

## Electrical Properties of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

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The conductivity, Seebeck effect, and optical transmission of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> have been analyzed using two alternative models. The first model assumes conduction to occur in the  $d$  levels of Fe ions and yields a quantitative fit to the data. Mobility behavior determined with this model is explained in terms of wavy bands. The second model assumes conduction in the  $sp$  bands of oxygen in addition to  $d$ -level conduction. It is shown qualitatively to be a reasonable model.

### 1. INTRODUCTION

IN a previous paper on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>1</sup> conductivity and Seebeck effect data were presented. An attempt was made to interpret the data in terms of the usual band theory for semiconductors. The behavior of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> differs in several important ways from the predictions of the theory. The following observations are difficult to explain. Intrinsic-like samples can be made  $n$  type or  $p$  type (judging from the sign of the Seebeck effect) without changing their conductivity; no normal Hall effect is found; mobility as determined from application of the band theory is unusually low and shows an anomalous temperature dependence; impurity concentration predicted from electrical results disagrees by several decades with chemical analysis. Similar results<sup>2</sup> for NiO have confirmed the idea that the conduction mechanism in these materials differs fundamentally from the mechanism found in silicon and germanium.

In this paper the results reported in reference 1 together with chemical analysis of the samples and optical transmission data are discussed. Two alternative models are proposed to explain these data. The first model to be considered assumes conduction to involve only electrons and holes in the  $d$  levels of Fe ions. This is consistent with low mobility carriers and the fact that no normal Hall effect is detected. The model leads to a quantitative fit of the data. Impurity concentration determined electrically agrees with that determined by chemical analysis. Mobility varies over the range  $10^{-6}$  to  $10^{-1}$  cm<sup>2</sup>/volt sec. It varies with impurity concentration and increases exponentially with temperature. This behavior suggests the presence of wavy bands. At high temperatures and at high-impurity concentrations, where wavy bands may be said to have been smoothed out by high carrier concentration, a mobility behavior is found in both Fe<sub>2</sub>O<sub>3</sub> and NiO having an apparent activation energy of  $\sim 0.1$  ev. The question is raised as to whether 0.1 ev represents the energy required to transfer a charge carrier from one Fe ion to another and whether this energy is related to the antiferromagnetic exchange energy  $kT_C$ .

The second model assumes conduction to involve  $d$  electrons and holes, and also  $sp$  electrons and holes in the bands associated with the O ions. So many unknown parameters are involved in this model that only a qualitative discussion can be given. This model is shown to be reasonable when applied to Fe<sub>2</sub>O<sub>3</sub>. It has been fitted quantitatively to the data for NiO which is believed to constitute a simpler case.

### 2. $d$ LEVEL CONDUCTION

Results of the previous attempt to analyze the data suggested the possibility that mobility in Fe<sub>2</sub>O<sub>3</sub> is unusually low. A rough estimate of the magnitude of mobility may be made by the following consideration. It is observed that about  $10^{-2}$  atom percent Ti must be added to Fe<sub>2</sub>O<sub>3</sub> in order to change its room temperature conductivity appreciably. To produce a comparable change in the conductivity of germanium only about  $10^{-7}$  atom percent of As need be added. It is concluded that the mobility of carriers in Fe<sub>2</sub>O<sub>3</sub> is the order of  $10^3 \times 10^{-7} / 10^{-2} = 10^{-2}$  cm<sup>2</sup>/volt sec. Failure to detect a Hall effect is consistent with this low mobility. Such behavior suggests that conduction is occurring in exceedingly narrow bands or in localized levels. The results of the analysis do not depend upon whether narrow bands or localized levels are assumed. However, in Sec. 2.3, mobility is shown to have an apparent activation energy. This suggests that conduction involves localized levels. These levels can probably be identified as the  $d$  levels of iron since the levels of oxygen constitute a wide band in ionic oxides such as Fe<sub>2</sub>O<sub>3</sub>.

An energy-level scheme is shown in Fig. 1. The  $d$  levels are shown lying between the filled and empty  $sp$  bands of oxygen. These bands are assumed in this section to be so far from the  $d$  levels that they play no part in conduction. The intrinsic ionization energy  $E_G$  represents the energy required to create an electron-hole pair, that is an Fe<sup>2+</sup> and an Fe<sup>4+</sup>. These diffuse from one cation site to the next by the exchange of an electron. Donor and acceptor ionization energies are represented in Fig. 1 by  $E_D$  and  $E_A$ . The distance of the Fermi level above the filled levels is represented by  $E_F$ .

Where energy bands are wide, carrier concentration depends upon the level density near the band edge. For bands less than  $kT$  wide or for localized levels, carrier

<sup>1</sup> F. J. Morin, Phys. Rev. **83**, 1005-1010 (1951).

<sup>2</sup> F. J. Morin, following paper [Phys. Rev. **93**, 1199 (1954)].

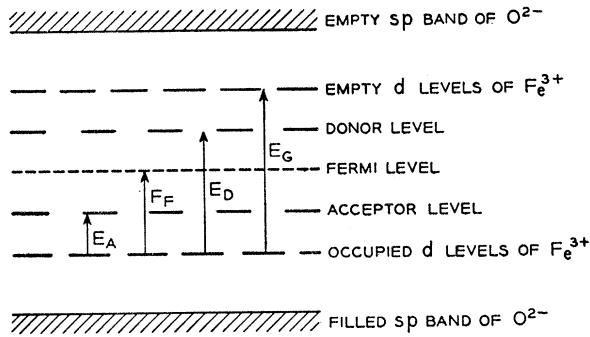


FIG. 1. Energy-level scheme assumed in the analysis of the data.

concentration must depend upon the total level density. It is assumed, therefore, that electron and hole concentrations are given by

$$n = N \exp[-(E_G - E_F)/kT], \quad (1)$$

$$p = N \exp(-E_F/kT), \quad (2)$$

where  $N = 4 \times 10^{22}$  iron atoms per  $\text{cm}^3$  of crystal. The assumption of narrow bands or localized levels also leads to the assumption that the kinetic energy term in the Seebeck effect is negligible so that for electrons alone,

$$QT = E_G - E_F, \quad (3)$$

and for holes alone,

$$QT = E_F, \quad (4)$$

where  $Q$  is the Seebeck effect in volts per degree. When both holes and electrons are involved two expressions are necessary, that for conductivity,

$$\sigma = \sigma_n + \sigma_p, \quad (5)$$

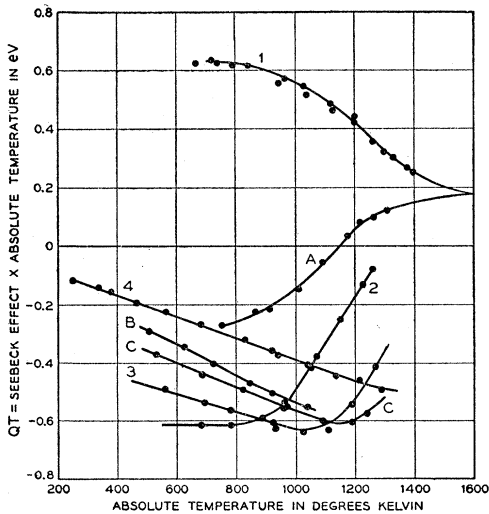


FIG. 2. The product of Seebeck effect and absolute temperature as a function of absolute temperature for samples of  $\alpha\text{-Fe}_2\text{O}_3$ . Sample composition given in Table I.

and that for Seebeck effect,

$$QT\sigma = -(E_G - E_F)\sigma_n + E_F\sigma_p. \quad (6)$$

Combining (5) and (6) yields

$$\sigma_n = \sigma(E_F - QT)/E_G. \quad (7)$$

One more equation is needed in fitting the data:

$$\sigma_n/\sigma_p = (\mu_n/\mu_p) \exp[(2E_F - E_G)/kT], \quad (8)$$

where  $\mu_n$  and  $\mu_p$  are electron and hole mobilities.

### 2.1 SEEBECK EFFECT

Seebeck effect data from reference 1 is shown replotted in Fig. 2. Sample *D* has been omitted for clarity. Sample 1 is *p* type, the others are *n* type.  $QT$  increases (negatively) with temperature in the range of impurity conductivity. It tends toward a positive value as conduction enters what is assumed to be the intrinsic range. An extrapolation of the data suggests that  $QT$  (sample 1) =  $QT$  (sample *A*) when  $T > 1600^\circ$ .

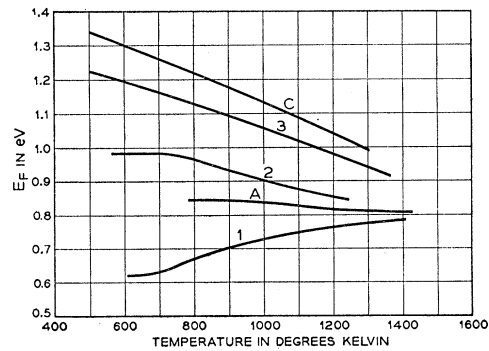


FIG. 3. Fermi energy as a function of absolute temperature computed as described in Sec. 2.1.

If this is assumed to represent an intrinsic region where  $E_F = E_G/2$  and  $n = p$ , then a positive  $QT$  may mean that  $\mu_p > \mu_n$ . By assuming a value for  $E_G$ , the ratio  $\mu_n/\mu_p$  can be computed from  $\sigma$  and  $QT$  measured in this range using Eqs. (5) and (7). The assumed value for  $E_G$  can then be checked using Eqs. (5) and (8) by computing a fit to measured  $\sigma$  and  $QT$  in the range where  $n \neq p$  but both are important. When this is done it is found that a fit can be obtained for samples 1, 2, and *A* when  $E_G = 1.6$  eV and  $\mu_n/\mu_p = 0.635$ , and a fit for samples 3 and *C* when  $E_G = 1.7$  eV and  $\mu_n/\mu_p = 0.650$ . The solid lines drawn on the  $QT$  plot represent values of  $QT$  used in the computation. Values of  $E_F$  found by this computation are shown in Fig. 3. For samples 4, *B*, and *D* it is assumed that  $QT = E_G - E_F$ .

The ionization energy of the impurities seems to change with impurity concentration. The flat portion of the  $E_F$  curves indicates an impurity level at 0.99 eV in sample 2, 0.85 eV in sample *A*, and 0.61 eV in sample 1. For the other samples,  $E_F$  behavior indicates the impurity levels to lie within 0.4 eV of the empty levels.

In these samples,  $E_F$  has left the neighborhood of the impurity level and is moving toward  $E_G/2$ . Consequently, the slopes of the carrier concentration curves for samples 3, 4, B, C, and D do not represent ionization energies of impurities.

## 2.2 CARRIER CONCENTRATION

Conduction electron concentration, computed from  $E_F$  values found in Sec. 2.1 and Eq. (1), is shown in Fig. 4. Impurity concentration can be estimated directly from the curves of Fig. 4 for samples 3, 4, B, C, and D. It can be determined for samples 1, 2, and A by fitting the curves using an expression of electrical neutrality. It should be recalled that, in addition to the titanium, donor centers were added to samples, A-D by reduction and acceptor centers added to samples 1-4 by oxidation. These additional centers are present in unknown amounts. However, because of the approximate way in which the data are being treated it seems worth while to compare the electrically determined impurity concentrations with those determined by chemical analysis. The comparison is made in Table I. The conclusion drawn from these data is

TABLE I. Impurity concentrations.

Sample No.	Titanium content in $10^{19}$ atoms/cm <sup>3</sup>	Electrical impurities in $10^{19}$ atoms/cm <sup>3</sup>
1	1.0	0.6
A	0.88	1.0
2	2.8	2.0
B	4.4	8.0
3	13.	2.5
C	13.	5.5
4	43.	46
D	72.	50

that there is good agreement between the electrical and chemical determination of impurity concentration. Since results obtained from the band model disagreed by several decades, the present agreement supports the assumptions leading to Eqs. (1), (2), (3), and (4).

## 2.3 MOBILITY AND WAVY BANDS

From  $n$  obtained in Sec. 2.2 and  $\sigma_n$  obtained by fitting  $QT$  data in Sec. 2.1 or measured directly,  $\mu_n$  has been calculated and is shown in Fig. 5. Two things are unusual about these results: the low values found for mobility, and the temperature dependence which suggests an activation energy associated with mobility. Two regions of different temperature dependence can be distinguished. At low temperature the activation energy depends upon impurity concentration. At high temperatures it decreases with temperature tending toward an activation energy of 0.1 ev. This same behavior is found for NiO, reference 2, Fig. 5, the mobility reaching an activation energy of 0.1 ev at high-impurity concentrations and at high temperature.

A reasonable explanation for some of this behavior is suggested by the idea of "wavy bands" as described

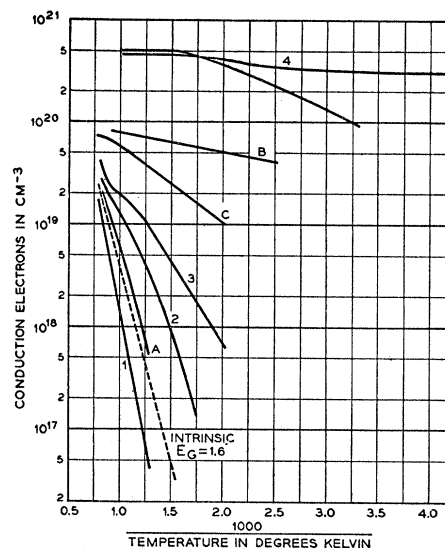


FIG. 4. Concentration of conduction electrons as a function of reciprocal absolute temperature computed with Eq. (1).

by Wannier<sup>3</sup> and James.<sup>4</sup> These are potential fluctuations produced by crystal imperfections and inhomogeneous distribution of impurities. In the present case, the potential fluctuations give rise to an activation energy for the motion of holes and electrons. If the potential wells are filled with carriers the fluctuations are smoothed out and the mobility activation energy decreased. This is brought about by increasing impurity concentration and by increasing temperature. The residual activation energy of 0.1 ev may be the energy

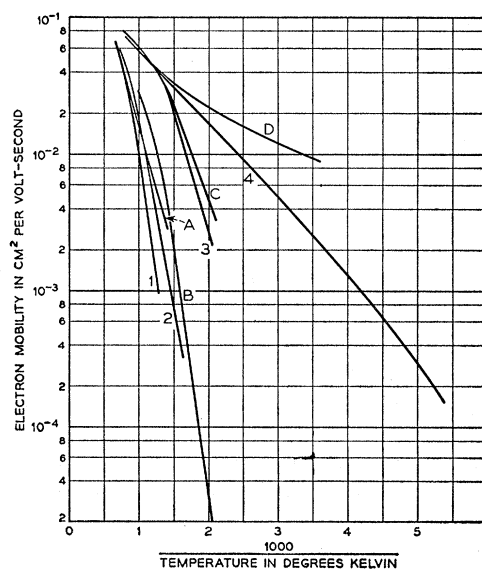


FIG. 5. Mobility of conduction electrons as a function of reciprocal absolute temperature computed from conductivity and conduction electron concentration.

<sup>3</sup> G. H. Wannier, Phys. Rev. **76**, 438-439 (1949).

<sup>4</sup> H. M. James, Science **110**, 254-256 (1949).

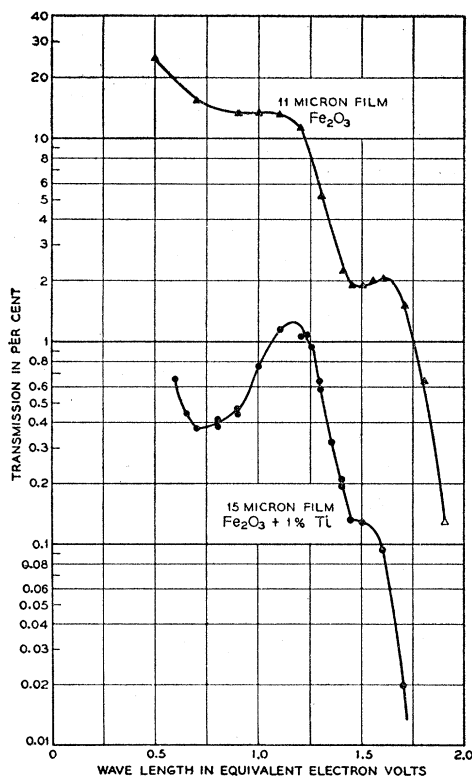


FIG. 6. Optical transmission as a function of wavelength for polycrystalline films of  $\alpha\text{-Fe}_2\text{O}_3$  sintered at  $1100^\circ\text{C}$  in air.

required for the fundamental transfer process of conduction, that is the energy required to transfer a carrier from the potential well of one cation to that of the next cation. In  $\text{Fe}_2\text{O}_3$  this process may be the drift of an  $\text{Fe}^{2+}$  electron or an  $\text{Fe}^{3+}$  hole among  $\text{Fe}^{3+}$  ions.

Since  $\alpha\text{-Fe}_2\text{O}_3$  is an antiferromagnet, the transfer energy just described may be related to the antiferromagnetic exchange energy. The Curie temperature for  $\alpha\text{-Fe}_2\text{O}_3$  is  $\sim 950^\circ\text{K}$ . Consequently the exchange energy  $kT_C$  is  $\sim 0.073$  ev as compared to 0.1 ev found above.

### 3. OPTICAL TRANSMISSION

Optical transmission is shown in Fig. 6 for a film of  $\alpha\text{-Fe}_2\text{O}_3$  11 microns thick and a film of ( $\alpha\text{-Fe}_2\text{O}_3 + 1$  atomic percent Ti) 15 microns thick. These films are polycrystalline, prepared by sintering a film of oxide powder at  $1100^\circ\text{C}$  in air. Three absorption regions can be distinguished: one at  $\sim 0.7$  ev seems associated with donor impurities since it is present before Ti is added and increases when Ti is added, one at 1.5 ev, and a fundamental absorption at  $\sim 1.9$  ev which may be associated with excitation from the filled  $sp$  band of oxygen to empty  $d$  levels or to empty  $sp$  levels.

In Sec. 2.1 it was pointed out that Fermi level behavior indicated donor levels at 0.85 ev and 0.99 ev above the filled levels. The separation of filled and

empty  $d$  levels was found to be 1.6–1.7 ev. This locates donor levels at 0.6–0.8 ev below the empty levels in agreement with the optical result of 0.7 ev. The results also suggest the absorption at 1.5 ev to be excitation from filled to empty  $d$  levels.

### 4. $sp$ BAND CONDUCTION

Assuming the optical absorption at 1.9 ev to involve the  $sp$  bands of oxygen leads to the possibility of conduction by  $sp$  holes and electrons. Judging from experience with  $sp$  band conduction in oxides such as  $\text{ZnO}$  and  $\text{Cu}_2\text{O}$ ,  $sp$  charge carriers can be expected to have mobilities in the range 10–100  $\text{cm}^2/\text{volt sec}$  at  $1000^\circ$ . This mobility range is greater than that found for  $d$  carriers by a factor of  $10^2\text{--}10^4$  at  $1000^\circ$  in pure  $\alpha\text{-Fe}_2\text{O}_3$ . Thus the  $sp$  carrier concentration can be small compared to  $d$  carrier concentration and still contribute to conduction.

In Fig. 1 the  $d$  levels are shown between the bands of oxygen. If the  $d$  levels lie near enough to the filled band, excitation from  $sp$  to  $d$  will occur. At high temperature this situation will provide high-mobility holes and low-mobility electrons in addition to the low-mobility carriers from  $d$  to  $d$  excitation. The conduction, with increasing temperature, may become dominated by high-mobility holes. Measured  $QT$  will tend to become large and positive as it becomes increasingly influenced by high-mobility holes lying far below the Fermi energy. Such  $QT$  behavior is observed in  $\text{NiO}$ .

If the  $d$  levels lie about midway between the  $sp$  bands and the  $sp$  bands are near enough together,  $sp$  to  $sp$  excitation can be expected. In this case the contribution to conduction by  $sp$  electrons will more or less balance that by  $sp$  holes and  $QT$  will be small. Its sign will depend upon location of the  $d$  levels with respect to the  $sp$  bands and upon the relative mobilities of  $sp$  holes and electrons. This seems to be the situation in  $\text{Fe}_2\text{O}_3$  assuming  $sp$  band conduction. The introduction of  $sp$  electrons in addition to  $sp$  holes prevents a quantitative fit to the data being made for  $\text{Fe}_2\text{O}_3$  because too many unknown parameters are involved. If the  $d$  levels are assumed to be midway between the  $sp$  bands, and the absorption at 1.9 ev is assumed to be an  $sp$  to  $sp$  transition, the Fermi level in pure  $\text{Fe}_2\text{O}_3$  will be at  $\sim 1.9/2 = 0.95$  ev above the filled  $sp$  band. Then  $sp$  carrier concentration will be  $\sim 4 \times 10^{15} \text{ cm}^{-3}$ . For the  $sp$  carrier to make a contribution to conduction at  $1000^\circ$  equal to that of the  $d$  carriers, the  $sp$  mobility will have to be

$$\begin{aligned} \mu_{sp} &= (n+p)_d \mu_d / (n+p)_{sp} \\ &= 8 \times 10^{18} \times 10^{-2} / 4 \times 10^{15} = 20 \text{ cm}^2/\text{volt sec}, \end{aligned}$$

which is a reasonable result.

### 5. SUMMARY

Conductivity, Seebeck effect, and optical transmission of  $\alpha\text{-Fe}_2\text{O}_3$  have been analyzed using two

alternative models. The first model assumes the following: conduction is in the  $d$  levels of iron; the Seebeck effect depends only on the location of the Fermi level; the level density involved in conduction equals the cation density. The model yields a quantitative fit to the data. Impurity concentration determined electrically agrees with that determined chemically. Electrical and optical results are consistent. Carrier mobility is found to be below 0.1 cm<sup>2</sup>/volt sec. It has an activation energy dependent upon impurity concentration and temperature which is explained

on the basis of "wavy bands". At high temperature and impurity concentration mobility activation energy tends towards a minimum value of 0.1 ev which may be the energy involved in the transfer of charge from one cation to another.

The second model assumes  $d$  level conduction and, in addition, conduction in the  $sp$  bands of oxygen by carriers having normal mobility behavior. A quantitative discussion of this model is not possible because of the number of unknown parameters involved. It is shown qualitatively to be a reasonable model.

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## Electrical Properties of NiO

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The conductivity, Seebeck effect, and optical transmission of NiO have been analyzed using two alternative models. The first model assumes conduction to occur in the  $d$  levels of Ni ions and yields a quantitative fit to the data. Mobility behavior determined with this model is explained in terms of wavy bands. The second model assumes conduction in the filled  $sp$  band of oxygen in addition to  $d$ -level conduction. It also yields a quantitative fit to the data which, however, is unsatisfactory because the concentrations and mobilities which result for  $d$  carriers appear unreasonable. Examples of grain boundary conduction are analyzed.

### 1. INTRODUCTION

**E**LECTRICAL conductivity, Seebeck effect, and optical transmission have been measured on sintered polycrystalline samples of NiO. This was done in continuation of the work on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub><sup>1,2</sup> with the object of understanding the conduction mechanism in oxides having partially filled  $d$  levels. NiO containing lithium or excess oxygen<sup>3,4</sup> provides a  $p$ -type system for comparison with the  $n$ -type system:  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> containing titanium. NiO also provides a simpler subject for study than  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; it is not ferromagnetic, its structure is NaCl cubic, and conduction is believed to involve fewer unknown parameters.

The general behavior of NiO is very similar to that of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Conductivity is insensitive to impurities in concentrations below  $\sim 10^{18}$  cm<sup>-3</sup>. No Hall effect is observed. NiO differs in one essential way from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: no  $n$ -type NiO is known. The data are analyzed in terms of the two models described in reference 2. The assumption of  $d$ -level conduction alone leads to the result that electron mobility is less than hole mobility by a factor of at least two decades.

Impurity ionization energy decreases with increasing impurity concentration. Lithium concentration determined electrically agrees with that determined chemi-

cally. Mobility activation energy decreases with increasing impurity concentration and temperature to the minimum value of 0.1 ev found for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. This behavior is described in reference 2 in terms of a wavy-band model.

The second model, which assumes conduction by  $d$  holes and electrons and by  $sp$  holes, fits the data. Several adjustable parameters are involved so that a fit can be obtained over a range of assumed values for some parameters. Only one set of assumed parameters has been used in detailed calculations. Some limits can be set on the range of assumptions which give a fit.

A conduction result is described which is believed to be an example of grain boundary conduction. Its temperature dependence fits a modified theory of Henisch<sup>5</sup> for conduction in inhomogeneous semiconductors.

### 2. METHODS

Nickel oxide was prepared by thermal decomposition of either chemically pure Ni(NO<sub>3</sub>)<sub>2</sub>, NiCO<sub>3</sub>, or NiC<sub>2</sub>O<sub>4</sub>. Stoichiometric NiO was prepared with difficulty since NiO tends to exist with excess oxygen in the lattice. It was found that the oxygen content of the sintered sample depended upon the salt from which it was prepared as well as upon sintering conditions. Stoichiometry was approached more closely using NiCO<sub>3</sub> and NiC<sub>2</sub>O<sub>4</sub>. This seems reasonable when the oxygen

<sup>1</sup> F. J. Morin, Phys. Rev. **83**, 1005-1010 (1951).

<sup>2</sup> F. J. Morin, preceding paper [Phys. Rev. **93**, 1195 (1954)].

<sup>3</sup> J. H. DeBoer and E. J. W. Verwey, Proc. Phys. Soc. (London) **49**, (extra part) (1937).

<sup>4</sup> E. J. W. Verwey, Chem. Weekblad **44**, 705-708 (1948).

<sup>5</sup> H. K. Henisch, Phil. Mag. **42**, 734 (1951).