

Electronic structure of cubic sodium tungsten bronze

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The electronic band structure of cubic NaWO_3 has been calculated self-consistently with the semirelativistic linear muffin-tin orbital method. The inclusion of the relativistic band shifts and the self-consistent charge transfer substantially modifies the position and width of the valence bands, bringing them into much better agreement with photoemission experiments than earlier calculations. Despite the fact that the Na $3s$ band lies above the Fermi level, there is a net transfer of charge of about one electron per atom to the Na sites from the W and O atoms.

Since the pioneering measurements of Danielson and his co-workers¹ in the 1950s, the electronic properties of the sodium tungsten bronzes Na_xWO_3 have been studied by many groups. The evidence which has accumulated since then has increasingly supported the hypothesis, originally formulated by Sienko,² that the conduction-band states in the metallic phases, which occur when x is greater than about 0.22, are primarily based on the W d orbitals. In particular NMR studies³ give experimental support to this viewpoint.

For x values greater than about 0.5, the crystal assumes the perovskite form, with the Na atoms at the corners of

the cubes, the W atoms at the body centers, and the O atoms at the face-centered positions. The electronic structures of a number of similar perovskites have been calculated by Mattheiss,⁴ and Kopp, Harmon, and Liu⁵ determined the band structure of NaWO_3 by the Korringa-Kohn-Rostoker method. A photoemission study of $\text{Na}_{0.85}\text{WO}_3$ by Höchst, Bringans, and Shanks⁶ was in general accord with these calculations, but a detailed analysis

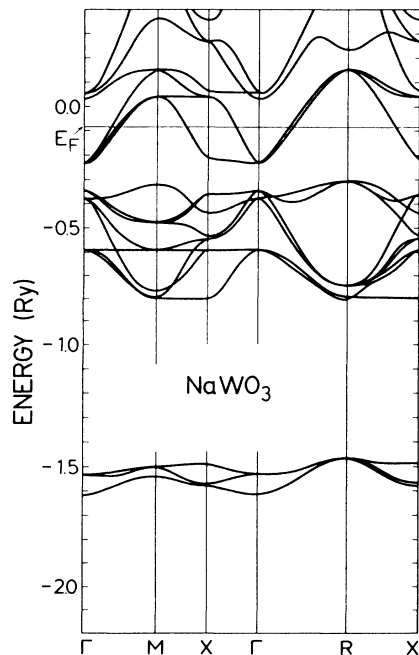


FIG. 1. Band structure of NaWO_3 calculated within the local-density approximation. The self-consistent LMTO calculation was performed with two energy panels, the lower covering the O $2s$ regime around -1.5 Ry. The lattice constant $a = 3.87$ Å.

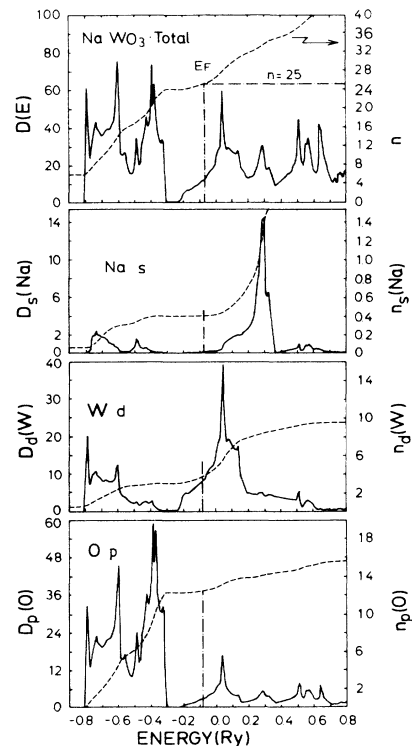


FIG. 2. Total density-of-states (DOS, solid curve) and number of states (n , dashed curve) (upper part) together with the most important partial functions, O p , W d , and Na s . [Only the energy range of the upper panel is shown; therefore $n_l(E)$ are nonzero at the left-hand edge of the figure.]

of the angle-resolved spectra led them "to conclude that the calculated position of the top of the valence band is too near the Fermi energy and that the valence-band width is too narrow." The calculations which have previously been made on perovskite crystals have suffered from two deficiencies: Firstly, relativistic effects were ignored, which leads to an error in the relative placement particularly of the W states and, more importantly, they were based on potentials which are not self-consistent. Charge-transfer effects are of particular interest in these compounds, since the process of donating electrons from the Na atoms to the W *d* bands, which is the basis of the Sienko model, would at first sight imply a corresponding transfer of charge, leading to positively charged Na sites. As we shall see, the reality is quite different, and self-consistency in the calculations is essential for the elucidation of such effects.

We have accordingly calculated the electronic structure of cubic NaWO₃ by the self-consistent scalar-relativistic linear muffin-tin orbital (LMTO) method,⁷ including the relativistic band shifts but neglecting the spin-orbit coupling. The energy bands in the symmetry directions of the simple-cubic Brillouin zone are shown in Fig. 1, while energies and wave-function symmetries at the points Γ and *X* are given in Table I. From these and the partial and total densities of states shown in Fig. 2 we confirm that the valence bands have predominantly O *p* and W *d*

character, but with a significant admixture of Na *s* (plus *p* and *d*). The lower part of the conduction band is also dominated by the W *d* and O *p* states, which together contribute over 90% of the density of states at the Fermi level. The Na 3*s* band lies well above the filled states. The lowest bands shown in Fig. 1 contain the six O *s* electrons.

The total charges within the different atomic spheres have also been calculated, and the occupation numbers are given in Table II. There is a substantial transfer of charge from W and O to Na, so that, from this viewpoint, the chemical formula may roughly be written Na^{-1.05}W^{+0.67}(O^{+0.13})₃. The actual values of the charges within each atomic sphere depend, of course, on the choice of the ratio between the sphere radii. This ratio was here chosen to be $S_{\text{Na}}:S_{\text{W}}:S_{\text{O}}=2:1.5:1$. This means that $S_{\text{Na}}=1.97$ Å, i.e., very close to the Wigner-Seitz radius of pure Na, 2.01 Å. The W sphere in NaWO₃ has in our case $S_{\text{W}}=1.48$ Å [$S(\text{bcc W})=1.56$ Å], and $S_{\text{O}}=0.98$ Å. Thus, the fact that we find that Na has one extra electron is not caused by a choice of an unreasonably large Na sphere radius. We may picture this distribution of charge as originating in the overlap from the WO₃ bonding valence electrons into the Na atomic sphere. We find, for example, that the standard potential construction of Kopp *et al.*,⁵ in which atomic charge densities placed on the lattice sites overlap to form the assumed charge density in

TABLE I. Eigenvalues at Γ and *X* in Ry and compositions of the states. The numbers in parenthesis give the degeneracies of the levels. The footnotes below the table (a–j) specify the projections onto cubic harmonics at each site. The coordinate system is chosen such that Na is at (0,0,0), W at (1,1,1)*a*/2, O⁽¹⁾ at (1,1,0)*a*/2, O⁽²⁾ at (1,0,1)*a*/2, and O⁽³⁾ at (0,1,1)*a*/2. The *X* point chosen has $\mathbf{k}=(0,1,0)2\pi/a$. The lattice constant $a=3.87$ Å.

Energy (Ry)	Na			Angular-momentum weights (percent)			W			Footnote
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>	
Γ										
(3) -0.591	0	11	0	0	67	0	0	22	0	
(3) -0.378	0	0	0	0	100	0	0	0	0	
(3) -0.345	0	5	0	0	89	0	0	0	0	
(3) -0.234	0	0	5	0	0	7	0	0	88	a
(1) 0.032	84	0	0	15	0	1	0	0	0	
<i>X</i>										
(1) -0.802	0	1	0	0	53	0	11	0	35	b
(2) -0.595	0	9	0	0	59	1	0	0	31	c
(2) -0.549	0	0	10	0	68	0	0	22	0	d
(1) -0.536	26	0	0	4	67	0	0	2	0	e
(1) -0.441	0	0	18	0	82	0	0	0	0	f
(2) -0.362	0	0	5	0	89	0	0	6	0	g
(1) -0.213	0	0	0	0	0	7	0	0	93	h
(2) 0.041	0	0	0	0	34	2	0	0	64	i
(1) 0.062	0	0	0	14	0	12	0	0	74	j

^aW($d_{T_{2g}}$).

^bO⁽²⁾(p_y , 53%), W($d_{x^2-y^2}$, 29%), W(d_{3z^2-1}).

^cO⁽²⁾(p_x , 59%), W(d_{xy} , 31%).

O⁽²⁾(p_z , 59%), W(d_{yz} , 31%).

^dO⁽¹⁾(p_z , 37%), O⁽³⁾(p_z , 30%), W(p_z , 22%).

O⁽¹⁾(p_x , 30%), O⁽³⁾(p_x , 37%), W(p_x , 22%).

^eNa(s , 26%), O⁽¹⁾(p_y , 34%), O⁽³⁾(p_y , 34%).

^fNa(d_{3z^2-1} , 18%), O⁽¹⁾(p_y , 41%), O⁽³⁾(p_y , 41%).

^gO⁽¹⁾(p_x , 55%), O⁽³⁾(p_x , 34%).

O⁽¹⁾(p_z , 34%), O⁽³⁾(p_z , 55%).

^hW(d_{xz} , 93%).

ⁱO⁽²⁾(p_z , 34%), W(d_{yz} , 64%).

O⁽²⁾(p_x , 34%), W(d_{xy} , 64%).

^jW(d_{3z^2-1} , 53%), W($d_{x^2-y^2}$, 21%).

TABLE II. Partial occupation numbers in the two panels used. Panel 1 covers the O $2s$ band range, whereas panel 2 includes the remaining states. The last column gives the partial density-of-states (DOS) values at the Fermi level $E_F = -0.084$ Ry.

	Occupation numbers n_l (states/formula unit)		DOS (E_F) D_l (E_F) (states/Ry)/formula unit
	Lower panel	Upper panel	
Na s	0.056	0.348	0.084
Na p	0.140	0.692	0.087
Na d	0.130	0.683	0.164
O s	4.880	0.128	0.045
O p	0.008	12.472	2.696
O d	0.004	0.126	0.516
W s	0.170	0.415	0.005
W p	0.261	0.809	0.011
W d	0.352	3.326	8.012
Total	6	19	11.620

the crystal, results in an excess of about 3.1 electrons within each Na muffin-tin sphere. This gives rise to a repulsive Madelung potential and raises the Na $3s$ states above the lowest WO_3 antibonding levels, so that a partially compensating reverse transfer occurs (note that the bottom of the Na $3s$ band, the almost pure level at Γ in Table I, is well above the Fermi level). The Na atoms, however, remain negatively charged with about one extra electron, when the potential is made self-consistent.

This charge transfer, together with the relativistic effects, has a significant effect on the relative position and width of the valence bands, as may be deduced by comparing our results with those of Kopp *et al.*⁵ We find the separation of the valence and conduction bands at Γ to be 0.11 Ry, compared with their value of 0.15 Ry, while our width of 0.51 Ry is much greater than their 0.35 Ry. These modifications of the valence band greatly improve the agreement with the photoemission results of Höchst *et al.*⁶ On our energy scale, their Fig. 6, which shows angle-resolved photoemission at normal emission, has the following features: an edge at -0.30 Ry, a sharp peak at -0.40 Ry, a broad peak centered at about -0.6 Ry and a

small hump at -0.7 Ry. They conclude that these data represent the one-dimensional state density along ΓX and that the bottom of the valence band is around -0.8 Ry. Even though there is some uncertainty in the interpretation of photoemission measurements, the agreement between experiment and Figs. 1 and 2 is striking.

This study has again illustrated the importance of charge-transfer effects in solid compounds. In contrast to the elements, where accurate results may frequently be obtained using *ad hoc* potential constructions, the attainment of self-consistency is crucial for obtaining accurate energy bands in materials containing several different kinds of atom. The nature of the charge transfer, which contains essential information about the electronic and cohesive properties of the solid, may not always be obvious from elementary considerations.

ACKNOWLEDGMENTS

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