Local Character of Many-Body Effects in X-Ray Photoemission from Transition-Metal Compounds: Na_xWO_3

M. Campagna and G. K. Wertheim
Bell Laboratories, Murray Hill, New Jersey 07974

and

H. R. Shanks
Ames Laboratory—USAEC, Iowa State University, Ames, Iowa 50010

and

F. Zumsteg*
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

and

E. Banks
Polytechnic Institute of New York, Brooklyn, New York 11201

(Received 27 January 1975)

X-ray photoemission spectra of W core levels in metallic sodium tungsten bronzes, Na_xWO_3, clearly show asymmetries due to many-body effects. Na and O core levels show only the expected plasmon satellite, demonstrating the importance of the local density of states in the screening of the core hole.

The importance of many-body effects in x-ray spectroscopy was pointed out in various theoretical papers a number of years ago.[1,2] Experimental evidence to support these theories has been sought in the x-ray threshold anomalies of simple metals like Li, Na, Mg, Al,[3] and the Mg_xSb_{1-x} alloys.[4] However, none of the theories seems to explain the data satisfactorily.[5] Many-body effects are also expected to be important in photoemission spectroscopy.[6] The effect of extra-atomic relaxation on binding energies[7] is, in a sense, a many-body phenomenon even though the leading term is Hartree-like. Neither this nor the well-known satellites are, however, many-body effects in the sense of Refs. 1–6. The discrepancy between the observed positive electron-spin polarization of photoelectrons from Ni and Co near threshold[8] and the prediction of negative polarization by the Stoner-Wohlfarth-Slater band theory of magnetism has been considered as among the first clear examples of the importance of these many-body interactions during the photoemission process.[9] The appearance of an asymmetry in the line shape of $3d$ and $4f$ core levels in x-ray photoemission spectroscopy (XPS) of $4d$ and $5d$ metals,[10] and similar observations in simple metals,[11,12] provide direct evidence for the fundamental role of the core-hole potential in photoemission data. The asymmetry was ascribed to the interaction of the suddenly created potential of the photohole with the conduction electrons. Apart from these first observations there is little other experimental information on the coupling between a hole state and conduction electrons in photoemission.

This Letter is a preliminary report of an XPS study of the sodium tungsten bronzes, Na_xWO_3. We show that these mixed-valence metallic oxides provide a unique opportunity for the investigation of the dependence of many-body effects on conduction-electron concentration, total density of states, local density of states at the site of a given atom in the solid, and nature of the wave functions forming the conduction band.

The cubic Na_xWO_3 are closely related to the ABO_3 ternary oxides with (distorted) perovskite structure, and have been the subject of numerous investigations.[13-15] Their electronic structure has been considered in detail from the theoretical point of view,[14] while experimental information has been derived mainly from optical studies.[15] Single-crystal specimens of Na_xWO_3 with ~ 16-mm^2 area were cut from larger single crystals obtained by electrolysis. Surfaces for the XPS study were prepared by cleaving as described by Wertheim *et al.*[16] Data were obtained with monochromatized Al $K\alpha$ radiation using an HP-5950A ESCA spectrometer.

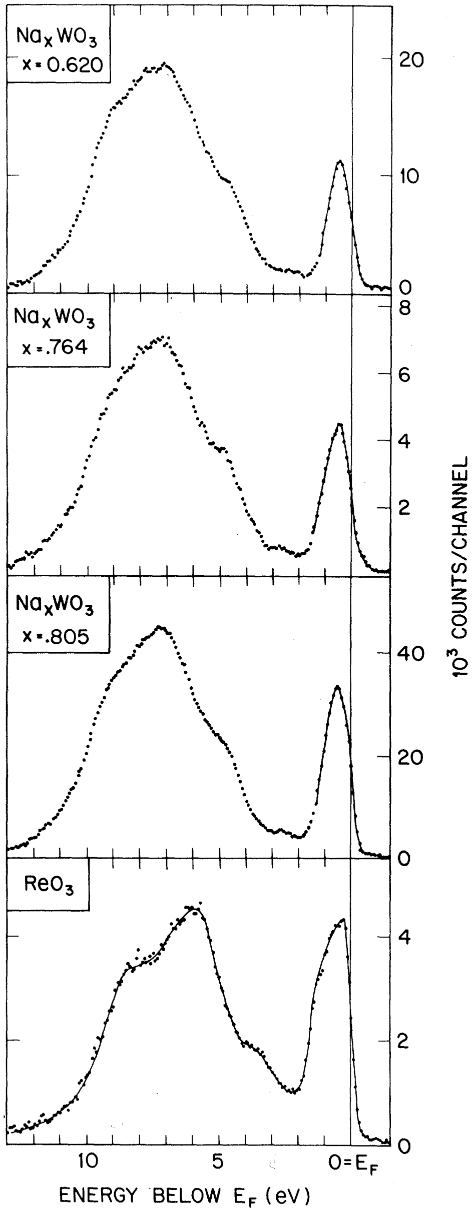

FIG. 1. Valence-band XPS spectra of vacuum-cleaved Na_xWO_3 and ReO_3.

In Fig. 1 we show the XPS valence band of Na_xWO_3 for the nominal compositions $x = 0.620$, 0.764, and 0.805, as determined from lattice-constant measurements. For comparison we also show the valence band of ReO_3.[16] From an inspection of Fig. 1 we conclude that the electronic structure of the Na_xWO_3 is very similar to that of ReO_3, and presumably representative of the ABO_3 perovskites. Note, however, that the XPS valence-band spectrum does not reproduce the *total* density of states, but is most sensitive to the covalent admixture of higher angular momentum states into the p band.[16] The heights of the spectra of the valence bands, centered about 7 eV below E_F, have been normalized in order to show that the area of the conduction-band peak near E_F increases in proportion to the Na content. The data provide a direct visualization of the filling of a conduction band in a solid with increasing electron concentration. In fact the width of the conduction band increases slightly from an experimental full width at half-maximum of 1.00 ± 0.05 eV to 1.15 ± 0.05 eV with increasing x. This demonstrates that the conduction band, although made up of a covalent admixture of W $5d$ and O $2p_\pi$ wave functions, is filled by electrons donated by the Na, with a conduction-electron concentration equal to the sodium concentration.[13, 14]

The data are in good agreement with the results of theoretical studies of the electronic structure of the perovskites,[13, 14] and thus support the view that the information obtained by XPS is mostly bulk information.

The most interesting, and initially puzzling result is provided by the W $4f$ spectra, shown in Fig. 2. The $4f$ region is not a simple spin-orbit doublet of symmetrical lines with 7:5 intensity ratio as one might expect on the basis of the $4f$ spectra of W or WO_3,[17] or from simple theoretical considerations. The dominant extraneous feature is provided by the third peak at 38.5 eV, 2 eV below the $4f_{5/2}$ line. This peak is clearly broader than the other two lines suggesting that it represents a plasmon energy loss and/or other many-body satellite.[18] The former is not an unlikely interpretation in view of similar, though weaker, energy-loss features on the Na and O $1s$ lines and the strong 2.1-eV peak observed in the energy-loss function in Ref. 15. Either alternative implies that there must be another satellite belonging to the $4f_{7/2}$ line, lying directly beneath the $4f_{5/2}$ line. The intensity ratio of the two satellites must also be approximately in the ratio 7:5. The shape of the $4f$ core lines also requires comment. An examination of Fig. 2 shows that there is a long tail toward greater binding energy in the $4f$ spectrum. This tail, although not so pronounced, is present on each W-core-level line. It is not due to the 2-eV plasmon because a similar tail is not found in the O and Na $1s$ spectra, shown in Fig. 3, which do exhibit the plasmon energy loss. The Na $1s$ line is clearly symmetrical, even though its width greatly exceeds the natural width. According to current theoretical investigations the interaction of the

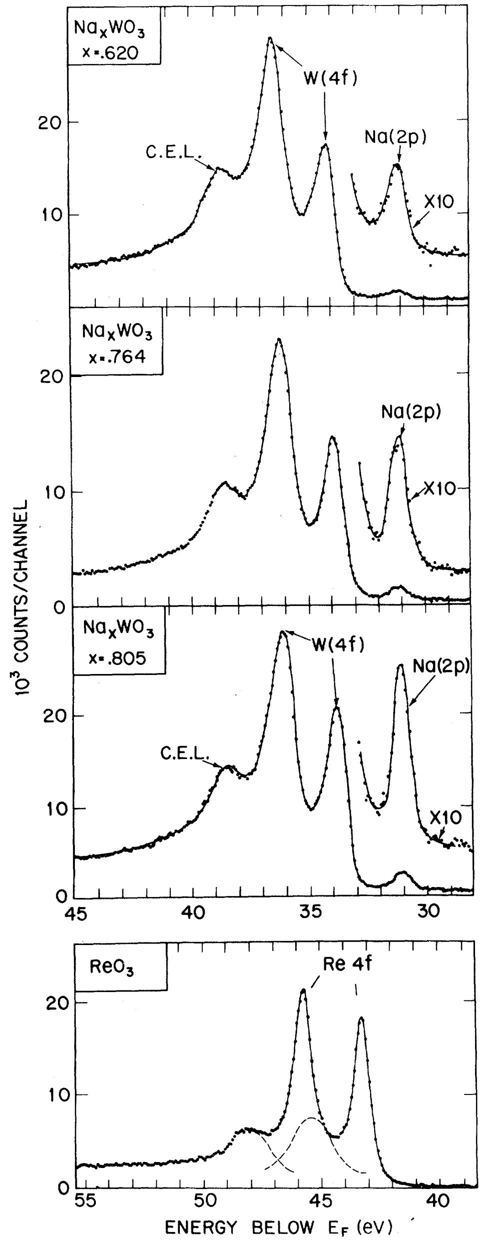

FIG. 2. XPS spectra of the $4f$ region of Na_xWO_3.

photoelectron with other electrons during escape from the solid can be neglected (except for plasmon excitation). We therefore ascribe the long tail of the W lines to the coupling of the core hole with the Fermi sea, as suggested by Doniach and Sunjic.[6] The asymmetry parameter, α, inferred from an analysis of the spectra in Fig. 2, lies in the range ~0.15 to 0.19, with a tendency to *decrease with increasing* x. It can be understood by assuming that the f hole is effectively screened by p and d phase shifts in the $5d$ conduction band.

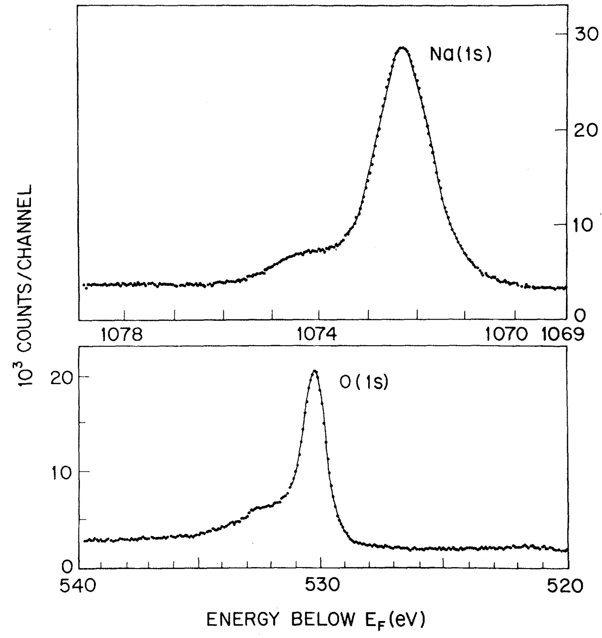

FIG. 3. XPS spectra of the Na and O $1s$ lines of $Na_{0.764}WO_3$.

From the absence of asymmetric broadening of the O and Na levels one concludes that the interaction of the core hole with the conduction electrons is a local effect, directly related to the nature of the wave functions forming the conduction band and not a simple "jellium" effect. The fact that the density of conduction electrons vanishes at the Na nuclei is reflected in the much weaker coupling between Na core holes and the conduction electrons. Core-level line-shape analysis therefore provides another technique for the study of covalent mixing in the conduction band.

A more precise picture of the satellites on the $4f$ lines can be obtained by subtracting the main lines under the assumption that they have the Doniach-Sunjic[6] line shape. Two broad symmetrical satellites with the proper 7:5 intensity ratio are obtained, but the strength relative to the $4f$ lines is much greater than expected on the basis of the plasmon satellites on the Na and O $1s$ lines. This suggests that the extra intensity is due to another mechanism, the most likely one being that proposed in a recent paper by Kotani and Toyazawa.[19] In their model photoionization of a core electron in a d-band metal may pull a normally empty d state below the Fermi energy. If that state is filled by an electron from the conduction band the asymmetrical main line is obtained; if it remains empty a lifetime-broadened satellite appears at greater binding energy. This corresponds very closely to what is found in Na_xWO_3; even the 2-eV separation corresponds well to the shift expected for removal of one electron.

A detailed discussion of (1) the relationship between the electronic structure of the bronzes and XPS valence-band data, (2) the connection between XPS binding energies of W and Na core levels and spin-relaxation[20] and Knight-shift[21] experiments, and (3) the implications of the detection of a unique W 4f doublet on conduction-electron delocalization will be published elsewhere. A more extensive investigation of the dependence of α on x and on the local environment is in progress.

---

*Present address: Central Research Department, Dupont Chemicals, Wilmington, Del. 19898.

[1] G. D. Mahan, Phys. Rev. 163, 612 (1967).

[2] P. Nozières and C. T. deDominicis, Phys. Rev. 178, 1097 (1969).

[3] J. D. Dow and B. F. Sonntag, Phys. Rev. Lett. 31, 1461 (1973).

[4] J. D. Dow, J. E. Robinson, J. H. Slowik, and B. F. Sonntag, Phys. Rev. B 10, 432 (1974).

[5] J. D. Dow, in Proceedings of the Fourth International Conference on Vacuum Ultraviolet Radiation Physics, Hamburg, West Germany, 22–26 July 1974 (unpublished).

[6] S. Doniach and M. Sunjic, J. Phys. C: Proc. Phys. Soc., London 3, 285 (1970).

[7] L. Ley *et al.*, Phys. Rev. B 8, 2392 (1973).

[8] G. Busch, M. Campagna, and H. C. Siegmann, Phys. Rev. B 4, 747 (1971).

[9] P. W. Anderson, Phil. Mag. 24, 203 (1971); S. Doniach, in *Magnetism and Magnetic Materials—1971*, edited by C. D. Graham, Jr., and J. J. Rhyne, AIP Conference Proceedings No. 5 (American Institute of Physics, New York, 1972), p. 549.

[10] S. Hüfner, G. K. Wertheim, D. N. E. Buchanan, and K. W. West, Phys. Lett. 46A, 420 (1974); S. Hüfner and G. K. Wertheim, Phys. Rev. B 11, 678 (1975).

[11] P. H. Citrin, Phys. Rev. B 8, 5545 (1973).

[12] L. Ley, F. R. McFeely, S. P. Kowalczyk, J. G. Jenkin, and D. A. Shirley, to be published.

[13] See P. Hagenmuller, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford, England, 1971), Vol. 5, p. 71, and references cited therein.

[14] J. B. Goodenough, Bull. Soc. Chim. Fr. 1965, 1200, and Progr. Solid State Chem. 5, 145 (1971); L. F. Mattheiss, Phys. Rev. B 6, 4718 (1972).

[15] D. W. Lynch, R. Rosei, J. H. Weaver, and C. G. Olson, J. Solid State Chem. 8, 242 (1973), and references cited therein.

[16] G. K. Wertheim, L. F. Mattheiss, M. Campagna, and T. P. Pearsall, Phys. Rev. Lett. 32, 997 (1974).

[17] T. A. Carlson and G. E. McGuire, J. Electron Spectrosc. Relat. Phenomena 1, 161 (1972/1973).

[18] The alternate interpretation of the W 4f spectrum in terms of separate contributions from W^{6+} and W^{5+} is not tenable for various reasons. The intensity ratios $[W^{5+}]/[W^{6+}] = x/(1-x)$ for the three samples range from 4.1 for $x = 0.805$ to 1.63 for $x = 0.620$. This is contrary to the data. Neither the x-dependent shift of the narrower line at smaller binding energy, nor the x-dependent change in the separation between the two sets of lines fits into this picture.

[19] A. Kotani and Y. Toyazawa, J. Phys. Soc. Jpn. 37, 912 (1974).

[20] W. H. Jones, Jr., E. A. Garbaty, and R. G. Barnes, J. Chem. Phys. 36, 494 (1962).

[21] A. T. Fromhold, Jr., and A. Narath, Phys. Rev. 136, A487 (1964).

---

dc Conductivity in an Isostructural Family of Organic Metals

S. Etemad, T. Penney, E. M. Engler, B. A. Scott, and P. E. Seiden
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 5 September 1974)

The tetracyano-p-quinodimethane salts of tetrathiafulvalene and its newly synthesized selenium analogs tetraselenafulvalene and *cis/trans*-diselenadithiafulvalene form an "isostructural" series of highly conducting organic salts. The electrical conductivity is remarkably similar and peaks at 59, 40, and 64°K, respectively. It is concluded that the conduction mechanism is of the same origin in spite of their varying molecular properties.

Considerable interest has been generated recently by the dc-conductivity properties of the crystalline organic charge-transfer salt tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ).[1-7] In order to understand this material better we have synthesized the selenium analog of TTF, tetraselenafulvalene (TSeF)[8] [Fig. 1(a)], and *cis/trans*-diselenadithiafulvalene (DSeDTF)[9] [Figs. 1(b) and 1(c)]. In this paper we report conductivity measurements on the TCNQ