instances, the field effect predominates initially (Fig. 7). Injection for either direction of current flow predominates after the surface states absorb the induced charge and at high currents. There is a point where the injection and extraction effects will just cancel. This point, however, is not a stable one because it is associated with the relaxation of the slow surface states.

CONCLUSION

The experiments discussed here have served to stress the importance of the surface in determining the nature of the characteristics for a metal to semiconductor contact. They have further served to clarify to some extent the role an insulating layer plays between the metal and the semiconductor. If an insulating layer of an appropriate thickness is present, the applied voltage can control the injection-extraction properties of the metal to semiconductor contact and unusual characteristics such as injection or extraction regardless of the direction of current flow may be exhibited by the contact. Such contacts do not lead to rectification. The purpose of these and other experiments now in progress is to develop a model which will form the basis for a more complete and quantitative theory of the metal to semiconductor contact for a two carrier system.

ACKNOWLEDGMENTS

The author has profited from discussions with Dr. P. H. Dowling, Dr. F. K. du Pré, and Dr. E. S. Rittner of Philips Laboratories. He is also indebted to Dr. H. Statz of Raytheon Manufacturing Company, for commenting on an earlier version of this paper.

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Effects of MnO and CoO on the 0.24-ev NiO Absorption Line

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Measurements are reported of the change in the 0.24-ev NiO absorption band due to additions of MnO and CoO to NiO crystals. The results support the interpretation that the band has its origin in an antiferromagnetic effect.

INTRODUCTION

A RECENT paper[1] reported the temperature dependence of an absorption band of NiO which is centered at 0.24 ev at 300°K.[2] Those measurements suggested that the band was connected with antiferromagnetic ordering in this crystal. A mechanism, due to Kane,[3] was proposed which involved the simultaneous optical excitation of spin waves and phonons of large k vector. Some preliminary calculations by Kane[3] indicated a rough agreement between the observed energy of the line and that calculated from a spin wave model. This interpretation of an optical absorption process is, to our knowledge, novel. It is therefore desirable to find additional supporting evidence for it in other systems. Obvious analogs to NiO are CoO and MnO. However, neither of these crystals shows an absorption band similar to that of the 0.24-ev band of NiO.[4] The Néel temperature, which may be taken as a measure of the antiferromagnetic interaction, is considerably lower in both MnO (120°K) and CoO (290°K) than in NiO (640°K).[5,6] It would, therefore, be expected, according to the proposed model for the absorption, that the energy of the absorption line would be lower than that which obtained in NiO. However, between 0.1 and 0.03 ev the strong lattice vibration absorption in these crystals eliminates the possibility of observation of such an absorption line[4] in either MnO or CoO. Also analogous to NiO are the mixed crystals of NiO and other transition metal monoxides. For example, mixed crystals of the type $Ni_xCo_{(1-x)}O$ or $Ni_xMn_{(1-x)}O$ form homogeneous solid solutions having the same crystal structure as NiO (i.e., NaCl structure). Such mixed crystals afford the opportunity for observing the effects on the 0.24-ev NiO band of small constitutional perturbations from pure NiO. Accordingly, a study of the effects on the 0.24-ev NiO band in such mixtures was undertaken.

EXPERIMENTAL

Crystals of NiO mixed with either MnO or CoO were prepared by the flame fusion technique.[7] Their composition is assumed to be that of the original powder charge. All showed good perpendicular cleavage. X-ray

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[1] R. Newman and R. M. Chrenko, Phys. Rev. **114**, 1507 (1959).

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

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

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[5] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 5-226.

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

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

diffraction measurements indicated that the boules were single crystals constituted as homogeneous solid solutions with lattice constants calculable by linear interpolation between the lattice constants of the pure components.

RESULTS AND DISCUSSION

Figure 1 shows representative absorption spectra in the 0.15- to 0.35-ev spectral range of crystals of $Ni_xMn_{(1-x)}O$ of various compositions. This system was examined more extensively both as to the number of crystals studied and the temperature dependence of their spectra than was the NiO-CoO case. Several general comments about these spectra can be made. First it can be noted that there is a gradual decrease in the energy and intensity of the absorption line with decreasing concentration of NiO. The band shape, as characterized by the width at half-height, is not appreciably altered. Comparing the effects of added MnO and CoO it was noted that for a given concentration of either substituent the effects of the MnO are larger than those of the CoO. In Figs. 2 and 3 the aforementioned comparisons are shown in graphical form. As mentioned above, the Néel temperature of MnO (120°K) is below that of CoO (290°K) and both are below that of NiO (640°K). The Néel temperature may be taken as a measure of the antiferromagnetic interaction energy. It would seem reasonable that the average antiferromagnetic interaction in mixed NiO crystals will be reduced by adding either CoO or MnO, but that it will be reduced more by the presence of a given mole fraction of MnO than by the same fraction of CoO. In this way the decreases in the energy of the band and the larger effects of the MnO than the CoO may be qualitatively understood.

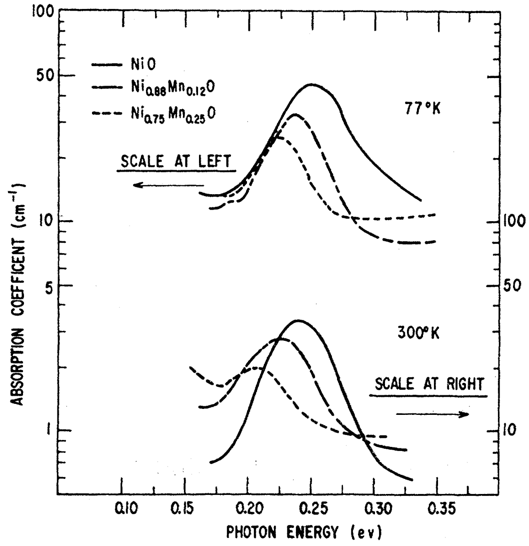

FIG. 1. Absorption spectra of crystals of $Ni_xMn_{(1-x)}O$ in the 0.15- to 0.35-ev region at 77°K and 300°K.

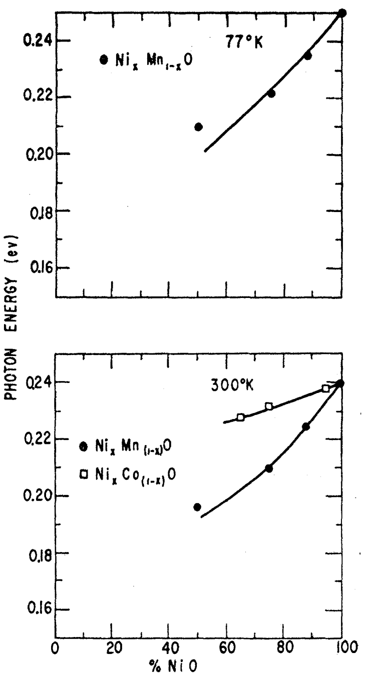

FIG. 2. Effects of the addition of MnO and CoO on the position of the 0.24-ev NiO absorption band.

We are not aware of any work describing the antiferromagnetism in the system we have chosen to study most intensively, i.e., NiO-MnO. Therefore we do not know the values of the Néel temperatures in our crystals. However, in similar systems (e.g., CoO-MnO) it would appear that the Néel temperature was a linear function of composition.[8,9] We will assume this to be true for our system as well. In the work on pure NiO[1] it was pointed out that the temperature dependence of the observed line intensity and that of the calculated magnetization of a magnetic sublattice were the same. In other words, the two quantities appear to be proportional to one another. We will assume in the present

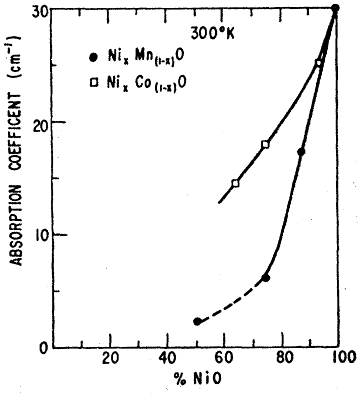

FIG. 3. Effects of the addition of MnO and CoO on the absorption coefficient of the 0.24-ev NiO absorption band.

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[8] Bacon, Street, and Tredgold, Proc. Roy. Soc. (London) **A217**, 252 (1953).

[9] N. Perakis and A. Serres, J. phys. radium **18**, 47 (1957).

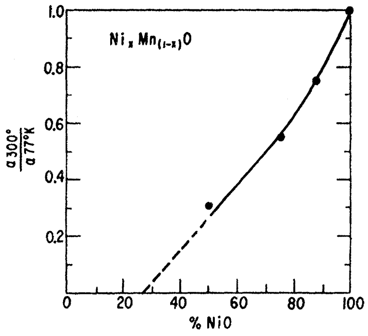

FIG. 4. Ratio of absorption coefficients $\alpha_{300°K}/\alpha_{77°K}$ in the $Ni_xMn_{(1-x)}O$ system.

case that for a material of any given composition that a similar relationship holds. For all the samples studied the estimated Néel temperature is large compared to 77°K (the lowest would be $Ni_{.5}Mn_{.5}O$ where $T_N \sim 380°K$). At 77°K then, the sublattice magnetization and the band intensity are close to the asymptotic values characterizing the ordered state. (For example, measurement at 20°K on a $Ni_{.75}Mn_{.25}O$ sample indicated no change in the absorption band from that at 77°K). Therefore, for a material of given composition, the ratio of the absorption coefficient at 300°K to that at 77°K will be proportional to the degree of sublattice magnetization at 300°K. In Fig. 4 the ratio $\alpha_{300°K}/\alpha_{77°K}$ is plotted against composition for the NiO-MnO system. The extrapolation of the optical data to the composition having a $\alpha_{300°K}/\alpha_{77°K}$ value of zero would characterize a material for which the Néel temperature was 300°K. The composition corresponding to this extrapolation occurs approximately at the composition for which a 300°K Néel temperature would be predicted by linear interpolation between the Néel temperatures of the pure oxides, namely $Ni_{.35}Mn_{.65}O$.

The line shape is the same for either the pure NiO or the various mixed crystals. This can be cited as some support for a spin wave interpretation of the absorption line. A mechanism which involved only a local interaction between nearest or next nearest neighbors would be more sensitive to disorder than would a mechanism which involved long-range averaging of the interactions.

There is a close similarity of the crystals NiO, CoO, and MnO and their mixtures with respect to such parameters as lattice constant, crystal structure, dielectric constants, and lattice frequencies. To account for our observation of differences in the optical absorption in these crystals it seems necessary to introduce the detailed electronic structure of the metal ion and its interaction with its environment. The various observations on the 0.24-ev line both in the pure NiO and in the mixtures suggest that this interaction may be most directly interpreted as arising from an antiferromagnetic effect.

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Magnetic Susceptibility of Thorium Metal in the Range 130–300°K

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The magnetic susceptibility of thorium has been measured in the temperature range, 130–300°K. Within the precision of measurement, the susceptibility was found to remain constant at a value of $+0.410 \pm 0.002$ emu/g. This susceptibility behavior is in contrast to the elastic behavior which indicates a change in the character of the interaction forces near 253°K.

THE elastic parameters of thorium have recently been measured.[1] It was found that the curves representing the temperature dependence of C_{12} and C_{44} cross[2] at 253°K, with C_{12} being greater than C_{44} above this temperature and less below. Since thorium is face-centered cubic with all atoms at centers of symmetry, one of the Cauchy conditions is fulfilled and the difference in magnitude of C_{12} and C_{44} must be a parameter associated with noncentral-force contributions. Starting with a model of a point lattice embedded in an electron gas, de Launay[3] has developed for fcc and bcc lattices relationships which equate the bulk modulus of the electron gas to $C_{12}-C_{44}$ and which show that the bulk modulus of the gas is proportional to the product of the electron density and the Fermi energy. Since the paramagnetism of the valence electrons is proportional to the density of states at the Fermi level, the simple electron gas approximation also leads to an expression[4]

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[1] Armstrong, Carlson, and Smith, J. Appl. Phys. **30**, 36 (1959).

[2] The temperature of equality of C_{12} and C_{44} was erroneously quoted in the abstract of the original paper as 271°K instead of 253°K.

[3] J. de Launay, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, pp. 276–284.

[4] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 160.