnetic field at room temperature for this sample. The estimated uncertainty in the values of voltage measured above saturation is 6.3%. The value of R_0 deduced from the differential measurement is $R_0 = -1.40 \times 10^{-10}$ volt-cm/amp-oersted. The value of N^* obtained from R_0 is $N^* = 4.46 \times 10^{20}$ electrons/cm^3. The room temperature Hall mobility is calculated to be $\mu_H = 0.0476$ cm^2/volt sec. In Fig. 5 is shown a plot of the resistivity of this sample as a function of reciprocal temperature.

Listed in Table II are some of the physical properties
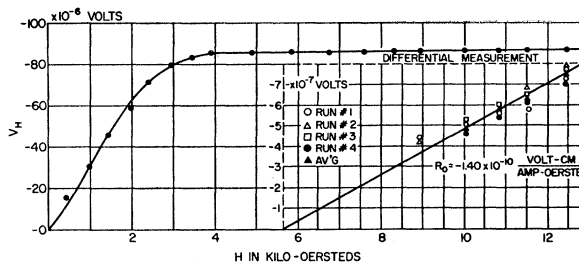

FIG. 4. The Hall voltage as a function of applied magnetic field for $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ at room temperature. Sample thickness, $t = 0.100$ inch; $I = 200$ ma.

TABLE I. Some physical properties of Fe_3O_4

Density (20°C)	$d = 5.185$ g/cm^3
Molecular weight	$w = 231.55$ g/mole
Number of molecules/cm^3	$n_0 = 1.35 \times 10^{22}$/cm^3
Conductivity	$\sigma = 250$ (ohm-cm)$^{-1}$
Activation energy obtained from conductivity data below room temperature	$E = 0.039$ electron volt
Upper limit of the ordinary Hall coefficient	$R_0 = -1.80 \times 10^{-11}$ volt-cm/amp-oersted
Lower limit of the effective number of electrons/cm^3 obtained from R_0	$N^* = 3.47 \times 10^{21}$/cm^3
Lower limit of the effective number of electrons/Fe_3O_4 molecule	$n^* = 0.257$/molecule
Upper limit of the Hall mobility	$\mu_H = 0.450$ cm^2/volt-sec
Extraordinary Hall coefficient	$R_1 = -3.28 \times 10^{-8}$ volt-cm/amp-gauss
Saturation magnetization at 0°K	$M_0 = 510$ gauss
Saturation magnetization	$M_s = 472.3$ gauss
Curie temperature	$T_c = 574$°C
Transition temperature	$T = -153.8$°C

of Linde Air Products Company sample 8/18/52A, $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$. All temperature-dependent values are room temperature (300°K) values unless otherwise stated.

(C) $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$

The sample of $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$ obtained from Linde Air Products Company was also a single crystal. No Hall measurements were made on this sample, but the resistivity was measured as a function of temperature. This is shown in Fig. 5. Some of the physical properties of this sample at room temperature (300°K) are listed in Table III.

DISCUSSION

(A) Fe_3O_4

The number of molecules/cm^3 in Fe_3O_4 at room temperature is $n_0 = 1.35 \times 10^{22}$/cm^3. On the basis of

Verwey's simple picture of one electron per Fe_3O_4 molecule contributing to the current, we expect a value of N^* close to n_0. The value of N^* observed, $N^* = 3.47 \times 10^{21}$/cm^3, represents a lower limit of the true value of N^* and is about $\frac{1}{4}$ the value of n_0. Thus, unless the small value of R_0 is due to partial compensation by carriers of opposite sign, the observed value of N^* suggests a large carrier density roughly in accord with Verwey's hypothesis.

The conductivity of synthetic single crystals of Fe_3O_4 grown by Smiltens has been measured by Calhoun.[2] Between −100°C and 200°C, the conductivity data have been fitted by the equation

$$\sigma = AT^{-\frac{3}{2}}e^{-E/kT}, \tag{5}$$

where $E = 0.039$ electron volt. If we rewrite Eq. (5)
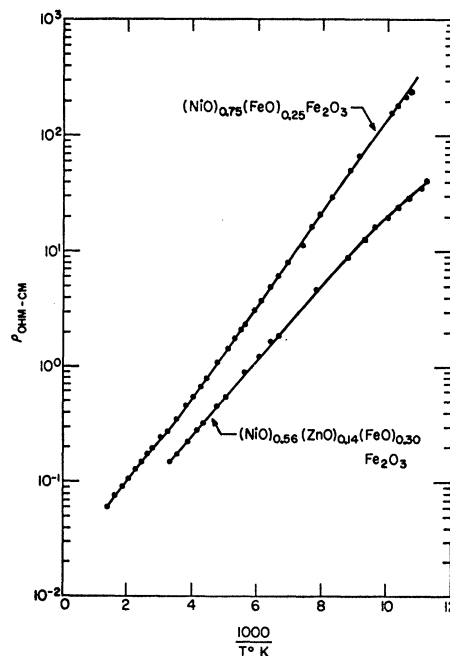
$$\sigma = n_0 e^{-E/kT} e\mu(T) = ne\mu(T), \tag{6}$$

FIG. 5. The resistivity of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ and $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$ as a function of reciprocal temperature.

TABLE II. Some physical properties of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$.

Density	$d = 5.35$ g/cm^3
Molecular weight	$w = 233.68$ g/mole
Number of molecules/cm^3	$n_0 = 1.38 \times 10^{22}$/cm^3
Conductivity	$\sigma = 3.40$ (ohm-cm)$^{-1}$
Activation energy obtained from conductivity data below room temperature	$E = 0.078$ electron volts
Ordinary Hall coefficient	$R_0 = -1.40 \times 10^{-10}$ volt-cm/amp-oersted
Effective number of electrons/cm^3 obtained from R_0	$N^* = 4.46 \times 10^{20}$/cm^3
Effective number of electrons/Fe$_3$O$_4$ molecule	$n^* = 0.129$/molecule
Hall mobility	$\mu_H = 0.0476$ cm^2/volt-sec
Extraordinary Hall coefficient	$R_1 = -16.4 \times 10^{-8}$ volt-cm/amp-gauss
Saturation magnetization at 0°K	$M_0 = 338$ gauss
Saturation magnetization	$M_s = 308$ gauss
Curie temperature	$T_c = 597$°C

where e is the charge of the electron, $\mu(T)$ is the temperature-dependent mobility, then n, the number of electrons/cm^3 contributing to the conductivity, is given by

$$n = n_0 e^{-E/kT}. \tag{7}$$

If we insert the value of $n_0 = 1.35 \times 10^{22}$/cm^3 and $E = 0.039$ electron volt, at room temperature we obtain $n = 2.98 \times 10^{21}$/cm^3, in good agreement with $N^* = 3.47 \times 10^{21}$/cm^3.

(B) $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$

The resistivity of stoichiometric NiOFe$_2$O$_3$ is greater than 10^6 ohm-cm. In NiOFe$_2$O$_3$ the ions in the octahedral sites are not identical, and hence the distribution of electrons on the octahedral ions is not random. Because of its low conductivity, we may assume that the Ni^{2+} ion does not readily contribute an electron to the conduction process.

In the sample of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$, however, one-fourth of the molecules are Fe$_3$O$_4$ molecules. Therefore, on the basis of the simple Verwey model we would expect a number of electrons equal to the number of Fe$_3$O$_4$ molecules in this sample. The value of n_0 of this sample is $n_0 = 1.38 \times 10^{22}$/cm^3, and the number of Fe$_3$O$_4$ molecules is one-fourth of this number, or 3.45×10^{21}/cm^3. The observed value of $N^* = 4.46 \times 10^{20}$/cm^3 is roughly 1/10 of the number of Fe$_3$O$_4$ molecules. However, if we calculate a value of n using Eq. (7) with a value of $E = 0.078$ electron volts

TABLE III. Some physical properties of $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$.

Density	$d = 5.24$ g/cm^3
Molecular weight	$w = 234.49$ g/mole
Number of molecules/cm^3	$N_0 = 1.35 \times 10^{22}$/cm^3
Conductivity	$\sigma = 6.67$ (ohm-cm)$^{-1}$
Activation energy obtained from the conductivity data below room temperature	$E = 0.066$ electron volt

derived from conductivity data (see Fig. 5) we obtain

$$n = (n_0/4)e^{-E/kT} = 1.68 \times 10^{20}/cm^3, \tag{8}$$

which is roughly one-third of the observed value of N^*.

In the case of Fe$_3$O$_4$, we assume that the electron conducts by hopping along Fe^{3+} ions in the octahedral sites. In the case of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$, we expect that the mobility will be reduced because we do not have similar ions in all of the octahedral sites. If we assume that the mobility of $(NiO)_{0.75}(FeO)_{0.25}$- (Fe_2O_3) is about $\frac{1}{4}$ the mobility of Fe$_3$O$_4$ because, on the average, each Fe$_3$O$_4$ molecule will be $\frac{3}{4}$ surrounded by NiO Fe$_2$O$_3$ molecules, and compare the ratio of the conductivities of Fe$_3$O$_4$ and $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ using the values of n obtained from Eqs. (7) and (8), we obtain at room temperature

$$\frac{\sigma(Fe_3O_4)}{\sigma[(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)]}$$

$$= \frac{1.35 \times 10^{22} e^{-0.039/kT} e\mu(T)}{(1.38/4) \times 10^{22} e^{-0.078/kT} e \times \frac{1}{4}\mu(T)} = 70.8. \tag{9}$$

The observed ratio of the conductivities at room temperature is 73.5.

(C) $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$

In the case of $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$, we expect the conductivity to be roughly the same order of magnitude as the conductivity of $(NiO)_{0.75}(FeO)_{0.25}$- (Fe_2O_3) since the number of Fe$_3$O$_4$ molecules is about the same. The conductivity observed at room temperature, $\sigma = 6.67$ ohm-cm^{-1}, is about a factor of 2 larger than the conductivity of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ at room temperature. We then compare the conductivity of $(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)$ with the conductivity of Fe$_3$O$_4$ at room temperature. We obtain n from Eq. (7) assuming that n_0 is equal to the number of Fe$_3$O$_4$ molecules or 3/10 of the total number of molecules, and we assume that the mobility is 3/10 the mobility of Fe$_3$O$_4$. Using a value of $E = 0.066$ electron volt derived from the data of Fig. 5, we obtain

$$\frac{\sigma(Fe_3O_4)}{\sigma[(NiO)_{0.56}(ZnO)_{0.14}(FeO)_{0.30}(Fe_2O_3)]}$$

$$= \frac{1.35 \times 10^{22} e^{-0.039/kT} e\mu(T)}{(3/10)(1.35 \times 10^{22}) e^{-0.066/kT} e(3/10)\mu(T)} = 31.4. \tag{10}$$

The observed ratio of the conductivities at room temperature is 37.5.

(D) Concluding Remarks

The conduction mechanism of the metal oxides, of which the ferrites are a special case, is presently not

very well understood. The conductivity of most transition metal oxides is very low, $\sigma < 10^{-7}$ ohm-cm^{-1}, in contradiction to the normally expected high conductivity of solids with incompletely filled bands. DeBoer and Verwey[21] and Mott[22] have suggested that these materials be treated in a way deviating fundamentally from the Wilson theory.[23,24] They have proposed that a suitable approximation to the state of such a system be obtained by starting with atomic wave functions and forming lattice wave functions analogous to the Heitler-London treatment of molecules. The transport of electricity is then associated with certain excited states of the metal ion.

The usual example of this mechanism is the conductivity of NiO. The Ni ion in the normal state is Ni^{2+}. An excited state giving rise to an electric current would be a state in which two Ni^{2+} are converted to one Ni^{3+} and one Ni^{+}. As may be expected, such a mechanism results in a negligibly small current, and the conductivity of pure, stoichiometric NiO is of the order of 10^{-8} ohm-cm^{-1}. However, if an excess of oxygen is introduced into the lattice, resulting in metallic deficiencies, then around each missing Ni^{2+} ion, two Ni^{3+} ions are created. Under these conditions, when a normal Ni^{2+} ion is excited to an Ni^{3+} state plus an electron, and if this electron becomes trapped by an Ni^{3+} ion in the vicinity of the metal deficit, then the electron deficit may propagate through the crystal. This mechanism can then provide a current as well as an activation energy for the process, which is observed. Thus, the presence of identical ions with different valence in identical lattice sites is seen to be a condition for conduction in this oxide.

In the case of Fe₃O₄, we have a similar but not identical situation. The presence of Fe^{2+} and Fe^{3+} ions in octahedral sites occurs as a consequence of the inverted spinel structure. Under these conditions, we would expect that an electron would be free to wander through the crystal with zero activation energy. Thus the presence of a small but finite activation energy in the region above the transition requires explanation, which has not been forthcoming.

Verwey and Haayman[1] have measured the conductivity of sintered bars of Fe₃O₄ with deviations from stoichiometry resulting in deficiencies of Fe^{2+} ions in octahedral sites. Their data indicate that above the transition the conductivity of Fe₃O₄, unlike that of NiO, decreases with increasing number of deficits, while the activation energy increases. They have associated the increase of activation energy with an increase of the average energy needed to prevent the electrons from being trapped somewhere in the lattice.

They suggest that the octahedral holes act as negative charge centers which tend to surround themselves with Fe^{3+} ions and hence disturb the random distribution of the electrons on the octahedral ions.

This may then suggest that in pure stoichiometric Fe₃O₄ the activation energy may approach zero. While this is a possibility, it is more than likely that Smiltens' crystals contain few octahedral ion deficiencies.

Below the transition, the work of Verwey,[25] Verwey and Haayman,[1,26] supported by the work of Calhoun[2] has indicated that Fe₃O₄ is in an ordered state. The activation energy observed below the transition may then be associated with the observed order. One may then speculate upon the existence of short-range order in the region above the transition. However, the order of magnitude of the activation energy below the transition does not agree very well with the energy difference between the ordered and disordered state calculated for an ionic crystal, and no calculations have been carried out above the transition.

Morin[27,28] has made measurements on sintered samples of αFe₂O₃ and NiO with deviations from stoichiometry. His Hall effect measurements were inconclusive, but he has inferred a value of N^* from thermoelectric measurements. The thermoelectric and conductivity data then indicate that an activation energy is to be associated with the mobility. At high temperature, this activation energy tends toward 0.1 electron volt for both the αFe₂O₃ and NiO samples. He has then suggested that the 0.1 electron volt may be the energy required for the fundamental transfer of an electron from the potential well of one cation to the potential well of the next cation.

It may be proper to associate the observed activation energy of Fe₃O₄ above the transition with the mobility, but no conclusive arguments for doing this have yet been presented. On the other hand, the association of the activation energy with the carrier density is also without supporting argument and was done to best fit the data. In this respect, the measurements reported here are inconclusive because they have not been made as a function of temperature.

These remarks simply point out the lack of a coherent picture of the conductivity of the metal oxides. The condition of similar ions with different valence in identical lattice sites seems to be a rather general condition for an appreciable conductivity, as has been pointed out again, more recently, by Verwey,[29] but even the mechanism by which the electron hops has not been clarified.

While the measurements reported here shed no light

[21] J. H. DeBoer and E. J. W. Verwey, Proc. Phys. Soc. (London) A49 (extra part), 59 (1937).
[22] N. F. Mott, Proc. Phys. Soc. (London) A62, 416 (1949).
[23] A. H. Wilson, Proc. Roy. Soc. (London) A134, 277 (1931).
[24] A. H. Wilson, Proc. Roy. Soc. (London) A134, 458 (1931).

[25] E. J. W. Verwey, Nature 144, 327 (1939).
[26] Verwey, Haayman, and Romeijn, J. Chem. Phys. 15, 181 (1947).
[27] F. J. Morin, Phys. Rev. 93, 1195 (1954).
[28] F. J. Morin, Phys. Rev. 93, 1199 (1954).
[29] E. J. W. Verwey, Semiconducting Materials (Butterworths Publications, Ltd., London, 1951), p. 151.

upon the conductivity mechanism, they do suggest that the number of electrons involved in the conductivity of Fe_3O_4 is large. While the possibility that the observed value of R_0 is small because of partial compensation by positive carriers is not to be ignored, nevertheless the low conductivity of Fe_3O_4 with respect to metals is probably due to a low mobility. The limited data reported here and the low conductivity of $NiOFe_2O_3$ also suggest that the condition of equivalent ions with different valence in identical sites is a necessary condition for conductivity in these materials.

Thermal Resistance due to Isotopes at High Temperatures

V. AMBEGAOKAR*
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania
(Received November 24, 1958)

In pure dielectric crystals, the isotopic variations of atomic mass contribute a temperature-independent thermal resistance at high temperatures. This resistance has been calculated using a Debye model of the vibrational spectrum. Umklapp processes are treated as the dominant scattering mechanism. The distribution of the heat current over the vibrational modes is known for low frequencies. This distribution is considered to apply over the whole frequency spectrum. The calculated result is compared with the experiments of Geballe and Hull on isotopically pure germanium. A satisfactory agreement with experiment is obtained.

IN many dielectric crystals heat is transported principally by lattice vibrations. A thermal resistance, or finite thermal conductivity, results from interactions between phonons and from the scattering of phonons by crystal imperfections. In pure crystals of a single chemical constituent, with which this paper is concerned, the natural isotopic variations of atomic mass will scatter phonons. In contrast to phonon-phonon scattering which increases with temperature, the scattering of phonons by mass variations is temperature independent. Thus, at high temperatures isotopic scattering does not affect the steady-state distribution of phonons in a temperature gradient and simply leads to an additional resistance independent of the temperature.[1] It is the aim of this paper to calculate that resistance.

The scattering of phonons by mass irregularities is calculable from first principles. Klemens[2] has shown that it is described by a relaxation time, τ_I, which in the Debye approximation is given by

$$1/\tau_I(\omega) = \Omega\Gamma\omega^4/4\pi c^3 \equiv A\omega^4,$$

where

$$\Gamma = \sum_i f_i(\Delta m_i/m)^2.$$

(1)

Here Ω is the volume per atom of the crystal, f_i is the fraction of atoms with mass variation Δm_i, m is the average mass of all atoms, c is the velocity of sound in the Debye model, and ω is the phonon frequency. We see that isotopes are most effective in scattering short-wavelength phonons. Even in this region, though, the temperature independence of isotope scattering will result in its being a small effect at high enough temperatures.

Umklapp processes are the dominant scattering mechanism at high temperatures. Umklapp scattering for low-frequency phonons has been treated by Klemens,[3] who has shown that at low temperatures it is describable to first order by a relaxation time, τ_U, such that

$$\tau_U \propto 1/\omega^2, \qquad \omega \ll \omega_D,$$

(2)

where ω_D is the Debye limiting frequency. The expression (2) can be shown to be also valid at high temperatures.

We shall consider that all long-wave phonons are scattered in the same way. In general, special consideration must be given to the long-wave longitudinal phonons, for it is well known that such phonons cannot take part in Umklapp processes. However, Herring[4] has shown that in crystals of high enough symmetry long-wave longitudinal phonons are converted into transverse phonons, by ordinary momentum conserving 3-phonon processes, rapidly enough to avoid a low-frequency catastrophe in the conductivity. In particular, for cubic materials the relaxation time for this process

* Permanent address: Department of Physics, Carnegie Institute of Technology, Pittsburgh 32, Pennsylvania.
[1] This point is discussed by R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, 1955), p. 52.
[2] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

[3] P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).
[4] C. Herring, Phys. Rev. **95**, 954 (1954).