Significant Differences between Hartree-Fock and Local-Exchange Energy Bands for TiO

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Hartree-Fock (HF) energy-band calculations on TiO are in qualitative disagreement with those obtained with use of statistical exchange ($X\alpha$). While all $X\alpha$ results have a 2–8-eV gap between the Ti $3d$ and O $2p$ bands, the HF results show largely overlapping $2p$-$3d$ bands. The HF result is supported experimentally by the absence of any gap in the experimental valence x-ray–photoemission–spectroscopy spectrum. Reasons for the apparent failure of $X\alpha$ theory on this material, and not on other materials are suggested.

While large quantitative differences exist between statistical-exchange ($X\alpha$) results and those obtained by solving the Hartree-Fock (HF) problem first and then adding correlation corrections appropriate to the solid at hand, qualitative agreement has been demonstrated in the past. Recent calculations by the authors on the rock-salt structure of TiO, using both approaches, have shown gross *qualitative* disagreement between the two methods. This is the first time that the two methods have yielded entirely different pictures of the fundamental nature of the bonding in any material (although the insulating transition-metal oxides are now showing qualitative difference also).[1]

The local-orbital method[2] was used to generate a density matrix for $\mathrm{Ti}^{++}\mathrm{O}^{--}$. This configuration was indicated by previous statistical-exchange results on this material. Bands were then generated from this density matrix using both HF and the full Slater exchange ($\alpha = 1$). The latter was chosen to permit comparison with previous results by Ern and Switendick,[3] and by Mattheiss.[4] Results by Neckel *et al.*,[5] using lower α values, have shown that the bands are relatively insensitive to the choice of α.

Results by the authors using the full Slater exchange are in substantial agreement with those of Ern and Switendick except that the O $2p$ bandwidth is somewhat greater. Relatively pure metal $3d$ bands lie above oxygen $2p$ bands by a 2-eV gap.[6] The $\mathrm{Ti}^{++}\mathrm{O}^{--}$ configuration is self-consistent with the bands.[7] Using the same basis set and program (except for replacing the Slater exchange by the HF exchange) entirely different bands result, as may be seen in Fig. 1. The density of states is seen in Fig. 2.

It is, of course, necessary to add correlation corrections to the HF bands. While these are difficult to determine precisely, they may be estimated as follows. These corrections are divided into long-range (polarizationlike) and short-range (relaxationlike) parts.[8] The former is found by the electron-polaron model[9] in the case of insulators, and may be estimated by Overhauser's model[10] for conductors. The latter is found from atomic (or ionic) calculations. Unlike materials as alkali halides[11] and lithium[12] or calcium[13] metal, the corrections are surprisingly small.

The derivation of the short-range correlation[8] relies on a small overlap between valence orbitals, which equivalently implies narrow bands and a long hole lifetime on one site. However, the valence bands in TiO are not only very wide (short lifetime) but also have extensive p-d hybridization which makes it meaningless to speak of an oxygen or titanium hole. Thus as argued in Ref. 8, the short-range correlations should be greatly reduced compared with those of the ionic solids where they amount to a few eV. In addition, the conduction-electron density in TiO is very low compared to other metals such as Ca or Li, thus causing a small long-range correction due to low screening. Most of the valence electrons are "frozen out" of the conduction process because of their involvement in the covalent and ionic bonds of the material. A similar situation is found, for example, in TiC and the Ni metal ***d*** electrons. Using a conduction-electron density of $0.0002e^-/a_0^3$ based on Hall-effect measurements (uncertain but of the correct magnitude) we estimate a valence-band compression of only 0.12 Ry. Thus the total correlation corrections are small, and we would expect the HF valence-band width to be in substantial agreement with the experimental x-ray–photoemission–spectroscopy (XPS) bandwidth, as is indeed the case. However, this is *not* the usual case. In Li metal, for example, the HF bandwidth is over twice the correlated bandwidth.[12]

This suggests a reason for the difference be-

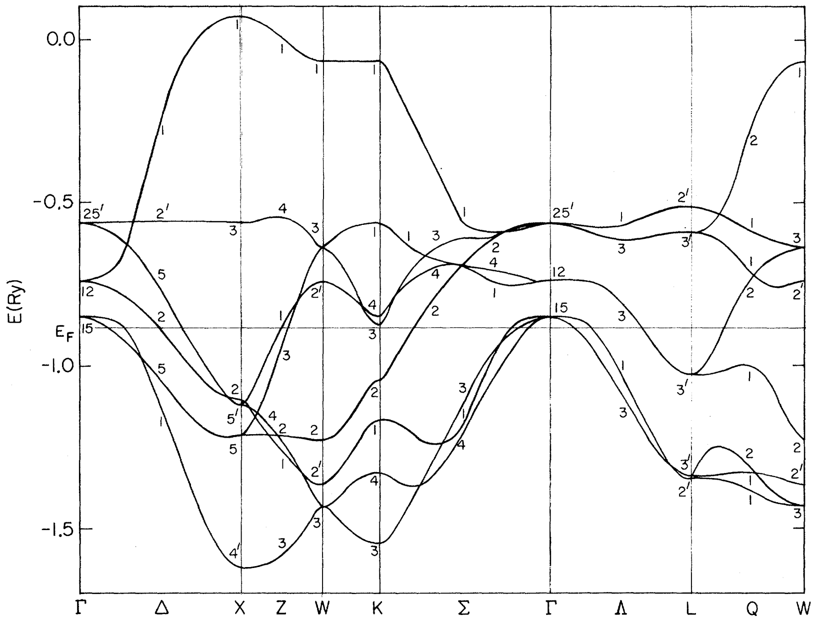

FIG. 1. Hartree-Fock energy bands for TiO. Note the complete *p*-*d* mixing as evidenced by the evolution of the lowest Δ_5 band Γ_{15} (pure *p*) to X_5 (pure *d*). This bonding band is filled, while the next higher (anti-bonding) Δ_5 band is empty in the region around $\Delta_{0.5}$, where the most *p*-*d* mixing occurs.

tween the HF and $X\alpha$ results: While the "HF-plus-correlation" approach tailors the correlation correction to the material at hand, the $X\alpha$ method "hardwires" the correction in a relation to the exchange energy appropriate to the free-electron gas.[15] Thus in TiO, in which we have a very high valence-electron density but a very small correlation correction, the $X\alpha$ method should and does yield results in substantial disagreement with HF-plus-correlation results.

We find several pieces of experimental evidence which strongly support the HF picture of TiO. Firstly, XPS measurements of Ichikawa *et al.*,[16] done over a wide range of compositions, *x*, of TiO_x, find no evidence for a band gap separating the Ti 3*d* and O 2*p* bands. The gap is supposedly (from $X\alpha$ calculations) 1.8–7.6 eV,[17] and the experimental resolution is 1 eV (see Fig. 3).

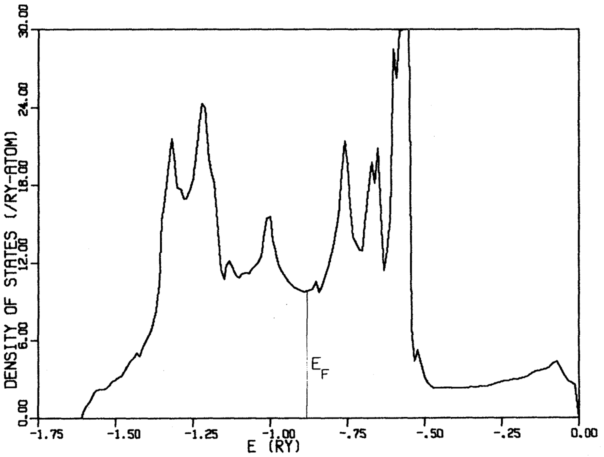

FIG. 2. Hartree-Fock density of states for TiO. Correlation effects will compress the valence band by-about 0.12 Ry. The predicted bandwidth is then about 8 eV.

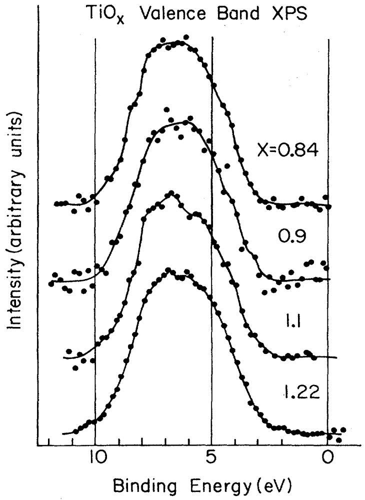

FIG. 3. TiO_x valence-band XPS, from Ichikawa, Terasaki, and Sagawa (Ref. 15). Resolution is 1 eV. Note lack of evidence of any band gap.

Since Ti 3*d* electrons are clearly visible above a gap in ultraviolet-photoelectron-spectroscopy measurements on Ti_2O_3,[14] matrix-element effects would probably not explain the absence of *d*-electron visibility above the supposed gap in TiO, where one-quarter (as compared to one-ninth in Ti_2O_3) of the valence electrons are in *d* bands. Secondly, Hall-effect measurements[18] on TiO_x show the Hall constant to be $+2.7\times10^{-4}$ cm^3/C for $x=0.8$, but -0.8×10^{-4} cm^3/C for $x=1.23$. Thus, two types of charge carriers are suggested. One is indeed hard pressed to find an explanation in any of the $X\alpha$ results; however, hole carriers are in obvious evidence around Γ in the HF results, while electron carriers arise from the *d* bands. A qualitative explanation for the Hall-measurement results may be obtained from a "rigid-band" model which suggests E_F moves upward as x increases from 1 (thus filling in the hole pocket) and downward as x decreases (thus creating a larger hole pocket).[19]

The comparison of the interatomic spacings of TiO to other monoxides, as was done by Mattheiss,[4] shows strong evidence for a different form of binding in TiO and VO. Indeed, while CaO and those oxides past VO have interatomic spacings which scale as the metal (M^{++}) ionic radii, TiO and VO have spacings even narrower than NiO which has the most compact doubly positive ion of the series (see Fig. 4). This is strong evidence for covalency. However, all $X\alpha$ band calculations produce bands for TiO and VO which are only quantitatively different from those of the other monoxides.[20] Our HF results show this covalency strongly as metal-oxygen *p*-*d* and metal-metal *d*-*d* bonding; while the former is present and may be important to the reactivity of the TiO surface, the latter is probably the dominant covalent contributor to the cohesive energy. We believe this to be true since the net charge on the oxygen ion seems to be only slightly less than that of a filled shell. The $X\alpha$ results, however, have a *d* band which is significantly narrower than the one for the HF results. The great difference in the *d* bands is solely a consequence of the difference in the exchange potentials, since our full-Slater-exchange *d* band is almost identical to that of Ern and Switendick.[3] The greater HF *d*-band width causes the penetration into the oxygen *p* band and the absence of any gap, in agreement with the above-mentioned XPS results.

Thus, several experimental facts suggest the correctness of the HF results. Other experimental evidence, such as soft-x-ray emission,[21] for example, does not distinguish as easily as XPS between the two results. More experiments, particularly on vacancy-free stoichiometric samples, would be helpful. If the present indications continue, however, one would be forced to conclude that the $X\alpha$ method is not applicable to TiO or other similar materials.

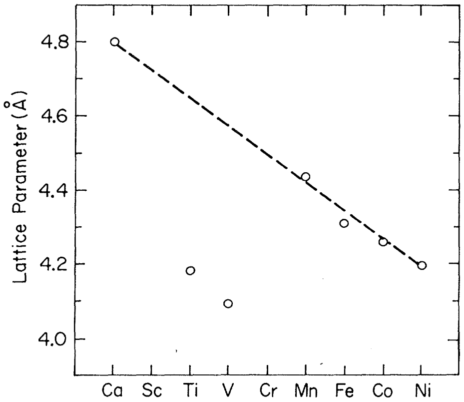

FIG. 4. Lattice parameters for the 3*d* transition-metal monoxides, from Mattheiss (Ref. 4).

A longer report, which will soon follow, will describe the computational details, discuss the effect of the albeit small correlation corrections on the density of states, and compare the HF results to other properties.

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[1] A. B. Kunz and G. T. Surratt, to be published.

[2] A. B. Kunz, Phys. Status Solidi 36, 201 (1969), and Phys. Status Solidi (b) 46, 385 (1971).

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

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

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

[6] The reuslts were so similar to Ref. 3 that they have not been drawn.

[7] No problems in self-consistency, such as those reported on VO by T. E. Norwood and J. L. Fry [Phys. Rev. B 2, 472 (1970)] were encountered.

[8] Sokrates T. Pantelides, Daniel J. Mickish, and A. Barry Kunz, Phys. Rev. B 10, 2602 (1974).

[9] A. B. Kunz, Phys. Rev. B 6, 606 (1972).

[10] A. W. Overhauser, Phys. Rev. B 3, 1888 (1971).

[11] Daniel J. Mickish, A. Barry Kunz, and T. C. Collins, Phys. Rev. B 9, 4461 (1974).

[12] Dwight R. Jennison, Bull. Am. Phys. Soc. 22, 444 (1977), and to be published.

[13] Daniel J. Mickish, A. Barry Kunz, and Sokrates T. Pantelides, Phys. Rev. B 10, 1369 (1974).

[14] Victor E. Henrich, G. Dresselhaus, and H. J. Zeiger, Phys. Rev. Lett. 36, 1335 (1976).

[15] A discussion of this point may be found in Ref. 10.

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

[17] Actual values obtained from the various calculations are as follows: Ref. 3 (using Ti$^+$O$^-$ and $\alpha = 1$), 1.8 eV; Ref. 4 (using neutral TiO and $\alpha = 1$), 7.6 eV; Ref. 5 ($\alpha_{\mathrm{Ti}} = 0.72$, $\alpha_{\mathrm{O}} = 0.74$; self-consistent; however, muffin-tin radii were set to neutral-atom values), 2.2 eV.

[18] S. Takeuchi and K. Suzuki, J. Jpn. Inst. Metals (Sendai) 33, 279, 284 (1969). These results are quoted in M. D. Banus, T. B. Reed, and A. J. Strauss, Phys. Rev. B 5, 2775 (1972).

[19] This "rigid-band" model should be valid at least for a vacancy concentration of up to 10%. See J. M. Schoen and S. P. Denker, Phys. Rev. 184, 864 (1969). The important point is that two carrier types are clearly indicated.

[20] See Ref. 4 for a comparison. The quantitative difference may be sufficient to explain the covalency TiO and VO if one assumes the increasing d-d overlap ultimately favors a delocalized bonding state rather than a localized magnetic state for the d electrons.

[21] Although evidence for overlapping $2p$ and $3d$ bands may also be found here. The d-like peak at -1.0 Ry in Fig. 2 lies 4 to 5 eV above the p-like peak at -1.25 to -1.35 Ry, in agreement with the 6-eV separation in the TiO$_3$ spectrum of Ref. 15 which is as good as the 7.6-eV separation predicted by $X\alpha$ theory (Ref. 3). Valence-band distortions produced by the core hole make comparisons closer than this to the emission spectra questionable.

Optical Theorem and Electronic States in Disordered Transition Metals

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In disordered systems, apparently reasonable decoupling procedures can lead to *negative* densities of electronic states near resonant d bands. By applying the optical theorem to the multiple-scattering series we can determine *a prior* whether a given decoupling will necessarily yield positive results. Since *none* of the extensions of the coherent-potential approximation to amorphous systems is found to meet this requirement, we propose a new scheme which is both self-consistent and guaranteed to give a positive spectrum.

Certain quantities in statistical physics are, by definition, nonnegative. However, when such quantities are calculated approximately one can obtain negative values.[1] In the present paper we (1) show that this issue arises in calculating electronic states in strong-scattering liquid and amorphous metals, (2) suggest that several apparently reasonable approximation schemes may encounter similar difficulties, and (3) establish a procedure whereby such unphysical results may be avoided.

In realistic calculations on d-band metals one usually begins with a muffin-tin single-particle Hamiltonian:

$$\mathcal{H} = -\nabla^2 + \textstyle\sum_\alpha v_\alpha(\vec{r}) \equiv H_0 + \mathcal{V}(\vec{r}). \tag{1}$$

The ions are centered at the sites $\{\vec{R}_\alpha\}$ and the potentials $v_\alpha(\vec{r}) \equiv v(|\vec{r} - \vec{R}_\alpha|)$ are taken to be nonoverlapping and spherically symmetric. Within this framework, the electronic spectrum is evaluated in terms of the scattering properties of the individual ions and a sequence of correlation functions $g(\alpha|\beta)$, $g(\alpha|\beta|\gamma), \ldots$, which describe the average arrangement of the atoms. [In practice only the pair distribution $g(\alpha|\beta)$ is readily available from experiment; higher-order correlations must somehow be approximated in terms of $g(\alpha|\beta)$.]

If the scattering by the ions is weak, all terms beyond second order in perturbation theory may be neglected and no significant problems arise. By contrast, in systems involving noble or transition metals, the atomic potentials exhibit resonances and a simple truncation of the perturbation series is not valid. Selected terms must be summed to all orders and it is here that unexpected difficulties can occur. To illustrate, we com-