Direct and Temperature-Modulated Reflectance Spectra of MnO, CoO, and NiO[†]

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Direct near-normal-incidence reflectance spectra were measured for MnO, CoO, and NiO between 3 and 27 eV at room temperature and below, and the corresponding dielectric response functions, $\epsilon = \epsilon_1 + i\epsilon_2$, were obtained by Kramers–Kronig inversion. Thermoreflectance (TR) spectra between 4 and 8 eV at various temperatures were also measured. Spectra for all three materials support a model containing both localized and one-electron band states. In MnO peaks with temperature coefficients of $\sim 10^{-3}$ eV/K were observed at 5.7 and 6.9 eV, temperature-independent structure occurred at 5.4, 6.3, and 7.2 eV, and spectral features with indeterminate temperature dependence were seen at 4.6 and 5.5 eV. The temperature-dependent structure was assigned to one-electron interband transitions associated with anion $2p$ and cation $4s$ states. The temperature-independent structure was assigned to crystal-field-split localized interionic transitions between the $3d$ states of neighboring Mn ions. The crystal field splitting of the $3d$ states was determined to be 0.9 eV. TR spectra for CoO exhibited temperature-dependent structure (9.5×10^{-4} eV/K) at 5.0, 6.0, and 7.2 eV and additional structure at 2.8, 3.2, 3.8, 4.2, 5.35, and 6.25 eV. Interpretations of the optical spectra of CoO and NiO analogous to those of MnO are proposed. The interband gap between the anion $2p$ and cation $4s$ bands was determined to be 5.7 eV in MnO, 6.0 eV in CoO, and 6.2 eV in NiO.

I. INTRODUCTION

Transition-metal compounds are of fundamental interest in solid-state physics. Their electronic properties appear to defy explanation solely in terms of conventional one-electron band theory. Mott[1] pointed out that most of their unusual properties are associated with the presence of partially filled d and f shells which, since their states have small wave-function overlap between nearest-neighbor ions, lead to narrow states. Band theory predicts that certain transition-metal compounds (e.g., MnO) have a partially filled conduction band arising from the transition-metal d states and are conductors. These materials are, in fact, good insulators. Mott noted that electron correlations must be included to explain this anomalous behavior. He also pointed out that all solids are excitonic insulators in the limit where the lattice constant is so large that the overlap between the wave functions of adjacent atoms is too small to permit conduction.

Various attempts have been made to include electron correlation effects. Hubbard[2] has considered a model Hamiltonian incorporating correlation effects. More recently augmented-plane-wave band-structure calculations for antiferromagnetic α-MnS, MnO, and NiO have been reported by Wilson[3]; in these the effective one-electron potential depends upon spin direction. Although these models predict insulating states for these materials, they do not fully explain their optical spectra.

The first-row transition-metal mono-oxides TiO, VO, MnO, FeO, CoO, and NiO are good candidates for experimental study. Some of the common properties of these materials are: (i) All are ionic crystals with rocksalt structure (above the respective Néel temperatures of those that are antiferromagnetic), and have lattice constants in the range 4.1–4.44 Å at 300 K. (ii) All are antiferromagnetic except TiO and possibly VO. (iii) The majority are insulators or semiconductors with the exception of TiO and VO, which are metals.

Determination of the electronic structure of these materials is essential to an understanding of these properties, and direct and modulated optical spectroscopy are powerful means for studying this structure. Previous studies have shown that these materials have complex optical spectra. Absorption and room-temperature reflectance data on NiO and CoO have been reported by Powell and Spicer,[4] Newman and Chrenko,[5] and Pratt and Coelho.[6] Their spectra show absorption lines and reflectance peaks between 0.025 and 20 eV in NiO and between 0.5 and 20 eV in CoO. Absorption spectra for MnO with structure between 1.7 and 3.6 eV were reported by Huffman, Wild, and Shinmei[7] and by Pratt and Coelho.[5] Electroreflectance spectra of NiO were reported by McNatt[8] between 3 and 5 eV and by Glosser and Walker[9] between 3 and 6.5 eV.

Recently empirical models involving a mixture of one-electron bands and localized states based on crystal or ligand field theory have been proposed by Adler and Feinleib and by Wilson.[10] Most of these studies are concerned with the electronic states of the oxygen $2p$ and transition-metal $3d$ and $4s$ states which bear upon the electrical, magnetic, and optical properties, below 30 eV, of the first-

row transition-metal mono-oxides. In both models the overlap between the $2p$ wave functions of adjacent oxygen ions as well as those of the metal $4s$ ions is so large that these states form bands. Conversely, the transition-metal $3d$ states are localized because of their small overlap. The separation in energy of these states is such that the $2p$ states are filled, the $3d$ states partially filled, and the $4s$ states empty at $T = 0$. Several types of transitions between these states are predicted. Below 4 eV localized excitons are expected in which the $3d$ electrons of a manganese ion are raised to an excited configuration. Near 4 eV and above transitions involving bands and/or localized $3d$ states, including interionic $3d$ transitions, may occur. Other transitions require much more energy and normally are not considered.

Previous MnO and CoO low-energy absorption spectra are in agreement with an interpretation involving transitions among $3d$ levels of an individual ion and based on the crystal field splitting calculated by Tanabe and Sugano.[11] The reflectance spectra of NiO and CoO and the electroreflectance spectrum of NiO have been interpreted in terms of some of the transitions mentioned above for the region around and above 4 eV.

In the present study, direct near-normal-incidence reflectance spectra of MnO, NiO, and CoO were obtained between 3 and 27 eV at two temperatures. In addition, temperature-modulated reflectance spectra were obtained between 3 and 8 eV at several temperatures. An interpretation of these spectra consistent with a mixed-band-localized-state model is proposed. In accordance with this interpretation, the values of the separation between the $2p$ and $4s$ bands, the crystal field splitting of the $3d$ states, the separation between the localized $3d^5$ level and the $4s$ band, and the energy required to remove a $3d$ electron from one cation and place it on another in each material are established.

II. EXPERIMENTAL PROCEDURE

Direct near-normal-incidence (6°) reflectance spectra were obtained with a stainless-steel high-vacuum reflectometer equipped with a vertically mounted rotatable, sodium-salicylate-coated, fiber optics light pipe. The freshly cleaved sample was mounted in a horizontal slide attached to the cold finger of a helium Dewar. In the reflectance position, the sample was located on the axis of rotation of the light pipe. Spectra were taken at a pressure of $\sim 10^{-8}$ Torr and below after evacuating the reflectometer with a 80-liter/sec vacuum pump aided by an auxiliary liquid-nitrogen shield which partially surrounded the sample. A dc hydrogen lamp was used for measurements below 12 eV and a pulsed condensed-discharge argon lamp was used from 10 to 30 eV.

Thermoreflectance spectra were obtained with a high-vacuum low-temperature-modulation reflectometer in which the entrance beam was focused with a toroidal mirror onto a specially prepared $5 \times 5 \times 0.25$-mm sample. Temperature modulation of approximately 0.2 K was produced by applying a 25-V, 10-Hz square wave with an average power of 0.5 W across a thin Ni film deposited on the sample surface. Control studies with an indirectly heated sample (with correspondingly smaller modulation) showed that no spurious features were introduced by the presence of the heating film. Both a 500-W xenon arc and the dc hydrogen source were employed.

III. RESULTS

A. Direct Reflectance

1. MnO

Direct near-normal-incidence (6°) reflectance spectra in the fundamental electronic region were obtained on samples of MnO from two different sources at a variety of surface conditions and temperatures. Freshly cleaved samples from a flame-fusion-grown crystal obtained from Ventron[12] were measured at 300 and 22 K over the region from 4 to 27 eV (Fig. 1).

The room-temperature spectrum exhibits reflectance peaks at 4.7, 5.1, and 6.9 eV, and shoulders at 5.6 and 6.6 eV. This structure is shifted and split at 22 K to give peaks at 4.6 (A), 5.2 (B), 5.5 (C), 6.3 (D), 6.6 (E), and 7.0 eV (F), whose positions are reproducible to within 0.1 eV. In addition to this structure, a broad peak is also seen at 16 ± 1 eV.

For comparison, additional measurements were made on cleaved samples obtained from Nakazumi Inc.[13] The spectra are similar to those of the Ventron samples but are inferior in revealing spectral structure. Peaks were broadened and some of the relative heights were slightly different.

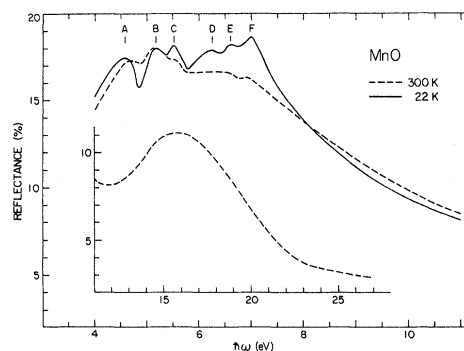The spectra were analyzed by means of the Kramers–Kronig relations using a method due to Roes-

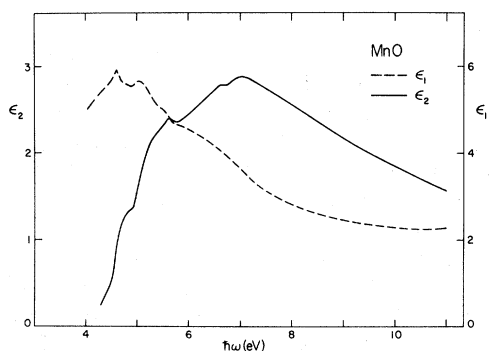
FIG. 1. Direct-reflectance spectra of MnO.

FIG. 2. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of MnO at 300 K.

sler[14] to yield the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) of MnO at 300 and 22 K. The results are displayed in Figs. 2 and 3. Structure in the dielectric function occurs at nearly the same positions as in the reflectance. However, a general loss of resolution introduced by the dispersion analysis and the usual shifts to higher energy of $\lesssim 0.1$ eV are observed. The imaginary part at 22 K exhibits structure at 4.7, 5.3, 5.6, 6.3, 6.6, and 7.0 eV.

2. NiO

Reflectance spectra of NiO were obtained between 2 and 11 eV at 300 and 22 K. These data are similar to the room-temperature spectra of Powell and Spicer,[4] but some slight differences were noted. In the portion of their spectrum below 11 eV, structure was observed at 4.0, 4.8, 5.9, 7.2, and 8.25 eV, with a maximum reflectance of 32% at 4.0 eV. This structure is seen in the present data at 4.0, 4.7, 5.9, 7.2, and 8.4 eV, with a maximum reflectance of 28.5% at 4.0 eV.

3. CoO

The reflectance of CoO was measured from 4 to 11 eV at 300 and 120 K. Again the data are similar to those of Powell and Spicer.[4] Their spectrum (room temperature) shows a peak which may be a doublet at 5.5 eV, where the reflectance attains its maximum value of 20%, and a shoulder at 7.5 eV. The present room-temperature spectrum shows only a single peak at 5.7 eV with a maximum reflectance of 21%. At 120 K, however, a shoulder appears at 8.5 eV. Because of the large discrepancy in position, it is not clear if this corresponds to the same structure observed in the previous data at 7.5 eV. The observed deviations between the two sets of data on both NiO and CoO may be due in part to differences in sample quality.

Some similarity exists between the reflectance spectra from 3 to 12 eV of MnO, NiO, and CoO.

In all three compounds, the structure is grouped between 4 and 8.5 eV with the reflectance dropping off below 4 eV and with a broad minimum between 9 and 12 eV. Here, however, the similarity appears to end. The fine structure revealed at low temperature is different for each material. MnO exhibits considerable fine structure (six peaks); NiO shows, at most, three peaks and two shoulders; and CoO has only one or two peaks and a shoulder. It is reasonable to assume, at this stage, that the spectral differences are intrinsic properties of the materials although some dependence on crystal quality may be present.

B. Temperature-Modulated Reflectance Spectra

1. MnO

Temperature-modulated reflectance spectra at near-normal incidence (20°) were obtained on freshly cleaved samples of Ventron MnO from 3.9 to 7.6 eV at three temperatures and at a pressure of 2×10^{-7} Torr. Spectra observed between 4.6 and 7.6 eV are shown in Fig. 4.

The modulation spectra consist of a complex mixture of relatively broad peaks and valleys together with sharper structure. Particular significance will be attached to the appearance of both temperature-dependent and temperature-independent spectral structure. Negative dips whose positions are independent of temperature appear at 5.4, 6.4, and 7.2 eV. Temperature-dependent dips which occur at 5.7 eV at 85 K and 6.9 eV at 200 K are shifted to lower energies by ~ 0.15 eV at 310 K. A negative dip and a positive peak whose temperature dependence and precise position are obscured by nearby large temperature-dependent structure appear at 4.8 and 5.5 eV, respectively, at 310 K (the 5.5-eV peak shifting to 5.43 eV at 85 K). Finally, a peak whose position is temperature independent appears at 4.9 eV.
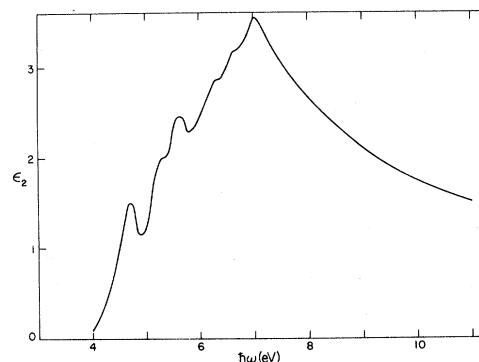

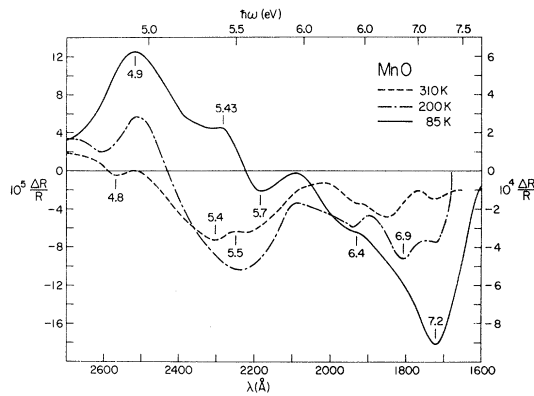FIG. 3. Imaginary part of the dielectric function of MnO at 22 K.

FIG. 4. Thermoreflectance spectra of MnO at 85 K (right-hand scale), and at 200 and 310 K (left-hand scale).

FIG. 6. Thermoreflectance spectra of CoO.

2. NiO

The thermoreflectance spectrum of NiO, which we recently reported,[15] is shown in Fig. 5. The most outstanding feature in this spectrum is a sharp dip at 6.2 eV which shifts by 3.6×10^{-4} eV/K to lower energy with increasing temperature.

3. CoO

The thermoreflectance spectra of CoO, shown in Fig. 6, reveal more pronounced structure than the direct reflectance spectra of this compound. Three pieces of structure are seen which shift to lower energy with increasing temperature by 9.5×10^{-4} eV/K. These are the two negative peaks and the one positive peak which appear at 5.0, 6.0, and 7.2 eV, respectively, at 80 K. Also observed are negative peaks at 4.2, 5.35, and 6.25 eV which appear only at 80 K and negative peaks at 2.8, 3.2, and 3.8 eV.
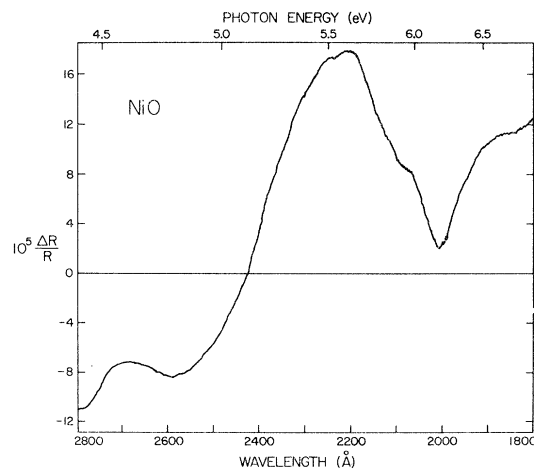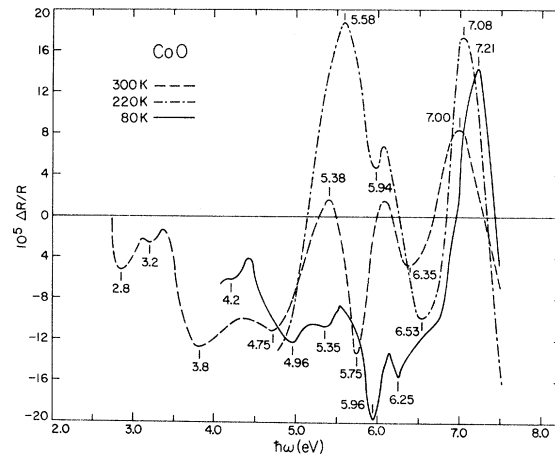
IV. DISCUSSION

Of the three materials studied, MnO is the only one for which no previous spectra beyond the localized d-exciton region have been reported. Surprisingly, it also revealed direct reflectance spectra richer in structure than either CoO or NiO. For this reason and since an understanding of MnO may provide a basis for interpreting the spectra of the other two compounds, its spectra will be treated first.

It is desirable first to establish a comparison between the direct reflectance and thermoreflectance spectra. The problem is simplified by the fact that the positions of structure differ only slightly ($\lesssim 0.1$ eV) between the dielectric function and the better resolved direct reflectance spectra. Since these differences are within the uncertainty (0.1 eV) in the positions of some of the direct-reflectance peaks, only the direct and modulated reflectance spectra need be examined. Although only a rough correspondence exists between thermoreflectance and the difference between the direct reflectance at two temperatures due to different broadening and band-edge shifting effects as a function of temperature, it can be used as a guide in interpreting the spectra. The position and temperature dependence of each piece of structure were determined from the spectra in which they are best resolved. It is important to note that in MnO, contrary to the situation in simpler materials where thermoreflectance uncovers new transitions, the majority of the spectral features are seen in both direct reflectance and thermoreflectance.

Examination of Fig. 4 reveals that the modulated reflectance signal is approximately seven times larger at 85 K than at the other two temperatures. A similarity exists between this spectrum and the difference between the spectra at 300 and 22 K of

FIG. 5. Thermoreflectance spectrum of NiO at 300 K.

Fig. 1. The large thermoreflectance peak at 4.9 eV corresponds to the direct reflectance dip at the same energy. The dips in modulated reflectance at 5.7, 6.4, and 7.2 eV correspond to the direct reflectance peaks at 5.5 (C), 6.3 (D), and 7.0 (F) eV, respectively. The dip at 6.9 eV in the thermoreflectance spectrum at 200 K also appears related to the direct-reflectance peak at 6.6 (E) eV. The general trend is for structure to appear at slightly higher energies in thermoreflectance.

There are three remaining pieces of thermoreflectance structure. Two of these, a negative dip at 5.4 eV and a positive peak at 5.5 eV, can be seen in both the 85- and 310-K spectra. The third, a negative dip at 4.8 eV, is seen most clearly in the spectrum at 310 K. That these are not seen in the difference between the direct reflectance spectra at 22 and 300 K is due to the fact that the difference between direct reflectance spectra gives only an average thermoreflectance spectrum over a wide range of temperature and that only large thermoreflectance effects appear in the difference between the direct spectra. However, judging by order and position, it seems reasonable to assume that the features at 4.8, 5.4, and 5.5 eV in the modulated spectra are related to the peaks at 4.6 (A) and 5.2 (B) eV and the sharp rise at 5.4 eV, respectively, in the direct reflectance spectra.

The energy of each electronic transition in MnO and its temperature dependence are estimated from those of the best resolved corresponding spectral feature. The modulated spectra present the most clearly defined structure in the majority of cases. These have temperature-independent transitions at 5.4 and 7.2 eV, transitions which shift to lower energies with increasing temperature at 5.7 and 6.9 eV, and a transition whose temperature dependence is indeterminate at 5.5 eV. The temperature coefficients of the structure at 5.7 and 6.9 eV are between 5×10^{-4} and 2×10^{-3} eV/K. The large positive thermoreflectance peak at 4.9 eV seems to be a manifestation of the dip between transitions in direct reflectance and not an indication of an additional transition. Although the position of the transition at 6.2 (D) eV is best resolved in direct reflectance, the fact that it is temperature independent can only be seen in thermoreflectance. The 4.6-eV peak (A) is most clearly defined in direct reflectance, but the temperature dependence of its position can be determined neither in direct reflectance, where the uncertainty in peak position prohibits it, nor in modulated reflectance, where it is obscured by other structure.

The models which appear most likely to be able to explain the properties of transition-metal compounds are mixed-localized-band models in which the metal-ion d states lead to localized states, while states of greater wave-function overlap de-

velop nearly one-electron-like bands. Adler and Feinleib[10] first proposed such a model in which the d states were treated by crystal field theory; recently Wilson[10] has suggested an extension of this model based on ligand field theory of the molecular cluster $(MO_6)^{-10}$.

The energy order of the levels involved in these models can be predicted on the basis of the effect of the Madelung energy on the atomic states as follows: The ionization energy of the free O^{--} ion $(3d^5)$ is 34 eV and the excited states with configuration $3d^4 4s$ of this ion lie approximately 8 eV above the ground state on the average.[16] This places the $3d$ states at -34 eV and the $4s$ states at -26 eV. The Madelung energy of an electron on a manganese ion in MnO is 23 eV,[2,17] which raises these levels to -11 and -3 eV, respectively. The free O^{--} ion has a negative ionization energy of 9 eV[9] and the Madelung energy is -23 eV in this case. Thus the $2p$ level is at -14 eV. X-ray photoelectron spectroscopy data reported by Hufner and Wertheim[18] confirm that the $2p$ band lies below (but close to) the $3d$ states in MnO, CoO, and NiO. These data also indicate that the $2p$ band is approximately 5 eV wide and that the $3d$ states are less than 1 eV in width. In first-row transition-metal mono-oxides at $T = 0$ the $2p$ band is filled, the localized $3d$ states are partially filled, and the $4s$ band is empty.

The following types of transitions are expected in such a model for MnO: (i) At energies lower than ≈ 4 eV localized excitons should occur where the $3d$ electrons of a particular manganese ion are excited. (ii) An electron can be excited from a localized $3d$ state into the $4s$ band. Wilson[10] estimated, using a spin-polarized band-structure calculation for MnO, that these transitions occur in the 4- or 5-eV region and are split into a doublet separated by about 1 eV by the crystal field splitting of the $3d$ levels. (iii) One-electron transitions can occur between the $2p$ and $4s$ bands. Wilson's band-structure calculation[3] estimates this energy gap to be about 6 eV. (iv) An electron can be excited from the $2p$ band into a localized $3d$ state. Wilson estimates that these transitions should occur at around 10 eV or above and should be crystal field split similarly to the type-(ii) transitions. (v) An electron can be raised from a $3d$ state of one Mn^{++} ion into a $3d$ state of another M^{++} ion creating a (Mn^+, Mn^{+++}) pair. An upper limit of 18 eV for the energy (neglecting crystal field splitting) of this transition can be estimated from the difference between the ionization potentials of Mn^+ and Mn^{++}. Screening by the other electrons present in the solid could, however, reduce this energy substantially.

The splitting of the type-(v) excitation can be determined in a first approximation from the one-electron picture represented in Fig. 7.[3] This fig-

ure shows the d-state splitting associated with the inclusion in the Hamiltonian of both an electron exchange term and the crystal field potential. The exchange term produces a spin dependence such that electrons of opposite spin see different potentials. The exchange splitting (Δ_{ex}) is thus the difference in energy between the states of majority spin direction ($3d_\alpha$) and minority spin direction ($3d_\beta$).

In the Mn^{++} ion the five $3d_\alpha$ levels are filled in accordance with Hund's rule and the $3d_\beta$ states are empty. An electron can be excited from either of the filled crystal-field-split $3d_\alpha$ states (t or e) of one ion into either of the empty $3d_\beta$ states (t or e) of another ion. This need not involve a spin flip since the α direction in one ion can be the same as the β direction in another ion. Since the crystal field splitting is the same for both spin directions, the transitions $t \to t$ and $e \to e$ have the same energy. Thus the result is an equally spaced triplet.

The transitions [(i)–(v)] discussed above should give rise to pronounced optical structure. [19,20] An identification of our optical data in terms of these transitions is proposed below.

The absorption peaks below 4 eV observed by Huffman, Wild, and Shinmei[7] and by Pratt and Coelho[6] in MnO and CoO, and by Newman and Chrenko[5] in NiO, have been interpreted as arising from excitons of type (i). The energies of these excitons, which involve only localized states, are independent of temperature or have much smaller coefficients of temperature dependence than do the energies of transitions involving one or more bands. Typically, because band edges are both shifted and broadened with temperature it is expected that the positions of excitations involving bands will shift by approximately 4×10^{-4} eV/K.[22,23] Therefore, the temperature dependence of spectral features observed in the present study may serve as a guide in their assignment to particular types of transitions.[24]

Photoconductivity measurements on MnO which show a steep rise above 4 eV have been reported by Drabkin, Emel'yanova, Iskenderov, and Ksendov.[25] This behavior is usually taken to indicate an electronic excitation involving an itinerant (band) state. The type-(ii) doublet is predicted to lie in the 4- or 5-eV region and involves an itinerant state while the observed excitations at 4.6 eV and either 5.4 or 5.5 eV are in agreement with this energy position and splitting. Since the position of the structure at 5.4 eV is temperature independent, however, it is unlikely that it arises from a transition involving the 4s band. Therefore, it is plausible to identify the excitations in MnO at 4.6 and 5.5 eV (even though their temperature dependence is indeterminate from the data) with the crystal-field-split 3d-to-4s transitions.
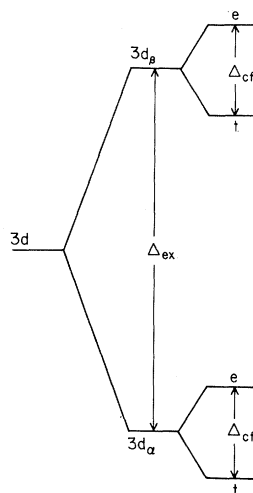
The excitations observed in MnO at 5.7 and 6.9

FIG. 7. Exchange (Δ_{ex}) and cubic crystal field (Δ_{cf}) splitting of the 3d states in a typical transition-metal mono-oxide.

eV both have the correct general temperature dependence for band-to-band transitions. They exhibit a negative temperature coefficient of between 10^{-3} and 10^{-4} eV/K characteristic of one-electron band states in simpler materials. Thus it appears reasonable to assign the transition at 5.7 eV to the one-electron energy gap between the 2p and 4s bands (estimated to be 6 eV) and to assume that structure in the density of states in one of these bands in responsible for the additional spectral structure at 6.9 eV.

The transitions observed in MnO which remain to be assigned are those at 5.4, 6.3, and 7.2 eV. In accordance with their temperature independence they are interpreted as transitions involving only localized states, the most likely candidates being the three equally spaced type-(v) excitations. The transition at 6.3 eV is interpreted as having the energy required to remove a 3d electron from one Mn ion and to place it on a nearest-neighbor Mn ion, while the transitions at 5.4 and 7.2 eV occur at this energy minus and plus the crystal field splitting. Thus the crystal field splitting of the 3d levels in MnO is approximately 0.9 eV, which agrees with the separation between transitions from the crystal-field-split 3d states to the 4s band at 4.6 and 5.5 eV. Previous estimates[7,26] (based on absorption data) of this splitting have ranged between 0.9 and 1.2 eV.

Figure 8 summarizes the electronic states of MnO discussed above as determined from its optical spectra. A diagram of this type was first used by Adler and Feinleib[10] to order the states of NiO.

Since the approximation that the crystal field splitting is independent of the number of electrons in the 3d shell has been used, the manner in which this splitting is presented in the diagram is somewhat arbitrary. In Fig. 8 the d^5 level is shown as
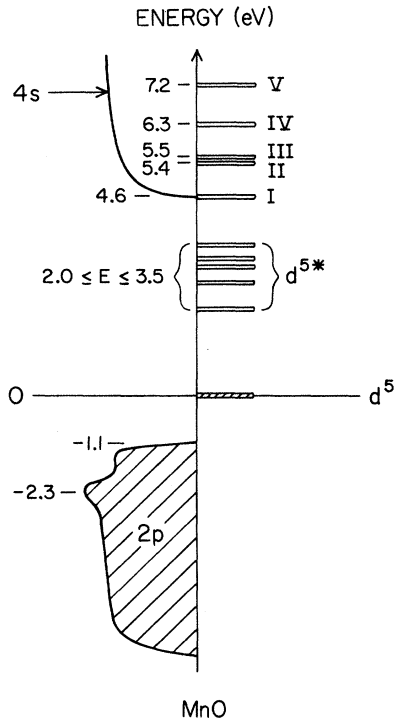
ENERGY (eV)

FIG. 8. Electronic states of MnO. One-electron bands are shown to the left of the vertical line, and localized states to the right. The states which are filled at $T = 0$ are shaded; the highest of these, $3d^5$ (the ground-state $3d$ configuration in MnO), is arbitrarily set at zero.

a singlet and the splitting is exhibited in the d^4 and d^6 states. The positions of the states of the right relative to those on the left are approximately set by placing the $4s$ band edge 4.6 eV above the localized d^5 level, since this is the lowest energy at which transitions occur between these two levels. The positions of the unshaded localized states represent the total energies of the previously discussed excitations. The final states of transitions, labeled by roman numerals, are as follows: I $= d^4(t_\alpha^3 e_\alpha) + 4s$, II $= d^4(t_\alpha^3 e_\alpha) + d^6(t_\alpha^3 t_\beta e_\alpha^2)$, III $= d^4(t_\alpha^2 e_\alpha^2) + 4s$, IV $= d^4(t_\alpha^3 e_\alpha) + d^6(t_\alpha^3 e_\alpha^2 e_\beta)$ and $d^4(t_\alpha^2 e_\alpha^2)$ $+ d^6(t_\alpha^3 t_\beta e_\alpha^2)$, V $= d^4(t_\alpha^2 e_\alpha^2) + d^6(t_\alpha^3 e_\alpha^2 e_\beta)$, where t, e, α, and β have the same meaning as in Fig. 7.

Augmented-plane-wave energy-band calculations have been reported by Mattheiss[27] for CaO, TiO, VO, MnO, FeO, CoO, and NiO. In the case of MnO, these calculations predict a direct gap of ~0.2 eV between the $3d$ and $4s$ bands, and no gap at all for indirect transitions. In MnO, FeO, CoO, and NiO, $3d$ bandwidths of around 3 eV are predicted.

In view of the observed onset of photoconductivity in MnO at 4 eV, the internal consistency of the

present interpretation of the optical spectra, and the fact that the observed $3d$ bandwidths of MnO, NiO, and CoO are no more than 1 eV, none of which agrees with the augmented-plane-wave calculations, their applicability to these transition-metal compounds is questionable.

It is reasonable to expect that the interpretation of temperature-shifted spectral structure as involving at least one band state applies to NiO and CoO as well as MnO. For NiO, the only spectral feature with well-defined temperature dependence is the thermoreflectance dip at 6.2 eV. The fact that this dip shifts to lower energy by 3.6×10^{-4} eV/K or ~0.1 eV as the temperature is raised from 80 to 300 K seems to indicate a transition involving a band state. This is consistent with our earlier interpretation (Glosser and Walker[9]) of the electroreflectance spectrum of NiO. We pointed out that the shape of the oscillation seen in the region of 6.2 eV is reminiscent of critical-point spectra observed in semiconductors and thus we attributed this feature to the onset of transitions between the $2p$ and $4s$ bands. As in the case of MnO, structure observed in direct reflectance and electroreflectance at around 4 eV in NiO arises from transitions between localized $3d$ states and itinerant $4s$ band states. This assignment was based partially on the facts that the observed electroreflectance signal between 3 and 5 eV was not typical of excitations between two bands, but photoconductivity measurements[28] indicated the involvement of an itinerant state.

Again, in CoO, thermoreflectance structure is seen with temperature dependence similar to that observed in MnO and NiO. The negative peaks at 5.0 and 6.0 eV and the positive peak at 7.2 eV all shift to lower energies by 9.5×10^{-4} eV/K with increasing temperature, which implies the involvement of band states. The negative peak at 3.8 eV is assumed to have this same temperature dependence for the purpose of interpretation, although there are no low-temperature data in this case. By analogy with MnO and NiO it seems likely that these spectral features result from transitions between the $2p$ and $4s$ bands and/or between localized $(3d)$ states and a band. Tentative Adler–Feinleib-type diagrams for NiO and CoO are presented in Figs. 9 and 10. The final states shown in these figures for NiO are the following: I $= d^7(t_\alpha^3 t_\beta^3 e_\alpha)$ $+ 4s$, II $= d^7(t_\alpha^2 t_\beta^3 e_\alpha^2) + 4s$, III $= d^7(t_\alpha^3 t_\beta^2 e_\alpha)$ $+ d^9(t_\alpha^3 t_\beta^3 e_\alpha^2 e_\beta)$, IV $= d^7(t_\alpha^3 t_\beta^3 e_\alpha) + d^9(t_\alpha^3 t_\beta^2 e_\alpha^2 e_\beta)$, V $= d^7(t_\alpha^2 t_\beta^3 e_\alpha^2) + d^9(t_\alpha^3 t_\beta^3 e_\alpha^2 e_\beta)$. For CoO these states are I $= d^8(t_\alpha^3 t_\beta e_\alpha^2) + 4s$, II $= d^8(t_\alpha^3 t_\beta e_\alpha^2) + d^8(t_\alpha^3 t_\beta^3 e_\alpha^2)$, III $= d^8(t_\alpha^3 t_\beta^2 e_\alpha) + 4s$, IV $= d^8(t_\alpha^3 t_\beta e_\alpha^2) + d^8(t_\alpha^2 t_\beta^3 e_\alpha^2 e_\beta)$ and $d^8(t_\alpha^3 t_\beta^2 e_\omega) + d^8(t_\alpha^3 t_\beta e_\alpha^2)$. (These last two states are approximately degenerate because $\Delta_{ex} \approx 2\Delta_{cf}$ in CoO.) V $= d^8(t_\alpha^2 t_\beta^3 e_\alpha^2) + 4s$, VI $= d^8(t_\alpha^3 t_\beta^2 e_\alpha)$ $+ d^8(t_\alpha^3 t_\beta^2 e_\alpha^2 e_\beta)$, VII $= d^8(t_\alpha^2 t_\beta^2 e_\alpha^2) + d^8(t_\alpha^3 t_\beta^2 e_\alpha^2 e_\beta)$.
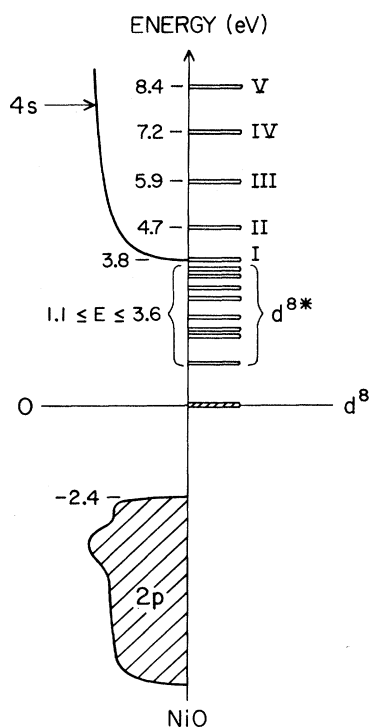
ENERGY (eV)

8.4 — V
4s →
7.2 — IV

5.9 — III

4.7 — II

3.8 — I

$1.1 \leq E \leq 3.6$ { } d^{8*}

O ———————— d^8

-2.4 —

2p

NiO

FIG. 9. Electronic states of NiO.

ENERGY (eV)

6.25 — VII
4s →
5.35 — VI
5.0 — V

4.2 — IV
4.0 — III
3.2 — II
3.0 — I

$1.0 \leq E \leq 2.6$ { } d^{7*}
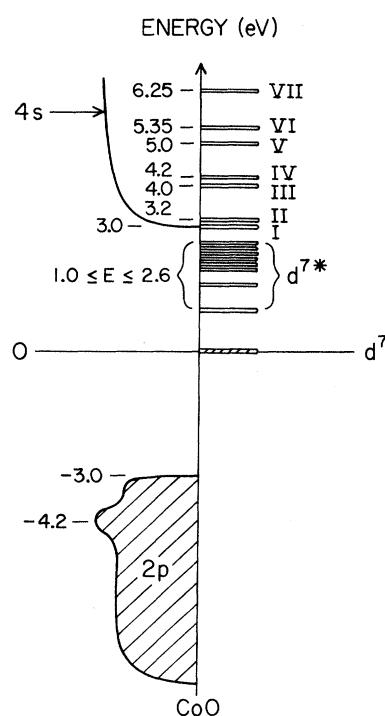
O ———————— d^7

-3.0 —
-4.2 —

2p

CoO

FIG. 10. Electronic states of CoO.

V. SUMMARY

The interpretation of the spectra obtained in this study is based on the following three premises: (1) Sharp temperature-dependent thermoreflectance structure is identified with the onset of transitions between the $2p$ and $4s$ bands. (2) Structure involving one or more bands is expected to shift with temperature while that involving only localized states is not. (3) The $3d$ levels in transition-metal mono-oxides are exchange split into a dou-

blet each member of which is crystal field split into another doublet.

The following assignments concerning the electronic states in MnO were made according to the proposed interpretation: (a) The energy gap between the $2p$ and $4s$ bands corresponds to the temperature-shifted thermoreflectance dip at 5.7 eV. (b) The separation between the $3d$ states and the $4s$ band is identified with the direct reflectance peak at 4.6 eV. (c) The crystal field splitting of the $3d$ states is approximately 0.9 eV. (d) The

TABLE I. Experimentally determined energies of electronic transitions in MnO, CoO, and NiO. d is direct reflectance, t is thermoreflectance, and e is electroreflectance.

	MnO ($n = 5$)		CoO ($n = 7$)		NiO ($n = 8$)	
	RT	LNT	RT	LNT	RT	LNT
$3d^n \rightarrow 3d^{n-1} + 4s$		4.6[a]d	2.8t 3.8t		3.8e, 4.0d	4.05[a]d
	5.5t	5.43t	4.75t	4.96t	4.7d	4.7[a]d
$02p \rightarrow M4s$	5.5–5.6t	5.7t	5.75t	5.96t	6.17t, e	6.25t
	6.7t	6.9[b]t	7.00t	7.21t		
$2(3d^n) \rightarrow 3d^{n-1} + 3d^{n+1}$	5.4t	5.4t	3.2t	4.2t	5.9d	5.9[a]d
	6.4t	6.4t, 6.3[a]d		5.35t	7.2d	7.2[a]d
	7.2t	7.2t		6.25t	8.4d	8.4[a]d
Δ_{cf}	0.9t	0.9t, d	0.95t	0.9t	1.05d, e	1.05d
Δ_{ex}			1.95t	2.15t	2.35d, e	2.35d

[a]22 K.   [b]200 K.

average energy required to remove a $3d$ electron from one Mn ion and place it on a nearest-neighbor Mn ion (i.e., the transition $d_\alpha^5 + d_\beta^5 \to d_\alpha^4 + d_\beta^5 d_\alpha$, where in this case α is the majority spin direction of the ion which looses an electron and β is the majority spin direction of the ion which gains an electron) is 6.3 eV.

In addition, it is noted that a temperature-shifted thermoreflectance dip was also observed at the previously suspected interband gap (6.2 eV) in NiO. Finally, it is suggested that the corresponding temperature-dependent structure at 6.0 eV in the temperature-modulated reflectance of CoO has a similar interpretation.

The results are summarized in Table I, which gives the energies determined for various electronic excitations in MnO, CoO, and NiO at room (RT) and liquid-nitrogen (LNT) temperatures. The experimental basis (direct, d; thermo, t; or electroreflectance,

e) for each assignment is indicated in this table.

It is interesting to note that in MnO and CoO certain similarities as well as differences appear in the thermoreflectance spectra above and below their respective Néel temperatures of 122 and 292 K. For example, in MnO the magnitude of the negative peak attributed to transitions between the $2p$ and $4s$ bands at 5.7 eV is approximately the same at 200 K as it is at 85 K, while magnitudes of the negative peaks assigned to localized inter-ionic $3d$ transitions at 6.4 and 7.2 eV are roughly ten times as large at 85 K as they are at 200 K. Such observations suggest that effects directly associated with the phase transition may be present and that further modulated reflectance studies on these compounds at or near their Néel temperatures may be important in the determination of the effect of antiferromagnetic ordering on the electron states of these materials.

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