(1960).

[2] G. Zally and J. Mochel, Phys. Rev. Lett. 27, 1710 (1971).

[3] H. Schmidt, Z. Phys. 215, 210 (1968).

[4] A. Schmid, Phys. Rev. 180, 527 (1969).

[5] Microscopic calculation actually results in a sum over "excited pair" energies. We have retained only the zero-energy term in Eq. (3) because it is expected to dominate near the transition. See P. A. Lee and M. G. Payne, Phys. Rev. Lett. 26, 1537 (1971), and 27, 170(E) (1971), and Phys. Rev. B 5, 923 (1972), for details.

[6] Lee and Payne, Ref. 5.

[7] L. G. Aslamazov and A. I. Larkin, Fiz. Tverd. Tela 10, 1104 (1968) [Sov. Phys. Solid State 10, 875 (1968)].

[8] For type-I materials the first-order phase transition intervenes and one has to use supercooling techniques to get close to T_{c2}.

[9] By nonlocal electrodynamics we refer to the complications that arise when higher-order terms in $\nabla/i + 2e\vec{A}/\hbar c$ are kept in Eq. (1), because different components of this operator do not commute. As a result the usual replacement of k^2 by $k_z^2 + (4eH/\hbar c)(n + \frac{1}{2})$ is not valid. See Ref. 6 for details.

[10] K. Maki, J. Low Temp. Phys. 1, 513 (1969).

[11] H. J. Mikeska and H. Schmidt, Z. Phys. 230, 239 (1970).

[12] K.-G. Usadel, Z. Phys. 227, 260 (1970).

[13] We should point out that for physical effects that do not arise *directly* from fluctuating pairs treated in the GL approximation, the kind of dimensionality change we discussed may not occur. Examples are the contribution to the conductivity from the Maki diagram [see K. Maki, Progr. Theor. Phys. 39, 897 (1968)] and fluctuation electronic density of states [E. Abrahams, M. Redi, and J. W. F. Woo, Phys. Rev. B 1, 208 (1970)].

[14] R. A. Ferrell, J. Low Temp. Phys. 1, 241 (1969).

X-Ray Photoemission Band Structure of Some Transition-Metal Oxides

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The valence-band structures of MnO, CoO, NiO, Cu_2O, CuO, and ReO_3 have been obtained by x-ray photoemission spectroscopy. It is found that in every case a narrow metal *d* band lies above the center of the oxygen 2*p* valence band.

The transition-metal oxides exhibit a wide variety of electric and magnetic properties[1]: There are magnetic insulators (e.g., NiO), compounds with a metal-to-insulator transition (e.g., V_2O_3), and metals (e.g., ReO_3), This wide variety makes these compounds an attractive subject for a systematic study of magnetic and electric properties. The most basic information required for an understanding of these properties is their band structure. Adler,[1] in a recent review of the properties of the transition-metal oxides, has shown that this knowledge is still incomplete, even in the most thoroughly investigated case, that of NiO. In fact, two different theoretical approaches[1,2] yield quite different band structures, clearly indicating the need for reliable experimental information. In this note we provide data which, for the first time, locate the O(2*s*), O(2*p*), and *d* bands of a number of transition-metal oxides quite accurately. We also show that x-ray photoemission spectroscopy (XPS) must be used with care even in the valence-band region because of the occurrence of multielectron excitations.

The XPS spectra were recorded with a Varian IEE 15 spectrometer, operated with Mg $K\alpha$ radiation at a linewidth of 1.2 eV. Samples consisting of thin layers of MnO, CoO, NiO, and Cu_2O were produced directly on the corresponding metals by exposing them to air under conditions such as to assure the formation of the desired oxide.[3] As a cross check we ran a sample made up from freshly crushed green NiO crystal mounted on double-sided Scotch tape. It gave results identical to those of NiO grown on Ni except for a charging shift of about 3 eV. The spectra of CuO and ReO_3 were obtained only from Scotch-tape-mounted samples. Figure 1 shows the typical valence-band spectra of the rock-salt-structure oxides MnO, CoO, and NiO; Fig. 2 shows the spectra of CuO, Cu_2O, and ReO_3. To facilitate comparison, the energy scales have been normalized to the O(2*s*) lines in each case.

The position of the Fermi energy shown in the figures has to be viewed with some caution. The Fermi energy of the instrument was determined from Ag and Au valence-band spectra. For the oxides produced directly on the metals there should be negligible charging effects; nevertheless, it is not certain that the concept of Fermi energy applies to a thin film of insulator or semiconductor under x-ray bombardment. The Fermi energy for CuO has been tentatively assigned the

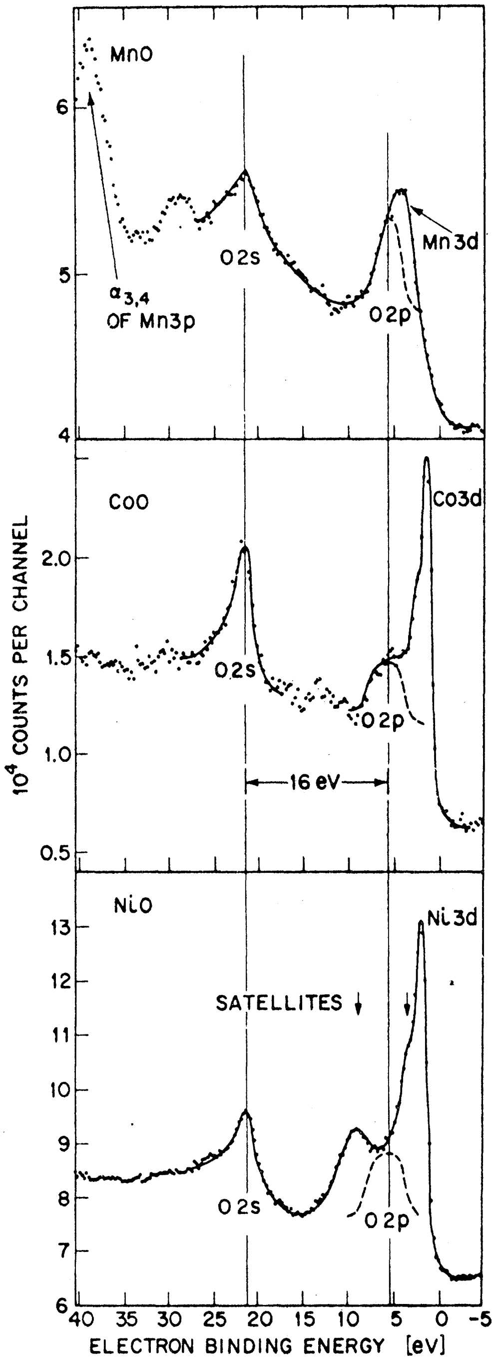

FIG. 1. XPS valence-band spectra of MnO, CoO, and NiO. Position of satellites in NiO deduced from the Ni(2*p*) spectra are indicated by arrows. Only very weak 2*p* satellites are observed in the CoO and MnO spectra. The position of O(2*p*) is indicated where not directly visible in the spectra.

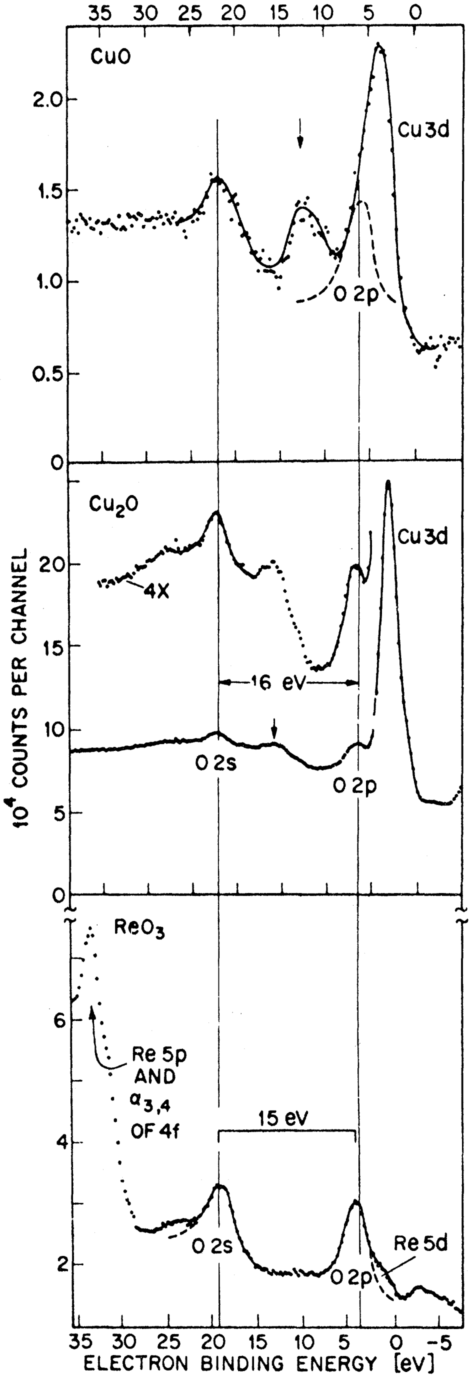

FIG. 2. XPS valence-band spectra of CuO, Cu_2O, and ReO_3. Satellite position in CuO and Cu_2O obtained from Cu(2*p*) spectra are indicated by arrows. (In the case of Cu_2O this may be an energy-loss peak.)

same position as in the oxide on metal samples, namely, 21 eV above the center of the O(2*s*) band. For ReO_3, the zero of energy was placed at the just visible Fermi edge in the data.

A remark regarding the comparison of XPS and ultraviolet photoemission spectroscopy (UPS), which is the main competitive method for determination of the density of states, is in order.

Eastman[4] has shown that UPS measurements with photon energies greater than 30 eV give similar results to those of XPS experiments, whereas UPS measurements with lower photon energies exhibit additional complexity introduced by the structure of the empty states. It must, of course, be kept in mind that the relative intensities of bands due to s, p, and d electrons are not correctly reproduced by either technique because of differences in the transition matrix elements of these electrons.

We next consider the general features of the valence bands, defined here to encompass the region of energy from 0 to 25 eV. At first glance the bands, even for the three oxides with the rock-salt structure in Fig. 1, appear strikingly different. The simplest spectrum is that of ReO_3 in Fig. 2 where the $O(2s)$ and $O(2p)$ bands are clearly discernible, and the $Re(5d)$ band shows up as a shoulder on the $O(2p)$ band. The interpretation of the other spectra depends on the realization that multielectron excitations may occur.[5,6] These give rise to satellite lines displaced to greater absolute binding energies with respect to the main line. Examples of satellites accompanying the sharpest lines in a transition-metal oxide, namely the metal $2p$ lines and the $O(1s)$ line, are shown for NiO in Fig. 3. The 6-eV satellite of the $2p$ line has been previously attributed to a $3d \rightarrow 4s$ excitation[5]; here the 1.5-eV satellites on both the $Ni(2p)$ and $O(1s)$ lines are attributed to a transition into an excited $3d$ state which occurs at just that energy according to the optical absorption data.[7,8] There is every reason to believe that these multielectron excitations will also occur in valence-band spectra. The strongest metal $2p$ satellites were found in NiO and CuO and their corresponding positions in the valence band have been indicated by arrows in Figs. 1 and 2. It seems very likely that the structures 1.5 and 6.9 eV below the $3d$ peak in NiO and 8 eV below the $3d$ peak in CuO are indeed due to a multielectron excitation and do not correspond to density of states in the normal band structure of the compound.

With this assignment the remaining features of the spectra show good agreement. The $O(2p)$ bands are clearly discernible in CoO, Cu_2O, and ReO_3; and their separation from the $O(2s)$ band is always between 15 and 16 eV. This suggests that in MnO, NiO, and CuO the centers of the $2p$ bands must fall just below the $3d$ band. This is clearly so in MnO, where no other structure identifiable as the $O(2p)$ band is visible, and extremely likely in NiO and CuO, because the hypothetical identification of the satellite as the $O(2p)$ band results in an $O(2s)$-$O(2p)$ separation which is much too small. Comments specific to individual oxides follow:

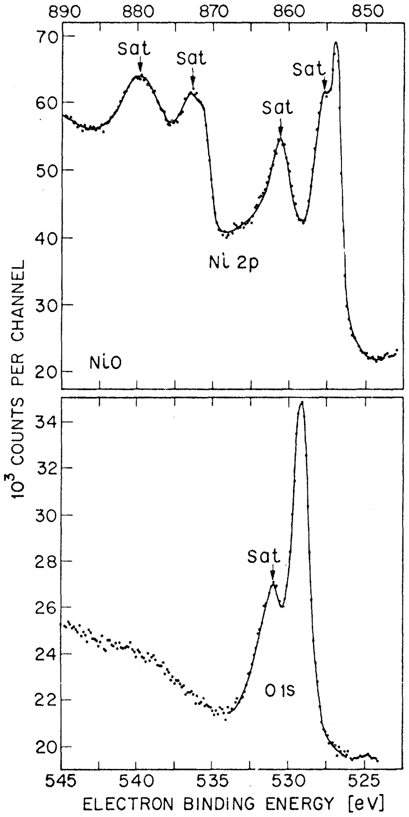

FIG. 3. XPS spectra of the $Ni(2p)$ and $O(1s)$ regions in NiO. The two-ion excitation satellite is readily visible.

NiO.—The band structure emerging from the XPS spectra is very similar to that proposed by Adler and Feinleib.[9] Judging from the shape of the d band, especially at the side near the Fermi edge, an upper limit close to the instrumental resolution of 1.2 eV can be set for its width; a large, 3-4-eV bandwidth seems very unlikely. The present results are very similar to the UPS measurements of Eastman and Cashion.[10] In view of the systematics presented in Figs. 1 and 2, it seems likely that the peak observed in their spectrum 5 eV below E_F is actually the $O(2p)$ band, whereas the 9-eV peak is most probably due to a satellite similar to that observed in the present XPS measurements.

MnO, CoO.—The band structures are very similar to that of NiO. CoO also has a narrow d band, whereas in MnO it appears broadened. Satellites observed on the $O(1s)$ line at 1 eV in

MnO and 2 eV in CoO can be attributed to multielectron excitations into excited *d* states by a comparison with the known absorption spectra.[11-13]

ReO_2.—Although ReO_3 is a metal, the O(2*s*)-O(2*p*) separation is only slightly reduced compared to that of the insulators. The 5*d* band lies at the Fermi energy, showing that it is responsible for the conductivity. This is in agreement with a model suggested by Feinleib, Scouler, and Ferritt.[14]

The present investigation has shown that transition-metal oxides of widely different structures and properties have very similar band structures when viewed with the limited resolution of current XPS techniques. An interpretation of the XPS valence-band spectra was obtained by comparing them with core-electron spectra and by searching for systematics in a series of oxides. The important characteristics of the band structures are (1) very similar O(2*s*)-O(2*p*) separations for all oxides investigated here, and (2) a substantial O(2*p*)-metal (*d*) overlap with a narrow *d* band lying above the center of the valence band. These experiments for the first time unambiguously determine the positions and approximate widths of these bands. They are in agreement with preliminary estimates[9] but do not confirm some more elaborate calculations.[2,15] Finally, intense multielectron excitations have been found to accompany the 3*d* spectra in those cases where satellites are observed in core-electron spectra. Also noteworthy is the fact that crossover excitations have been observed in these materials. Their occurrence could have been anticipated by a comparison with similar phenomena in x-ray emission experiments. The large O(2*p*)-metal (*d*) overlap in these compounds makes these transitions more likely than would appear at first sight.

In summary, this investigation has given a clear picture of the energy bands of the transition-metal oxides, and has shown that XPS can be employed as a powerful and very promising technique for the study of valence bands of relatively complicated systems.

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[1] D. Adler, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1968), Vol. 21.

[2] L. F. Mattheiss, Phys. Rev. B 5, 290, 306 (1972).

[3] The Cu(2*p*) spectrum of the Cu_2O reported here is like that obtained by T. Novakov and R. Prins, in Proceedings of the Conference on Electron Spectroscopy, Asilomar–Pacific Grove, California, 1971 (North-Holland, to be published), after heating in vacuum rather than like that reported by T. Novakov, Phys. Rev. B 3, 2693 (1971). The Ni(2*p*) spectra of the green NiO used in the present experiments are qualitatively similar to those of Novakov and Prins, but we do not confirm the positions of most of the satellites indicated by them.

[4] D. E. Eastman, in Proceedings of the Conference on Electron Spectroscopy, Asilomar–Pacific Grove, 1971 (North-Holland, to be published).

[5] A. Rosencwaig, G. K. Wertheim, and H. J. Guggenheim, Phys. Rev. Lett. 27, 479 (1971), and references cited therein.

[6] G. K. Wertheim and A. Rosencwaig, Phys. Rev. Lett. 26, 1179 (1971).

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

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

[9] D. Adler and J. Feinleib, Phys. Rev. B 2, 3112 (1970).

[10] D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. 27, 1520 (1971).

[11] G. W. Pratt, Jr., and R. Coelho, Phys. Rev. 116, 281 (1959).

[12] D. R. Huffman, R. L. Wild, and M. Shimmei, J. Chem. Phys. 50, 4092 (1969).

[13] W. Low, Phys. Rev. 109, 256 (1958).

[14] J. Feinleib, W. J. Scouler, and A. Ferritt, Phys. Rev. 165, 765 (1968).

[15] L. F. Mattheiss, Phys. Rev. 181, 987 (1969).