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Integer versus noninteger valence properties revealed by a comparative photoemission study of Na_xWO_3 and ReO_3

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Fano-type resonances in the 5*d* conduction-band intensity spectra have been observed at the $5p_{1/2}$ and $5p_{3/2}$ photoabsorption thresholds for Na_xWO_3 ($0.4<x<0.85$), ReO_3, WO_2, and W. The Na_xWO_3 tungsten-bronze spectra exhibit a characteristic double resonance structure different from the simple resonance peaks measured for ReO_3, WO_2, and W. These results could be related to a mixed-valence character of the metallic bronzes in the final state of the photoemission process. The complex structure of the photoelectron core-level 4*f* spectra for Na_xWO_3 and ReO_3 is discussed on the basis of these new findings.

I. INTRODUCTION

The sodium tungsten bronzes form a family of nonstoichiometric compounds with the formula Na_xWO_3. The sodium atoms are inserted into the interstitial sites of the WO_3 lattice and x can be varied between 0 and 1. The WO_3 network consists of oxygen octahedra with W in the center sharing common corners. These bronzes exist in a series of crystal structures, depending on the concentration of the sodium atoms and the temperature. The most common phase is metallic pseudocubic perovskite with $x>0.4$.

The Na_xWO_3 bronzes present a variety of interesting electronic properties depending on x. In particular, a nonmetal-metal transition occurs at $x\sim0.25$.[1] The electronic properties of the bronzes have been shown to be related to the filling of a W 5*d*-type conduction band of the WO_3 matrix by electrons from donor Na atoms. The Na_xWO_3 properties are often interpreted on the basis of the band-structure calculations for ReO_3,[2] because ReO_3 is isoelectronic to Na_1WO_3 and because of the similarity of optical,[3] energy-loss,[4] and photoemission[5] data for these compounds. Despite a great number of studies, fundamental questions like the origin of the nonmetal-metal transition and the evolution with x of the density of electronic states at the Fermi level remain controversial.

Photoelectron spectroscopy is a probe of the electronic density of states and should provide information on these problems. However, the core-level photoemission process in these narrow-band metallic materials is complicated and so far no consensus exists for interpretation of the complex W 4*f* x-ray photoemission spectroscopy (XPS) spectra of Na_xWO_3.[6,7] In previous photoemission XPS measurements[8,9] the relatively low energy resolution of conduction-band spectra (used to examine the electron density of states), coupled with uncertainty in the Fermi-level position and problems with surface preparation of samples has prevented drawing definitive conclusions on the x-dependent properties of the electronic structure.

In this paper we present results on $Na_{0.83}WO_3$, $Na_{0.4}WO_3$, and ReO_3 obtained with high-resolution angle-integrated photoemission experiments using synchrotron radiation in the photon-energy range 20—130 eV. These measurements are compared with data obtained on WO_2 and W. We focus mainly on the photoemission process. Besides photoemission spectra we present resonance studies near the metal 5*p* excitation threshold. The data concerning the x-dependent properties of the conduction band are reported elsewhere.[10] We show that the resonance of the 5*d* conduction-band intensity observed for these materials in the (40—60)-eV photon-energy range by constant-initial-state (CIS) spectra is the result of a Fano-type interference occurring at the 5*p* photoabsorption threshold. We observe differences in the shape of the CIS curves between Na_xWO_3 and ReO_3, WO_2, or W which may be characteristic of a mixed-valence character in the final state of Na_xWO_3.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin–Madison using a two-dimensional electron spectrometer[11] combined with a toroidal grating monochromator. The overall experimental resolution was better than 300 meV. The Na_xWO_3 and ReO_3 crystals were cleaved along a (100) plane at pressure of 2×10^{-10} Torr and measured at 5×10^{-11} Torr. Figure 1 shows the energy-distribution curves (EDC's) in the region of the $4f$ core levels measured at 110 eV. The corresponding valence (O $2p$) and conduction-band [W $5d$ (Re $5d$)] spectra taken at 60 eV are reported in Fig. 2. The valence-band spectra are qualitatively similar to published XPS spectra[5,6]; however, the sharp structures close to the Fermi level associated with the conduction band appear less intense in ultraviolet photoemission spectroscopy (UPS) than in XPS. This is due to a lower value for the W $5d$ (Re $5d$) to O $2p$ cross-section ratio. More interesting are the differences between the shape of the conduction band and the valence-conduction gap when we compare $Na_{0.83}WO_3$ and ReO_3. Figure 2 shows clearly that ReO_3 has a wider conduction band while the gap of 1.6 eV in $Na_{0.83}WO_3$ is reduced to a simple minimum in the density of states for ReO_3.

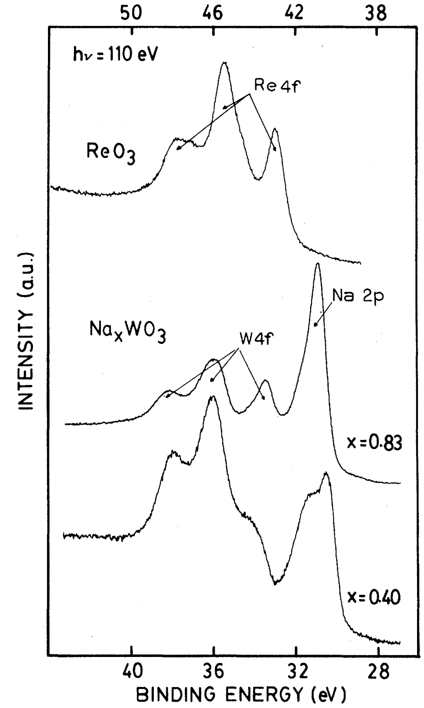

FIG. 1. 110-eV $4f$ core-level spectra of $Na_{0.4}WO_3$, $Na_{0.83}WO_3$, and ReO_3. The bottom binding-energy scale corresponds to the bronzes, the top scale to ReO_3. The reference level is the Fermi level.

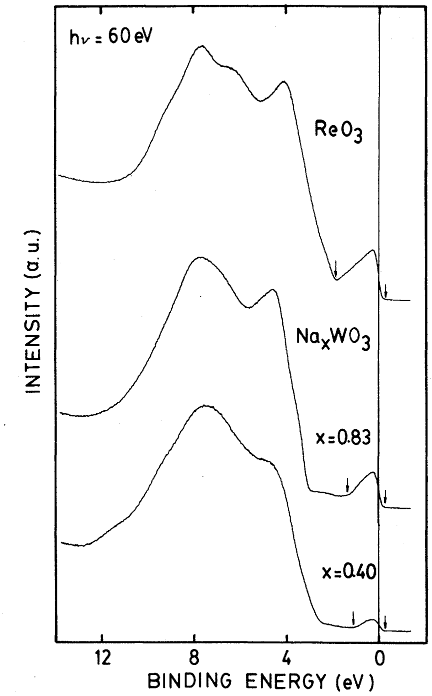

FIG. 2. Energy-distribution curves of the valence region from $Na_{0.4}WO_3$, $Na_{0.83}WO_3$, and ReO_3 measured at a photon energy of 60 eV. The vertical arrows show the integration range for the $5d$ conduction-band intensities reported in Fig. 3.

The core-level spectra display again the same trends as in XPS except for a much higher cross section for the Na $2p$ core level in UPS. However, in UPS the Na $2p$ spectra present a surface-sensitive component appearing at 0.7 eV higher binding energy than the bulk one. This does not affect the shape of the W $4f$ spectra since we measured similar W $4f$ spectra for $Na_{0.73}WO_3$ at 110 and 1486.6 eV in XPS (Ref. 10) (less surface sensitivity). The shape of the 110-eV W $4f$ spectra can therefore be related to the bulk properties of the bronzes. The $4f$ core-level photoelectron spectra of Na_xWO_3 and ReO_3 do not show the simple spin-orbit doublet observed for W, Re, or WO_3 but present a complex structure consisting of at least two overlapping spin-orbit doublets.

In a CIS experiment, the photon energy is varied with the kinetic energy of the collected electrons to maintain a constant photon-energy minus kinetic-energy value. The CIS curves reported in Fig. 3 correspond to the variation of the whole conduction-band intensity extracted from a series of EDC's for $Na_{0.4}WO_3$, $Na_{0.83}WO_3$, ReO_3, WO_2, and W in the photon-energy range 30–80 eV. All the spectra show a double modulation of the 5*d* conduction-band emission. The ReO_3, WO_2, and W spectra only differ by the exact position of the maxima and minima. For the two Na_xWO_3, a splitting occurs giving four maxima; the curves are quite similar to the results of Benbow *et al.*[12] obtained for $Na_{0.7}WO_3$.

III. DISCUSSION

A. The photoemission core-level spectra of the tungsten bronzes

The 4*f* core-level spectra of Na_xWO_3 and ReO_3 are characterized by two overlapping $4f_{5/2}$, $4f_{7/2}$ doublets whereas W or WO_3 show only one doublet. In a general discussion on the shape of core-level photoemission spectra of metallic compounds, Chazalviel *et al.*[6] have pointed out that three quantities must be taken into account: the core-hole valence Coulomb interaction *Q*, the valence correlation interaction *U*, and the bandwidth *W*. If any of these quantities is negligible it is possible to describe the spectra with a known model, e.g., with the intrinsic plasmon excitation model for negligible *Q*, with the Friedel exciton model for negligible *U*, and with the mixed-valence model for negligible *W*. In the case of the bronzes, the existence of plasmon excitations can be ruled out because the observed splitting in the photoemission spectra is different from the value determined by optical[3] or electron energy-loss spectroscopies.[4,13] Two kinds of models remain to describe the spectra.

Focusing on the metallic Na_xWO_3 results, Chazalviel *et al.*[6] described the doublet at low binding energy as the fundamental lines and the doublet at higher binding energy as satellites whose origin is due to excitations of the conduction band during photoemission, probably through a Friedel exciton mechanism where in the final state the 4*f* hole pulls some of the 5*d* states below the Fermi level.[14] In this model the satellite is a manifestation of core-hole screening effects in the final state of the photoemission process. The satellite and the fundamental peaks can also be referred to as the "poorly-screened" (or, more usually, shake-up) and "well-screened" peaks in the Schönhammer-Gunnarsson treatment of this problem.[15] Recently, Beatham *et al.*[16] suggested that the results and conclusions obtained by Chazalviel *et al.* for the Na_xWO_3 bronzes could be extended to a wide range of *narrow-band metallic oxides,* including WO_2 and implicitly ReO_3. In this picture the Na_xWO_3 bronzes are simply considered as ordinary metals and *no distinction* with ReO_3 is made.

The second kind of model is related to the mixed-valence concept. It is usual to invoke a mixed-valence situation in two cases, i.e., either when the bandwidth *W* decreases to zero (the situation in some rare-earth materials) or when there is a noninteger number of valence electrons[17] (the situation in certain complex ions or compounds). The tungsten bronzes belong to this latter category be-

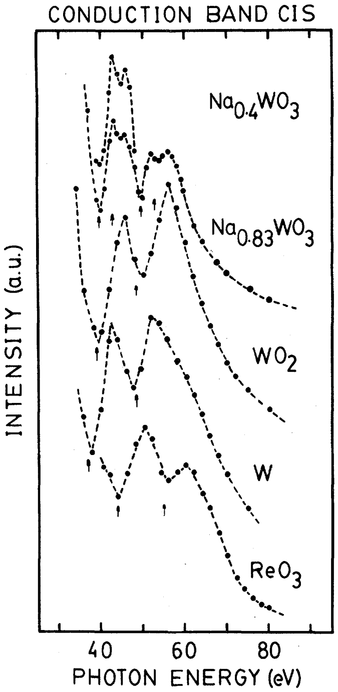

FIG. 3. 5*d* conduction-band (see Fig. 2) intensity vs photon energy for $Na_{0.4}WO_3$, $Na_{0.83}WO_3$, WO_2, W, and ReO_3. The data have been normalized with respect to variation in photon flux and monochromator transmission but not with respect to electron-energy-analyzer efficiency and electron mean free path. The different sets of data have been arbitrarily normalized in intensity. The vertical arrows correspond to resonance minima near the $5p_{1/2}$ and $5p_{3/2}$ ionization energies. The integer valence compounds show simple structures whereas the tungsten bronzes exhibit a double resonance structure.

cause they have less conduction electrons than tungsten atoms (x per WO_3 cell). In the classification of Robin and Day,[17] the semiconductor bronzes are called inhomogeneous mixed-valence compounds (two oxidation states W^{6+} and W^{5+} exist in the neutral system,[18] whereas the metallic bronzes are called homogeneous mixed-valence materials. More generally, two pictures have been used to describe the photoemission process in mixed-valence compounds, an "initial-state" approach[19] involving the fluctuating (hopping) time τ and the photoemission time t, and a "final-state" approach[20,21] taking into account the core-hole valence Coulomb interaction Q, the valence correlation interaction U, and the bandwidth W. In fact, these two descriptions become equivalent in the narrow-band limit since they assume the same stationary initial ground state, the same energy shift between the two final-state configurations, and the same important parameter, i.e., the bandwidth W. If the conduction band is narrow enough, the hopping time h/W of one electron between two tungsten sites becomes longer than the photoemission time and the Coulomb interaction Q becomes high enough ($Q > W$) to induce a localization in the final state. Thus, two final configurations are expected in both cases. However, the relative intensity of these states and their energy separation (roughly a measure of Q) are the same in the two descriptions only when the width value decreases to zero ($Q \gg W$ and $\tau \gg t$) (see Ref. 20). According to these criteria, the applicability of a mixed-valence model to describe the Na_xWO_3 data would be questionable since, in this case, W is about 2—3 eV and the doublets' energy separation is ~ 2.5 eV whereas $t \times 10^{-16}$ sec (Ref. 22) and $\tau \approx 2 \times 10^{16}$ sec ($W \approx Q$ and $t \approx \tau$). We suggest that an important additional parameter is the existence of a noninteger number of conduction electrons and that the instantaneous charge distributions $d^0(W^{6+})$ and $d^1(W^{5+})$ can be revealed by the photoemission process. This model was used to interpret data on semiconducting and metallic H_xWO_3 (Ref. 23) bronzes which showed a direct relation between the satellite to fundamental peak intensity ratio and the expected W^{6+}-W^{5+} configuration ratio. In this picture one configuration d^1 is expected for ReO_3 and the satellite is explained by a model of the first class. In the case of the Na_xWO_3 bronzes a decision between the two models cannot be made based only on the existing photoemission spectra due to the lack of quantitative theoretical studies.

One experimental approach to resolve the problem would be to vary parameters by tuning the excitation energy $h\nu$ to the threshold of photoionization of the core levels. In a "shake-up" model the satellite to fundamental peak intensity ratio is expected to vary with $h\nu$ at threshold whereas it is expected to be constant in a mixed-valence situation. Unfortunately, when $h\nu$ decreases to the core-level photoionization threshold the $4f$ photoionization cross section decreases to zero and the $5p$ peaks are too broad to be analyzed. We used the resonance effects to overcome these difficulties.

B. Resonant photoemission

Figure 3 shows the intensity profile of the conduction bands for ReO_3, WO_2, and W and the positions of the $5p_{1/2}$ and $5p_{3/2}$ levels in these compounds. It is seen that the double modulation of the $5d$ conduction band occurs just above the photoabsorption threshold of the $5p$ spin-orbit doublet. Such resonances of the primary emission structure or of a satellite structure have been already observed[24] in the valence $3d$, $4f$, or $5f$ cross sections of numerous elements and compounds. They have been explained by a Fano effect[25] related to the interference of two excitation channels leading to the same final state. Following the same model we explain the enhancement of the $5d$ emission by an autoionization decay process following $5p \rightarrow 5d$ absorption transitions, which interfere with the direct $5d$ emission. For example, in the case of ReO_3, the configuration d^2 can occur when a $5p$ hole is created by a photoabsorption process giving

$$5p^6 5d^1 + h\nu \rightarrow 5p^5 5d^2 ,$$

the $5p^5 5d^2$ configuration can decay through an autoionization process

$$5p^5 5d^2 \rightarrow 5p^6 d^0 + e ,$$

where e denotes electron, which interferes with the direct photoionization process

$$5p^6 5d^1 + h\nu \rightarrow 5p^6 d^0 + e$$

giving the resonance phenomenon.[25]

It is the first time, to our knowledge, that such $5p \rightarrow 5d$ resonances have been shown in $5d$ compounds. Williams *et al.*[26] only observed $4f \rightarrow 5d$ resonances in Pt at the $4f$ photoabsorption threshold. The resonance curves of ReO_3, WO_2, and W have simple Fano-type line shapes which indicate that multiplet splitting effects are negligible. This is confirmed by the W $4f$ EDC spectra of W which is free of multiplet splitting. In the absence of multiplet splitting effects band-structure effects should be taken into account. The CIS curves of Na_xWO_3 present four maxima. Benbow *et al.*[12] suggested that this kind of oscillation could be a consequence of the structure of the multiply-connected Fermi surface in the repeated zone scheme but they did not exclude the occurrence of $5p \rightarrow 5d$ excitations. We note that in ReO_3 which is characterized by the same Fermi surface as Na_xWO_3 such double structures are not detected and conclude that the oscillations predicted by Benbow *et al.* do not play a major role in the (40—60)-eV energy region. In the same way, we exclude any effect due to a possible Na $2p$ excitation (there are no Na empty states at the Fermi level[27] and only one additional peak in the CIS spectrum would be expected) or to a surface segregation effect (no such effect is detected in the W $4f$ EDC spectra). We therefore assume that the origin of the four structures is related to a Fano resonance at the $5p$ excitation threshold as in W, WO_2, and ReO_3.

We will now discuss these results in view of the two models evoked to interpret the EDC spectra of ReO_3 and Na_xWO_3. In the case of the shake-up model, we expect two peaks in the EDC core-level spectra and one peak in CIS's. This has been observed for CuO and NiO.[28] In a rare-earth mixed-valence system, we expect two peaks in both EDC and CIS curves. In the case[29] of SMB_6 the features related to the two valence states $4f^5$ and $4f^6$ have been observed both in EDC's and CIS's. The similarity of the CIS curves for ReO_3, WO_2, and W confirms that the satellite in ReO_3 can be seen as occurring from a shake-up or a plasmon-excitation process like those described in Ref. 6. It is tempting to relate the double structure seen in the bronze case to a mixed-valence character. However, the shape of of the double structure seems independent of the Na concentration as seen in Fig. 3 and only the overall intensity is proportional to the number of occupied $5d$ states. Moreover, in the simple atomic model used above to describe the resonance phenomenon in ReO_3, the $5d^0$ state cannot show any emission; hence, we would have to assume a possible final-state "hybridization" of the $5p^5 5d^2$ and $5p^5 5d^1$ configuration to explain the results. Consequently, the double structure seen in the CIS curves of Na_xWO_3 can be explained neither by a shake-up model nor by a simple mixed-valence model but it definitively reveals differences in the photoemission process between materials of noninteger and integer number of valence electrons.

IV. CONCLUSION

In conclusion, we have observed simple Fano-type resonances in the $5d$ conduction-band CIS curves of ReO_3, WO_2, and W and characteristic double resonances for the Na_xWO_3 bronzes. We suggest from a comparison of EDC's and CIS curves that at the scale of photoemission process the Na_xWO_3 bronzes possibly reveal an intermediate valence character whereas the related compound ReO_3 has integer valence. More theoretical and experimental work on such compounds is needed to show if the observed effect is characteristic of the sodium bronzes or more generally of narrow-band metallic compounds with noninteger valence.

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