

trons occupied the e_g orbitals. Since Mo^{+3} contains only three $4d$ electrons, all would be in the t_{2g} levels with parallel spins, and there would be no difference between this ion and the corresponding ion, Cr^{+3} , of the iron-group series. However, both Pd^{+3} and Ru^{+3} would have only one unpaired electron instead of three and five, respectively, which would be expected if Hund's rule were applicable. In the current investigations, the sensitivity of the measurements was insufficient to observe paramagnetic scattering from ions with a spin-only magnetic moment from a single electron, and the rapid decrease of the $4d$ -magnetic form factor would have

prevented the detection of magnetic ordering unless the antiferromagnetic structure produced reflections at small scattering angles. It would be of considerable interest to obtain the magnetic moment values in these two compounds from paramagnetic susceptibility measurements.

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Effect of High Pressure on Electrical Properties of NiO , CoO , CuO , and Cu_2O †

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The effect of pressure on electrical resistance and Seebeck coefficient at or near room temperature in NiO , CoO , CuO , and Cu_2O has been determined. Equations relating the Seebeck coefficient to hole concentration have been used to calculate the effect of pressure on hole mobility. In all materials examined, hole mobility was decreased by pressures to 60 000 atm. It has been proposed that NiO charge transport occurs by the motion of holes trapped at local sites by polarization of the surrounding lattice. The effect of pressure on the diffusion of self-trapped holes has been considered. Motion of self-trapped holes in an ionic crystal and of vacancies in a metal may be similar to the extent

that the motion of either probably involves cooperative movements of surrounding ions or atoms. Some inward relaxation probably occurs around either a hole trapped at a local site in an ionic crystal or around a vacancy in a metal. In either case pressure would be expected to decrease the jump frequency for motion of the defect. It is proposed that in NiO , CoO , and CuO , the decreased hole mobility with pressure was due to a decrease in diffusion rate of self-trapped holes. The explanation for pressure effects in Cu_2O may be more complicated since Cu_2O is generally regarded as a wide-band semiconductor.

INTRODUCTION

THE band model of solids predicts that materials such as NiO , CoO , and CuO with incompletely filled $3d$ shells should be expected to exhibit metallic conductivity. However, NiO , CoO , and CuO in pure stoichiometric condition are as good insulators as Cu_2O , which has a completely filled $3d$ shell. Mott¹ and Verwey² have proposed that materials such as NiO are insulators because the Ni^{++} ions are too far apart for appreciable overlap of $3d$ orbitals. Room temperature electrical conductivity in both NiO and Cu_2O may be increased several orders of magnitude by the presence of excess oxygen or by addition of certain impurities such as Li to NiO .

According to Verwey,³ in excess-oxygen or Li-doped NiO , hole transfer between localized sites occurs by a chain of transitions $\text{Ni}^{++} + \text{Ni}^{+++} \rightarrow \text{Ni}^{+++} + \text{Ni}^{++}$. It has been suggested,⁴ on the basis of effects of oxygen

pressure on electrical conductivity, that charge transfer in either NiO or Cu_2O occurs to the Verwey model, that is, by electron exchange between divalent and trivalent nickel ions or monovalent and divalent copper ions, respectively. In NiO , the lack of a detectable Hall effect at room temperature and an apparent increase in hole mobility with temperature are in accord with the Verwey model.⁵ Cu_2O , however, exhibits a measurable Hall effect at room temperature and an apparent decrease in hole mobility with temperature, suggesting hole transport in a wide valence band.⁶ It should be mentioned, however, that the temperature dependence of hole mobility in Cu_2O may be reversed in some ranges of temperature and oxygen pressure.⁷ Interpretation of electrical data from sintered Cu_2O samples is complicated by the presence of surface layers, which may under some conditions carry most of the current.⁸

The purpose of this work was to determine the effects of pressure on electrical properties of excess-oxygen or doped NiO , CoO , CuO , and Cu_2O . The effects of pressure on resistivity and Seebeck coefficients of these materials were measured on powder compacts at or

† This work was done under the auspices of the Air Force Office of Scientific Research.

¹ N. F. Mott, *Proc. Phys. Soc. (London)* **A62**, 416 (1949).

² J. H. deBoer and E. J. W. Verwey, *Proc. Phys. Soc. (London)* **49** (extra part), 49 (1937).

³ E. J. W. Verwey, *Semiconducting Materials* (Butterworths Scientific Publications Ltd., London, 1951), p. 151.

⁴ O. Kubaschewski and B. E. Hopkins, *Oxidation of Metals and Alloys* (Butterworths Scientific Publications Ltd., London, 1953), p. 30.

⁵ F. J. Morin, *Phys. Rev.* **93**, 1195 (1954).

⁶ W. H. Brattain, *Revs. Modern Phys.* **23**, 203 (1951).

⁷ P. Schmidt, *Ann. Physik* **14**, 265 (1954).

⁸ J. Bloem, *Philips Research Rept.* **13**, 167 (1958).

near room temperature. Since compacting was achieved by high pressure rather than by presintering, the samples were of uniform chemical composition.

The effect of pressure on the electrical properties of all of the above materials was similar. The resistivity either increased or remained nearly constant with pressure. In all of the materials examined, hole mobility was decreased by pressures up to 60 000 atm. It is shown that a decrease in hole mobility with pressure would be expected in NiO if charge transport occurs, as has been proposed,^{9,10} by thermally activated motion of holes self-trapped at local sites by lattice polarization.

A similarity in pressure effects on electrical properties of NiO and Cu₂O might be expected if the charge transport mechanism were similar in the two materials. However, the decrease in hole mobility in Cu₂O might also have been due to pressure-induced interband scattering or to other scattering effects. It was not possible from investigation of powder compacts to distinguish between various possible explanations for pressure effects in Cu₂O.

Mott¹ has suggested that if a substance such as NiO were subjected to very high pressure, it should suddenly show metallic conduction for some value of the pressure. In this investigation metallic conduction in NiO was not found at pressures up to 200 000 atm.

EXPERIMENTAL METHODS

To measure electrical resistivity under pressure, powder compacts were squeezed between two tungsten carbide pistons in an apparatus of the Bridgman-anvil type. The arrangement of sample and pistons was similar to that used by Griggs *et al.* for measuring resistivity of LiH.¹¹ The material was introduced into the pressure cell by centering a catlinite ring gasket on the lower piston, then heaping powder over the hole in the ring. After precompacting to 10 000 atm, more powder was added near the center of the piston to insure a nearly equal distribution of the load over the gasket and sample.

Sample resistance was measured by a four terminal current-voltage method or by a Wheatstone bridge. Electrical contact was made to the piston holders which were insulated from the press by mica spacers. Because of parallel conduction through the catlinite ring and the mica spacers, materials with resistivity greater than 10⁶ ohm-cm could not be measured by this method.

The pressure on the sample was calculated by dividing piston load by piston area. At room temperature, the calculated pressure probably approximated the real pressure on the sample quite closely up to 150 000 atm.¹¹

⁹ R. R. Heikes and W. D. Johnston, *J. Chem. Phys.* **26**, 582 (1957).

¹⁰ J. Yamashita and T. Kurosawa, *J. Phys. Chem. Solids* **5**, 34 (1958).

¹¹ D. T. Griggs, W. G. McMillan, E. D. Michael, and C. P. Nash, *Phys. Rev.* **109**, 1858 (1958).

Above 150 000 atm, the piston area was increased by plastic flow of the tungsten carbide resulting in average pressure lower than calculated. Also the sample shape was changed when the piston was deformed. There is, therefore, increasing uncertainty concerning effect of pressure on sample resistivity at pressures above 150 000 atm.

During the first pressure cycle, the powder compacted and the sample configuration changed. There were effects of nonhydrostatic stresses on the sample resistance. In an effort to separate these from the effects of hydrostatic pressure, resistance measurements were made during successive increasing and decreasing pressure cycles. After a certain number of cycles, it was generally found that the resistance at a given pressure remained nearly constant during successive cycles. It was assumed that the variation in resistance was then due mainly to hydrostatic pressure. The effects of hydrostatic pressure were, of course, superimposed on the effects of previous nonhydrostatic stresses. Line broadening in x-ray diffraction patterns indicated that there was always some residual lattice strain introduced by nonhydrostatic stresses.

Seebeck coefficients were measured by compressing powder compacts between preflattened thermocouples. The details of the pressure cell for determining Seebeck coefficients have been described elsewhere.¹² The mean temperatures of Seebeck samples were between 65°C and 90°C; temperature differences across samples were between 10 and 35 degrees depending on the material and sample thickness.

Seebeck data were taken from samples which had been cycled until the sample resistance and temperature on either side of the sample indicated that the sample configuration was stable. It was found that the Seebeck coefficients were generally lower in subsequent cycles than during the first cycle. The decrease in the Seebeck coefficient on cycling depended somewhat on the sample thickness, which could be controlled by the amount of powder used. Seebeck coefficients were generally lower in thick samples. Examination of samples thicker than 0.006 in. showed extrusion of the powder outside the periphery of the flattened thermocouples. Since heat transfer between the pistons and sample was via the thermocouples, and temperature gradients were obtained by heating the top piston, sample extrusion outside the thermocouple area decreased the average temperature difference between top and bottom sample surfaces resulting in decreased thermoelectric power. To obtain pressures up to 60 000 atm without failure by short circuit between the thermocouples, it was necessary to use samples, in which some extrusion occurred. It was assumed that in stabilized samples where extrusion occurred, the effect temperature gradient, and, therefore, the measured Seebeck coefficients were low by a constant factor over the pressure range from 10 000

¹² A. P. Young, P. B. Robbins, W. B. Wilson, and C. M. Schwartz, *Rev. Sci. Instr.* **31**, 70 (1960).

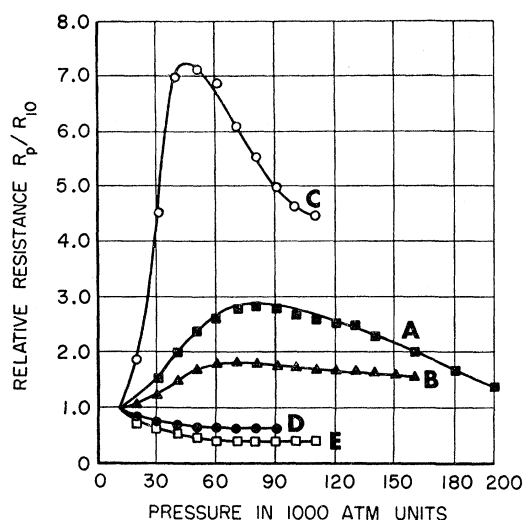


FIG. 1. Resistance of NiO samples as a function of pressure during the first increasing pressure cycle. The quantity R_p/R_{10} is the ratio of sample resistance at pressure to resistance at 10 000 atm.

to 60 000 atm. Therefore, Seebeck coefficients from these thick samples were corrected by a constant factor of the order of 15% which provided a fit between the Seebeck data from thick and thin samples at 10 000 and 20 000 atm.

RESULTS

NiO

All materials examined are listed in Table I. NiO materials *D* and *E* were obtained from Morin, who has described their electrical properties at normal pressure.⁵ Since the starting material for the high-pressure measurements had to be in powder form, the sintered materials *D* and *E* were powdered in a glass mortar.

The effect of pressure on electrical resistivity was similar in materials *A*, *B*, and *C*. During the first pressure cycle the resistivity increased with pressure up to a pressure of 60 000 to 80 000 atm at which point the resistivity began to decrease slowly. The effect of pressure on electrical resistivity of materials *A*, *B*, and *C* during the first cycle is shown in Fig. 1. The curves are normalized. R_p/R_{10} is the ratio of sample resistance, at pressure p , to resistance at 10 000 atm.

It was found on reducing the pressure that much of the resistance increase in materials *A*, *B*, and *C* was residual. R_p/R_{10} curves, where R_p and R_{10} were resistances of precompressed samples, are shown in Fig. 2. The difference in the curves of Figs. 1 and 2 is greatest in the low-pressure range. In all materials examined, the effect of precompression on resistance decreased with pressure until at 80 000 atm the difference in resistance during the first pressure cycle and subsequent cycles was negligible.

There was a possibility that some or most of the residual increase in resistance and change in nature of

TABLE I. Description of materials examined at high pressure.

Material designation	Source ^a
NiO <i>A</i>	J. T. Baker Reagent NiO, green powder
NiO <i>B</i>	J. T. Baker Reagent NiO, black powder
NiO <i>C</i>	Johnson-Matthey Specpure NiO
NiO <i>D</i>	Morin Sample 5 (reference 5)
NiO <i>E</i>	Morin Sample 6 (reference 5)
CoO	A. D. Mackay
CuO	J. T. Baker Reagent
Cu ₂ O	J. T. Baker Reagent
Cu ₂ S	Baker and Adamson Reagent
Ag ₂ S	A. D. Mackay
CdS	Baker and Adamson Reagent

^a All materials were examined by x-ray diffraction for detection of minor phases. None were found.

the curves in Figs. 1 and 2 could have been due to loss of contact between the sample and the pistons when the pressure was reduced. For another check on the effect of precompression on the residual resistivity and the shape of R_p/R_{10} vs pressure curves, several samples of materials *A*, *B*, and *C* were compressed to pressures of approximately 100 000 atm. The resulting coherent samples of each material were powdered in a mortar. Samples prepared with this powder were then run in the usual way. The initial resistance at 10 000 atm was considerably higher than that found in samples of the as-received powder. Also the resistivity vs pressure curves in the initial cycle in the precompressed and reground samples resembled the curves of Fig. 2 rather than Fig. 1. It was concluded, therefore, that the increase in residual resistance and change in shape of the curves in Figs. 1 and 2 was due mainly to changes within the samples rather than to changes in contact resistance on reduction of pressure.

The effects of pressure on the resistance of samples made from materials *D* and *E* are shown in Figs. 1 and 2. The differences in R_p/R_{10} ratios during the first pressure cycle and subsequent cycles were much less in

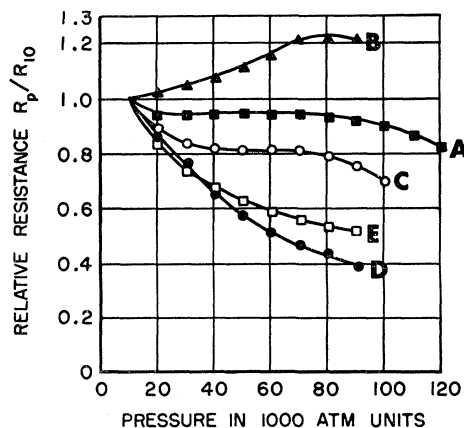


FIG. 2. Resistance of NiO samples as a function of pressure after precompression. The samples were cycled several times to pressures over 100 000 atm until the resistance at given pressure was nearly constant during successive pressure cycles.

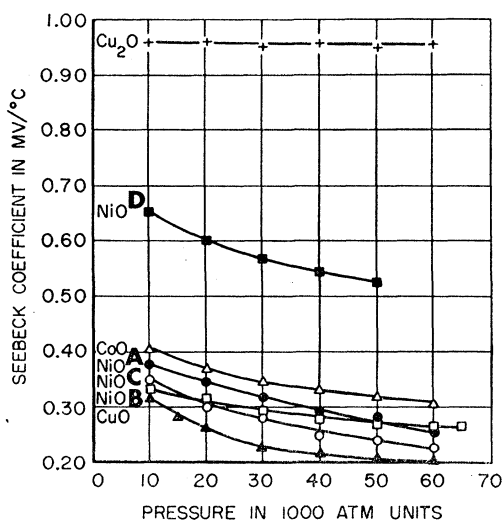


FIG. 3. Seebeck coefficients of NiO, CoO, CuO, and Cu₂O samples as a function of pressure.

materials *D* and *E* than in *A*, *B*, and *C*. Some prior lattice strain was probably introduced by grinding the sintered materials *D* and *E*, thus reducing the effects of further strain on the resistance. Effects of prior grinding on resistance of powder compacts have been noted by other investigators.¹³

The Seebeck coefficients of all NiO materials decreased with pressure as shown in Fig. 3. The curve for NiO *E*, not shown, was very close to the curve for NiO *B*. The NiO materials were all *p* type.

CoO, CuO, and Cu₂O

The effects of pressure on the resistance of CoO and of NiO materials *A*, *B*, and *C* were similar to the extent that the resistance of CoO samples increased during the first pressure cycle and that much of the resistance increase was residual. However, the resistance increase in CoO with pressure during the first cycle was much greater than in any NiO material. There was also a

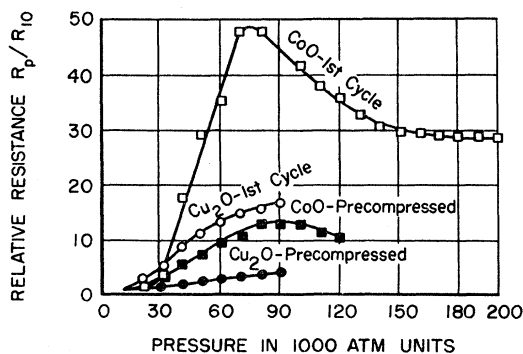


FIG. 4. Resistance of CoO and Cu₂O samples as a function of pressure during the first pressure cycle and after precompression.

¹³ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 69.

considerable increase in resistance with pressure of pre-compressed CoO samples as shown in Fig. 4.

The resistance of CuO samples during the first cycle decreased by about 30% between 10 000 and 30 000 atm, and then leveled off. On release of pressure from 30 000 atm, the resistance stayed nearly constant at the R_{30} value. Resistance of precompressed samples was nearly constant. The initial decrease in resistance of CuO samples was probably related to powder compaction. Pressures of about 20 000 atm were required for production of CuO pellets, whereas hard coherent pellets of most other materials investigated were formed at pressures of less than 10 000 atm.

Cu₂O samples were obtained from two sources. The electrical characteristics under pressure of samples from the two materials were nearly the same. Pressures attainable with Cu₂O powder compacts were limited by blowout of the catlinite rings. Apparently the coefficient of friction of Cu₂O on tungsten carbide is lower than that of NiO and CoO. Up to pressures of about 90 000 atm, resistance increased with pressure both during the first cycle and on recycling as shown in Fig. 4.

The Seebeck coefficient of CoO and CuO decreased with pressure, as shown in Fig. 4, but in the case of Cu₂O, was nearly constant under pressure. This was confirmed in several samples of each reagent grade material. The results of one run are shown in Fig. 3. The Seebeck coefficient of Cu₂O samples was approximately 1 mV/°C. The conductivity of CoO, CuO, and Cu₂O was *p* type.

Ag₂S, CdS

Some materials other than 3d transition metal oxides and Cu₂O were examined to determine whether large changes in resistance, such as Bridgman¹⁴ found in some compound semiconductors, would be observed with the methods of this investigation.

The resistance of powder compacts made from Ag₂S dropped by a factor of approximately 400 between 10 000 and 50 000 atm. The pressure effect on resistance was reversible in cycling. The resistance of samples of CdS dropped by a factor of more than 150 000 between 10 000 and 50 000 atm. Much of this resistance decrease was irreversible as the resistance at 10 000 atm on the decreasing pressure cycle dropped below its initial value by a factor of about 15 000. X-ray analysis showed that the CdS was predominantly hexagonal wurtzite structure before compression; after compression it was predominantly cubic zincblende structure.

DISCUSSION

Morin¹⁵ proposed an energy-band scheme for impure or nonstoichiometric NiO in which localized 3d levels lie in the energy gap between the filled and empty *sp*

¹⁴ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **81**, 169 (1952).

¹⁵ F. J. Morin, *Semiconductors*, edited by N. E. Hannay (Reinhold Publishing Corporation, New York, 1959), p. 600.

oxygen bands. Holes are created in the $3d$ levels by electron transitions from the $3d$ levels to low-lying acceptor levels. A $3d$ hole freed from a cation defect is presumed to consist of a Ni^{+++} ion with normal Ni^{++} cation neighbors for some distance around it. The hole can diffuse about the cation lattice by exchanging an electron with a Ni^{++} neighbor. When an external electric field is applied to the crystal, a net drift of holes occurs, resulting in current flow. The Morin energy-band picture is consistent with the Verwey model in which hole transfer between localized sites occurs by transitions of the type $\text{Ni}^{++} + \text{Ni}^{+++} \rightarrow \text{Ni}^{+++} + \text{Ni}^{++}$.

The Morin assumption of conduction in localized $3d$ levels led to equations relating the Seebeck coefficient Q to the hole concentration p :

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

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

where E_F is the energy separation between the Fermi level and the filled d levels from nickel ions, and $N = 5.6 \times 10^{22}$ nickel atoms per cc of crystal. The hole concentration p is the number of $3d$ holes freed from cation defects, which is equivalent to the number of Ni^{+++} ions removed from the neighborhood of cation defects. Hole mobility is dependent on the jump frequency for motion of Ni^{+++} ions in the cation lattice.

Equations (1) and (2) have led to a quantitative fit with the data in investigations of doped NiO samples.^{5,16} Similarities in electrical properties of doped NiO, CoO, and CuO have been noted.⁹ Equations (1) and (2) were assumed to be applicable to NiO, CoO, and CuO, and were used to determine the effects of pressure on hole concentrations in these materials. There has been no experimental evidence that these equations are applicable to Cu_2O . However, there must be a relationship between hole concentration and Seebeck coefficient in Cu_2O . The Seebeck coefficient of Cu_2O was nearly constant throughout the pressure range from 10 000 to 60 000 atm. Effects of pressure on hole concentration may have been offset by other pressure effects to maintain a constant Seebeck voltage over the whole pressure range. However, if the changes in hole concentration had been large, their effect on the Seebeck voltage would probably not have been offset throughout the pressure range. It was assumed, therefore, that to a first approximation, hole concentration in Cu_2O was unaffected by pressure.

The effects of pressure on hole mobilities are shown in Fig. 5. The quantity μ_p/μ_{10} is the ratio between hole mobility at pressure and at 10 000 atm. In examining the curves of hole mobility vs pressure it should be kept in mind that the Seebeck coefficient data were approximate. Only quite large differences in behavior among various materials should be regarded as significant. For instance, among the NiO materials, only NiO E differed significantly from the others. NiO E

was a Li-doped material with nearly 10% Li addition. At this concentration each Ni^{+++} ion would have on the average at least one Li^+ ion as a nearest neighbor. For such heavily doped material there are no Ni^{+++} ions far removed from the neighborhood of cation defects. The meaning of the expression for hole concentration p in Eq. (2) for such heavily doped material is doubtful because it is apparent that $3d$ holes can never be considered to be freed from cation defects.

Consider first, the pressure effects in NiO. Morin found that the hole mobility in Li-doped NiO samples was quite low, and that it increased exponentially with temperature at normal pressure. Low hole mobilities denote, in the Verwey model, low jump frequencies for motion of higher valency ions. This low jump frequency

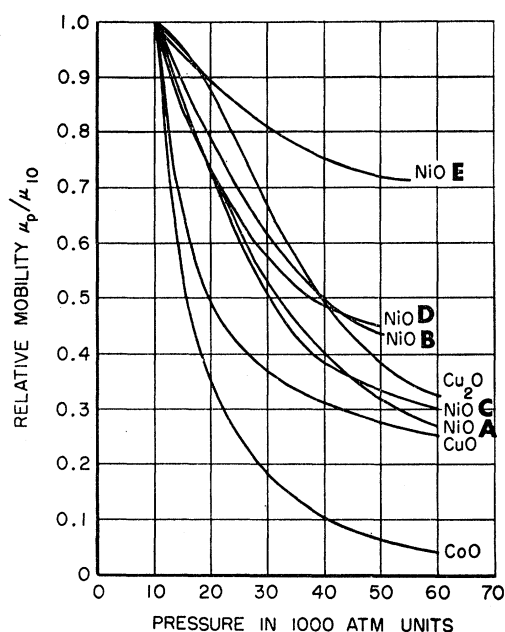


Fig. 5. Hole mobility of NiO, CoO, CuO, and Cu_2O samples as a function of pressure. Hole concentration as a function of pressure was determined from the Seebeck data of Fig. 3 by use of Morin's equations (reference 5). The quantity μ_p/μ_{10} , the ratio of hole mobility at pressure p to hole mobility at 10 000 atm, was computed from pressure effects on hole mobility and on resistance of recompressed samples.

may be accounted for by a trapping process first proposed by Gurney and Mott.¹⁷ If an electron or a hole remains on an ion for a time, which is long compared to the natural vibrational period of the lattice, the surrounding medium will be polarized. If polarization of the lattice around a higher valency ion such as Ni^{+++} occurs, motion of the ion in the lattice will involve more than the motion of electrons alone.^{9,10} Because the polarizing effect also moves with the Ni^{+++} ion, the ion movements are not isolated events, but are co-operative movements involving a number of ions. In

¹⁶ G. Parravano, J. Chem. Phys. **23**, 5 (1955).

¹⁷ R. W. Gurney and N. F. Mott, Proc. Phys. Soc. (London) **49**, 32 (1957).

this respect, the motion of higher valency ions in a polarized medium may resemble the motion of vacancies in a metal, since vacancy motion may also involve co-operative movements among the atoms surrounding the defect.

Nachtrieb¹⁸ has proposed that in the vacancy mechanism for diffusion in a metal, transport does not occur by movement of simple vacancies but rather by the movement of small regions of disorder through the crystal. Removal of an atom from the interior of a metallic crystal probably results in an inward movement of its nearest former neighbors. Nachtrieb has used the term "relaxion" to describe the disordered region around a vacancy. Motion of a Ni^{+++} ion in a polarized lattice and of a vacancy in a metal crystal may be similar in that the polarizing effect or the relaxions moves with the defect. In either case, before a Ni^{+++} ion or a vacancy can move, this theory suggests that work must be done on the surrounding ions or atoms to restore them to their normal positions.

The diffusion rate of Ni^{+++} ions or relaxions is given by an equation of the type

$$D = \gamma a^2 \nu \exp(-\Delta F/RT), \quad (3)$$

where ν is the average lattice vibrational frequency, a is the lattice parameter, and γ is a constant determined by the lattice geometry and the assumed jump mechanism. The quantities, a^2 , ν , and ΔF all depend on pressure. Since a^2 and ν vary in opposite ways with pressure, it seems likely the direction of change in D with pressure will depend on the exponential term. The free energy ΔF is related to the work required to restore surrounding atoms or ions to their normal positions. One would expect this work to be increased by pressure if the relaxation around a defect is inward. The jump frequency for motion of the defect would decrease with pressure. Measurement of pressure effects on self diffusion of several crystalline materials indicates that the jump frequency of vacancies is decreased by pressure.¹⁹

The exact nature of ion displacements around a higher valency ion such as Ni^{+++} will depend on the forces of attraction and repulsion between ions in the crystal. The surrounding oxygen ions should be moved inward around the Ni^{+++} ion from their normal positions; the nearest Ni^{++} ions somewhat further away will be moved outward. Because the Ni^{++} ions will be partially shielded from the Ni^{+++} ion by the polarized O^{--} ions and also because the Ni^{+++} ion has a smaller radius than Ni^{++} , there is probably a net inward re-

laxation of ions around a Ni^{+++} ion. The relaxation around a Ni^{+++} ion may be quite small because of the rapid increase in repulsive forces on closer ion approach; nevertheless, one might expect some increase, with pressure, in the work required to restore ions around a Ni^{+++} ion to normal positions. However, with sufficient pressure, the general lattice compression will cause the ion configurations around a Ni^{+++} ion and neighboring Ni^{++} ions to become more nearly degenerate. There may, therefore, be a limiting pressure above which the activation energy for Ni^{+++} ion diffusion begins to decrease. The trend of resistivity and Seebeck coefficients in NiO samples indicates that there may be a reversal in hole mobility at some pressure above 60 000 atm.

The NiO, CoO, CuO, and Cu_2O materials examined were similar to the extent that none of them exhibited the large decreases in resistance with pressure found in some other semiconducting compounds. In particular, CoO and Cu_2O were similar in that the resistance of each of these materials increased with pressure both during the first cycle and after precompression. The effects of pressure on electrical properties of NiO, CoO, CuO, and Cu_2O were consistent with a process in which conduction occurs by diffusion of self-trapped holes. This does not mean that there was no other possible explanation for the effects of pressure on the electrical properties of these materials. It was not possible on the basis of Seebeck coefficient and resistivity data from powder compacts to distinguish definitely between various possible effects of pressure on electrical properties. It is possible that in Cu_2O resistivity was increased because of interband scattering or other complicated effects such as have been observed in germanium above 10 000 atm.²⁰ For more quantitative data and more detailed consideration of charge transport mechanisms, experiments with single crystals are required. Consideration is being given to methods of determining pressure effects on single crystals of these relatively high resistance materials.

Mott¹ has suggested that there may be a critical interatomic spacing in NiO for which the energy of the crystal with a large number of electron and hole pairs will be less than the energy of the crystal with no pairs. One would expect then that at some value of high pressure, the effective number of free electrons in NiO would suddenly jump to about one per atom and metallic conduction would occur. The results of the present investigation indicate that the critical pressure for metallic transition in NiO or CoO is greater than 200 000 atm.

¹⁸ N. H. Nachtrieb and G. S. Handler, *Acta Met.* **2**, 797 (1954).
¹⁹ L. A. Girifalco and H. H. Grimes, NACA Technical Note 4408, September, 1958 (unpublished).

²⁰ W. Paul and H. Brooks, *Phys. Rev.* **94**, 1128 (1954).