PHYSICAL REVIEW VOLUME 114, NUMBER 6 JUNE 15, 1959

Optical Properties of Nickel Oxide*

R. Newman† and R. M. Chrenko
General Electric Research Laboratory, Schenectady, New York

(Received January 28, 1959)

The absorption spectrum of single crystal NiO has been measured in the 0.1 to 6 ev range and its reflectivity spectrum from 0.025 to 10 ev. The absorption spectrum shows a series of lines from 1 to 3.5 ev arising from internal transitions of the Ni ion. A continuous background absorption occurs in the range from 0.1 to 3.5 ev whose magnitude increases with impurity concentration. The absorption coefficient rises steeply above 3.5 ev and reaches a value of 10^6 cm^{-1} at and above 4 ev. An absorption line at 0.24 ev is found to be temperature sensitive in both intensity and frequency in the range above 300°K. Its behavior suggests that it is connected with the antiferromagnetic ordering. The reststrahlen spectrum was observed with the following parameters: high- and low-frequency dielectric constants 5.4 and 12, respectively; energies of longitudinal and transverse optical mode vibrations are 0.076 and 0.044 ev, respectively.

THE properties of the monoxides of the iron group of transition metals are of interest in several branches of solid state physics. They are simple examples of variable valence semiconductors[1–4] and antiferromagnets.[5–7] Their crystal structure[8] (NaCl type) affords conceptual simplicity. As such, a thorough study of their various physical properties in systems which are well defined in as many respects as possible (e.g., stoichiometric single crystals) is both intrinsically interesting and valuable as a point of departure for quantitative understanding of more complicated materials of practical interest (e.g., ferrites). In this paper we shall describe some results of optical measurements on single crystal NiO.

EXPERIMENTAL

Single crystals were prepared by two different techniques. The first of these was the flame fusion method.[9] Here, crystals about 0.5 cm in diameter and several cm long were grown in an oxygen rich oxyhydrogen flame from NiO powder. The latter was obtained by pyrolysis of reagent $NiCO_3$ (chief impurity, Co, 0.1%).

Crystals were also prepared by halide decomposition.[10] In this method, epitaxial growth at 700°C of single crystal films of NiO on single crystals of MgO is obtained by decomposition of $NiBr_2$ with H_2O vapor. Films could be grown with thicknesses in the range from about 1 to 10^2 microns and several cm^2 in area. The thickness of the films was measured in a micrometer microscope for thicknesses in excess of a few microns. The thickness of the thinner films was not measured directly. Their thickness was obtained by fitting optical absorption data obtained from them to previously established data points. To obtain thick specimens, of order one mm thick, growth was achieved on previously prepared thin NiO films which had been freed from their MgO backing by chemical dissolution of the latter.

Crystals prepared by the two techniques had the same x-ray lattice constants to within experimental error (4.176±0.001 a.u.). They differ in their optical properties (see below) in such a direction as to indicate that the flame fused crystals have a higher nonstoichiometric excess of oxygen. This is also indicated by the electrical resistivities. The flame fused crystals had resistivities of order 10^6 ohm-cm, the halide decomposition crystals were about 10^{10} ohm-cm. Since the halide decomposition crystals are prepared at a much lower temperature it might be expected that they should be more perfect with respect to stoichiometry.

For some of the optical work it was necessary to obtain very thin specimens with thicknesses of a few hundred angstroms. For this purpose Ni was evaporated in vacuum onto polished fused quartz sheets. The thickness of the nickel film was measured optically by measurement of the transmission in the visible and ultraviolet using some recently obtained values of the optical constants of Ni.[11] The Ni films were then oxidized by heating in air at 900°C. The thickness of the NiO films was calculated from the Ni film thickness correcting for the change in density upon oxidation.

RESULTS

Figure 1 shows the reflectivity spectrum, Fig. 2 the absorption spectra of NiO. The reflectivity spectra obtained from halide decomposition crystals and flame fused crystals were identical. The absorption data shown were taken with crystals prepared by halide decomposition unless otherwise noted. The absorption

---

* This work supported in part by the U. S. Air Force (Wright Air Development Center).

† Present address: Materials Research Laboratory, Hughes Products, Newport Beach, California.

[1] E. J. W. Verwey *et al.*, Phillips Research Repts. **5**, 173 (1950).

[2] J. H. DeBoer and E. J. W. Verwey, Proc. Phys. Soc. (London) **49** (extra), 59 (1937).

[3] R. R. Heikes and W. D. Johnson, J. Chem. Phys. **26**, 582 (1957).

[4] F. J. Morin, Phys. Rev. **93**, 1199 (1954); Bell System Tech. J. **37**, 1047 (1958).

[5] C. H. LaBlanchetais, J. phys. radium **12**, 765 (1951).

[6] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

[7] J. R. Singer, Phys. Rev. **104**, 929 (1956).

[8] H. P. Rooksby, Acta Cryst. **1**, 226 (1948); N. C. Tombs and H. P. Rooksby, Nature **165**, 442 (1950).

[9] E. J. Scott, J. Chem. Phys. **23**, 2459 (1955).

[10] R. E. Cech and E. I. Alessandrini, General Electric Research Laboratory Report No. 58-RL-1983, 1958 (unpublished) and Trans. Am. Soc. Metals (to be published).

[11] S. Roberts (unpublished results).

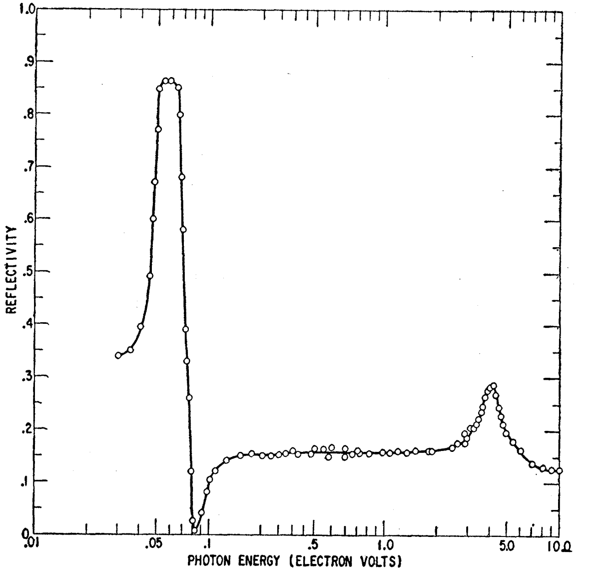

FIG. 1. Reflectivity spectrum of NiO at 300°K.

spectra differed in certain details for the two kinds of crystals. This will be discussed below. It will be convenient to divide the spectrum into three parts for purposes of discussion. We will first discuss the spectrum for $h\nu > 0.1$ ev, with the exception of the line at about 0.24 ev, then the 0.24-ev line and finally the region for $h\nu < 0.1$ ev.

A. $h\nu > 0.1$ ev

Starting at about 1 ev and proceeding upward in energy to about 3.5 ev there is a series of absorption lines. A portion of this line spectrum has previously been observed.[4] These lines are most clearly resolved from one another at low temperatures. There is a close correspondence between the spectrum of these lines and the spectra of Ni^{++} ions in either a cubic crystal such as MgO,[12] in the pseudo cubic environment found in aqueous solution of some nickelous salts[13] or in crystals with hydrated Ni ions [i.e., the $Ni(H_2O)_6{}^{++}$ ion].[14] The spectra in these analogous cases have been shown to arise from the cubic field Stark splitting of the energy levels of the Ni^{++} ion.[15,16] The theoretical procedures for the analysis of this situation were developed originally to treat the case of the magnetic susceptibility of magnetically dilute paramagnetic ions in a crystal and were extended to deal with the spectroscopic problem.[17] In brief, the procedure involves setting up a cubic field potential which perturbs the energy levels of the free ion. The perturbing potential is described in terms of a coefficient Dq and is quartic in the crystal coordinates. To first order the separation of the energy levels from the ground state are calculable from the levels of the free ion and Dq. In practice some changes from the values of the levels of the free ion are required to obtain satisfactory agreement between observed and calculated crystal spectra.[12]

In Table I, we show the observed frequencies, the proposed assignment, and, as a check, the values of the spectroscopic terms that can be independently calculated using the energy level parameters evaluated from the energies of other lines in the spectrum. We also show a comparison of our data with that of the spectrum of Ni^{2+} in MgO.[12] It is most convenient to calculate the Dq value from the lowest energy absorption line for which the theory predicts $\hbar\omega = 10\ Dq$. It can be noted from the table that all the observed transitions are forbidden by one or more selection rules (e.g., $g \rightarrow g$ is forbidden). It is through an interaction with lattice vibrations, that the lines develop intensity. This is consistent with the relatively low values of absorption coefficient (e.g., $\alpha = 10^2$ to 10^3 cm^{-1} above background) observed. The free ion levels and the Dq value (0.113 ev, 910 cm^{-1}) found here are approximately those found for the analogous systems mentioned above.[12–14] Thus a tight binding approximation gives a reasonably good representation of the observed energy level spectrum for the internal transitions of the Ni^{2+} ion in NiO. From the observed width of some of the absorption lines one would estimate that the width of the Ni^{2+} ion $3d$-band in this material is less than 0.25 ev wide.

NiO shows antiferromagnetism and one might have anticipated some evidence of superexchange in the spectrum (e.g., splitting of the lines). To test this idea, spectral measurements were made at various temperatures in the range from about 700°K (i.e., above the Neel point, 640°K) down to 20°K. With increasing temperature only slight increases in the intensities of the absorption lines and small shifts toward lower energy in the positions of the peaks were observed.

TABLE I. Optical spectrum of NiO at 300°K. (Energy level parameters for NiO $D_q = -0.113$ ev, $E_p = 1.56$ ev, $E_D = 1.26$ ev, $E_G = 2.38$ ev.)

Assignment and crystal symmetry representations of excited states[a]		Observed absorption lines[b] (electron volts)		Calculated absorption lines (electron volts)	Absorption coefficient (cm^{-1})
$\Gamma_5(^3F)$	$^3T_{2g}$	1.13	(1.07)		380
$\Gamma_3(^1D)$	^1E_g	1.75	(1.68)	1.62[c]	950
$\Gamma_4(^3F)$	$^3T_{1g}$	1.95	(1.83)	1.85[c]	450
?	?	2.15			230
$\Gamma_5(^1D)$	$^1T_{2g}$	2.75	(2.69)		950
$\Gamma_4(^3P)$	$^3T_{1g}$	2.95	(3.04)		1900
$\Gamma_1(^1G)$	$^1A_{1g}$	3.25	(3.21)		9000
$\Gamma_4(^1G)$	$^1T_{1g}$	3.52	(3.50)		12000

[a] The ground state has a $\Gamma_2(^3F)$, $^3A_{2g}$ representation.
[b] Values in parenthesis are Ni^{2+} in MgO [W. Low, Phys. Rev. **109**, 247 (1958)].
[c] Calculated using energy level parameters listed above which were obtained from other observed lines.

---

[12] W. Low, Phys. Rev. **109**, 247 (1958).

[13] C. K. Jorgensen, Acta Chem. Scand. **9**, 1362 (1955).

[14] H. Hartmann and H. Muller, Trans. Faraday Soc. (to be published).

[15] R. Schlapp and G. Penney, Phys. Rev. **42**, 666 (1932).

[16] R. Finkelstein and J. H. Van Vleck, J. Chem. Phys. **8**, 790 (1940).

[17] L. E. Orgel, J. Chem. Phys. **23**, 1004 (1955).

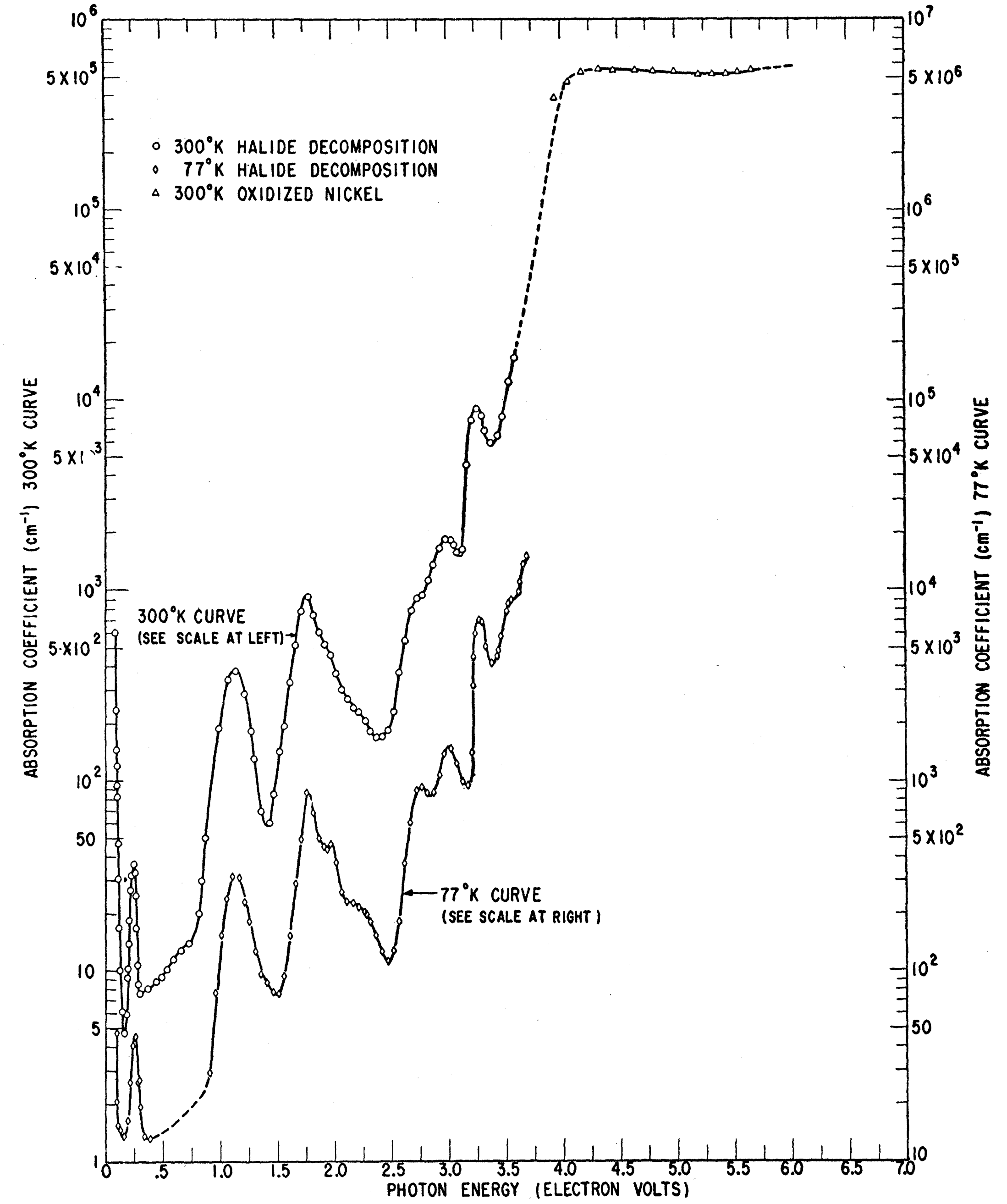

FIG. 2. Absorption spectrum of NiO at 300°K, 77°K. Dashed lines are interpolations.

These phenomena are explicable as phonon and lattice dilation effects. We conclude that exchange interactions are not important in determining the observed spectral pattern in this region. We would note that the temperature dependence of the frequency of the line at about 1 ev indicates that $d|Dq|/dT = -3\times10^{-5}$ ev/°C in the range from 300 to 630°K.

At approximately 4 ev the absorption spectrum is characterized by a rapid increase in absorption coefficient followed by a plateau at higher energy. The same effect is manifested in the reflectivity spectrum by the presence of a peak at 4 ev. In the range from 4 to about 6 ev, our measurements on polycrystalline films failed to indicate any fine structure in the plateau. The absorption coefficient in the plateau region is about 10^6 cm^{-1}. The form of the spectrum suggests a photoionization process with an ionization energy of about 4 ev. The magnitude of the absorption coefficient implies that it is an allowed transition. The first allowed internal transition of the free Ni^{++} ion is $3d^8 \rightarrow 3d^7 4p$, this corresponds to a term value of 14 ev in the free ion.[18] A reduction in this value to 4 ev by effects due to the crystal lattice is unlikely in view of the success of the tight binding approximation in accounting for the discrete spectrum up to about 3.5 ev. A more reasonable hypothesis is that one is seeing a charge transfer spectrum[19] as in alkali halides. That is, in terms of a tight binding model

$$Ni^{2+}+O^{2-}+\hbar\omega \rightarrow Ni^{+}+O^{-}.$$

In the charge transfer spectrum of the oxides[20] (e.g., MgO) the absorption is usually characterized by one or more absorption peaks, followed by an absorption continuum with an absorption coefficient of order 10^6 cm^{-1}. In our measurements at 300°K no peaks are observed.[21] Possibly they would be more obvious at low temperatures. The interpretation of the absorption as due to charge transfer, indicates that a lower limit for the energy of the virtual charge transfer process appearing in the theories of superexchange would be about 4 ev for NiO.[22]

We should like to make one further comparison of our spectrum with that obtained in crystals containing $Ni(H_2O)_6^{2+}$ ions. This is simply that whereas starting at about 0.1 ev our spectrum shows a continuing rising characteristic with increasing energy leading to a very high absorption coefficient plateau above 4 ev, this behavior is not shown by crystals such as $NiSO_4\cdot(H_2O)_6$.[14] The absence of a high absorption in this region of energy (i.e., $h\nu > 4$ ev) is understandable for the hydrated ions. For in this case a charge transfer process would occur at a much higher energy corresponding to the larger energy required to remove an electron from an H_2O molecule than from an O^{2-} ion.

In the range from about 0.1 to 3.5 ev the appearance of the spectrum suggests a superposition of two components. These are the line spectrum which we have discussed and a continuous background absorption. The latter increases with increasing energy to join with the high absorption continuum at about 4 ev. The magnitude of the continuous background absorption is determined by the stoichiometry of the crystals.

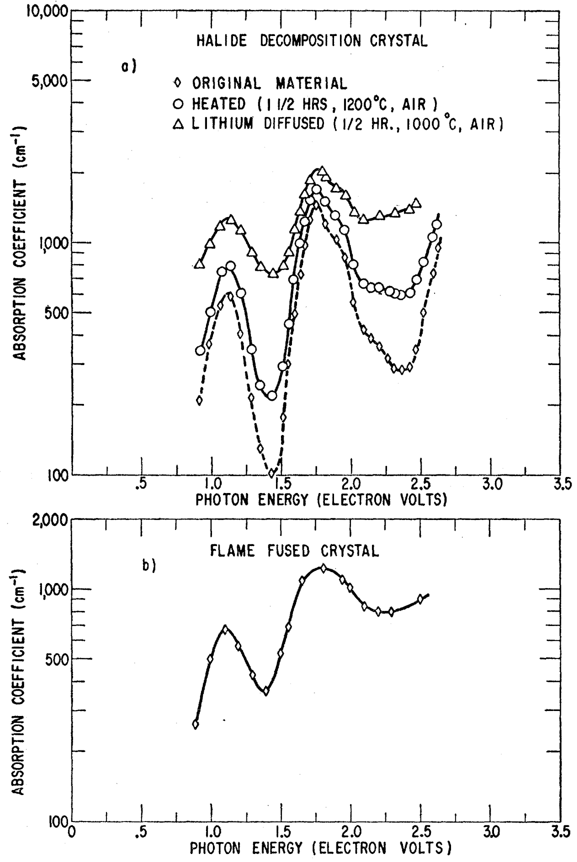

FIG. 3. Effects of oxygen on the absorption spectrum of NiO in the visible. (a) halide decomposition crystal, (b) flame fused crystal.

A general description of the effects of non-stoichiometry is that it increases the magnitude of the continuous absorption background in the entire range from 0.1 to about 3.5 ev. This is shown in Figs. 3 and 4. As one example of this effect we will consider the visible region of the spectrum. It is a well-known fact that NiO that is closely stoichiometric appears green, whereas material that has an excess of oxygen tends more toward a black appearance. To illustrate in a quantitative way the nature of this color change optical measurements were made on crystal films that were (a) heated in oxygen (1000°C) or (b) into which lithium oxide was diffused. Both methods produce increases in the O/Ni ratio. In the accepted model[1,2] the former method introduces an Ni vacancy and two Ni^{3+} ions for each excess oxygen, the latter method introduces a Li^{+} ion, at a cation (i.e., Ni^{++}) site and a Ni^{3+} ion for each excess oxygen. In the present experiments the lithium oxide diffusion introduces a higher O/Ni ratio than does the diretc oxygenation method as judged from the magnitude of the optical and electrical effects (see below). We assume in this discussion that the two different methods of altering the O/Ni ratio are for the present purposes equivalent. In Fig. 3(a) are shown portions of the absorption spectra of a single crystal film (50μ), as grown, after heating in oxygen at 1000°C for an hour and after heating in O_2 in the presence of Li_2O. For further comparison, Fig. 3(b) shows a portion of the spectrum of a flame fused crystal. The spectra indicate the following:

---

[18] *Atomic Energy Levels,* National Bureau of Standards Circular No. 467, edited by C. E. Moore (U. S. Government Printing Office, Washinton, D. C., 1952), Vol. 2, p. 102.

[19] W. P. Doyle and G. A. Lonergan, Trans. Faraday Soc. (to be published).

[20] G. H. Reiling, thesis, University of Missouri, 1956 (unpublished). MgO is the nonmagnetic oxide which is closest to the NiO structure.

[21] Data presented in reference 19 indicate a small peak, which is not shown in our measurements.

[22] P. W. Anderson, Phys. Rev. 79, 350 (1950).

(1) The positions of the absorption maxima remain unchanged with oxygenation.

(2) The absorption coefficients of the maxima are increased by only small amounts with oxygenation.

(3) The largest changes occur in the "transparency" regions between the bands.

In other words, the main effect is an increase in the magnitude of the continuous background with increased oxygen content. The spectra give a quantitative explanation of the dependence of the NiO color on oxygen content. Stoichiometric NiO is green because of strong absorption bands in the red (1.75 ev) and in the violet (2.75, 2.95 ev) with a "transparency" range ($\alpha \sim 10^2$ cm^{-1}) in the green. The effect of the excess oxygen is to increase the absorption coefficient in the green "transparency" range, tending to make the material more uniformly absorbing through the visible, or in other words, black.

The magnitude of the absorption of the continuous background qualtitatively describes the degree of stoichiometry. We would characterize the flame fused material as having a higher oxygen excess than either the unoxygenated or oxygenated film but not as high as the Li doped material. The same relationship is indicated by the resistivity of these samples[1,3,4]: ρ(halide film) $\sim 10^{10}$ ohm-cm, ρ(flame fusion) $\sim 10^6$ ohm-cm, ρ(Li-doped halide film) $\sim 10^2$ ohm-cm. As a further example, Fig. 4 shows a comparison of the absorption spectra of pure and Li-doped flame fused crystals and a crystal grown by halide decomposition in the range below 1 ev where there is less complication from a line spectrum. It would be interesting to test for a quantitative correlation between the magnitude of the continuous absorption in this range and the Li concentration in a series of doped crystals.

We should like to understand the origin of the continuous absorption and its relation to the oxygenation effects. The continuous nature of the background absorption without evidence for additional line structure rules out of consideration any internal transitions in either Ni^{2+} or Ni^{3+} ions. A satisfactory theory of the effect should be able to account for the energy range of the effect (0.1 to 3.5 ev) and the magnitude and spectral distribution of the absorption. At the present time we are unable to establish a unique mechanism to account for our results. Some of the possible mechanisms are listed below.

1. Charge transfer involving Ni^{2+} ions in the electrostatic field of an impurity.
2. Charge transfer involving Ni^{3+} ions.
3. Charge transfer effects involving the tail of the oxygen band.[23]

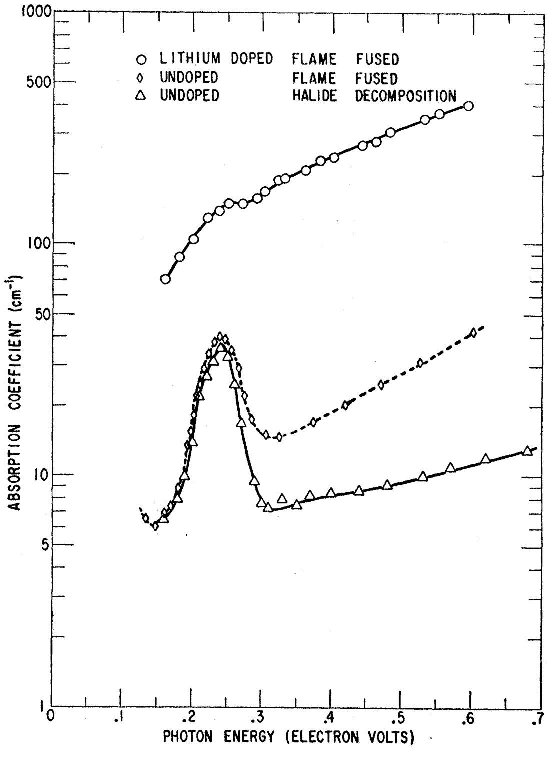

FIG. 4. Effects of oxygen on the absorption spectra of halide decomposition and flame fused NiO crystals below 1 ev.

4. Charged carrier effects either as a photoionization of a hole from an impurity center or as an optical activation of a hole out of a self trapped position.

The continuous absorption in the 0.1 to 3.5 ev region can be represented by a formula of the following form

$$\alpha = \text{const } (h\nu - E_0)^{-4},$$

where $E_0 = 4$ ev. It is interesting that a model which localized the absorption event at some point in the lattice a distance r away from some unique point (e.g., an impurity) and for which the absorption energy was given by

$$h\nu = E_0 - \text{const}/r$$

would then give an absorption coefficient with the inverse 4th power dependence on energy noted above.

B. $h\nu = 0.24$ ev

The absorption line located at 0.24 ev at room temperature has been observed previously in flame fused material.[24] It was believed to be an impurity effect.[24] We have observed it in our flame fused crystals, in Linde flame fused crystals and in crystals obtained by halide decomposition with the identical absorption co-

---

[23] In crystals similar to NiO, such as MgO or FeO that were examined by soft x-ray emission, a tail was found in the oxygen band. [H. M. O'Brian and H. W. B. Skinner, Proc. Roy. Soc. (London) **A176**, 229 (1940)]. The viewpoint taken here is that the tail may represent a density of states beyond the band edge that a perfect crystal would possess. This density of such states is assumed to increase with the concentration of nonstoichiometric oxygen.

[24] R. W. Johnson and D. C. Cronemeyer, Phys. Rev. **93**, 634 (1954).

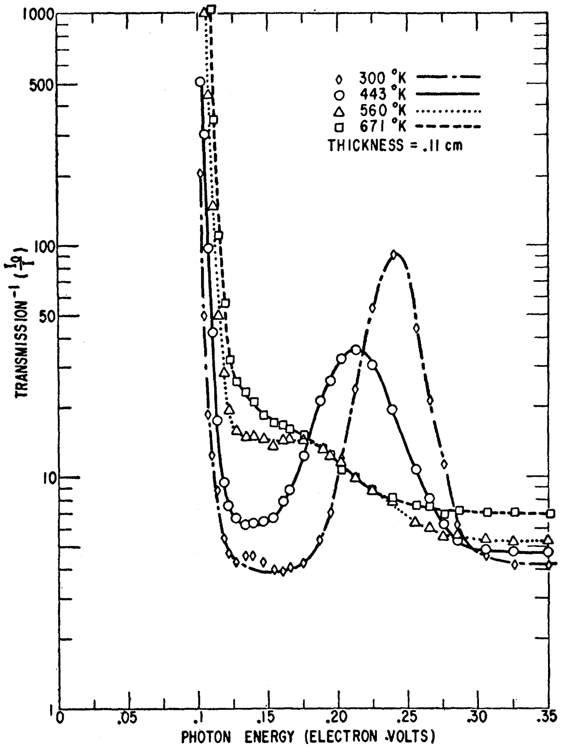

FIG. 5. Temperature dependence of 0.24-ev absorption line of NiO.

efficient (30 cm^{-1} above background) as was previously found. Since crystals prepared by the different techniques will have rather different concentrations of structural defects and such impurities as, excess oxygen, alkali and alkaline earth metals etc., it seems more natural to assume that the band in question is an intrinsic property of NiO rather than an impurity effect. As further evidence that this is the case, flame fused crystals of neither MnO or CoO show an absorption band at this energy. One would expect that these MnO and CoO crystals would have impurities and imperfections similar to those found in the flame grown NiO crystals.

The temperature dependence of this band is of interest as a clue to its origin. Figure 5 shows a series of absorption spectra for a halide decomposition crystal at various temperatures. Flame fused crystals behaved in an analogous manner. There is little change from low temperatures until a temperature above 300°K is reached. Then as the temperature increases the peak becomes less intense and moves toward lower energies. By the Neel temperature (640°K)[7] the band has almost disappeared into the background. This behavior suggests that the band is connected with the antiferromagnetic ordering in the crystal.

As NiO passes from the paramagnetic to the antiferromagnetic state two changes occur. First there is a very slight distortion of the crystal lattice from cubic to rhombohedral.[8] Second there is an ordering of the spins. The ordering increases with decreasing temperature. Small crystal distortions, per se, can not produce an absorption band of the type we are considering. The ground state of a Ni^{2+} ion even in a cubic field is a state without orbital angular momentum. Thus, even in the distorted cubic (i.e., rhombohedral) field no further splittings should arise. The vibrational spectrum would not be expected to be appreciably altered by the crystal distortion. For the high-energy tail ($h\nu < 0.1$ ev) of the vibrational absorption band, the changes are slight. Thus, we are drawn to the conclusion that the 0.24-ev band is associated with the ordering of the spins rather than with a small crystal distortion. As further evidence, some preliminary studies of mixed crystals of NiO with CoO or MnO have shown changes in the frequency and intensity of the band which also suggest a connection with an antiferromagnetic effect. This work will be described at a later time.

A rough quantitative correlation with the spin ordering can be made. For example, a comparison, as a function of temperature, of the calculated degree of magnetization of a magnetic sublattice and the integrated intensity of the absorption band shows that the two quantities are directly proportional. We should like to establish a model to account for the 0.24-ev line. In the ground state of the antiferromagnet all the spins are ordered. An excited state would be one in which, for example, a single spin would be inverted from its orientation in the ground state. Such an excited state could be reached by the absorption of radiation through a magnetic dipole transition. This description is somewhat analogous to a magnetic resonance in which the external magnetic field is here conceptually replaced by the crystalline exchange field.

In the optical region of the spectrum magnetic dipole transitions are usually of negligible importance compared to electric dipole transitions. However, a rough calculation of the absorption coefficient to be expected for the magnetic dipole transition appropriate to this case shows that it is, in fact, larger than the observed intensity. The observed value (corrected for background) of the absorption maximum is 30 cm^{-1}. The calculated value is 200 cm^{-1}, employing the observed frequency and line width and an appropriate magnetic dipole matrix element. (If phonons are involved, the intensity would probably be less.)

Kane has shown[25] that the energy to be expected on this simple model is $g\beta H_{\text{eff}}$ which is given by

$$g\beta H_{\text{eff}} = 3kT_c/S+1 = 0.085 \text{ ev}$$

for NiO with $T_c = 640°\text{K}$, $S=1$. The value 0.085 ev is a thermal energy. Although the optical energy would be higher, it is difficult to account for the factor of 3 necessary to get agreement with experiment. An even more serious objection to this simple model is the fact that the assumed excited state is not an eigenstate of the

---

[25] E. O. Kane (private communication).

spin system. The correct eigenstates of the spin system are spin waves. The light interacts directly only with spin waves of very small k vector which have nearly zero energy. Only the large k-vector spin waves have energies of the order $g\beta H_{\mathrm{eff}}$ as estimated above.

The maximum spin wave energy most probably occurs at the zone boundary in one of the symmetry directions. Kane has calculated the energy in the [100] and [111] directions at the zone edge using a method similar to that described by Nagamiya.[26] The energies were determined to be 0.078 and 0.13 ev, respectively by use of the parameters $T_c = 640°\mathrm{K}$, $\theta = 2000°\mathrm{K}$. In order to optically excite a spin wave with a nonzero k-vector it is necessary to use a phonon. If optical phonons (see Sec. C) are involved, then the maximum energy that could be absorbed would be about $0.13 + 0.06 = 0.19$ ev. The absorption spectrum for such a process would not be a symmetrical line, as we observe, but rather a continuous absorption which increased with increasing energy up to a maximum at about 0.19 ev. However, the density of both spin wave and phonon states is greatest at a zone boundary. This would tend to concentrate the absorption intensity near the maximum energy. This might give the absorption the appearance of a line rather than a continuum.

Note added in proof.—An alternative process is the creation of two spin waves of large energies having large and opposite k vectors through an intermediate state involving a single spin wave of small k vector [J. Van Kranendonk and J. H. Van Vleck, Revs. Modern Phys. **30**, 1 (1958)].

C. $h\nu < 0.1$ ev

At about 0.1 ev the absorption coefficient increases very rapidly with decreasing energy. A study of the reflectivity in this region is therefore more convenient. The reflectivity spectrum (Fig. 1) in the range $h\nu < 0.1$ ev is most reasonably interpreted in terms of the absorption of light by optical mode lattice vibrations. An examination of the reflectivity data indicate the following: ϵ_0 = static dielectric constant = 12, ϵ_∞ = high-frequency dielectric constant = 5.4, $\hbar\omega_t$ = transverse optical mode energy = 0.044 ev, $\hbar\omega_l$ = longitudinal optical mode energy = 0.076 ev. These quantities are theoretically connected[27] by the relationship

$$\omega_l/\omega_t = (\epsilon_0/\epsilon_\infty)^{\frac{1}{2}}.$$

The observed values satisfy this relationship. It was of interest to check the value of the low-frequency dielectric constant by a direct measurement. For this purpose single crystal films of NiO prepared by halide decomposition about 50μ in thickness and from 0.2 to 1.5 cm^2 in area were freed from the MgO backing. They were then coated on opposite large area surfaces with silver paint for electrodes. The capacities of the condensers thus formed were measured on a capacity bridge at 1 Mc/sec. Capacities were in the range 30 to 250 $\mu\mu$f. The dielectric constant obtained from these results was 11.8 ± 0.5. (The major error arises from variations of about 5% in the thickness of the films over their area.) This value is in good agreement with the value obtained optically.

ACKNOWLEDGMENTS

We are indebted to R. E. Cech who generously furnished many of the crystals used in this work and helped us with our own crystal growing operation. We appreciate discussions with I. S. Jacobs and W. L. Roth on antiferromagnetism. We are especially indebted to E. O. Kane for discussing many aspects of the present work at length and with great profit to the authors.

---

[26] T. Nagamiya, K. Yosida, and R. Kubo, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.

[27] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), p. 85.