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 cm²/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

ELECTRICAL conductivity, Seebeck effect, and optical transmission have been measured on sintered polycrystalline samples of NiO. This was done in continuation of the work on α-Fe_2O_3[1,2] with the object of understanding the conduction mechanism in oxides having partially filled d levels. NiO containing lithium or excess oxygen[3,4] provides a p-type system for comparison with the n-type system: α-Fe_2O_3 containing titanium. NiO also provides a simpler subject for study than α-Fe_2O_3; 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 α-Fe_2O_3. Conductivity is insensitive to impurities in concentrations below $\sim 10^{18}$ cm^{-3}. No Hall effect is observed. NiO differs in one essential way from α-Fe_2O_3: 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 chemically. Mobility activation energy decreases with increasing impurity concentration and temperature to the minimum value of 0.1 ev found for α-Fe_2O_3. 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[5] for conduction in inhomogeneous semiconductors.

2. METHODS

Nickel oxide was prepared by thermal decomposition of either chemically pure $Ni(NO_3)_2$, $NiCO_3$, or NiC_2O_4. 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 approched more closely using $NiCO_3$ and NiC_2O_4. This seems reasonable when the oxygen

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[1] F. J. Morin, Phys. Rev. **83**, 1005–1010 (1951).

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

[3] J. H. DeBoer and E. J. W. Verwey, Proc. Phys. Soc. (London) **49**, (extra part) (1937).

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TABLE I. Sintering conditions.

Sample No.	Starting material	Temperature °C	Atmosphere	Time hours	Lithium concentration Spectro.	Lithium concentration Electrical
1	$NiCO_3$	1150	1000 N_2+1 H_2	15		
	resintered	1250	1000 N_2+1 H_2	15	slight trace	...
2	NiC_2O_4	1250	1000 N_2+0.3 H_2	15	slight trace	3.6×10^{17}
3	$NiCO_3$	1150	500 N_2+1 H_2	15	slight trace	3×10^{18}
4	$NiC_2O_4+Li_2CO_3$[a]	1250	1000 N_2+0.3 H_2	15	$\sim6\times10^{18}$	3×10^{18}
5	$NiC_2O_4+Li_2CO_3$[a]	1250	1000 N_2+0.3 H_2	15	6.0×10^{19}	5×10^{19}
6	$Ni(NO_3)_2+LiNO_3$[b]	1100	O_2	16	4.2×10^{20}	7×10^{21}
7	$Ni(NO_3)_2$	1200	O_2	16	...	...
8	$Ni(NO_3)_2$	1500	air	2	...	...

[a] Mechanical mixing.
[b] Melted together.

content and gaseous decomposition products of the salt are considered. Stoichiometry is roughly indicated by the color of the sample. Pure stoichiometric NiO is a pale green. After some experience had been obtained, conductivity and Seebeck effect were used as indicators of very close approach to stoichiometry.

Grain boundary behavior must be considered in polycrystalline oxide samples. When such samples are cooled from sintering temperature in an atmosphere containing oxygen, they oxidize more rapidly at grain boundaries than within grains. This produces grain boundary resistance in *n*-type oxides and grain boundary conductivity in *p*-type oxides. To eliminate grain boundary conductivity, samples to be studied were sintered in a reducing atmosphere. To check the absence of grain boundary conductivity, the conductivity temperature-dependence of these samples is compared in Sec. 3 with that of a single crystal (assumed to contain no boundaries) and with samples sintered and cooled in oxygen to produce grain boundary conductivity. Table I summarizes sample preparation conditions and lithium concentration determined electrically and by spectrochemical analysis.

3. CONDUCTIVITY

Conductivity is shown in Fig. 1. Samples 1, 2, and 3 represent attempts to achieve stoichiometry. Samples 4, 5, and 6 contain increasing amounts of lithium and unknown amounts of excess oxygen. The fact that the conductivity of samples 2, 3, and 4 blend into sample 1 above 1000° suggests that the conductivity of 1 in this region represents intrinsic behavior and, therefore, that 1 is the most nearly stoichiometric sample. Samples 4 and 5 were sintered under the same conditions as 2 so that, judging from conductivity, the amount of excess oxygen in 4 and 5 is much smaller than the amount of lithium. Sample 6 was sintered under the same conditions as 7 in which the major impurity is excess oxygen. Therefore, judging from conductivity, the amount of excess oxygen in 6 is much less than the amount of lighium. The single-crystal conductivity is included for comparison with polycrystalline conductivity. Samples 7 and 8 were sintered and cooled in oxygen to produce examples of grain boundary conductivity. A qualitative comparison of the conductivity curves supports the idea that samples 1, 2, 3, and 4 have no grain boundary conductivity and that samples 7 and 8 do have grain boundary conductivity. Samples 7 and 8 are described in detail in Sec. 9.

4. SEEBECK EFFECT

Seebeck results are shown in Fig. 2. QT indicates the movement of the Fermi level with temperature and impurity concentration. QT is found to be always positive. Ordinarily it will decrease at high temperature as the Fermi level nears the middle of the forbidden energy region and carriers of opposite sign become appreciable in number. This was the case for α-Fe_2O_3. The high-temperature behavior of samples 1, 2, and 3 is unusual, therefore, and suggests that electron mobility is less than hole mobility by a factor of at least two decades. The tendency of QT for samples 1, 2, and 3 to approach the same value at high temperature is consistent with their conductivity behavior and the idea that they are entering the range of intrinsic conductivity.

The Fermi level tends to level off with temperature when passing through an impurity level. The low temperature QT behavior for samples 4, 5, and 6 indicate the location of acceptor levels whose ionization energy changes with lithium concentration from 0.10 to 0.46 ev. QT for samples 2 and 3 indicates an impurity level around 0.5 ev and the hump in 4 indicates a higher-lying level around 0.7 ev. The slowness with which QT for 2, 3, and 4 approaches QT for 1 at high temperature suggests levels lying around 0.8–0.9 ev. These are more easily seen on examination of carrier concentration curves.

5. HALL EFFECT

No Hall effect was observed on the sintered samples. There was the possibility, however, that grain boundaries reduced mobility enough to make the Hall effect undetectable. Accordingly an attempt was made to measure Hall effect on the single crystal. Measurement was made at 600°K. Hall coefficient is given by

$$R_H = V_H t \times 10^8 / HI \text{ cm}^3/\text{coul},$$

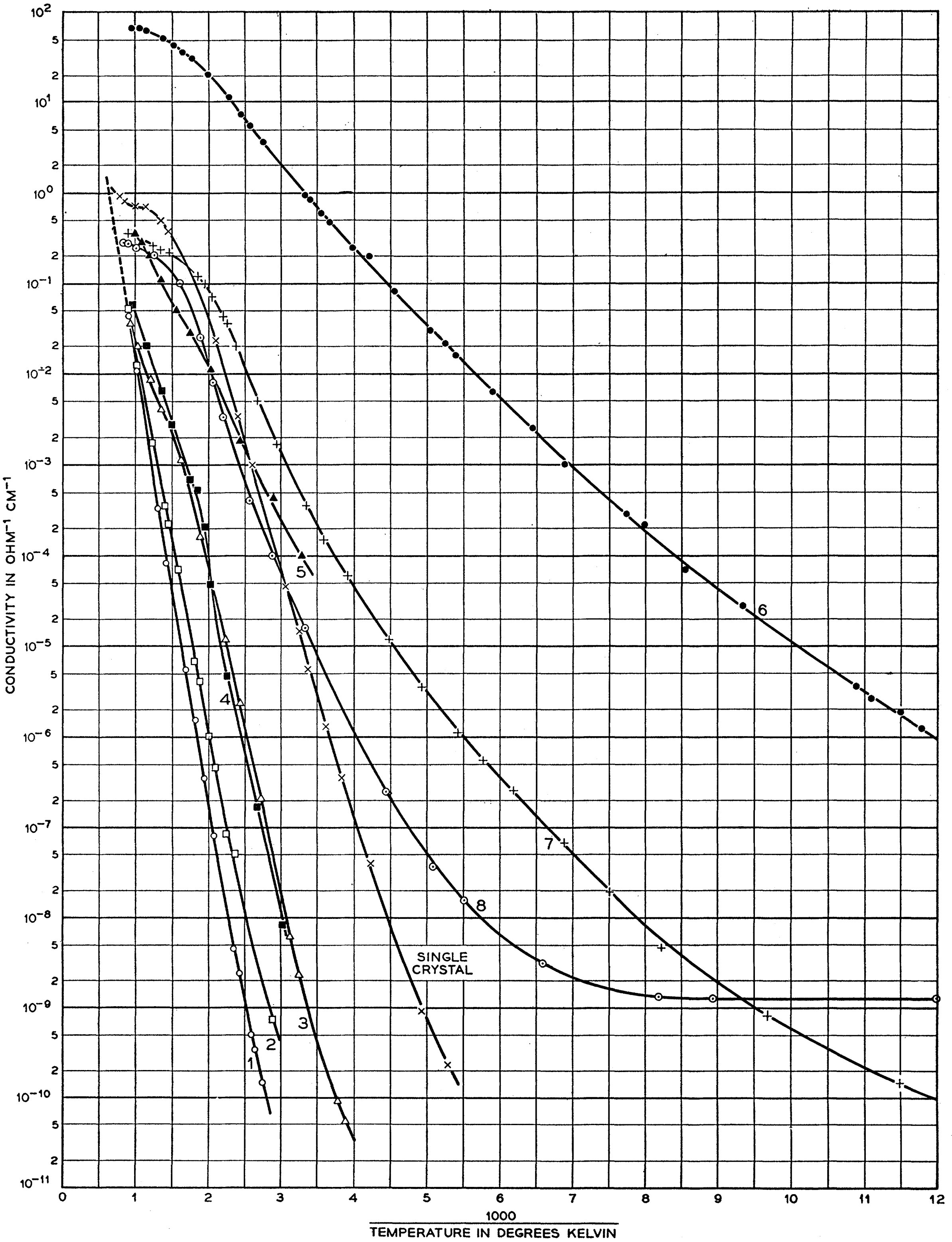

FIG. 1. Conductivity of nickel oxide samples as a function of reciprocal absolute temperature. Composition of samples given in Table I.

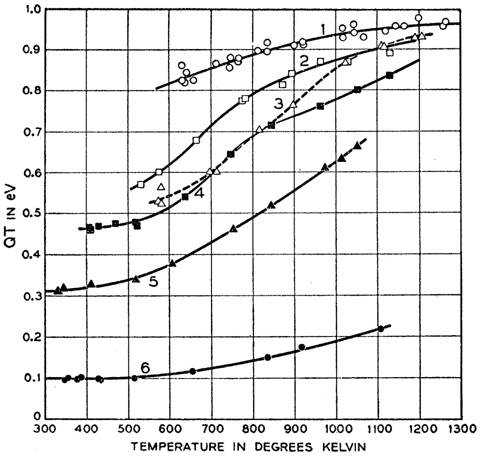

FIG. 2. The product of Seebeck voltage and absolute temperature as a function of absolute temperature for nickel oxide samples. Composition of samples given in Table I.

where V_H is Hall voltage, t thickness of sample, H applied field, and I current through the sample. No Hall voltage was detected under conditions where a potential change of 10^{-5} volts was measurable. Therefore,

$$R_H < 10^{-5} \times 0.0142 \times 10^8 / 5 \times 10^3 \times 5 \times 10^{-3} < 0.57.$$

At 600°K conductivity $\sigma = 0.17$, so that the Hall mobility is given by $R_H \sigma < 0.10$. This is consistent with the mobility results described in Sec. 6.

6. *d*-LEVEL CONDUCTION

The assumptions made concerning *d*-level conduction are described in reference 2, Sec. 2. The Fermi level measured from the filled levels is given by

$$QT = E_F. \quad (1)$$

Hole concentration is given by

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

where $N = 5.6 \times 10^{22}$ Ni atoms/cm^3 of crystal. Using Eqs. (1) and (2) hole concentration has been computed from the curves drawn through Seebeck data and is shown in Fig. 3. It is easy to see where the lower lying impurity levels become ionized in samples 2, 3, 4, 5, and 6 and to estimate their concentration. Higher-lying levels are indicated in 2, 3, and 4 by their slowness to go intrinsic at high temperature. The QT hump pointed out in Sec. 4 for sample 4 shows up clearly as a level having a concentration of $\sim 10^{19}$ cm^{-3}. It is assumed that the lower-lying levels in 2, 3, and 4 are lithium. The lithium concentration determined from these results is compared with spectrochemical analysis in Table I. Agreement is good for samples 4 and 5 and is taken as evidence supporting the assumptions leading to Eqs. (1) and (2). The lack of agreement found for sample 6 has not been explained.

Mobility has been computed from hole concentration and conductivity and is shown in Fig. 4. The results are very much like those reported for α-Fe$_2$O$_3$.[2] Mobility has an activation energy which depends upon impurity concentration and which tends to decrease at high temperature. This behavior suggests the wavy-band model discussed in reference 2. A minimum activation energy of 0.1 ev is reached at high temperature and impurity concentration. A value of 0.1 ev was also found for α-Fe$_2$O$_3$ with 1 percent titanium. This result is somewhat inconsistent with the idea advanced in reference 2 that the minimum activation energy may be the antiferromagnetic exchange energy since $kT_C(\text{NiO}) = 0.056$ and $kT_c(\alpha\text{Fe}_2\text{O}_3) = 0.073$. The mobility of sample 1 appears to be irregular with respect to the other samples. This may be an indication of the presence of *sp*-band conduction. Since sample 1 is the most nearly intrinsic of all the samples it would be expected to have the greatest proportion of *sp*-band conduction.

7. OPTICAL TRANSMISSION

Optical transmission is shown in Fig. 5 for two 14-micron films of NiO. These films were prepared by oxidizing high-purity Ni foil at 1100°C for 20 hours, one in air and the other in wet CO$_2$. The films are polycrystalline.

Three absorption bands can be distinguished. They are similar to the three bands found in α-Fe$_2$O$_3$ but are somewhat stronger and occur at shorter wavelengths. The band at $\sim$1.0 ev may be associated with excess oxygen and the levels noticed in the QT data existing

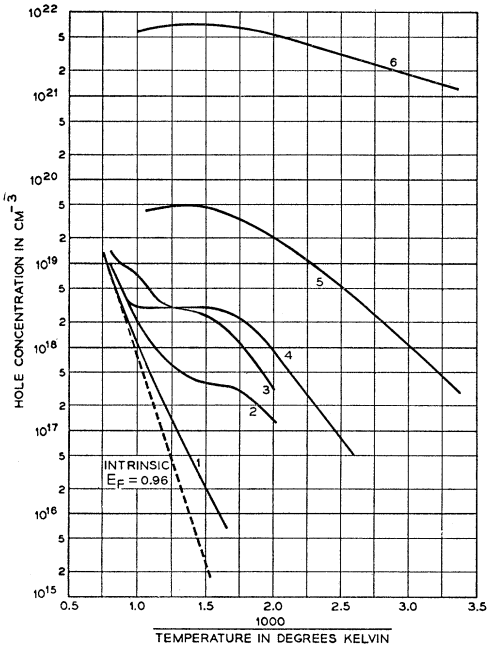

FIG. 3. Concentration of conduction holes as a function of reciprocal absolute temperature computed from Seebeck effect using Eq. (2).

at 0.8–0.9 ev. The band at 1.9 ev may be associated with the forbidden region indicated by the QT results for sample 1 which suggests this region to be $0.96\times 2=1.92$ ev wide. The absorption band at 2.7 ev is probably associated with excitation of electrons from the filled *sp* band of oxygen into an empty *sp* band.

8. *sp* BAND CONDUCTION

The possibility of *sp*-band conduction has been discussed in reference 2, Sec. 4. As pointed out there, the QT behavior of NiO sample 1 at high temperature suggests that the d levels may be nearer to the filled *sp* band then to the empty *sp* band. Several models have been investigated on the assumption that *sp* holes but no *sp* electrons contribute to conduction. So many unknown parameters are involved in computing a fit to the data that a detailed discussion of all the computations does not seem worthwhile. As an example of the methods used, one model will be described.

Conduction by *sp* holes can be combined with d-level conduction by means of the following equations. If it is assumed that *sp* holes, d holes, and d electrons contribute to the conduction process, then

$$\sigma=\sigma_{sp}+\sigma_{dp}+\sigma_{dn}, \tag{3}$$

and the Seebeck effect becomes

$$QT=[(QT)_{sp}\sigma_{sp}+(QT)_{dp}\sigma_{dp}-(QT)_{dn}\sigma_{dn}]/\sigma. \tag{4}$$

To obtain QT in terms of the Fermi level it is necessary to assume an energy level system. Measuring from the filled *sp* band let E_{dp} be the filled d level, E_{dn} the empty d level, and E_F the Fermi level. Then QT can be rewritten in more useful form

$$\sigma_{dp}=\sigma(E_F-QT)/(E_{dp}+E_{dn}\sigma_{dn}/\sigma_{dp}). \tag{5}$$

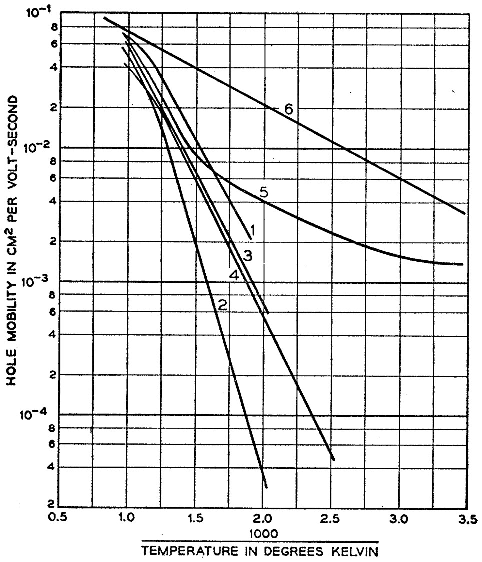

FIG. 4. Mobility of conduction holes as a function of reciprocal absolute temperature computed from conductivity and carrier concentration.

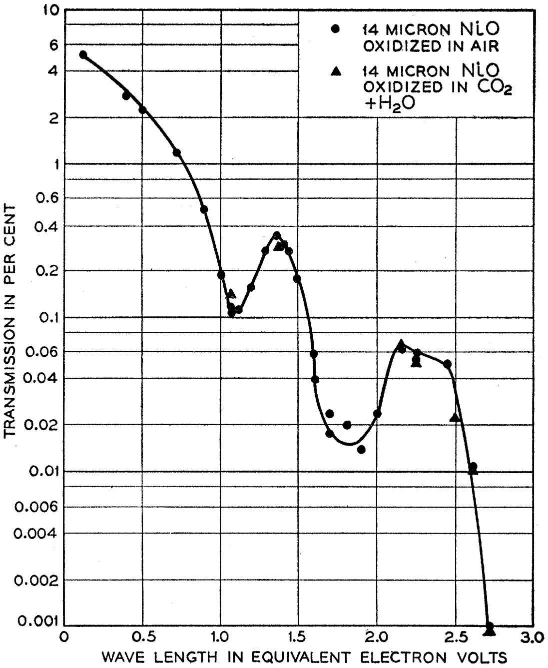

FIG. 5. Optical transmission as a function of wavelength for polycrystalline films of nickel oxide sintered at 1100°C for 20 hours.

If it is assumed that mobility of d holes = mobility of d electrons, the ratio σ_{dn}/σ_{dp} can be written

$$\sigma_{dn}/\sigma_{dp}=\exp[-(E_{dn}+E_{dp}-2E_F)/kT]. \tag{6}$$

Computation is made in the following sequence:

1. assume values for energy levels;
2. substitute an assumed E_F and compute σ_{sp}, σ_{dn} and σ_{dp} from (3), (5), and (6);
3. assume some reasonable behavior for *sp* mobility and compute p_{sp} from σ_{sp};
4. from p_{sp} compute E_F and compare with assumed E_F;
5. repeat process until computed E_F = assumed E_F.

Data for samples 1 to 5 have been fitted in this way. Results are disappointing. At the present time it does not seem possible to learn anything conclusive about *sp* conduction from the small amount of data available.

9. GRAIN BOUNDARY CONDUCTIVITY

Henisch[5] has derived an expression for the temperature dependence of conductivity in an inhomogeneous semiconductor having potential barriers of various heights. The effective barrier height φ for a series arrangement of barriers along any filamentary conduction path is given by

$$\varphi=\bar{\varphi}+S^2/2kT, \tag{7}$$

where $\bar{\varphi}$ is the mean barrier height and S the standard deviation in barrier height. This situation applies to α-Fe_2O_3 in which high-resistance grain boundaries are

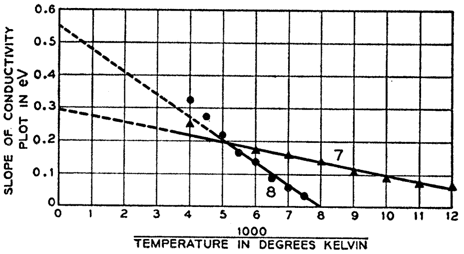

FIG. 6. Temperature dependence of the conductivity slope.

in series with conducting grains. In NiO the grain boundaries are conducting and therefore act in parallel with the grains. For this situation it can be shown that Eq. (7) becomes

$$\varphi = \bar{\varphi} - S^2/2kT. \tag{8}$$

Grain boundary conductivity was introduced into samples 7 and 8 by cooling them from sintering temperature in an oxidizing atmosphere. Conductivity is shown in Fig. 1. The low-temperature conductivity behavior is in accord with Eq. (8) if the slope of the Fig. 1 curves is taken to be effective barrier height. The temperature dependence of the conductivity slope is shown in Fig. 6 as plotted points. Straight lines are drawn through the points to determine the intercept at $1/T=0$ which is $\bar{\varphi}$ and the slope which is $S^2/2k$. Points deviate from straight line behavior at 200°K probably because the normal conductivity process becomes comparable to grain boundary conductivity. From these results $\bar{\varphi}=0.30$ ev and $S=0.059$ ev for sample 7, and $\bar{\varphi}=0.55$ ev and $S=0.108$ ev for sample 8.

10. SUMMARY

Conductivity, Seebeck effect, and optical transmission of NiO have been analyzed using two alternative models. The first model assumes the following: conduction is in the *d* levels of nickel; the Seebeck effect depends only upon 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^2/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 filled *sp* band of oxygen by holes having normal mobility behavior. A quantitative investigation has been made of this model with unsatisfactory results. The idea of *sp*-band plus *d*-level conduction is shown to be reasonable.

Two instances of grain boundary conduction are presented and analyzed in terms of a modified theory of Henisch.

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Drift Mobilities in Semiconductors. II. Silicon

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The drift mobility of holes in *n*-type silicon and electrons in *p*-type silicon has been measured as functions of impurity concentration and temperature. In single crystals of resistivity greater than 10 ohm-centimeter, the mobility at 300°K of holes is $\mu_P=500\pm50$ cm^2/volt-sec and of electrons is $\mu_N=1200\pm100$ cm^2/volt-sec. For this high-resistivity material, the temperature dependence of mobility in the same units is $\mu_N=5.5\times10^6T^{-1.5}$ and $\mu_P=2.4\times10^8T^{-2.3}$.

INTRODUCTION

THIS paper constitutes a companion paper to one dealing with the drift mobilities in germanium.[1] The drift mobility of holes and electrons has been measured in silicon single crystals grown from starting material of relatively high purity. Drift measurements were made on samples that were cut from crystals whose resistivity values ranged from 0.3 to 30 ohm-centimeter at 300°K. The variation of mobility with temperature was measured over a temperature range of 150°K to 300°K in two of these samples. Calculated from the experimental data are curves giving the relationship between the number of impurity centers and the resistivity, and the ratio of the electron mobility to the hole mobility in *n*-type and *p*-type silicon as a function of the number of impurity centers.

A discussion of the experimental techniques, preparation of samples, sources of error, and methods for combining the results of various scattering mechanisms is given in I.

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[1] M. B. Prince, Phys. Rev. 92, 681 (1953) hereinafter referred to as I.