PHYSICAL REVIEW B VOLUME 19, NUMBER 10 15 MAY 1979

Comments on "Significant differences between Hartree-Fock and local-exchange energy bands for TiO"

Karlheinz Schwarz and Adolf Neckel

Institute of Technical Electrochemistry, Technical University of Vienna, A-1060 Vienna, Austria

(Received 2 December 1977)

The recent controversy over the bonding in TiO, particularly with respect to O-2p–Ti-3d band overlap, is reexamined. The soft-x-ray emission spectra (SXS) are recalculated within the $X\alpha$ formalism and agree well with experimental results. The x-ray photoemission spectroscopy (XPS) data are discussed and it is found that discrepancies between theory and experiment exist for both the $X\alpha$ and Hartree-Fock calculations. From the SXS and XPS spectra it is concluded that the O-2p–Ti-3d mixing is better represented by the $X\alpha$ band structure.

In a recent Letter Jennison and Kunz[1] reported on their Hartree-Fock (HF) energy bands for TiO, which are in qualitative disagreement with those obtained using the local-exchange model ($X\alpha$). Whereas the $X\alpha$ results produce a 2.2-eV energy gap between the Ti 3d and the O 2p bands,[2] the HF results give 2p and 3d bands that overlap considerably. These authors argue that x-ray photoemission spectroscopy (XPS) experiments support the HF results, and they comment on the " apparent failure of $X\alpha$ theory on this material." Qualitative agreement between $X\alpha$ and HF methods has been obtained in many cases by adding correlation corrections to the HF results. However, these corrections are expected to be small for TiO,[1] and there are thus two different pictures of the bonding in TiO. In our opinion there is also experimental evidence for the $X\alpha$ results, although some discrepancies remain, but equally the HF results differ from experiment. Therefore, only a critical analysis of both sets of results can help settle this controversy.

Band-structure calculations using the augmented-plane-wave (APW) method have been performed for several transition-metal compounds which crystallize in the rocksalt structure, especially for carbides, nitrides, and oxides.[2,3] According to these calculations, the bonding changes in character for the series TiC, TiN, and TiO, with the nonmetal 2p and the Ti 3d bands strongly overlapping in the case of the carbide, but showing a small gap for the oxide.[4] For TiO, at least four APW energy-band calculations have been published,[2,5-7] including two non-self-consistent calculations using full Slater exchange ($\alpha=1$).[5,6] The work of Ern and Switendick,[5] who constructed the crystal potential from the ions Ti^{+} and O^{-}, resulted in a gap of 1.8 eV between the O 2p and Ti 3d bands. A second calculation by Mattheiss[6] using neutral atoms to construct the potential gave an O-2p–Ti-3d gap of 7.6 eV. The third calculation, which produced an O-2p–Ti-3d gap of 2.2 eV is described in detail below, since it is the basis for the following discussion. The fourth calculation used the virtual-crystal approximation to study the effect of vacancies and nonstoichiometry on calculated band structures.[7]

The third APW calculation[2] is quasi-self-consistent (within the muffin-tin approximation for the potential and charge density), and consequently does not depend on the ionicity and the electronic configuration of the constituent atoms in contrast to the other calculations mentioned above. Exchange is treated by the $X\alpha$ method, where inside the atomic spheres the optimized atomic exchange parameters $\alpha_{\rm vt}$ (from the virial theorem[8]) are taken ($\alpha_{\rm O}=0.74387$ and $\alpha_{\rm Ti}=0.71648$), and between the spheres an α value of $\frac{2}{3}$ is used. It has been shown for VC that a reduction of the exchange parameter from $\alpha=1$ to the $\alpha_{\rm vt}$ values broadens the bands somewhat, but leaves the relative positions of the p and d bands almost unchanged.[9] Comparison with atomic calculations suggests that a similar insensitivity of the band structure to the exchange parameter will hold for TiO.

Since the muffin-tin model has been shown to be a good approximation for TiC,[10] it is important to demonstrate that the results obtained in Ref. 2 are not critically dependent on the parameters and approximation used there. The atomic-sphere radii, $R_{\rm O}$ and $R_{\rm Ti}$, the other parameters apart from the exchange approximation which enter into the APW calculation, were determined by the intersection of the superposed O and Ti potentials in the $\langle 100\rangle$ direction. In carrying out the self-consistent iterations, these radii were kept fixed, but relaxing this constraint results in a change of only 1% in the radii. A comparison of two sets of self-consistent APW calculations on VC showed that band energies were shifted by less than 0.02 Ry when the ratio of the atomic sphere radii $R_{\rm C}/R_{\rm V}$ was drastically changed from 0.899 to 0.645.[11] Thus the choice of the muffin-tin radii is not critical for the present discussion. If the HF calculation is convergent and is as insensitive to changes in model parameters as the APW calculation, then the qualitative disagreement between the results of the two methods must arise from the different treatment of exchange.

Another point raised by the authors of Ref. 1 is the "questionable" comparison of theoretical calculations in Ref. 2 with the soft-x-ray emission spectra (SXS) owing to valence-band distortions produced by the core hole. However, for the series of transition-metal compounds MX (M = Ti, V, or Nb; X = C, N, or O) it is possible to interpret the SXS (Ref. 12) in terms of partial local densities of states $\chi_l^t(E)$ obtained from $X\alpha$-APW calculations.[2] Using radial transition probabilities in the calculation of SXS, good overall agreement is obtained [for instance, for VC and VN (Ref. 13) and for NbC (Ref. 3)], although valence-band distortions are not taken into account. Owing to this neglect of distortion, the results for SXS from $X\alpha$-APW calculations must be treated with some caution, though for the nitrides, for example, we find that the separation between M d and N p bands tends to be *smaller* by, at most, 1 eV in the $X\alpha$-APW results than in the experimental SXS. Furthermore, the separation of the X s and X p bands is only 1–2 eV smaller than the corresponding peaks in the metal K spectra. Thus we conclude that it is reasonable to compare SXS data with theoretical results obtained by the method of Ref. 13. For the present discussion we follow the procedure adopted in Ref. 13 and compute the SXS of TiO including the radial transition probabilities. For the broading of the SXS, the following parameters were used [full width at half maximum (FWHM) see Ref. 13 for definitions]: Γ_0 (core) = 0.4 eV for O K and 0.6 eV for Ti K and Ti L_{III}; W (valence) = 1 eV and S (spectrometer) = 0.6 eV. The comparison between theory and experiment is shown in Fig. 1, and the following points emerge:

(i) The O K spectrum [Fig. 1(a)], which reflects the local O-p density of states (DOS), $\chi_p^O(E)$, shows good agreement with experiment.[14]

(ii) The Ti L_{III} spectrum, which is determined primarily by the large Ti-d component of the DOS, $\chi_d^{Ti}(E)$, is compared with the experimental spectrum of Fischer[15] in Fig. 1(c). Another spectrum obtained by Ichikawa *et al.*[16] agrees well with that shown in Fig. 1(c) except that it does not show the small peaks labeled C and D. Peak C, which also appears in the spectra of TiC and TiN, can be readily understood from the $X\alpha$-APW results as a contribution from the nonmetal s band.

(iii) The $X\alpha$ and HF band structures differ in the amount of O-p and Ti-d mixing. The good agreement of the peak separation and their relative intensities for the O K and Ti L_{III} spectra, which reflect the main components of the DOS, lends support to the $X\alpha$ results.

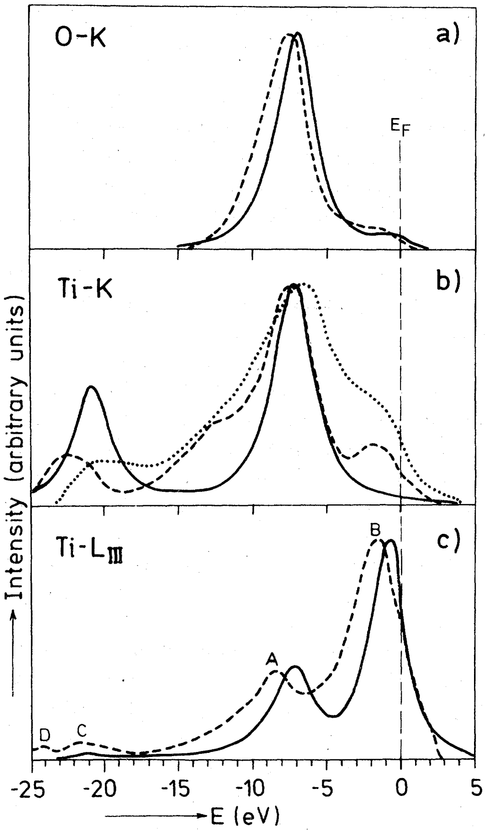

FIG. 1. Soft-x-ray emission spectra of TiO, theory (solid line) and experiments: (a) O K spectrum from Menshikov *et al.* (Ref. 14) (dashed line); (b) Ti K spectra from Nemnonov and Kolobova (Ref. 17) (dashed line) and from Ramqvist *et al.* (Ref. 18) (dotted line); (c) Ti L_{III} spectrum from Fischer (Ref. 15) (dashed line).

(iv) The two experimental Ti K spectra[17,18] are shown in Fig. 1(b). The theoretical spectrum is determined by the rather small component $\chi_p^{Ti}(E)$, which, near E_F, is so small[12] that it cannot be seen after broadening, and consequently the peak or shoulder in the experimental spectrum just below E_F is not explained in this calculation. In addition, this experimental spectrum gives a rather smaller separation between the O p and Ti d bands than is indicated by the $X\alpha$ results. However, one should bear in mind that the Ti K spectrum correlates with $\chi_p^{Ti}(E)$, which, since it is a small component, is very sensitive to small changes in the band structure and to valence-band distortions. It could be considerably increased even by a small reduction of the O-p–Ti-d band separation, while such a small change would not drastically alter the major components of the DOS, and therefore the interpretation of the O K and Ti $L_{\rm III}$ spectra would remain valid. A situation similar to that of TiO is also found for VO.[12]

Another point of dispute between the $X\alpha$ and HF results, the valence-band width, cannot easily be obtained from SXS, since too many broadening effects are involved, but it can be estimated from XPS data for the valence band. These measurements, which have been carried out by Ichikawa *et al.*[16] (who estimated the energy resolution of their spectrum to be about 1 eV for FWHM), since they do not show a band gap separating the Ti-d and O-p bands as seen in the $X\alpha$ DOS, have been adduced as evidence supporting the HF results.[1] Figure 2 illustrates the comparison between the experimental XPS and the total DOS obtained after convolution with a 1-eV broadening function for both the HF results [Fig. 2(a)] and the $X\alpha$-APW calculations [Fig. 2(b)], for which the band gap disappears after broadening. In our opinion *neither* the HF *nor* the $X\alpha$ results give good agreement with experiment; in comparison to the XPS data, the HF results give too high a peak energy (main peak) and too large a bandwidth, whereas the $X\alpha$ results give too low a peak energy and too small a bandwidth. The XPS spectrum of Ref. 16 shows no intensity just below E_F, as if TiO were nonmetallic, though TiO is known to exhibit metallic conductivity and there is considerable intensity near E_F in the Ti $L_{\rm III}$ spectrum [Fig. 1(c)]. Since *both* the $X\alpha$ and HF results predict intensity near E_F, and this is missing in the XPS, it is desirable that further work on this discrepancy be carried out. In order to estimate how the matrix elements would affect the XPS valence-band spectrum in TiO, obtained by using the $X\alpha$ method, we have also convoluted the partial DOS. For example, we show in Fig. 2(b) that the convolution of only the O-2p DOS $\chi_p^0(E)$ leads to a peak, corresponding to the 2p band, which is almost unchanged in comparison to the curve derived from the total DOS, but the peak near E_F is dramatically reduced in size, since it corresponds mainly to Ti-d DOS. Therefore the relative intensities of these two peaks depend strongly on the matrix elements, which can be roughly estimated from the ratio of the partial-ionization cross sections for O 2p and Ti 3d electrons. If the ionization cross section for the O 2p electrons were larger than that for the Ti 3d electrons, the O-2p peak would dominate in the XPS spectrum, thus providing one possible explanation of the XPS spectrum[16] within the $X\alpha$ formalism. It is unlikely that a similar explanation could be advanced for the results obtained by the HF method, since there is much stronger p-d mixing compared to the $X\alpha$ bands. In Ref. 1 it is argued that the Ti-3d electrons should be visible in ultraviolet-photoemission spectroscopy (UPS) of $\mathrm{Ti_2O_3}$. However, since the matrix elements for XPS could be significantly different from those for UPS, this is a weak argument. For Mg $K\alpha$ radiation the relative photoionization cross sections have been measured and are 0.7 and 1.2 for O 2p and Ti 3d electrons, respectively.[19] Using these values for estimating matrix elements in TiO, the d band peak in Fig. 2(b) would be enhanced relative to the p-band peak in contrast to the present XPS data.[16] However, according to new preliminary XPS experiments, which are currently being carried out at the University of Lyon,[20] two pronounced peaks corresponding to the O 2p and Ti 3d bands are found, providing evidence in favor of the $X\alpha$ band structure.

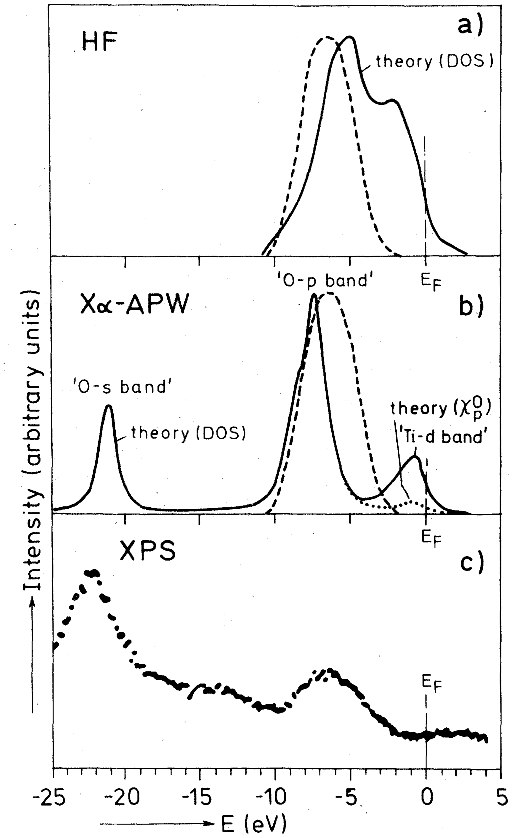

FIG. 2. XPS valence-band spectra from Ichikawa *et al.* (Ref. 16) (dashed line) are compared with theoretical DOS convoluted with a 1 eV FWHM broadening function: (a) HF–total DOS from Ref. 1 (solid line); (b) APW–total DOS taken from Ref. 2 (solid line), O-p component $\chi_p^0(E)$ alone (dotted line); (c) XPS taken from Ref. 16.

The separation between the O 2s and O 2p bands (which is not yet available for the HF case) is about 2 eV smaller for the $X\alpha$ case than for the

XPS data,[16] a result which is consistent with the SXS spectra.

To summarize, we conclude that there is no clear-cut conflict between the $X\alpha$ and HF methods in the case of TiO, especially since both methods show discrepancies with experimental data. In order to bring the $X\alpha$ results into better agreement with experiment, the separation between the O *p* and Ti *d* bands should be reduced by about 1.5 eV, a process which would broaden the O-*p* and increase the small Ti-*p* component near E_F (thus explaining the Ti *K* SXS). However, in our opinion the gross features of the O-*p*–Ti-*d* mixing are better represented by the $X\alpha$ band structure than by the HF results, using the O *K* and Ti L_{III} SXS as a criterion and allowing for matrix-element effects to account for the XPS data.

The new preliminary XPS experiments[20] differ significantly from those reported in Ref. 16, and lend support to the $X\alpha$ band structures.

Note added in proof. New XPS and UPS experiments[21,22] show clear evidence for an energy gap between the O 2*p* and the Ti 3*d* bands in agreement with the $X\alpha$ band structure suggested here. Both groups have found that the earlier work of Ichikawa *et al.*[16] was affected by surface contamination due to poor preparation of samples and that the Japanese workers were effectively measuring the spectrum of TiO_2, not TiO.

ACKNOWLEDGMENTS

The authors are very grateful to Dr. L. Porte and Dr. M. Demosthenous for making their preliminary new XPS data available to us prior to publication. We are also pleased to acknowledge valuable discussions with Dr. C. P. Mallett. This work has been supported by the Fonds zur Förderung der wissenschaftlichen Forschung.

---

[1] D. R. Jennison and A. B. Kunz, Phys. Rev. Lett. 39, 418 (1977).

[2] A. Neckel, P. Rastl, R. Eibler, P. Weinberger, and K. Schwarz, J. Phys. C 9, 579 (1976).

[3] K. Schwarz, J. Phys. C 10, 195 (1977).

[4] A. Neckel, K. Schwarz, R. Eibler, P. Weinberger, and P. Rastl, Ber. Bunsenges., Phys. Chem. 79, 1053 (1975).

[5] V. Ern and A. C. Switendick, Phys. Rev. 137, A1927 (1965).

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

[7] J. M. Schoen and S. P. Denker, Phys. Rev. 184, 864 (1969).

[8] K. Schwarz, Phys. Rev. B 5, 2466 (1972).

[9] A. Neckel, P. Rastl, P. Weinberger, and R. Mechtler, Theor. Chim. Acta 24, 170 (1972).

[10] H. R. Trebin and H. Bross, J. Phys. C 8, 1181 (1975).

[11] K. Schwarz, K. Pechter, and A. Neckel, J. Phys. C 8, 1663 (1975).

[12] A. Neckel, K. Schwarz, R. Eibler, P. Rastl, and P. Weinberger, Microchim. Acta (Vienna) Suppl. 6, 257 (1975).

[13] K. Schwarz and A. Neckel, Ber. Bunsenges. Phys. Chen 79, 1071 (1975).

[14] A. Z. Menshikov, I. A. Brytov, and E. Z. Kurmaev, Phys. Status Solidi 35, 89 (1969).

[15] D. W. Fischer, in *Band Structure Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and L. M. Watson (Academic, London, New York, 1973), p. 669.

[16] K. Ichikawa, O. Terasaki, and T. Sagawa, J. Phys. Soc. Jpn. 36, 706 (1974).

[17] S. A. Nemnonov and K. M. Kolobova, Fiz. Metal. Metalloved 22, 680 (1966) [Phys. Met. Metallogr. (USSR) 22, 36 (1966)].

[18] L. Ramqvist, B. Ekstig, E. Källne, E. Norelund, and R. Manne, J. Phys. Chem. Solids 30, 1849 (1969).

[19] A. Calabrese and R. G. Hayes, Chem. Phys. Lett. 27, 376 (1974).

[20] L. Porte and M. Demosthenous (private communication).

[21] G. K. Wertheim and D. N. E. Buchanan, Phys. Rev. B 17, 2780 (1978).

[22] V. E. Heinrich, H. J. Zeiger, and T. B. Reed, Phys. Rev. B 17, 4121 (1978).