

surface Coulomb sums for many surface faces of NaCl, CsCl, wurtzite, and zinc-blende lattices. Calculations of  $\mu$  are made for 46 ionic crystal halides, oxides, and sulfides of the form  $MX$ . Because the effective charge  $z$  of these crystals is fractional in general, a simple procedure is used to calculate an effective  $\epsilon(z)$ . This flexible feature of handling fractional charges enables electrostatic principles to be applied to zinc blende and wurtzite crystals which are known to be partly ionic and partly covalent. Electrostatic criteria show that checkerboard-like surfaces are expected to be more stable than layer-like surfaces. Numerical calculations of the 48 crystals investigated show that surface states should lie closest to band center for HgS, CdS, and ZnS, and they should lie closest to the band edges for the alkali halides. Various effects can be incorporated in the above theory, if desired. They are band broadening, subsurface states, symmetry properties of the general  $M_nX_m$  crystal, surface relaxations of an initially unstable  $MX(L)$  surface, ion core repulsions, and the addition of partial covalency.

For the  $(11\bar{2}0)$  face of CdS, detailed analysis has been made leading to an estimate of 0.2–0.4 eV for surface

trap depths. Each surface  $Cd^{2+}$  ion is an electron trap and each surface  $S^{2-}$  ion is a hole trap.

Intrinsic surface states were detected on the  $(11\bar{2}0)$  surfaces of vapor-phase-grown insulating CdS single crystal platelets with photoconductivity experiments. The intrinsic surface states were observed only when the surface was free of chemisorbed ions. The experimentally detected surface states have the following features in common with the computed intrinsic surface states: (1) The surface states function as traps for carriers from the bulk; (2) there are surface states that trap electrons as well as surface states that trap holes; (3) electrons and holes can be trapped in nearly equal numbers on an  $MX(C)$ -type surface; (4) the energy depth of the traps is bracketed by the limits of 0.2 and 0.7 eV. It is also shown that a large minority carrier lifetime plays a double role in the detection of the intrinsic surface states by photoconductivity measurements. First, it makes possible the isothermal desorption of chemisorbed ions that otherwise interfere with the detection of the intrinsic surface states. Second, it makes possible the surface-compensated filling of the intrinsic surface states.

## Mechanism of the Electrical Conduction in Li-Doped NiO

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The electrical conductivity and the Seebeck effect are measured in the temperature region of 100 to 1300°K in NiO doped with Li. From the results it is concluded that the mobility of the charge carriers involves no activation energy. The temperature dependence of the conductivity is almost completely determined by the charge-carrier concentration. In order to calculate from the measurements the mobility  $\mu$  as a function of temperature, the behavior of the density of states  $N_V$  must be known.  $\mu$  has been calculated for two cases, viz.,  $N_V$  independent of temperature and  $N_V$  proportional to  $T^{3/2}$ . The resulting values of  $\mu$  at room temperature are 0.5 and 5 cm<sup>2</sup>/V sec, respectively. In the discussion the results of Hall-effect measurements are also considered.

### I. INTRODUCTION

**M**ANY of the transition-metal oxides, if pure and stoichiometric, are insulators. This was explained by Verwey and De Boer<sup>1,2</sup> by assuming the  $3d$  electrons to be localized at the metal ions. According to these authors a necessary condition for an appreciable conductivity in these oxides is the presence of ions of the same element with different valency at crystallographically equivalent lattice points. In NiO this can be

achieved by creating Ni vacancies or more easily by substituting Li for Ni at Ni sites. Each  $Li^{1+}$  ion is then compensated by a  $Ni^{3+}$  ion (principle of controlled valency<sup>3</sup>). At low temperatures the holes formed by the  $Ni^{3+}$  are bound to the, effectively negative,  $Li^{1+}$  ions. At high temperatures the holes are free and can move through the lattice by the interchange of electrons between  $Ni^{3+}$  and  $Ni^{2+}$  ions. It was assumed that no activation energy is needed for this process. The activation energy occurring in the conductivity must then be the energy needed for loosening the holes from the  $Li^{1+}$  ions.

<sup>1</sup> E. J. W. Verwey and J. H. Boer, *Rec. Trav. Chim.* **55**, 531 (1936).

<sup>2</sup> J. H. de Boer and E. J. W. Verwey, *Proc. Phys. Soc. (London)* **49**, 59 (1937).

<sup>3</sup> E. J. W. Verwey, *Semiconducting Materials* (Butterworths Scientific Publications Ltd. London, 1951), pp. 151–161.

In later years<sup>4-11</sup> it was concluded from experimental data that the model mentioned above had to be changed. If the free holes could move through the lattice without an activation energy, one would expect the mobility to be almost independent of temperature. This did not seem to be in agreement with the experiments, which pointed to a mobility increasing exponentially with temperature. The activation energy thus introduced in the mobility was in many cases much larger than the binding energy of the holes to the  $\text{Li}^{1+}$  ions, which was taken as an indication that the activation energy in the conductivity was mainly due to the mobility and not to a variation in charge-carrier concentration. The values of the mobility at room temperature deduced from such an interpretation were found to be very small ( $10^{-3}$ – $10^{-6}$   $\text{cm}^2/\text{V sec}$ ).

According to Heikes and Johnston<sup>5</sup> the conduction mechanism could be considered as a thermally activated diffusion process (hopping model). The activation energy for this diffusion process is a consequence of the trapping of the holes by the lattice polarization (and the accompanying lattice distortion) induced by the hole itself.

The conception of a mobility with an activation energy was first introduced by Morin<sup>4</sup> for interpreting conductivity and Seebeck-effect measurements on NiO doped with different amounts of Li. In his analysis the density of states was assumed to be constant and equal to the number of ionic sites ( $5.5 \times 10^{22}/\text{cm}^3$ ). The transport term occurring in the expression for the Seebeck effect was assumed to be zero. Then the activation energy in the mobility was found to be 0.1 eV or more. In later years different authors<sup>6,7,11,12</sup> also using conductivity and Seebeck-effect measurements arrived at similar conclusions.

Other arguments used in literature to confirm the idea of a thermally activated hopping process are the following:

(a). At high Li concentrations ( $> 5$  at.%) the activation energy in the conductivity is still rather large. At such concentrations, however, nearly all Ni ions have Li neighbors, so that the holes can move through the lattice without leaving the  $\text{Li}^{1+}$  ions. The temperature dependence of the resistivity then must be due to the mobility.<sup>5,7</sup>

(b). The conductivity at room temperature is pro-

portional to the Li concentration.<sup>8</sup> The simplest explanation is that the number of free holes is equal to the Li concentration. The activation energy in the conductivity cannot then be due to the variation in the charge-carrier concentration.

(c). The low values calculated for the mobility were in agreement with the fact that no Hall effect could be detected.

(d). The existence and the behavior of the mechanical and dielectric losses.<sup>13-16</sup> In these experiments the movements of holes around the  $\text{Li}^{1+}$  ions to which they are bound are studied. At high Li concentrations the activation energy for this process is of the same order of magnitude as that obtained from conductivity measurements in the same temperature region.

Recently, however, Hall-effect measurements have been published,<sup>17-19</sup> giving for the Hall mobility at room temperature values varying from  $5 \cdot 10^{-3}$ – $3 \cdot 10^{-1}$   $\text{cm}^2/\text{V sec}$ . These values are much larger than those calculated from the Seebeck effect and conductivity measurements using the hopping model. Moreover, the Hall mobility did not increase exponentially with temperature as one would expect from the hopping model but decreased with temperature in the region from 300 to 500°K. Although the interpretation of the Hall effect in crystals with magnetic ions is not yet completely clear, these results nevertheless suggest that the thermally activated hopping model is not correct for NiO.

In this paper we will present further measurements of the conductivity and Seebeck effect on NiO doped with small amounts of Li. From these measurements the mobility  $\mu$  as a function of temperature has been calculated. Our results show that in the case of NiO the use of the hopping model is indeed not correct.

## II. EXPERIMENTAL

Ceramic samples were prepared by prefiring an intimate mixture of NiO and  $\text{Li}_2\text{CO}_3$  at 700°C in air. After milling the product obtained, it was pressed to bars and thereafter these bars were pressed hydrostatically. The bars were fired at 1300°C in oxygen for 24 h and thereafter cooled in the furnace. From 1000°C to room temperature the samples were cooled in air. The amount of  $\text{Li}^{1+}$  and  $\text{Ni}^{3+}$  was determined by chemical analysis. The density of the samples was about 93% of the x-ray

<sup>4</sup> F. J. Morin, *Phys. Rev.*, **83**, 1005 (1951); **93**, 1195 (1954); **93**, 1199 (1954); *Bell System Tech. J.* **37**, 1047 (1958).

<sup>5</sup> R. R. Heikes and W. D. Johnston, *J. Chem. Phys.* **26**, 582 (1957).

<sup>6</sup> R. R. Heikes, A. A. Maradudin and R. C. Miller, *Ann. Phys. (Paris)* **8**, 733 (1963).

<sup>7</sup> S. van Houten, *J. Chem. Phys. Solids* **17**, 7 (1960).

<sup>8</sup> G. H. Jonker and S. van Houten, *Halbleiterprobleme VI*, (Frederick Vieweg und Sohn, Braunschweig; Germany, 1961), p. 118.

<sup>9</sup> S. P. Mitoff, *J. Chem. Phys.* **35**, 882 (1961).

<sup>10</sup> S. Koide, *J. Phys. Soc. Japan* **20**, 123 (1965).

<sup>11</sup> M. Nachman, L. N. Cojocarn, and L. V. Ribo, *Phys. Status Solidi* **8**, 733 (1965).

<sup>12</sup> G. Parravano, *J. Chem. Phys.* **23**, 5 (1954).

<sup>13</sup> R. G. Miller and R. R. Heikes, *J. Chem. Phys.* **28**, 348 (1958).

<sup>14</sup> S. van Houten, *J. Phys. Chem. Solids* **23**, 1045 (1962).

<sup>15</sup> S. van Houten and A. J. Bosman, in *Informal Proceedings of the Buhl International Conference on Materials, Pittsburgh, 1963*, edited by E. R. Schatz (Gordon and Breach Science Publishers, Inc., New York, 1966).

<sup>16</sup> A. J. Bosman and S. van Houten, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1965), p. 1203.

<sup>17</sup> P. V. Zhuze and I. A. Shelykh, *Fiz. Tverd. Tela* **5**, 1756 (1963) [English transl.: *Soviet Phys.—Solid State* **5**, 1278 (1963)].

<sup>18</sup> M. Ksendzov, N. L. Ansel'm, L. L. Vasileva, and V. M. Latysheva, *Fiz. Tverd. Tela* **5**, 1537 (1963) [English transl.: *Soviet Phys.—Solid State* **5**, 1116 (1963)].

<sup>19</sup> M. Roilos and P. Nagels, *Solid State Commun.* **2**, 285 (1964).

density. The length of the finished bars was about 15 mm, their cross sections about 10 mm<sup>2</sup>.

One of the samples was heated to 1000°C and then slowly cooled in nitrogen to see whether in this temperature region the gas atmosphere had any influence on the conductivity and Seebeck effect.

The conductivity and Seebeck effect were measured from 100 to 1300°K in air. For the conductivity a four-point method was used. To be sure that the measured values of the conductivity indeed represent the conductivity of the bulk, ac measurements were performed up to 5 Mc/sec.

Below room temperature the Seebeck effect was determined by measuring the thermal emf and the temperature difference with thermocouples mounted in copper blocks soldered at the end of the NiO bar. Such a unit was clamped between two large copper blocks, one of which could be heated. For the measurements above room temperature the thermocouples were mounted in narrow and deep holes in the sample.

Hall-effect measurements in the temperature region 300–1100°K were also performed.<sup>20</sup> The magnetic field used was 30 000 Oe.

### III. RESULTS

Figure 1 gives log<sub>10</sub>ρ for NiO containing 8.8×10<sup>-2</sup> at.% Li as a function of the reciprocal temperature. Sample 1 was cooled in air and sample 2 in nitrogen. It is seen that there is a considerable difference in the dc conductivity. The ac measurements, however, show that the bulk resistivity has not been changed by the different heat treatment. The ac values of both samples lie practically on the dc curve of sample 1. This means that on cooling in nitrogen grain-boundary effects completely dominate the dc measurements. All further resistivity

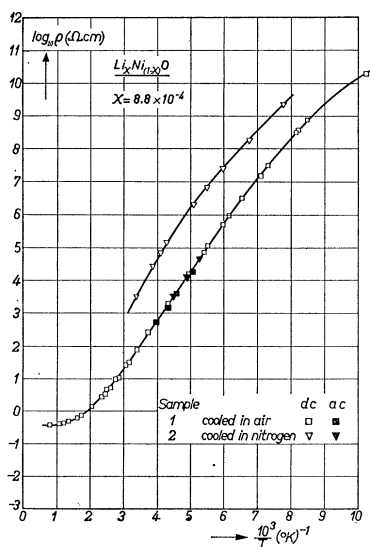


FIG. 1. Resistivity as a function of reciprocal temperature for NiO containing 8.8 × 10<sup>-2</sup> at.% Li. Owing to grain-boundary effects, the sample cooled in nitrogen (2) has a much larger dc resistivity than the sample cooled in air (1). For the latter sample the dc and ac resistivities coincide.

<sup>20</sup> A. J. Bosman, H. J. van Daal and G. F. Knuvers, Phys. Letters 19, 372 (1965).

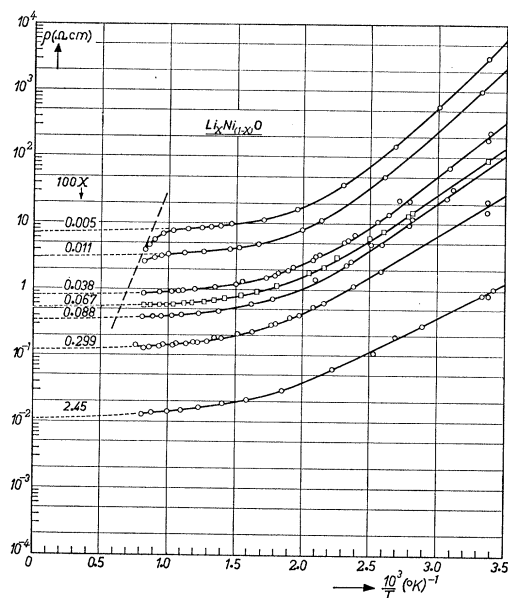


FIG. 2. Resistivity as a function of reciprocal temperature for NiO doped with different amounts of Li. The Li concentrations are determined by chemical analysis, except the value of 5×10<sup>-3</sup> at.% which was calculated from the amount of Li<sub>2</sub>CO<sub>3</sub> added to the pure NiO. The dashed line represents the resistivity of pure NiO in equilibrium with oxygen (1 atm) measured on a single crystal (see Ref. 9).

values given in this paper have been obtained from dc measurements performed on samples cooled in air.

In Fig. 2 the results of the resistivity measurements in the temperature region of 300 to 1300°K on different samples are given. The dashed line represents the resistivity of NiO being in equilibrium with oxygen (1 atm) as measured by Mitoff<sup>9</sup> on an undoped single crystal. The saturation value of the conductivity at high temperatures is seen to be proportional to the Li concentration (Fig. 3), indicating that the conductivity is brought about by the Li added, and not by an unknown impurity or a deviation from stoichiometry by oxidation. Only for the sample with the smallest amount of Li (0.005 and 0.011 at.%) at high temperatures oxidation seems to influence the conductivity.

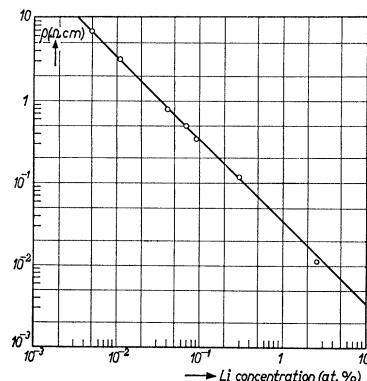


FIG. 3. Resistivity at high temperatures as a function of the Li concentration. The values of the resistivity are obtained from Fig. 2 by extrapolating the measurements to 1/T=0.

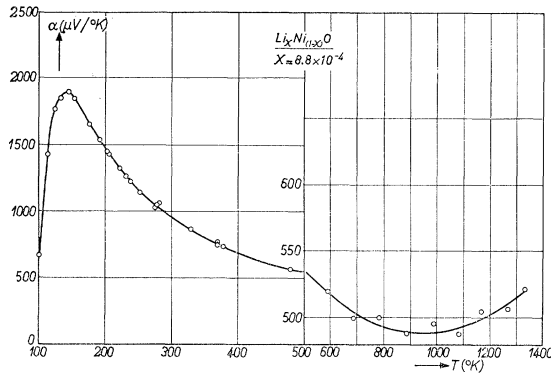


FIG. 4. Thermoelectric power  $\alpha$  as a function of temperature for NiO containing  $8.8 \times 10^{-2}$  at. % Li. Note the change in both scales at  $500^\circ\text{K}$ .

In Fig. 4 we have plotted the thermoelectric power  $\alpha$  of NiO containing  $8.8 \times 10^{-2}$  at. % Li (sample 1 in Fig. 1). At about  $140^\circ\text{K}$  the thermoelectric power shows a maximum. Below this temperature  $\alpha$  decreases rapidly. This decrease is not believed to be due to a systematic error in the measuring method for high Ohmic samples since heavier doped samples with much lower resistivity show the same phenomenon. Above  $140^\circ\text{K}$  the thermoelectric power decreases with temperature and reaches a minimum value at about  $900^\circ\text{K}$ .

The thermoelectric power of sample 2 in Fig. 1 is the same as that of sample 1. Thus the thermoelectric power is not influenced by grain-boundary effects caused by cooling in nitrogen.

#### IV. DISCUSSION

##### A. Conduction Mechanism above $140^\circ\text{K}$

As can be seen in Fig 1 the resistivity of sample 1 (NiO containing  $8.8 \times 10^{-2}$  at. % Li and cooled in air) changes by a factor of  $10^{11}$  in the temperature region of 100 to  $1300^\circ\text{K}$ . Since the ac measurements show that grain-boundary effects are absent, this curve represents the behavior of the bulk. In the temperature region of 140 to about  $400^\circ\text{K}$   $\log_{10}\rho$  depends linearly on the reciprocal temperature. The corresponding activation energy amounts to 0.30 eV. At temperatures higher than  $400^\circ\text{K}$  the temperature dependence gradually decreases. Below  $140^\circ\text{K}$  the temperature dependence also decreases. The behavior of the conductivity at these temperatures will be treated in the next section.

The question which now has to be answered is whether the activation energy of 0.30 eV originates from the charge carrier variation, or from the mobility, or from both.

In Fig. 2 it is seen that the temperature dependence of the conductivity practically disappears at high temperatures, indicating that the temperature dependence of the mobility is also small. However, this fact itself cannot be used as an argument to reject the hopping model. According to this model the mobility is pro-

portional to  $(1/T) \exp(-q/kT)$ , where  $q$  is the activation energy for the hopping process. If  $q$  were of the order of 0.1 eV, such a mobility would also become almost constant at temperatures around  $1200^\circ\text{K}$ .

From Fig. 4 it is seen that the thermoelectric power  $\alpha$  depends markedly on temperature. It is clear that at room temperature the number of free holes  $p$  is by no means constant and equal to the dope concentration, because then  $\alpha$  would be constant with respect to temperature. The fact that  $\alpha$  decreases up to high temperatures is already an indication that the variation in charge carrier concentration plays an important part in the conductivity.

If the conduction can be ascribed to one kind of charge carrier we can write for the thermoelectric power  $\alpha^{21}$ :

$$\alpha = -\left(\frac{k}{e} \frac{E_F}{kT} + A\right) = -\left(\ln \frac{N_V}{p} + A\right) = 2.3 \log_{10} \left(\frac{N_V e^A}{p}\right). \quad (1)$$

Here  $E_F$  is the Fermi level,  $A$  is a term connected with the kinetic energy of the free holes,  $N_V$  is the density of states and  $p$  is the number of free holes. If we compare  $\alpha/(2.3k/e) = \log_{10}(N_V e^A/p)$  and  $\log_{10}\rho = \log_{10}(1/pe\mu)$  we see that the temperature dependence of  $\alpha$  is determined by that of  $p$  if  $N_V$  and  $A$  are constant, and the temperature dependence of  $\rho$  by that of  $p$  and  $\mu$ . If the mobility  $\mu$  involves an activation energy the temperature dependence of  $\rho$  must be stronger than that of  $\alpha$ .

In Fig. 5 we have plotted the measured values of  $\alpha$  (see Fig. 4) in units of  $2.3k/e = 198 \mu\text{V}/^\circ\text{K}$  as a function of the reciprocal temperature. We have also plotted  $\log_{10}\rho$ .

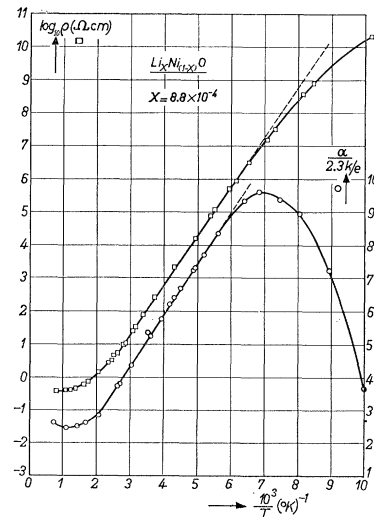


FIG. 5. Resistivity and thermoelectric power as a function of reciprocal temperature for NiO doped with  $8.8 \times 10^{-2}$  at. % Li. Above  $170^\circ\text{K}$  the temperature dependence of  $\log_{10}\rho$  is practically identical to that of  $\alpha/2.3(k/e)$ , indicating that their common origin is the variation in charge carrier concentration. The behavior of  $\rho$  and  $\alpha$  below  $170^\circ\text{K}$  can be ascribed to impurity conduction.

<sup>21</sup> A. F. Ioffe, *Physics of Semiconductors* (Infosearch Limited, London, 1960).

As can be seen the linear parts of these curves are parallel, indicating that the corresponding temperature dependences are the same. The large value of the activation energy (0.30 eV) found from the conductivity measurements is therefore completely due to the variation in free hole concentration. The temperature dependence of the mobility thus seems to be very slight. This means that the change in slope of  $\log_{10}\rho$  versus the reciprocal temperature above 400°K is due to exhaustion of the acceptors.

This result is completely in contradiction with the thermally activated hopping model and points to conduction in a band. In Sec. C we will give a more quantitative analysis of the conductivity and Seebeck-effect measurements.

### B. Conduction Mechanism below 140°K

The change in the temperature dependence of the conductivity at low temperatures was already found by Morin<sup>4</sup> and ascribed to an extra conduction along grain boundaries originating from oxidation. However, this behavior at low temperatures is also found in highly doped NiO. In this case it is almost impossible that the conductivity in the grain boundaries due to oxidation is larger than the conductivity in the bulk due to the Li. Moreover, measurements on single crystals<sup>19</sup> having a Li content of the same order of magnitude (0.2 at. %), show the same phenomenon. Therefore it is likely that this effect is a real bulk effect, most probably caused by impurity conduction<sup>18</sup> as was also found in SiC, Ge, etc. Ksendzow *et al.*<sup>18</sup> suppose that in consequence of the simultaneous presence of donors in the form of oxygen vacancies an equal amount of Li<sup>1+</sup>-Ni<sup>3+</sup> acceptors have accepted an electron at low temperatures. Owing to the presence of unoccupied Li<sup>1+</sup>-Ni<sup>3+</sup> centers these electrons can give rise to impurity conduction becoming noticeable at low temperatures. In Subsec. C it will be shown that the measurements above 140°K demonstrate that the samples are partly compensated, proving that donors are indeed present.

In Fig. 5 it is seen that at about 140°K, where the temperature dependence of  $\rho$  starts to change, the thermoelectric power  $\alpha$  has a maximum. Below this temperature we assume the simultaneous presence of two different conduction mechanisms. For the conductivity we can then write

$$\sigma = \sigma_p + \sigma_i, \quad (2)$$

where  $\sigma_p$  is the free-hole conductivity and  $\sigma_i$  the impurity conductivity. For the thermoelectric power we can write<sup>21</sup>

$$\alpha = - \left[ \frac{k}{e} \frac{\sigma_p}{\sigma} \left( \frac{E_F}{kT} + A \right) + \frac{\sigma_i}{\sigma} \left( \frac{E_F - E_A}{kT} \right) \right], \quad (3)$$

where  $E_A$  is the energy level of the acceptors with respect to the transport level. From the theory of partly

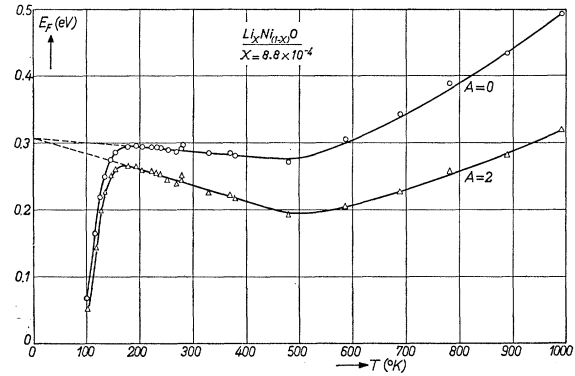


FIG. 6. The Fermi level  $E_F$  as a function of temperature, calculated from the thermoelectric power  $\alpha$  (Fig. 4) using the equation  $E_F = e\alpha T - AkT$ . This equation is not valid when more than one type of charge carriers is present, which clearly is the case below 170°K.

compensated semiconductors<sup>22</sup> it is known that at low temperatures the Fermi level is given by

$$E_F = E_A - kT \ln((N_A - N_D)/N_D), \quad (4)$$

where  $N_A$  and  $N_D$  are the concentrations of acceptors and donors, respectively. Here it is assumed that the factor describing the impurity spin degeneracy is equal to one. According to Eq. (4) the Fermi level at  $T=0$  coincides with the acceptor level and is lowered with increasing temperature,  $E_F - E_A$  becoming negative. From Eq. (3) it is seen that the first term dominates as long as  $\sigma_i/\sigma \ll 1$ . When the temperature is lowered, starting say at  $T=300$ °K, the thermoelectric power initially increases with decreasing temperature. However, as soon as  $\sigma_i$  becomes comparable with  $\sigma_p$  the first term in Eq. (3) decreases, while the second, negative term increases. This explains the maximum in the  $\alpha$ - $T$  curve.

### C. Quantitative Analysis

In Subsec. B it was assumed that the behavior of the conductivity and Seebeck effect below 140°K can be ascribed to impurity conduction, made possible by the presence of donors. The measurements above 140°K give reason to believe that the samples are indeed partly compensated. If the conduction can be ascribed to one kind of charge carrier Eq. (1) gives the relation between the thermoelectric power  $\alpha$  and the Fermi level  $E_F$ . In Fig. 6 we have plotted  $E_F = e\alpha T - AkT$  as a function of temperature for two values of  $A$ . It is seen that the presence of impurity conduction already becomes noticeable at about 170°K. Below this temperature Eq. (1) can no longer be used to calculate  $E_F$ . Above this temperature the Fermi level decreases with increasing temperature. This is in accordance with Eq. (4), which holds for the case of partial compensation.

In Subsec. A we saw that the activation energy cal-

<sup>22</sup> J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962).

culated from the conductivity measurements amounted to 0.30 eV. From Fig. 6 it can be concluded that this energy represents the distance between the acceptor level and the conduction level. For if we extrapolate the measurements above 170°K to  $T=0$  it is found that  $E_F=0.31$  eV. According to Eq. (4) the value of  $E_F$  at  $T=0$  equals  $E_A$  and not  $\frac{1}{2}E_A$ .

For a more quantitative calculation we have plotted in Fig. 7 on a large scale  $-\alpha/2.3(k/e)=\log_{10}(p/N_V e^A)$  as a function of the reciprocal temperature. If we should assume that  $N_V=5.5 \times 10^{22}$  and  $A=0$  according to Morin<sup>4</sup> then curve 1 would represent the variation of  $p$  with temperature. The saturation value  $p_{\text{sat}}$  is then found to be  $17 \times 10^{19}/\text{cm}^3$ , which is larger than the number of Li ions ( $4.9 \times 10^{19}/\text{cm}^3$ ). Since the amount of  $\text{Ni}^{3+}$  found by chemical analysis is practically the same as the Li content, the value of  $p_{\text{sat}}$  can not be larger than  $4.9 \times 10^{19}/\text{cm}^3$ . The assumption that  $N_V=5.5 \times 10^{22}$  and  $A=0$  is therefore not correct. In various publications<sup>4,11,12</sup> Seebeck-effect measurements have been analyzed with the values of  $N_V$  and  $A$  mentioned above. The calculated values of  $p_{\text{sat}}$  are invariably much larger than the Li concentration found chemically.

The measurements of the thermoelectric power  $\alpha$  at high temperatures show the presence of a minimum. This minimum in  $\alpha$  corresponds to a maximum in  $\log_{10}(p/N_V e^A)$ . This effect can be explained quite simply by assuming that  $N_V$  increases with temperature. Let us assume that  $N_V \propto T^{3/2}$  as is the case for a broad-band semiconductor. Replacing  $N_V$  by  $N_{V(300^\circ\text{K})}$

$\times (T/300)^{3/2}$  we have

$$\log_{10} \frac{p}{N_{V(300^\circ\text{K})} e^A} = \log_{10} \frac{p}{N_V e^A} + \frac{3}{2} \log_{10} \frac{T}{300}. \quad (5)$$

From the value of  $\log_{10} p/N_{V(300^\circ\text{K})} e^A$  at  $1/T=0$  (see Fig. 7, curve 2)  $N_{V(300^\circ\text{K})} e^A$  can be calculated to be  $1.75 \times 10^{21}$  using for  $p_{\text{sat}}$  a value of  $4.9 \times 10^{19} \text{ cm}^{-3}$ . To calculate  $N_{V(300^\circ\text{K})}$  the value of the transport term  $A$  has to be known. The following analysis will show that an estimate of  $A$  can be made from the measurements.

Since the acceptors are partly compensated by donors we have

$$p = \frac{N_A - N_D}{N_D} N_V \exp\left(-\frac{E_A}{kT}\right), \quad (6)$$

if  $p \ll N_A$  and  $p \ll N_D$ . A further indication that the assumption of partial compensation is correct can be found from the fact that the linear parts of the  $\log_{10} \rho$  versus  $1/T$  curves for NiO doped with different amounts of Li give values for  $\rho_{T=\infty}$  of about  $5.10^{-4} - 10^{-3} \Omega\text{cm}$  upon extrapolation to  $1/T=0$ . In accordance with Eq. (6) this means that  $(N_A - N_D)/N_D$  and therefore the ratio of donors to acceptors is of the same order of magnitude for all Li concentrations. If there were no compensation at all, this extrapolated value of  $\rho_{T=\infty}$  should be proportional to  $N_A^{-1/2}$ . From Eq. (6) it follows that

$$\log_{10} \frac{p}{N_V e^A} = \log_{10} \frac{N_A - N_D}{N_D e^A} - 0.43 \frac{E_A}{kT}. \quad (7)$$

Applying this equation to our case (Fig. 7, curve 1) we find that  $(N_A - N_D)/N_D e^A = 2$ . From the differences between the experimental points and the extrapolated line at high temperatures (curve 1 in Fig. 7), and the change of  $p$  calculated with curve 2 in Fig. 7, the value of  $(N_A - N_D)/N_D$  can be calculated.<sup>23</sup> It is found that  $(N_A - N_D)/N_D \approx 10$ , indicating that  $e^A \approx 5$ . This value of  $e^A$  gives  $N_{V(300^\circ\text{K})} \approx 3.5 \times 10^{20}$ . This is much lower than the value of  $5.5 \times 10^{22}$  for the case of completely localized levels. The magnitude found for  $N_V$  points to the existence of a fairly narrow band, having a band width which is still large compared with  $kT$ . However, we must keep in mind that the relatively low value of  $N_{V(300^\circ\text{K})}$  is a consequence of the assumption that  $N_V \propto T^{3/2}$ .

The analysis given above has been based on the assumption that the acceptors are partly compensated by donors. This led to Eq. (6) for the number of free holes  $p$ . If it would have been assumed that the number of donors  $N_D$  is so small that always  $N_D \ll p$  then

$$p = (N_A N_V)^{1/2} \exp(-E_A/2kT) \quad (8)$$

and

$$\log_{10} \frac{p}{N_V e^A} = \log_{10} \left\{ \left( \frac{N_A}{N_V} \right)^{1/2} \frac{1}{e^A} \right\} - 0.43 \frac{E_A}{2kT}. \quad (9)$$

<sup>23</sup> H. J. van Daal, W. F. Knippenberg, and J. D. Wasscher, J. Phys. Chem. Solids 24, 109 (1963).

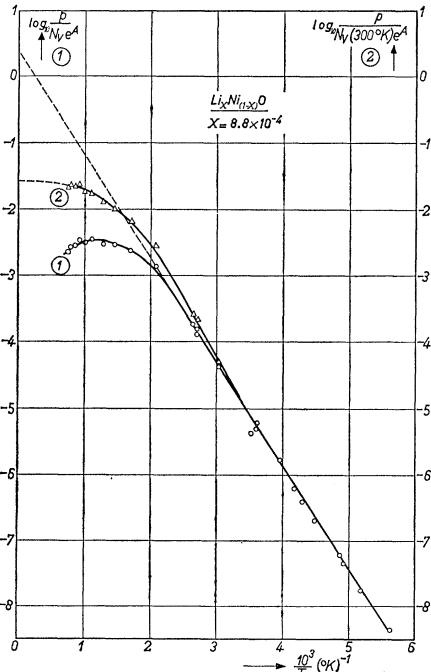


FIG. 7. The thermoelectric power  $\alpha$  of Fig. 4 plotted in units  $(-2.3k/e)$  versus the reciprocal temperature (curve 1), giving  $\log_{10} p/N_V e^A$ . Curve 2 shows  $\log_{10} p/N_{V(300^\circ\text{K})} e^A$  versus  $1/T$  and has been calculated from curve 1 with  $N_V = N_{V(300^\circ\text{K})} (T/300)^{3/2}$ .

From Fig. 7 it would follow that at room temperature  $(N_A/N_V)^{1/2}1/e^A \geq 2$ . If we now assume that  $N_V$  is independent of temperature and  $A=0$  (hopping model) it is found that  $N_V \approx 10^{19} \text{ cm}^{-3}$  instead of  $5.5 \times 10^{22} \text{ cm}^{-3}$ . If we assume that  $N_V$  increases with temperature and  $e^A \approx 5$  (band model) than  $N_V \leq 4.10^{17} \text{ cm}^{-3}$ . This is also much too small. Thus it is seen that in both cases absurd results are obtained if compensation effects are neglected.

In the analysis of the results we have found four physical reasons to justify the assumption of partial compensation:

1. The occurrence of impurity conduction at low temperatures.
2. The lowering of the Fermi level with increasing temperature.
3. The fact that the values of the conductivity extrapolated to high temperatures are about the same for all concentrations.
4. The values found for the density of states on the assumption of practically no compensation are definitely too small.

TABLE I.  $\text{Li}^{1+}$  and  $\text{Ni}^{3+}$  concentrations as determined by chemical analysis.

$[\text{Li}^{1+}]$ at. %	$[\text{Ni}^{3+}]$ at. %	$\frac{[\text{Ni}^{3+}]}{[\text{Li}^{1+}]}$	$\frac{N_D}{N_A}$	$\frac{N_A - N_D}{N_D}$
0.011	0.011	1.0		
0.038	0.037	0.97	0.03	37
0.067	0.062	0.93	0.07	12
0.088	0.084	0.96	0.04	47
0.299	0.245	0.82	0.18	4.5
2.45	2.35	0.96	0.04	42

We have tried to see whether it would be possible to determine the degree of compensation by chemical analysis. The results are given in Table I. One sees that for the samples with a Li concentration  $\geq 0.067$  at. % the ratio  $[\text{Ni}^{3+}]/[\text{Li}^{1+}]$  is significantly smaller than one, indicating that these samples are indeed partly compensated. For the samples with a Li concentration  $< 0.067$  at. % the uncertainty in the determination of  $[\text{Ni}^{3+}]$  is too large to decide whether these samples are partly compensated or not. The degree of compensation is in first approximation independent of the Li content, indicating that a certain fraction of the  $\text{Li}^{1+}$  is compensated by oxygen vacancies or Li interstitials which both act as donors. The magnitude of the degree of compensation found chemically agrees very well with the physically found value. This is a strong support for the analysis given.

D. Temperature Dependence of the Mobility

From the conductivity measurements (Fig. 1) and the values of  $p$ , calculated from the Seebeck effect (Fig. 7) and  $p_{\text{sat}} = 4.5 \times 10^{19} / \text{cm}^3$ , the mobility  $\mu$  as a function

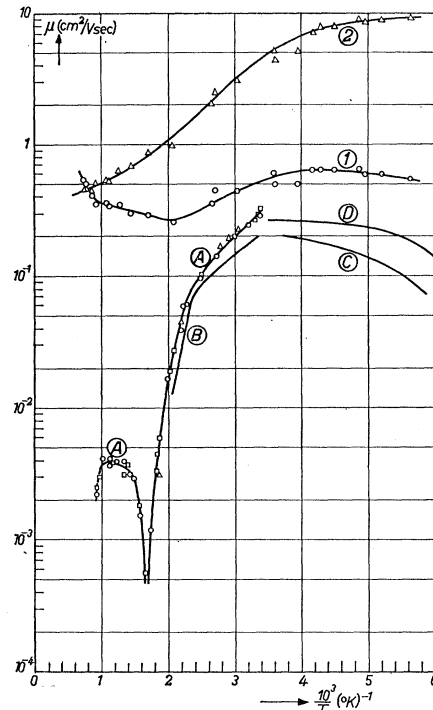


FIG. 8. Mobility  $\mu$  (1 and 2) and Hall mobility  $\mu_H$  (A, B, C and D) as a function of the reciprocal temperature. 1 and 2 are calculated from conductivity and Seebeck-effect measurements on NiO doped with  $8.8 \times 10^{-2}$  at. % Li using  $N_V = \text{constant}$  and  $N_V \propto T^{3/2}$ , respectively. A (see Ref. 20) was obtained on ceramic NiO containing  $8.8 \times 10^{-2}$   $\Delta$ ,  $1.1 \times 10^{-2}$   $\square$  and  $5 \times 10^{-3}$  at. % Li  $\circ$ . The curves B (Ref. 17) and C, D (Ref. 19) were obtained on single crystals, undoped and doped with about 0.2 at. % Li, respectively.

of temperature can be derived (see Fig. 8). Curve 1 is for  $N_V$  independent of temperature and curve 2 for  $N_V \propto T^{3/2}$ . We have also plotted the Hall mobility  $\mu_H = R_H \sigma$  (curve A) measured on ceramic samples of  $\text{NiO}^{20}$  containing  $8.8 \times 10^{-2}$ ,  $1.1 \times 10^{-2}$ , and  $5 \times 10^{-3}$  at. % Li and  $\mu_H$  obtained by different authors on single crystals of NiO (curves B,<sup>17</sup> C,<sup>19</sup> and D<sup>19</sup>). As can be seen from Fig. 8 the values of  $\mu_H$  obtained on ceramic samples are in agreement with those obtained on single crystals. The mobility  $\mu$  obtained from the Seebeck-effect data, however, is considerably larger than  $\mu_H$ . The discrepancy between  $\mu$  and  $\mu_H$  increases at high temperatures. The measurements above 600°K have shown that the Hall coefficient is extremely small in this temperature region and even has the negative sign.<sup>20</sup>

At high temperatures curves 1 and 2 in Fig. 8 give about the same value for the mobility. At these temperatures the calculated value of  $\mu$  is almost independent of the interpretation of the Seebeck effect. The conductivity measurements in this temperature region already lead directly to a value for the mobility if it is assumed that  $p \approx p_{\text{sat}} \approx [\text{Li}]$ . The temperature dependence of  $\mu$  at high temperatures, however, does depend on the interpretation of the Seebeck effect. The assumption that  $N_V$  is constant leads to an improbable decrease of  $p$  at high

temperatures (see Fig. 7, curve 1) resulting in an increase of  $\mu$  with temperature. The assumption that  $N_V \propto T^{3/2}$  leads to a behavior of  $p$  as one would expect (see Fig. 7, curve 2). The mobility in this case decreases with temperature in the whole temperature region.

At lower temperatures there is a considerable difference between curves 1 and 2. At this moment we have no further indication of which assumption on the behavior of  $N_V$  is the most appropriate. However, if we survey the different arguments we prefer curve 2. The decrease of  $p$  at high temperatures when  $N_V$  is assumed to be constant cannot be true. Moreover, the degree of compensation obtained from the analysis in which  $N_V \propto T^{3/2}$  has the same order of magnitude as found chemically. Unfortunately, the preference for curve 2 is not supported by the behavior of the Hall mobility. However, in view of the behavior of the Hall effect at high temperatures it is not yet clear how to interpret the Hall-effect measurements.

## V. CONCLUSIONS

From the analysis given above it is clear that a study of both Seebeck effect and conductivity does not lead to the thermally activated hopping process as was stated by many authors. The value of the mobility at room temperature is relatively large and decreases with increasing temperature. How then is it to be explained that so many authors have arrived at the hopping model from their experimental results? First of all we have seen that due to grain-boundary effects the gas atmosphere in which the samples are cooled has a very marked influence on the results obtained from dc conductivity measurements. It is quite probable that the presence of these effects has in many cases affected the experimental results and led to erroneous conclusions. Another source of errors may have been a wrong interpretation of the Seebeck effect. Most measurements were carried out on NiO doped with large amounts of Li. It appears, however, that for NiO doped with 0.5 at.% Li or more the Seebeck effect at temperatures only just below room temperature cannot be described with one type of charge carrier. If this nevertheless is done, the values found for the energy  $E_A$  will be much too small.

In the Introduction we mentioned some other arguments used in the literature in favor of the hopping

model. (a) and (b) both were concluded from conductivity measurements only. However, we think it is impossible to arrive at definite conclusions from measurements of one kind only. Moreover, concerning argument (a), the supposition that the loosening energy must become zero at large Li concentrations need not be correct. One may expect that it is precisely at high concentrations that new centers will be formed consisting of neighboring Li ions to which  $Ni^{2+}$  is strongly bound. Further, concerning argument (b), it can be seen in Fig. 2 that at room temperature the linear relationship between the conductivity and the dope concentration does not exist. The third argument (c) has already been overruled by the results obtained from Hall-effect measurements. The results from mechanical and dielectric-loss measurements on doped NiO finally appeared to give the best support for the hopping model. In the case of small dope concentrations it was already concluded<sup>15,16</sup> from dielectric measurements that the activation energy  $q$  for the jumping of a hole around a  $Li^{1+}$  ion is much smaller than the activation energy  $Q$  occurring in the conductivity. Only for large dope concentrations do mechanical loss measurements indicate that  $q$  is comparable to  $Q$ . However, these measurements were always performed at low temperatures, where impurity conduction is thought to dominate. It may be that the mechanical losses are not only due to the jumping of holes around the  $Li^{1+}$  ions. Electrons jumping from one center to another can also give rise to mechanical losses.

Summarizing we can conclude that the conductivity, Seebeck effect, and Hall effect clearly demonstrate that there is no coercive reason to introduce the model of thermally activated hopping in the case of NiO. From an analysis of the experimental data it even follows that employment of the band model leads to reasonable results.

## ACKNOWLEDGMENTS

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