

## X-Ray Photoelectron Band Structure of Some Transition-Metal Compounds

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The valence-band structures of MnO, CoO, NiO, CuO, Cu<sub>2</sub>O, NiCl<sub>2</sub>, NiS, and KNiF<sub>3</sub> have been obtained by x-ray photoelectron spectroscopy. Band widths and positions are obtained, and are compared with the results of band-structure calculations. Bandwidths for the oxides are in accord with augmented-plane-wave calculations. Bands positions are better described by shifting free-ion energy levels according to the Madelung energy. The structure of the *d* band of NiO is compared with other experimental and theoretical results.

### INTRODUCTION

The detailed interpretation of the optical and transport properties of transition-metal compounds remains an elusive goal in spite of many years of effort. Although considerable progress has been made<sup>1-3</sup> there is as yet no agreement on such fundamental properties as the band structure and the electronic density of states for many materials of basic importance.

The attempt to treat the electrons in transition-metal compounds by the Bloch-Wilson band theory leads to partially filled bands, implying metallic conductivity for all of these materials. This is, of course, contrary to the experimental facts and requires some elaboration of the theory. The most satisfactory explanation is due to Mott<sup>4</sup> who pointed out the importance of correlations between *d* electrons on the band structure. Full implementation of this suggestion in a band-structure calculation remains a formidable problem, and theoretical and experimental work to determine why a particular compound is a metal, insulator, or semiconductor continues. In this paper we will explore the application of x-ray photoelectron spectroscopy,<sup>5</sup> XPS or ESCA, to these problems. This technique, whose power in the study of band structures has already been demonstrated in the case of metals and alloys,<sup>6</sup> can provide a direct picture of the occupied electronic bands. Although the resolution provided by this technique is still limited, it has the advantage of probing more deeply into the density of states than do most other measurements, which provide information mainly about the electrons near the Fermi energy. XPS makes core as well as valence electrons accessible and thus provides the opportunity to test band-structure calculations in greater detail than ever before.

To interpret the results of XPS experiments it becomes essential to establish the connection between the core and outer electrons. Core electrons are localized and exist in states like those in free atoms. Outer or valence electrons generally form bands. In the Madelung description of

an ionic solid the core and valence state energies are simply obtained by correcting the free-ion energy levels by the electrostatic potential existing at the site of each ion. This approach is very successful for core levels, but cannot give a good description of valence electrons because it neglects the effects of wave-function overlap, which leads to band formation and hybridization.

A better representation requires a full-fledged band-structure calculation. These have been very successful in describing, for example, the Fermi surface of simple metals. Calculations for many of the materials of interest in this paper have been done by Mattheiss<sup>7-10</sup> and will be discussed in greater detail in connection with the experimental results. It should be recognized at the outset that these calculations which utilize Hartree-Fock methods exclude intra-atomic exchange and electron-electron correlation effects. They consequently cannot account for the magnetic, optical, and transport properties. Their chief contribution is to establish bandwidths and band positions.

The inclusion of intra-atomic exchange can account for the insulating properties only in certain special cases,<sup>11</sup> e. g., those of  $3d^5$  and  $3d^8$ . The real origin of the insulating nature of these materials is found within the framework of the theory outlined by Mott and developed by Hubbard.<sup>12</sup> Mott<sup>4</sup> pointed out that *d*-band transport in a material with a partially filled band requires transitions of the form

$$3d^n + 3d^n - 3d^{n-1} + 3d^{n+1}.$$

The energy for this process is the greater the more localized the *d* electrons, or the narrower the band. When this correlation energy *U* becomes sufficiently large, i. e., larger than the bandwidth, transport becomes impossible. A Hamiltonian containing these ideas, now widely used to discuss the properties of narrow-band materials, was introduced by Hubbard<sup>12</sup>:

$$H = \sum_{i,j\sigma} T_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_i n_{i+1}$$

where  $c^\dagger$  and  $c$  are creation and annihilation operators,  $T_{ij}$  is the Fourier transform of the Bloch energies, and  $U$  is the Coulomb repulsion energy between two electrons with opposite spin on the same site. The important parameters which determine the metal-insulator transition within the framework of this Hamiltonian are the bandwidth  $\Delta$  and the Coulomb repulsion  $U$ . The transition occurs when  $\Delta \approx U$ , an insulator being characterized by  $\Delta \ll U$  and a metal by  $\Delta \gg U$ . Experimentally determined values for these parameters are essential for a meaningful discussion of the properties of materials within the framework of the Hubbard Hamiltonian.  $\Delta$  can in principle be obtained directly from experimental data, but the magnitude of  $U$  is generally based on semiempirical estimates.<sup>1-3</sup>

A systematic investigation by XPS of a series of compounds like the transition-metal monoxides or monosulphides which have already been thoroughly studied by other techniques provides an attractive line of attack. These compounds include examples of all three types of conductivity. Of particular interest are compounds like NiS which exhibit a metal-to-nonmetal transition as a function of temperature.

The transition-metal monoxides have attracted considerable attention because, except for CrO, they exist as an isostructural series from TiO (metal) to NiO (insulator). Except for small lattice distortions which accompany magnetic transitions they have the simple NaCl structure. Among them NiO has often served as a test case for theoretical approaches. It is also the most thoroughly studied of these materials from the experimental point of view, and will therefore serve as a focus for our work as well.

The properties of NiO have been dealt with extensively in recent reviews.<sup>9,13-15</sup> We shall here summarize only the salient points. Stoichiometric NiO is a wide-gap insulator and its optical spectra for energies below 3.5 eV are very similar to those of dilute Ni<sup>2+</sup> in MgO. It has been argued that this is no proof of the localized nature of the 3d electrons because the states produced by photoabsorption may be excitonic states. Sharp excitonic states in conjunction with wide bands are well known in, for example, the elemental semiconductors. However, delocalization of the *d* states in NiO relative to those of Ni<sup>2+</sup> in MgO can be due only to considerable *d*-wave-functions overlap. This in turn would most likely affect the wave functions, implying different energy levels in the two systems. This is counter to experimental fact. It therefore follows that the similarity of the energy levels of Ni<sup>2+</sup> in NiO and MgO is an indication of localization in NiO. The high Néel temperature, 520 °K, shows that the magnetic interactions in this material are produced by strong superexchange via the

O-2p<sup>6</sup> orbitals which must be quite extended<sup>2</sup> and describable in a band picture.

The optical properties show a sharply rising absorption at 3.8 eV which resembles the behavior of a semiconductor at the gap energy. This energy has often been attributed to an excitation from the 3d band into the 4s band. However, Powell and Spicer<sup>15</sup> who made the most thorough study of the optical properties did not obtain sufficient evidence to distinguish between 3d → 4s and 2p → 3d assignments. In the region between 4 and 26 eV, many transitions have been detected in reflectivity measurements but little agreement exists regarding the interpretation.

The most ambitious attempt to set up a band structure for NiO is that of Adler and Feinleib.<sup>14</sup> They use free-ion energy levels corrected by the Madelung energy to approximate the positions of the energy bands and use auxiliary information to determine their width. The 3d electrons are assumed to be effectively localized in a band only 0.01 eV wide, lying close to the Fermi energy. The oxygen 2p valence band is taken to be 4 eV wide lying in the interval from 1.5 to 5.5 eV below  $E_F$ .

#### EXPERIMENTAL

All data were taken with a Varian IEE-15 spectrometer. The instrumental resolution, as measured by the full width at half-maximum of the Au 4f lines, was 1.8 or 1.3 eV depending on the count rate available. Samples were of two kinds, either freshly crushed powders or films grown on the metal. The films were grown by exposing the metal under the appropriate thermal conditions to the gas that ensured the formation of the desired compound. The films were always clearly visible showing that they had thicknesses larger than 1000 Å ensuring that their properties were representative for the solid. This type of sample has the advantage that charging effects are small. For powder samples a charging correction must be applied. Normally the carbon 1s line due to volatile contaminants was used to normalize data by shifting the whole spectrum so as to place the carbon line at 285 eV. The absolute zero of the energy scale itself was determined from the Fermi edge as measured with a silver sample.

XPS binding energies are normally expressed relative to the Fermi energy. It should be recognized, however, that the Fermi energy of an insulator can assume any position within the band gap, depending on doping. Moreover, the Fermi energy, which is an equilibrium property, is not well defined in an insulator exposed to a high flux of x rays which generate a substantial number of free carriers. The data taken with films on metallic substrates suggest that the effective refer-

ence level lies near the middle of the gap. It is clear from these remarks that in all cases the energy scales have to be considered as uncertain from an absolute point of view and their position can also vary between different compounds depending on their electrical properties. Therefore for comparison with other data some well-defined spectral features, such as the edge of the valence band, should be used as a reference.

The chief advantage of XPS over other techniques such as low-energy ( $h\nu \leq 11$  eV) ultraviolet photoelectron spectroscopy (UPS) is that it directly reflects the density-of-states structure of the *filled* bands alone although the latter technique has much better resolution. The final state of the photoexcited electron lies in a region of the empty band structure  $\sim 1250$  eV above the Fermi energy, where there is no density-of-states modulation. In low-energy UPS an unfolding of the joint initial- and final-state structure is required. The success of XPS in giving a fairly accurate representation of the density of occupied states of metals has been adequately documented. Recently, Shevchik *et al.*<sup>16</sup> have shown that high-energy UPS can give a good representation of the density of states near the Fermi energy and that by combining XPS and UPS results a more detailed representation of the density of states can be obtained. On the other hand, when XPS is used for the investigation of energy bands in insulators and semiconductors, complications may, in principle, arise from multielectron satellites. This phenomenon is well documented<sup>17</sup> for core levels of transition-metal ions and is generally attributed to the excitation of an electron from the valence region simultaneous with the photoelectric emission of the core electron. For the compounds considered in this paper these excitations must involve metal *p*- or ligand *d*-band electrons. Unfortunately, the exact nature of these excitations remains uncertain. If core level satellites are due to charge transfer transitions to metal *3d* states, then there are no valence-band satellites at the same energy due to this mechanism. All structure is then density-of-states structure. On the other hand, charge transfer to empty *4s* orbitals would allow valence band as well as core level satellites at the same energy. At present there is no definitive evidence to confirm or deny the existence of satellites in valence-band spectra.

The valence-band density of states is defined by a process in which one electron is removed. In insulators with localized *d*- or *f*-electrons the final state after photoemission need not be the ground state of the system. This effect is well documented for the *4f* spectra of rare-earth trifluorides,<sup>18</sup> but can also be found in certain transition-metal compounds.<sup>19</sup> It is most readily seen in systems with an electron configuration contain-

ing one more electron than a half-filled shell. In a weak crystal field this corresponds to a half-filled shell of spin-up electrons and one spin-down electron. It is immediately apparent that photoionization of the single spin-down electron leads to the ground state, whereas photoionization of a spin-up electron leads to excited states. This gives rise to final-state structure, which at first sight appears to be only distantly related to the electronic properties of the system under study. However, this final-state structure corresponds to the density of states defined in the usual sense.

## RESULTS

We begin our examination of XPS valence bands with a few simple systems to establish the power of the technique and then progress to systems of increasing complexity. We include here systems with no *d* electrons, with filled *d* shells, and systems with partially filled shells in which the *d* electrons are clearly localized or delocalized.

### Titanium Dioxide, $\text{TiO}_2$ , $3d^0$

The spectrum in Fig. 1 clearly shows the bands derived from the O-*2s* and O-*2p* atomic wave functions. The latter makes up the valence band and exhibits a bandwidth significantly greater than the 1-eV instrumental resolution. (Throughout this paper we will use the atomic tight-binding designation of the electron states, fully cognizant of the fact that hybridization may be appreciable.) We had earlier stressed<sup>20</sup> that the separation between the oxygen *2s* and *2p* states in many of these insulators is close to the free-atom value of 16 eV.

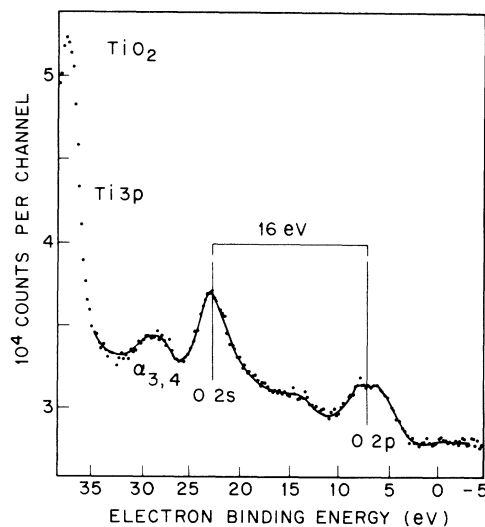


FIG. 1. XPS spectrum of the valence-band region of  $\text{TiO}_2$ . The O-*2s* band and the O-*2p* band are clearly discernible (from Ref. 19).

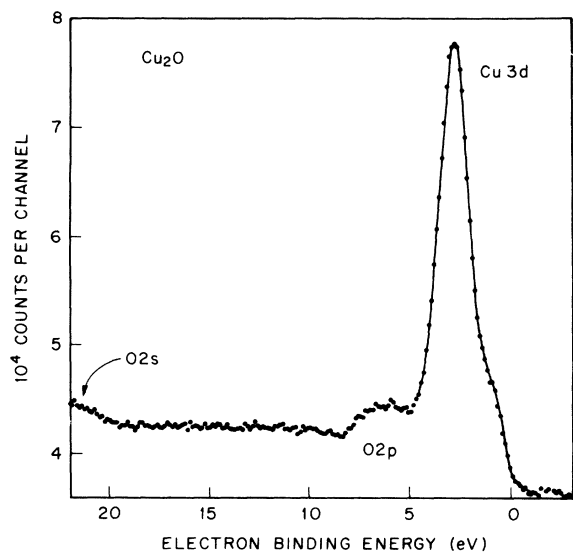


FIG. 2. XPS valence-band structure of  $\text{Cu}_2\text{O}$  (from Ref. 21).

This is of course implicit in the Madelung energy description of ionic solids. Deviations are expected whenever there is band overlap and hybridization between anion and cation states. A valence-band structure with similar O-2s-O-2p separation has also been obtained for MgO, a sodium chloride structure oxide. This will be useful in the consideration of the transition-metal monoxides in a later section of this paper.

#### Cuprous Oxide, $\text{Cu}_2\text{O}$ , $3d^{10}$

This spectrum, Fig. 2, was obtained from a thin film grown on a copper substrate.<sup>21</sup> The compound is a semiconductor with filled Cu-3d and O-2p shells. The 3d band clearly overlaps the oxygen 2p derived valence band. Some structure is resolved in the 3d band which has a width of 1.5 eV at half-height, much narrower than the 3d band of copper metal. Weak satellite structure seen in our earlier spectrum<sup>20</sup> is absent in this thin sample indicating that it was probably due to plasmon excitation by electrons originating deeper within the sample. Comparison of this spectrum with the band structure calculated by Dahl and Switendick<sup>22</sup> is instructive. Although a density-of-states histogram is not available, it is clear that there is satisfactory agreement with regard to the width and location of the oxygen 2p and copper 3d states. The location of the oxygen 2s states is, however, not correctly given by the band-structure calculation.

#### Potassium Nickel Fluoride, $\text{KNiF}_3$ , $3d^8$

The data for this transparent insulator compound are shown in Fig. 3. They were obtained with a

sample made from freshly crushed single-crystal material. The *d* electrons are localized. This is one of the first materials to which molecular orbital calculations were successfully applied to explain the magnetic properties.<sup>23</sup> The comparison of the XPS density of states with a recent theoretical augmented-plane-wave (APW) calculation shows that the latter<sup>10</sup> overestimates the F-2p-Ni-3d energy separation. The data clearly illustrate both the usefulness and the limitations of current XPS densities of states. They serve to locate the position of bands to within  $\sim 0.2$  eV and can thus provide a useful guide for band-structure calculations, but have only barely sufficient resolution to reveal structural details. Ni *d*-band structure is discussed below in connection with NiO and  $\text{NiCl}_2$ .

#### Cobaltous Oxide, $\text{CoO}$ , $3d^7$

This material can clearly be described as a Mott insulator since neither intra-atomic exchange nor the crystal field can account for its insulating properties. The data shown in Fig. 4 were taken on a thin film grown on a metallic substrate. The growth conditions were such as to avoid the formation of  $\text{Co}_3\text{O}_4$ . Of all the monoxides investigated CoO shows the important features of the valence band most clearly. The O-2s<sup>2</sup> band stands out at 22 eV, the O-2p<sup>6</sup> band is clearly visible at 6 eV.

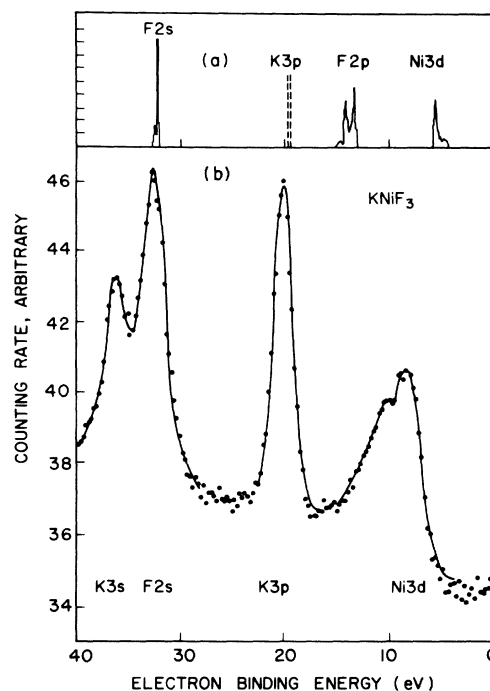


FIG. 3. Valence band for  $\text{KNiF}_3$ . (a) Calculated density of states after Mattheiss, Ref. 10; (b) XPS density of states.

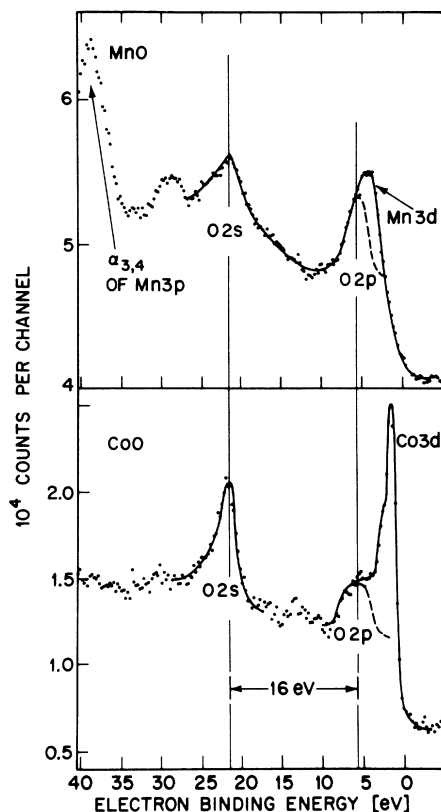


FIG. 4. XPS valence-band structure of MnO (upper part) and CoO (lower part) (from Ref. 20).

The separation is 16 eV. The  $3d$  band, at 2 eV, is considerably narrower than in MnO (see below) and shows some resolved structure. This structure may be described as the crystal-field splitting of the  $3d^6$  final state of photoemission. The width of the  $d$  band is 2.5 eV before correction for instrumental resolution.

#### Manganous Oxide, MnO, $3d^5$

Data for this compound are also shown in Fig. 4. The material was prepared on a metallic manganese substrate by oxidation in air followed by argon ion sputtering to remove higher oxides. The latter were dominant on bulk MnO samples. The data show the oxygen  $2s$  band and a band near the Fermi energy comprising the oxygen  $2p$  derived valence band and the manganese  $3d$  band. The combined band is relatively wide,  $\sim 5$  eV. The data suggest overlap between the O- $2p$  and Mn- $3d$  bands which would result in strong hybridization of the two bands with an attendant increase in bandwidth. This interpretation differs significantly from that of Wilson<sup>1</sup> who shows a 1.5-eV wide  $d$  band ( $t_{2g}$  and  $e_g$ ) located 2 eV above the edge of the valence band. An interesting comparison is pro-

vided by the results of a molecular cluster calculation recently reported by Johnson *et al.*<sup>24</sup> They treat an  $\text{MnO}_6^{10-}$  cluster, using the  $X\alpha$  method to approximate the exchange, and the transition state concept to calculate photoionization energies. They find two  $d$  bands, separated by 2.3 eV, sufficient to account for the observed bandwidth. The location of the  $2s$  and  $2p$  bands are also compatible with the experimental results.

#### Nickel Sulphide, NiS, $3d^8$

NiS is a metal at room temperature, and undergoes a metal-to-nonmetal transition at 260 °K.<sup>24</sup> The sample was produced by heating a Ni foil to 500 °C, then briefly exposing it to  $\text{H}_2\text{S}$ , and cooling it rapidly to room temperature. This procedure should preferentially produce NiAs structure material.<sup>25</sup> The Ni- $2p$  spectra showed no satellite structure at temperatures between 70 and 400 °K. Satellites had previously been found in all insulating paramagnetic Ni compounds, only Ni itself having no resolved satellite structure. This tends to con-

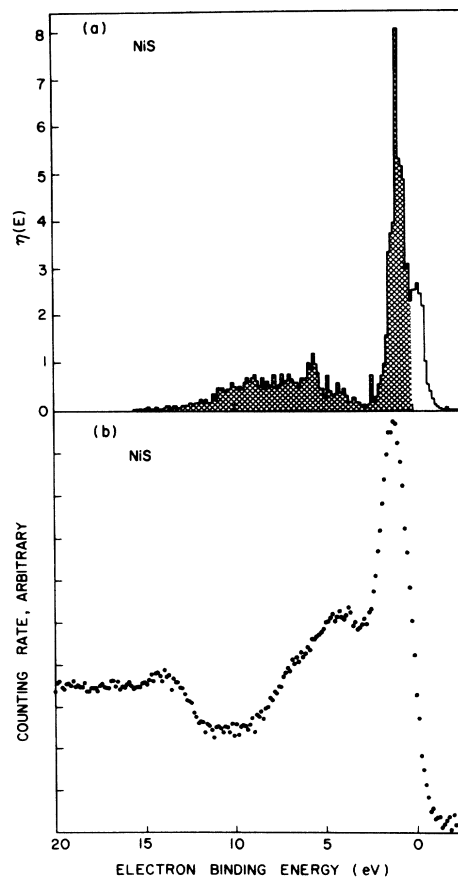


FIG. 5. Valence band of NiS. (a) Calculated density of states after Tyler and Fry, Ref. 26; (b) XPS density of states.

firm that we are dealing with a metal in this experiment. The agreement with the density of states calculated in a tight-binding approximation<sup>26</sup> is only fair (see Fig. 5). The most serious disagreement lies in the width of the S-3*p* band which is much narrower in the experiment than in the calculation where it almost overlaps the experimental S-3*s* band. (The 3*s* band was not included in the calculations.) As is the case in other transition-metal compounds, it appears that the *p*-*d* separation is overestimated by the calculations.

A detailed discussion of the electronic structure and its relation to the observed properties of NiS has been given by White and Mott.<sup>27</sup> Some of their findings are substantiated by the present data. Their main point is that there is considerable *d*-*p* overlap, so that the screening by the *p* electrons reduces the Coulomb energy to a very small value, making metallic conductivity possible. The XPS spectrum, Fig. 5, shows that the *d* and *p* bands fall quite close together lending support to this argument. Another interesting feature of the XPS data on NiS is the splitting of the Ni-3*s* spectrum. Since no satellites were found in other core electron spectra this splitting can only be attributed to the 3*d*-3*s* exchange interaction. The observed splitting of 2.6 eV corresponds to a magnetic moment of  $1.65\mu_B$ , provided the 3.1-eV splitting in NiF<sub>2</sub> is attributed to a moment of  $2\mu_B$  and  $\langle r^{-3} \rangle$  is the same in both compounds. This moment is close to that observed in nonmetallic NiS ( $1.5\mu_B$ ), but it had been found in other measurements that the moment vanished in the metallic phase.<sup>25</sup> A possible resolution of this contradiction lies in the lifetime of the charge fluctuations in NiS. These may be sufficiently long so that the multiplet splitting can be observed in the  $10^{-16}$  sec time domain of the XPS experiment, while neutron diffraction and magnetization measurements which sample over a time interval much longer than that of the charge fluctuations may only see a vanishing time-average moment.<sup>3</sup>

#### Nickel Oxide, NiO, 3*d*<sup>8</sup>

Much of the work undertaken to elucidate the problems of the metal-nonmetal transition has utilized NiO as a model compound. A great deal of experimental information has been accumulated and many calculations have been performed, but the attempt to obtain a consistent picture relating the experimental facts to a band structure has not been entirely successful. In this section we point out difficulties which are encountered in the attempt to interpret the XPS valence-band spectrum of NiO, and to relate it to earlier work.

The problem becomes apparent from an inspection of Fig. 6, which shows a Ni-2*p* and a valence-band spectrum of a NiO sample. The NiO was

grown as a thin film on Ni metal under conditions which ensure the formation of NiO. The spectrum is identical to one obtained from freshly crushed NiO single crystals, except for a shift due to charging. The 2*p* spectrum shows a number of extra lines marked as satellites in addition to the expected 2*p*<sub>1/2</sub> and 2*p*<sub>3/2</sub> lines. The nature of the electronic process responsible for these satellites is still open to discussion, but there is evidence that the 6.5-eV satellite corresponds to a O-2*p* → Ni-3*d* charge transfer excitation. It should be mentioned at this point that core electron satellite lines were considerably weaker in the other materials discussed so far in this paper. The problem with respect to an analysis of the valence-band spectrum becomes apparent from an examination of the lower part of this figure. It shows that the valence band exhibits four clearly resolved structures. The peak at 22 eV is the O-2*s* level, and the peak at 2 eV is due to the Ni-3*d* level. A comparison with

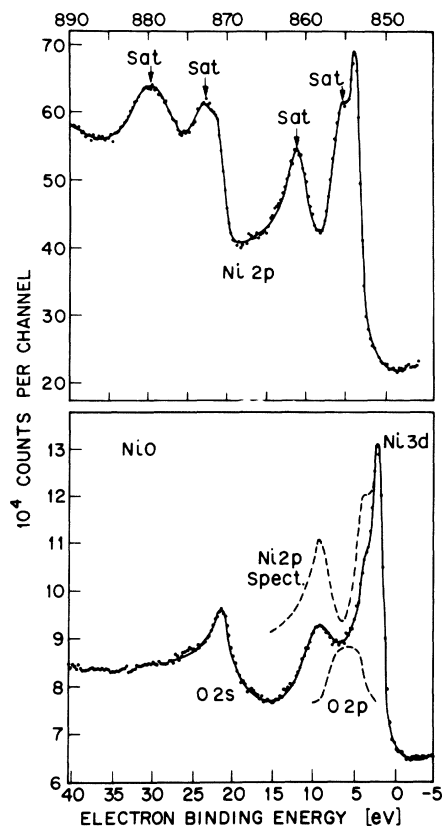


FIG. 6. XPS spectrum of the Ni-2*p* region of NiO (upper part). In addition to the 2*p* lines separated by the spin-orbit splitting, a number of extra satellite lines ("sat") are observed. These are most likely due to multi-electron excitations. Valence-band region of NiO, with the Ni-2*p* region superimposed (lower part). The 2*p* line has been made to coincide with the Ni-3*d* line.

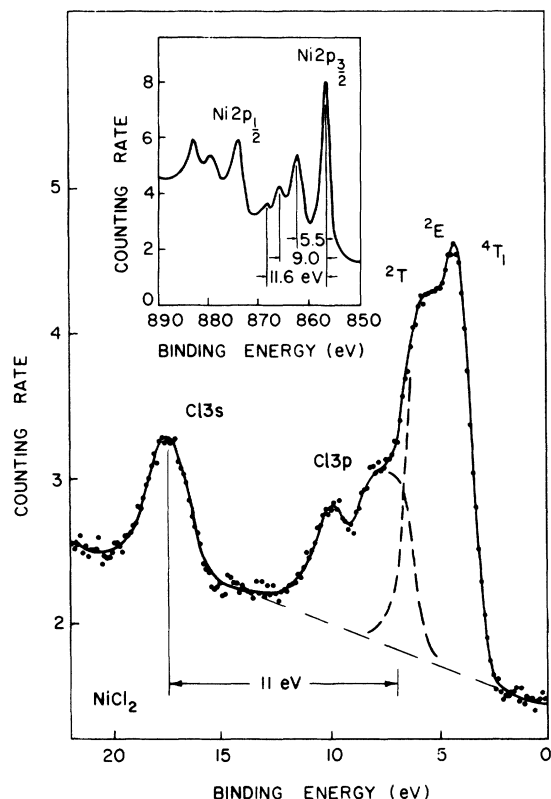


FIG. 7. Valence-band region of  $\text{NiCl}_2$ . The structure in the  $3d$  band may be interpreted as final-state structure in the  $3d^7$  configuration using weak crystal-field notation. The expected position of the  $\text{Cl-}3p$  band is also indicated. The insert gives the  $\text{Ni-}2p$  region for comparison.

the  $\text{Ni-}2p$  spectrum suggests that the structure at 9 eV and the shoulder at 3.8 eV may be due to multielectron transitions. This assignment is supported by the fact that the  $\text{O-}2p$  band in  $\text{CoO}$  (or  $\text{TiO}_2$ ,  $\text{MgO}$ , etc.) falls far from these supposed satellites. A change in the  $\text{O-}2p$  band sufficiently large to reconcile all the structure observed in  $\text{NiO}$  with the  $\text{O-}2p$  band is initially hard to support. On the other hand, the valence-band spectrum of  $\text{KNiF}_3$  does not exhibit satellite structure although the  $2p$  spectrum of this material contains strong satellites. A further counter example is provided by the valence band and  $\text{Ni-}2p$  spectra of  $\text{NiCl}_2$ , Fig. 7, in which it is evident that the two spectra have little in common. There is a close correspondence only between the 5.5-eV but not the 9.0-eV satellite in the  $\text{Ni-}2p$  spectrum and structure in the valence-band spectrum. Thus it appears that the similarity between the  $\text{Ni-}2p$  and the  $\text{Ni}$  valence band spectra of  $\text{NiO}$  is clearly accidental. We therefore conclude that the 1.8-eV satellites observed in  $\text{NiO}$  as a shoulder in both the  $\text{Ni-}2p$  spectrum and the valence band have nothing to do

with each other. This strengthens the view that the nearby satellite in the valence band represents band structure which can be understood in terms of a final-state effect. A comparison of the valence band of  $\text{NiO}$  with that of  $\text{NiF}_2$  (Fig. 8) supports the points just made. These two compounds do have very similar  $\text{Ni-}2p$  spectra, but the 1.8-eV satellite is missing in  $\text{NiF}_2$ . The valence band of  $\text{NiF}_2$ , though very similar to that of  $\text{NiO}$  shows not only a structure where one would expect the 6-eV satellite to occur but also a weak shoulder where one would expect the  $\text{F-}2p$  spectrum according to a comparison with  $\text{FeF}_2$ .

The observations can be summarized as follows. Structure in the  $3d$  band is almost certainly not due to multielectron satellites and therefore most probably reflects genuine  $3d$  band structure. As far as the anion bands go, two alternative interpretations remain open. On the one hand, satel-

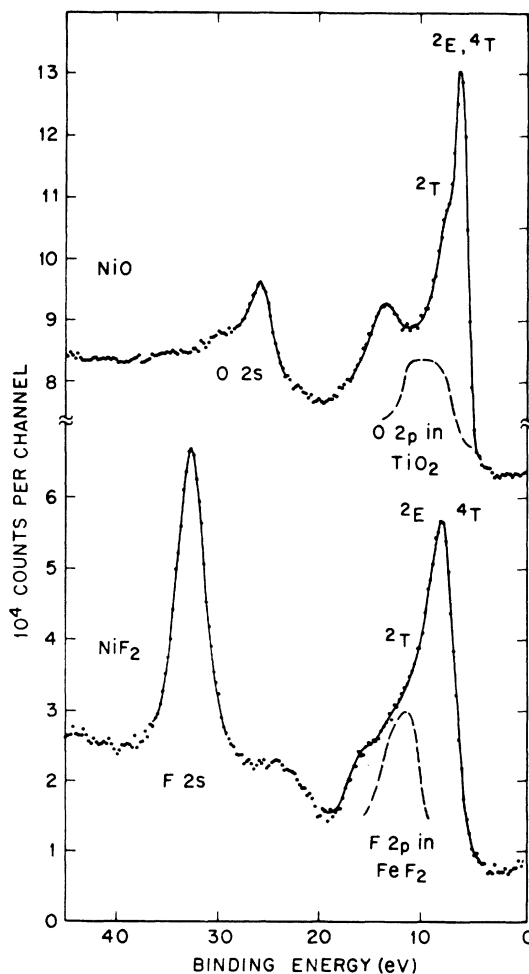


FIG. 8. Valence-band spectra of  $\text{NiO}$  and  $\text{NiF}_2$ . Final state  $3d^7$  crystal-field splitting in the  $3d$  band is indicated.

lite structure observed in the core spectra may also be visible in the valence bands accompanying the  $3d$  levels and may thus have to be subtracted from the valence band in order to reveal the true anion valence bands. (These bands would then be similar to those observed in materials where there are no strong satellites in the core spectra.) On the other hand, because of the decrease in the  $p$ - $d$  gap in the Ni compounds there may be much stronger hybridization than in the other materials considered so far and all the structure seen in the valence band may be "real" valence-band structure. We know of no experimental approach that would distinguish between these alternatives and therefore proceed now with a comparison of the XPS data with the results of other work.

The empirical systematics of Wilson<sup>1</sup> provide the most immediate comparison with the results of optical spectroscopy. He shows a  $d$ -band consisting of filled  $t_{2g}^{(\alpha)}$ ,  $t_{2g}^{(\beta)}$ , and  $e_g^{(\alpha)}$  bands each of the order of 1 eV in width, with the latter two overlapping and lying above the  $t_{2g}^{(\alpha)}$  band. The total width is  $\sim 2.5$  eV. This distribution of states is compatible with the XPS data provided the shoulder on the main peak is indeed part of the  $d$  band.

A similar conclusion follows from the work of Johnson *et al.*<sup>24</sup> who calculate the energy levels for a  $(\text{NiO}_6)^{10-}$  cluster self-consistently, taking exchange into account by the  $X_\alpha$  method, in which it is approximated by an extra Coulomb interaction.<sup>28</sup> By using the transition state concept<sup>29</sup> they calculate ionization energies which correspond closely to what is actually measured in a photoemission experiment. (This approach makes it possible to take into account the relaxation of the final state by calculating the energies of the initial and final states for an occupation number half-way between them.) This type calculation does not, of course, give a density of states, but a weighted average of the calculated orbitals should reproduce the XPS density of states. The calculations show strong hybridization between O  $2p$  and Ni  $3d$  resulting in a very broad valence band encompassing all the structure found in the XPS valence band. The  $3d$ -band components coincide with the main line and its shoulder, which accordingly comprise the  $d$  band. The peak at 9 eV contains part of the O- $2p$  states, but may nevertheless contain contributions from multielectron excitations.

Comparisons with the UPS results on NiO of Powell and Spicer<sup>15</sup> and on oxidized Ni by Eastman<sup>30</sup> lead to similar conclusions as far as the valence band is concerned. In each case structure is observed extending 10 eV below the Fermi energy, including the peak which could be due in part to multielectron excitation.

A comparison of the XPS results on NiO with other optical and photoemission work, as well as

with theoretical approaches is shown in Fig. 9. For convenience the energies have been normalized such that the position of the  $3d^8$  configuration is at  $E=0$  eV. The bottom trace shows the energy levels obtained by shifting the free-ion energy levels<sup>31</sup> by the Madelung energy of 24 eV.<sup>15</sup> Configurations for which the charge of an ion is changed by one unit, e. g., charge transfer transition of the type  $2(d^8) \rightarrow d^7 + d^9$  or  $p^6 + d^8 \rightarrow p^5 + d^9 4s$ , have been purposely left out, because their energy is difficult to estimate. See the Appendix for a discussion of this point.

It can be seen from Fig. 9 that the Madelung levels approximate the experimental position of the various bands fairly well. Adler and Feinleib<sup>14</sup> start from the Madelung picture, broaden those energy levels thought to be bands states (O  $2p$ , Ni  $4s$ , Ni  $4p$ ), but leave the Ni- $3d^8$  level very narrow. The Ni- $3d^8$  and O- $2p^6$  bands in their estimate also agree with the XPS density of states. On the other hand, they almost certainly overestimate  $U$  which they obtain on an atomic basis with only a small screening correction. Therefore, except for the Ni- $3d^7 4s$  band, the position of the excited states in Ref. 14 may be less reliable.

The ideas presented by Goodenough<sup>2</sup> are very similar to the results of Adler and Feinleib.<sup>14</sup> He also places a narrow  $3d$  band above a broad O- $2p$  band and places the  $4s$  band above the  $3d$  band by an amount which is close to the optically observed

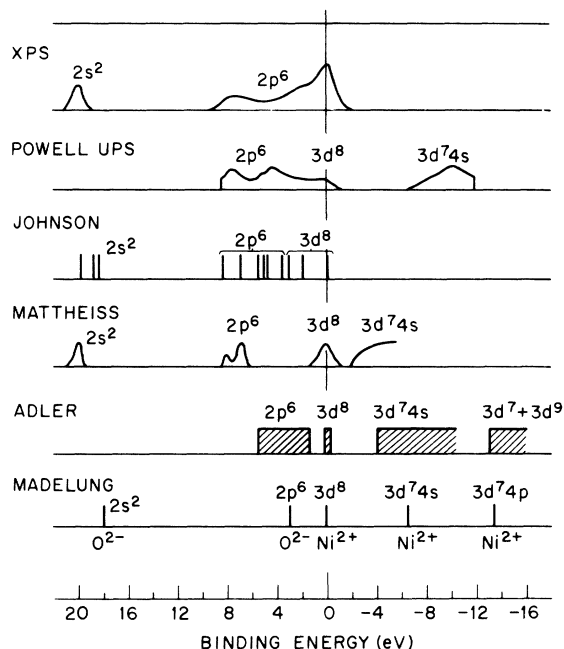


FIG. 9. Experimental and theoretical results for NiO. In every case the zero of energy has been made to coincide with the center of the  $3d$  band.



energy gap. He points out that in NiO the  $3d^7 4s$  band lies only a few tenths of an eV below the  $3d^8 4s$  band, thus stressing the itinerant nature of that band. Because his band structure is so similar to that of Adler and Feinleib, it has not been shown separately in Fig. 9.

Mattheiss<sup>7-10</sup> has made extensive calculations for a great number of transition-metal compounds, among them the transition-metal oxides. He uses an APW calculation yielding one-electron bands. The parameters entering these calculations were then fitted to a linear combination of atomic orbitals (LCAO) interpolation scheme. The main deficiency of this calculation is the lack of self-consistency. As Mattheiss notes, this lack may introduce errors in the relative position of the oxygen and metal bands of as much as a few electron volts. Calculations along similar lines were performed by Wilson,<sup>11</sup> who used a spin-polarized APW procedure. His calculations also lack self-consistency. Detailed comparison with experiment is difficult because density-of-states curves were not calculated. The calculations of both Mattheiss<sup>9</sup> and Wilson<sup>11</sup> give bandwidths of  $\sim 2$  eV for the  $3d$  electrons, compatible with the XPS data. The 7-eV Ni- $d^8$ -O- $2p^6$  separation in the calculation of Mattheiss is very large, while the 2-eV gap, presumably the Ni- $d^8$ -Ni- $d^7 4s$  transition, is small compared to the measured 3.7 eV. In this respect Wilson's calculations come somewhat closer to the experimental values, namely,  $\sim 3.8$  eV for the Ni- $d^8$ -O- $2p^6$  separation and 2.7 eV for the gap.

An attempt to reconcile the experimental valence-band structure with the results of optical spectroscopy runs into difficulties because there is no agreement on assignments. Since the position of the occupied bands is reasonably well described by the Madelung approach, and therefore similar to that of Adler and Feinleib,<sup>14</sup> one is led to similar assignments for the optical transitions. It would be premature, however, to assume that these assignments are unique. For example, the 4-eV band gap attributed to  $3d \rightarrow 4s$  by Adler and Feinleib<sup>14</sup> has been attributed to  $2p \rightarrow 3d$  by Wilson<sup>1</sup> and Johnson<sup>24</sup>; the 6-eV structure may be due to  $2p \rightarrow 4s$  according to Wilson<sup>1</sup> and Messick *et al.*,<sup>32</sup> although the  $3d \rightarrow 3d$  charge transfer transition has also been placed in this range. Unfortunately, the interpretation here remains far from clear.

#### Cupric Oxide, CuO, $3d^9$

The situation in this compound is quite similar to that in NiO. There are strong satellite lines in the core electron spectra. Valence-band data exhibit structure that correlates well with the core electron satellites.<sup>20,21</sup> The satellite structure

falls 6 eV below the location of the O- $2p$  valence band expected according to the Madelung calculation, or found in Cu<sub>2</sub>O. It would appear that this shift is too large to be accounted for by  $p$ - $d$  hybridization, but molecular cluster calculations for CuO<sub>6</sub><sup>10-</sup> again reproduce all the features of the experimental data.<sup>33</sup>

#### DISCUSSION

In many materials XPS measurements clearly reveal the essential features of the occupied band structure. The position of bands is obtained to  $\pm 0.2$  eV. Bandwidth can be measured with similar accuracy, but the detailed structure of bands is not obtainable at present because of the 1-eV width of the MgK $\alpha$  radiation used for photoexcitation. Ambiguities arise when structure in the valence band matches prominent satellites associated with core level spectra.

Comparison of core level binding energies and valence-band centroids with values derived from free-ion energy levels using the Madelung energy show that these materials are sufficiently ionic so that this approach is valid. Hybridization of metal  $3d$  with anion  $2p$  states can perturb these states when there is strong  $p$ - $d$  overlap. Such overlap is, of course, an important feature of these materials, as evidenced by the high Néel temperature of NiO due to strong Ni-O-Ni superexchange.

Comparison with band-structure calculations reveals a number of problems. Tight-binding calculations, exemplified by those for NiS, apparently do not yield an accurate picture of the valence-band region. APW calculations fail to reproduce the relative positions of anion and cation derived levels accurately. The anion  $2p$  to metal  $3d$  separations is generally too large, while the metal  $3d$  to  $4s$  separation is too small. These difficulties may be traced to the lack of self-consistency in these calculations, but one may nevertheless assume that they give a reasonable picture of the bandwidths.

The shape and width of the  $d$  bands in the monoxides is certainly the most interesting (and controversial) question. Two of the bands, those of NiO and CoO clearly have components less than 1 eV in width, but it is clear that this is not the entire  $d$  band. A guide to the interpretation of these  $d$  band spectra is provided by the calculations of Johnson *et al.*<sup>24</sup> and the systematics of Wilson.<sup>1</sup> The latter suggests that the shoulder corresponds to the spin-up  $t_{2g}$  band. A similar conclusion can be reached under the assumption that the final state of photoionization is localized. One can then analyze the photoemission process in terms of the crystal-field splitting of the final states,<sup>19</sup> which are the states of Ni<sup>3+</sup>,  $3d^7$ . The states produced

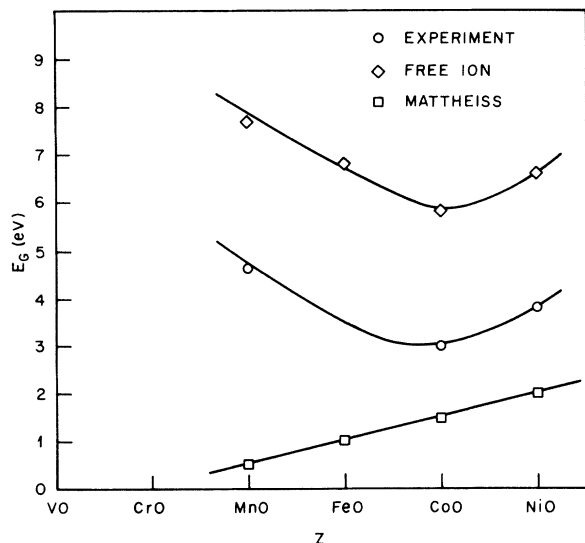


FIG. 10. The  $3d^n - 3d^{n-1}4s$  gap energy in transition-metal oxides according to Refs. 31, 32, and 36.

by photoionization of the  $^3A_2$  state of  $Ni^{2+}$  include  $^4T_1$ ,  $^2E$ , and  $^2T$ . On the Tanabe-Sugano diagram<sup>34</sup>  $^4T_1$  and  $^2E$  are degenerate at  $Dq/B \sim 2$ , the value appropriate for  $Ni^{3+}$ , and corresponds to the main line of the photoemission spectrum. The  $^2T$  state lies at  $E/B \sim 20$  and corresponds to the shoulder.

XPS measurements on TiO and VO have not been made because of surface oxidation. We therefore have no new experimental information bearing on the question why these two oxides are metallic, but soft x-ray emission spectra are available.<sup>35</sup> Heine and Mattheiss<sup>36</sup> have suggested that metallic conductivity is due to the meeting of the 4s and 3d bands, rather than to the breakdown of Mott insulation. Although the band separations are not reliably given by the APW calculations, the empirical data of Wilson<sup>1</sup> seem to support this interpretation. On the other hand, White and Mott<sup>27</sup> question this interpretation. Their position is supported by the data in Fig. 10, which compares the  $d^n - d^{n-1} 4s$  gap calculated by Mattheiss,<sup>36</sup> with that obtained from atomic optical spectra,<sup>31</sup> and that measured directly in NiO, CoO, and MnO.<sup>32</sup> Although the data are so far very limited, it looks as though the atomic spectra give a better guide to the  $d-s$  gap of the oxides than the APW calculations.

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#### APPENDIX

The problem will be sketched briefly with respect to  $2(d^8) - d^7 + d^9$ . An upper limit for the energy of this excitation can be obtained from the atomic energy levels.<sup>31</sup> The ionization potential of  $Ni^{2+}(3d^8)$  is 36 eV and that of  $Ni^{2+}(3d^9)$  is 18 eV, thus the above transition requires 18 eV of energy. This, of course, grossly overestimated the amount of energy required in the solid, because it neglects screening which is certainly present in the solid. We shall try to estimate this screening in various ways.<sup>37</sup> First of all, we assume that the 4-eV band gap in NiO is the energy required to produce a  $3d^7 4s$  state out of a  $3d^8$  state. The  $3d^7 4s$  state is a band state in which the electron has the ability to move through the crystal.<sup>2</sup> This of course creates charge fluctuations on other Ni ions of the type  $3d^8 4s$ . This state lies within 1 eV of a free ion  $3d^9$  state. This then would yield an estimate 4 eV for the process  $2(d^8) - d^7 + d^9$ .

Another estimate can be obtained as follows. Assume NiO is a metal by virtue of an extra electron in its 4s state, thus producing  $d^8 4s$  states. Now it takes  $\sim 4.5$  eV to produce a  $d^7 4s^2$  state and one gains 0.5 eV in going to the  $d^9$  state giving a total of  $\sim 5$  eV for  $2(d^8) - d^7 + d^9$ . (Here we have used the values for atomic  $Co^+$  because those for  $Ni^+$  are not available, but for an order of magnitude estimate, the errors introduced by this procedure should not be relevant.)

These estimates, inaccurate as they may be, show that in transitions which involve the transfer of an electron, the energies which one would estimate from a free-ion picture have to be reduced considerably because of charge fluctuations.<sup>37</sup>

Estimates for  $U$  in the literature vary between wide limits. Adler and Feinleib<sup>14</sup> give 13 eV, Messik, Walker, and Glosner<sup>32</sup> give 5.9–8.4 eV, Wilson<sup>1</sup> gives 4 eV, and Austin and Mott<sup>38</sup> give 1–5 eV.

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<sup>1</sup>J. A. Wilson, *Adv. Phys.* **26**, 143 (1972).

<sup>2</sup>J. B. Goodenough, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, New York, 1971), Vol. 5, p. 145.

<sup>3</sup>N. F. Mott and Z. Zinamon, *Rep. Prog. Phys.* **33**, 881 (1970).

<sup>4</sup>N. F. Mott, *Proc. Phys. Soc. Lond. A* **62**, 416 (1949).

<sup>5</sup>K. Siegbahn *et al.*, *Nova Acta R. Soc. Sci. Ups.* **20** (1967).

<sup>6</sup>See, for example, *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972).

<sup>7</sup>L. F. Mattheiss, *Phys. Rev.* **181**, 987 (1969).

<sup>8</sup>L. F. Mattheiss, *Phys. Rev. B* **2**, 3918 (1970).

<sup>9</sup>L. F. Mattheiss, *Phys. Rev. B* **5**, 290 (1972); *Phys. Rev. B* **5**, 306 (1972).

- <sup>10</sup>L. F. Mattheiss (unpublished).
- <sup>11</sup>T. M. Wilson, *Int. J. Quantum Chem.* **35**, 757 (1970).
- <sup>12</sup>J. Hubbard, *Proc. R. Soc. A* **276**, 238 (1963).
- <sup>13</sup>D. Adler, *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 21, p. 1.
- <sup>14</sup>D. Adler and J. Feinleib, *Phys. Rev. B* **2**, 3112 (1970).
- <sup>15</sup>R. J. Powell and W. E. Spicer, *Phys. Rev. B* **2**, 2182 (1970); see also R. J. Powell, Stanford Electronic Laboratory Technical Report No. 52, p. 20-1, 1967 (unpublished).
- <sup>16</sup>N. V. Shevchik, J. Tejada, D. W. Langer, and M. Cardona, *Phys. Status Solidi B* **57**, 245 (1973).
- <sup>17</sup>A. Rosencwaig, G. K. Wertheim, and H. J. Guggenheim, *Phys. Rev. Lett.* **27**, 479 (1971), and references cited therein.
- <sup>18</sup>G. K. Wertheim, A. Rosencwaig, R. L. Cohen, and H. J. Guggenheim, *Phys. Rev. Lett.* **27**, 505 (1971).
- <sup>19</sup>G. K. Wertheim, H. J. Guggenheim, and S. Hüfner, *Phys. Rev. Lett.* **30**, 1050 (1973).
- <sup>20</sup>G. K. Wertheim and S. Hüfner, *Phys. Rev. Lett.* **28**, 1028 (1972).
- <sup>21</sup>A. Rosencwaig and G. K. Wertheim, *J. Elect. Spectr.* **1**, 493 (1973).
- <sup>22</sup>J. P. Dahl and A. C. Switendick, *J. Phys. Chem. Solids* **27**, 931 (1966).
- <sup>23</sup>S. Sugano and R. G. Shulman, *Phys. Rev.* **130**, 517 (1963).
- <sup>24</sup>K. H. Johnson, R. P. Messmer, and J. W. D. Connolly, (unpublished).
- <sup>25</sup>J. T. Sparks and T. Komoto, *Rev. Mod. Phys.* **40**, 752 (1968).
- <sup>26</sup>J. M. Tyler and J. L. Fry, *Phys. Rev. B* **1**, 4604 (1970).
- <sup>27</sup>R. M. White and N. F. Mott, *Philos. Mag.* **24**, 845 (1971).
- <sup>28</sup>J. C. Slater, *Phys. Rev.* **81**, 385 (1951).
- <sup>29</sup>J. C. Slater and K. H. Johnson, *Phys. Rev. B* **5**, 844 (1972).
- <sup>30</sup>D. E. Eastman and J. K. Cashion, *Phys. Rev. Lett.* **27**, 1520 (1971).
- <sup>31</sup>C. E. Moore, *Atomic Energy Levels*, NBS Circ. No. 467 (U. S. GPO, Washington, D. C., 1949).
- <sup>32</sup>L. Messick, W. C. Walker, and R. Glosser, *Phys. Rev. B* (to be published).
- <sup>33</sup>K. H. Johnson (private communication).
- <sup>34</sup>See, for example, S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).
- <sup>35</sup>D. W. Fischer, *J. Appl. Phys.* **41**, 3922 (1970).
- <sup>36</sup>V. Heine and L. F. Mattheiss, *J. Phys. C* **4**, L191 (1971).
- <sup>37</sup>C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. IV.
- <sup>38</sup>I. G. Austin and N. F. Mott, *Adv. Phys.* **18**, 41 (1969).