

## Theoretical Study of the Band Structure of Oxides Crystallizing in the Rocksalt Structure: TiO\*

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The band structure of solids crystallizing in the rocksalt structure has been studied for arbitrary directions in reciprocal space using the parametrized tight-binding method. The results are specified in terms of a secular determinantal equation containing a minimal set of independent transfer integrals. Account is taken of nearest and next-nearest neighbor interactions, using  $4s$ ,  $4p$ , and  $3d$ -like orthogonalized basis functions for the cation and  $2s$  and  $2p$ -like orthogonalized basis functions for the anion. The analysis was then specialized to the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  symmetry directions in reciprocal space.

After discarding the contributions arising from the  $4p$  states, the 24 remaining transfer integrals were evaluated for the case of TiO by optimally fitting the eigenvalues of the various specialized secular determinantal equations to energy values calculated at selected points of the Brillouin zone by Ern and Switendick who employed the APW procedure. The numerical results show that to the extent to which the APW calculation provides an adequate description one cannot generally separate energy contributions associated with one set of atomic states from those contributed by others with compatible symmetry. Thus, direct cation-cation overlap is competitive with cation-anion interactions.

### Introduction

The metallic properties of transition metal monoxides crystallizing in the rocksalt structure have been the subject of several recent studies (1-7). Therefore, it seemed of interest to investigate the band structure of this class of materials on the basis of the LCAO (tight-binding) theory. We first develop the general theory in terms of a secular determinantal equation in parametrized form. We then specialize to the case of TiO by evaluating the parameters through optimization of the fit to prior calculations based on the APW approach.

We begin with a minimal survey of the pertinent features of the LCAO method which is closely patterned after the procedure developed by Slater and Koster (8); for additional details see

Refs. (9, 10). Basically the desired information is conveyed in terms of a secular determinantal equation of the form

$$|\langle l'_j | H | l_j \rangle - \lambda(\mathbf{k}) \delta_{l'_j l_j}| = 0 \quad (1)$$

whose solution indicates for every band how the energy  $\lambda$  changes with wave vector  $\mathbf{k}$  of the electron. The transfer integrals are defined by

$$\langle l'_j | H | l_j \rangle \equiv \sum_{\mathbf{n}} e^{i\mathbf{k} \cdot (\mathbf{R}_n + \boldsymbol{\rho}_{j'j})} \times \int d^3r u_{l'_j}^*(\mathbf{r}) H u_{l_j}(\mathbf{r} - \mathbf{R}_n + \boldsymbol{\rho}_{j'j}) \quad (2)$$

where the following symbols have been used: (a)  $H$  is the Hamiltonian operator for an electron in the periodic lattice array; (b)  $|l_j\rangle \equiv u_{l_j}(\mathbf{r})$  is an orthogonalized atomic orbital; (c)  $j'$  and  $j''$  designate the translationally and/or chemically distinct lattice atoms in an arbitrarily designated unit cell; (d)  $l$  symbolizes the three quantum

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numbers  $n, l, m_l$  associated with atom  $j$  or  $j'$ ; (e)  $\mathbf{R}_n \equiv n_1 \hat{\mathbf{e}}_1 a_1 + n_2 \hat{\mathbf{e}}_2 a_2 + n_3 \hat{\mathbf{e}}_3 a_3$  is the set of lattice vectors, the  $n_i$  being integers and the  $\hat{\mathbf{e}}_i$  being unit vectors and  $a_i$  edge lengths coinciding with the three edges of the primitive unit cell; (f)  $\boldsymbol{\rho}_{j'j}$  is the vector distance between atoms of the type  $j'$  and type  $j$  in the same primitive unit cell; (g)  $\delta$  is the Kronecker delta.

The use of orthogonalized atomic wave functions has the virtue of eliminating all overlap integrals in (1) in favor of the Kronecker delta. These wave functions are formed from the ordinary atomic orbitals by well-established procedures (11) and possess the same symmetry characteristics as the atomic functions from which they are formed (8).

For rocksalt structures the unit translation vectors are given by  $\hat{\mathbf{e}}_1 a_1 = (a/2)(\hat{\mathbf{i}} + \hat{\mathbf{j}})$ ,  $\hat{\mathbf{e}}_2 a_2 = (a/2)(\hat{\mathbf{j}} + \hat{\mathbf{k}})$ ,  $\hat{\mathbf{e}}_3 a_3 = (a/2)(\hat{\mathbf{k}} + \hat{\mathbf{i}})$ , where  $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$  are unit vectors along the three cubic axes of the crystal and  $a$  is the lattice parameter. Equation (1) calls for the evaluation of matrix elements of the operator  $H$  connecting  $u_{l'j'}^*$  to  $u_{lj}$ ; the latter is centered about an atom  $j$  at the distance  $\mathbf{R}_n + \boldsymbol{\rho}_{j'j}$  from atom  $j'$ . This distance also appears in the exponential term in (2). It is useful to introduce a vector  $\mathbf{R}_q \equiv (a/2) \times (q_1 \hat{\mathbf{i}} + q_2 \hat{\mathbf{j}} + q_3 \hat{\mathbf{k}}) = \mathbf{R}_n + \boldsymbol{\rho}_{j'j}$ , where  $q_i$  are integers, and to designate the transfer integrals by the symbol

$$E_{l'j'l_j}(q_1 q_2 q_3) \equiv \int d^3 \mathbf{r} u_{l'j'}^*(\mathbf{r}) H u_{lj}(\mathbf{r} - \mathbf{R}_q) \quad (2a)$$

When summing over  $q_1, q_2, q_3$  in Eq. (2a) it is convenient to do so with the magnitude  $|\mathbf{q}|$  fixed at successively larger values. For each fixed  $|\mathbf{q}|$ , i.e., within each coordination sphere, one ordinarily obtains interrelations among the different  $E$  parameters, such that Eq. (1) assumes the general form

$$\left| \sum_{|\mathbf{q}|} S_{j'j}(\mathbf{k}, \mathbf{q}) E_{l'j'l_j}(\mathbf{q}) - \lambda \delta_{l'j'l_j} \right| = 0 \quad (3)$$

(all  $l', l_j$ )

where for each fixed  $\mathbf{q}$  the exponential terms in Eq. (2), interrelated by linear dependences among corresponding  $E_{l'j'l_j}(\mathbf{q})$ , have evolved into structure factors  $S_{j'j}(\mathbf{k}, \mathbf{q})$ . The important feature of tight-binding methodology resides in the fact that, within the present approximation scheme and for a given type of crystal structure, the structure factors are uniquely determined; only the  $E$  parameters are altered as one proceeds from one case to the next.

## Elements of the Secular Determinantal Equation for the Rocksalt Structure

The elements in the secular determinantal Eq. (3) will now be determined for the defect-free rocksalt structure. Here we must first recognize the existence of two distinct types of lattice units, namely the cations labeled  $j'$ ,  $j=c$ , and the anions labeled  $j'$ ,  $j=a$ . For cationic states it seems reasonable to consider the orthogonalized atomic orbitals derived from the  $(n-1) d, n s$ , and  $n p$  wave functions indexed by  $l'_c$ ,  $l'_c = xy, xz, yz; x^2 - y^2, 3z^2 - r^2 \equiv z^2; s_c; x_c, y_c, z_c$ . For anionic states the orthogonalized atomic orbitals corresponding to the  $n's$  and  $n'p$  wave functions  $l'_a, l'_a = s_a, x_a, y_a, z_a$  are deemed relevant. In the present approximation all other states are excluded from consideration; this leads to a  $13 \times 13$  secular determinantal equation.

In the next step we restrict the summation over  $\mathbf{q}$  to: (a) the individual atoms whose energies in the crystal are characterized by the transfer integrals  $E_{l'j'l_j}(000)$ ; (b) nearest neighbors whose interactions are characterized by parameters such as  $E_{l'_c l'_a}(100)$  or  $E_{l'_a l'_c}(100)$ ; and (c) next-nearest neighbors with interactions specified by parameters such as  $E_{l'_c l'_c}(110)$  or  $E_{l'_a l'_a}(110)$ .

The various entries of the secular determinantal equation may now be constructed by evaluating the elements  $\sum_{|\mathbf{q}|} S_{j'j}(\mathbf{k}, \mathbf{q}) E_{l'j'l_j}(\mathbf{q})$  in (3), subject to the restrictions set forth above, and in conformity with standard procedures detailed elsewhere (8-10). The number of transfer integrals was confined to a minimal, linearly independent set, by examining whether for a given  $|\mathbf{q}|$ , crystal symmetry operations interrelate superficially distinct  $E_{l'j'l_j}(\mathbf{q})$  parameters. Interrelations among transfer integrals involving  $d$ -type basis functions are cited in Ref. (10).

The nonvanishing entries are summarized in Tables I-III, and the symbols are defined in Table VII. Despite the simplifications introduced so far the results are very complex: the secular determinant contains 137 nonvanishing entries involving 36 distinct  $E$  parameters. Careful examination of the tabulations shows that every basis function is connected to the 12 others through a large number of off-diagonal matrix elements. As will become clear from later discussion, and as has been detailed in another connection (12), one cannot introduce a further set of physically reasonable simplifying assumptions to decouple the large secular determinant into smaller subsets.

TABLE I

LISTING OF NONVANISHING MATRIX ELEMENTS FOR ENTRIES IN THE SECULAR DETERMINANTAL EQUATION FOR TiO PERTAINING TO TITANIUM-TITANIUM INTERACTIONS<sup>a</sup>

Entries	Notes and scheme for advancement of numerical indices $i, j$ , in $C_i$ or $S_j$
$\langle s_c   H   s_c \rangle = \eta + 4\zeta(C_1 C_2 + C_1 C_3 + C_2 C_3) - \lambda$	
$\langle s_c   H   x_c \rangle = 4iBS_1(C_2 + C_3)$	Advance all indices with $ x_c\rangle$
$\langle s_c   H   (z) \rangle \equiv \langle s_c   H   xy \rangle = -4\mu S_1 S_2$	Advance all indices with $ (z)\rangle$
$\langle s_c   H   x^2 - y^2 \rangle = 2\sqrt{3}8C_3(C_2 - C_1)$	
$\langle s_c   H   z^2 \rangle = -28(C_1 C_3 + C_2 C_3 - 2C_1 C_2)$	
$\langle x_c   H   x_c \rangle = D + 4EC_1(C_2 + C_3) + 4FC_2 C_3 - \lambda$	Advance all indices with $ x_c\rangle$
$\langle x_c   H   y_c \rangle = -4MS_1 S_2$	Advance index 1 with $\langle x_c  $ and index 2 with $ y_c\rangle$ ; ( $x_c \neq y_c$ ).
$\langle x_c   H   (z) \rangle \equiv \langle x_c   H   xy \rangle = 4iS_2(KC_1 + LC_3)$	
$\langle x_c   H   (y) \rangle = 4iS_3(KC_1 + LC_2)$	
$\langle y_c   H   (z) \rangle = 4iS_1(KC_2 + LC_3)$	
$\langle y_c   H   (x) \rangle = 4iS_3(KC_2 + LC_1)$	
$\langle z_c   H   (y) \rangle = 4iS_1(KC_3 + LC_2)$	
$\langle z_c   H   (x) \rangle = 4iS_2(KC_3 + LC_1)$	
$\langle x_c   H   x^2 - y^2 \rangle = 2\sqrt{3}iAS_1(C_2 + C_3) + 2iNS_1(C_2 - C_3)$	
$\langle y_c   H   x^2 - y^2 \rangle = -2\sqrt{3}iAS_2(C_1 + C_3) - 2iNS_2(C_1 - C_3)$	
$\langle z_c   H   x^2 - y^2 \rangle = 4iNS_3(C_2 - C_1)$	
$\langle z_c   H   z^2 \rangle = 4iAS_3(C_1 + C_2)$	
$\langle (z)   H   (z) \rangle \equiv \langle xy   H   xy \rangle = a + 4cC_1 C_2 + 4eC_3(C_1 + C_2) - \lambda$	Advance all indices with $(z)$
$\langle (z)   H   (y) \rangle \equiv \langle xy   H   xz \rangle = -4gS_3 S_2$	Advance $S_2$ with $ (y)\rangle$ and $S_3$ with $\langle (z)  $ ; ( $(z) \neq (y)$ )
$\langle xy   H   z^2 \rangle = -4\tau S_1 S_2$	$\langle xy   H   x^2 - y^2 \rangle = 0$
$\langle xz   H   x^2 - y^2 \rangle = 2\sqrt{3}\tau S_1 S_3$	
$\langle yz   H   x^2 - y^2 \rangle = -2\sqrt{3}\tau S_2 S_3$	
$\langle xz   H   z^2 \rangle = 2\tau S_1 S_3$	
$\langle yz   H   z^2 \rangle = 2\tau S_2 S_3$	
$\langle x^2 - y^2   H   x^2 - y^2 \rangle$	
$\langle z^2   H   z^2 \rangle = \left. \begin{array}{l} \alpha + 3 \left\{ \begin{array}{l} \beta \\ \gamma \end{array} \right\} C_3(C_1 + C_2) \\ + 4 \left\{ \begin{array}{l} \gamma \\ \beta \end{array} \right\} (C_1 C_2 + \frac{1}{4}C_1 C_3 + \frac{1}{4}C_2 C_3) - \lambda \end{array} \right\}$	
$\langle x^2 - y^2   H   z^2 \rangle = \sqrt{3}(\beta - \gamma)C_3(C_1 - C_2)$	

<sup>a</sup>  $S_i \equiv \sin(k_i a/2)$ ;  $C_j \equiv \cos(k_j a/2)$ ; subscripts (1, 2, 3) correspond to (x, y, z);  $a$  is the lattice constant.

Consequently, we were led to examine the secular determinantal equation along specific directions of high symmetry in reciprocal space. Considerable simplification now results because some of the structure factors vanish under these special conditions, and because many of the remaining entries are duplicated in corresponding positions of different rows and columns. One can then take suitable linear combinations of these, which transform the original basis functions to a

symmetry-adapted basis set. The transformed secular determinantal equation now splits into a number of subdeterminants in a manner which depends on the choice of the symmetry direction. Here, we shall consider the following cases: (a) the  $\langle 100 \rangle$  direction for which  $k_x \equiv k$ ,  $k_y = k_z = 0$ ; (b) the  $\langle 110 \rangle$  direction for which  $k_x = k_y \equiv k$ ,  $k_z = 0$ ; (c) the  $\langle 111 \rangle$  direction for which  $k_x = k_y = k_z \equiv k$ .

Results obtained under these special conditions

TABLE II

LISTING OF NONVANISHING MATRIX ELEMENTS FOR ENTRIES IN THE SECULAR DETERMINANTAL EQUATION FOR TiO, PERTAINING TO TITANIUM-OXYGEN INTERACTIONS<sup>a</sup>

Entries	Notes and scheme for advancing of indices
$\langle s_c   H   s_a \rangle = 2\rho(C_1 + C_2 + C_3)$ $\langle s_c   H   x_a \rangle = 2i\sigma S_1$	Advance $S_1$ in step with $ x_a\rangle$
$\langle x_c   H   s_a \rangle = 2iGS_1$	Advance $S_1$ in step with $\langle x_c  $
$\langle x_c   H   x_a \rangle = 2HC_1 + 2I(C_2 + C_3)$	Advance all indices in step with $\lambda = x, y, \text{ or } z$ ; $\langle \lambda_c   H   \lambda_a \rangle \equiv 0$ if $\lambda \neq \lambda'$
$\langle (z)   H   x_a \rangle \equiv \langle xy   H   x_a \rangle = 2ivS_2$	Index on $S_i$ corresponds to and is to be advanced with letter $\lambda'$ missing from the $\langle (\lambda)   H   \lambda_a \rangle$ sequence; also, $\langle (\lambda)   H   \lambda_a \rangle \equiv 0$
$\langle x^2 - y^2   H   s_a \rangle = \sqrt{3}\epsilon(C_1 - C_2)$ $\langle z^2   H   s_a \rangle = \epsilon(2C_3 - C_1 - C_2)$	
$\langle x^2 - y^2   H   x_a \rangle = \sqrt{3}i\xi S_1$ $\langle x^2 - y^2   H   y_a \rangle = -\sqrt{3}i\xi S_2$	$\langle x^2 - y^2   H   z_a \rangle = 0$
$\langle z^2   H   x_a \rangle = -i\xi S_1$ $\langle z^2   H   y_a \rangle = -i\xi S_2$ $\langle z^2   H   z_a \rangle = 2i\xi S_3$	

<sup>a</sup>  $S_i \equiv \sin(k_i a/2)$ ;  $C_j \equiv \cos(k_j a/2)$ ; subscripts (1, 2, 3) correspond to (x, y, z);  $a$  is the lattice constant.

by standard manipulations are displayed in Tables IV–VI, using definitions listed in Table VII. The use of broken lines is explained below.

### Application of Results to TiO

The above results have the advantage of being analytic and of being applicable to any solid crystallizing in the rocksalt structure, so long as the Wilson-Bloch model is applicable under the restrictions noted earlier. However, to determine the band structures for rocksalt crystals it is necessary to carry out numerical calculations of the various  $\lambda(\mathbf{k})$ . In principle this could be done by *a priori* calculations of the transfer integrals  $E_{V_j, t_j}(\mathbf{q})$ . However, as is well known, meaningful calculations can only be carried out if the basis functions  $|l_j\rangle$  are specified with a high degree of precision. In the absence of such information we adopted a curve-fitting procedure, by specializing to the case of TiO and by adjusting the  $E$  parameters until an optimal fit with prior band structure calculations was attained.

TABLE III

LISTING OF NONVANISHING MATRIX ELEMENTS FOR ENTRIES IN THE SECULAR DETERMINANTAL EQUATION FOR TiO, PERTAINING TO OXYGEN-OXYGEN INTERACTIONS<sup>a</sup>

Entries	Notes and scheme for advancement of entries
$\langle s_a   H   s_a \rangle = \kappa + 4\epsilon(C_1 C_2 + C_1 C_3 + C_2 C_3) - \lambda$ $\langle s_a   H   x_a \rangle = 4imS_1(C_2 + C_3)$	Advance all indices in step with $ x_a\rangle$
$\langle x_a   H   x_a \rangle = \rho + 4rC_1(C_2 + C_3) + 4tC_2 C_3 - \lambda$	Advance all indices in step with $ x_a\rangle$
$\langle x_a   H   y_a \rangle = -4zS_1 S_2$	First index in step with $\langle x_a  $ Second index in step with $ y_a\rangle$ ; ( $\langle \lambda_a   \neq   \lambda_a \rangle$ )

<sup>a</sup>  $S_i \equiv \sin(k_i a/2)$ ;  $C_j \equiv \cos(k_j a/2)$  where  $a$  is the lattice constant; subscripts (1, 2, 3) correspond to (x, y, z).

The case of TiO was chosen because of the detailed set of numerical calculations by Ern and Switendick (13) against which the present work could be checked. Their paper likewise contains extensive tabulations of eigenvalues which are needed as input parameters in our work. Moreover, their calculations have received experimental support. Various investigators using X-ray photoelectron spectroscopy (ESCA techniques) (14, 15) or soft X-ray emission (16–18) have found good agreement between their spectra and the density-of-states curves computed in Ref. (13). In agreement with the basic assumption underlying the theoretical treatment, the experiments indicate that up to one electron per Ti has been shifted from cationic to anionic states. The theoretical calculations (13) have received further confirmation from more recent calculations by Schoen and Denker (19) based on the APW-VCA approach. These latter computations have the advantage of making allowance for the existence of up to 15 at. % of vacancies in both sublattices to TiO. However, the numerical results are much less extensive than those of Ref. (13); moreover, the band structures arrived at in both cases are in substantial agreement.

In their numerical work Ern and Switendick (13) specified only a very limited number of eigenvalues derived from cationic  $p$ -states. Experience with our own calculations shows that this number is insufficient to permit a reliable

TABLE IV  
SECULAR DETERMINANTAL EQUATION FOR TiO ALONG THE  $\langle 100 \rangle$  DIRECTION IN RECIPROCAL SPACE<sup>a</sup>

$$a + 4c + 8eC - \lambda = 0 \quad (\Delta_2) \quad (IV.1)$$

$$\alpha + 6\beta C + 2\gamma(2 + C) - \lambda = 0 \quad (\Delta_2) \quad (IV.2)$$

$(p_c)$	$(p_a)$	$(t_{2g})$		
$D + 4E(1 + C) + 4FC - \lambda$	$2H + 2I(1 + C)$	$4i(K + L)S$	} = 0	(IV.3)
	$p + 4r(1 + C) + 4tC - \lambda$	$-2ivS$		
		$a + 4cC + 4e(1 + C) - \lambda$		

$(p_c)$	$(e_g)$	$(s_c)$	$(s_a)$	$(p_a)$		
$D + 8EC + 4F - \lambda$	$8iAS$	$-8iBS$	$2iGS$	$2HC + 4I$	} = 0	(IV.4)
	$\alpha + 2\beta(2 + C) + 6\gamma C - \lambda$	$4\delta(1 - C)$	$-2\epsilon(1 - C)$	$2i\xi S$		
		$\eta + 4\zeta \times (1 + 2C) - \lambda$	$2\rho(2 + C)$	$2i\sigma S$		
			$\kappa + 4I(1 + 2C) - \lambda$	$8imS$ $p + 8rC$ $+ 4t - \lambda$		(A <sub>1</sub> )

<sup>a</sup>  $k_x \equiv k$ ;  $k_y = k_z = 0$ ; Eq. (IV.3) is doubly degenerate;  $S \equiv \sin(ka/2)$ ;  $C \equiv \cos(ka/2)$

calculation of bands derived primarily from these cationic  $p$ -states. Moreover, it was found that with the 38 available input values of  $\lambda$  the system was not sufficiently overdetermined to permit reliable evaluation of the 36 distinct  $E$  parameters. We therefore elected to strike the first rows and columns from Eqs. (IV.3), (IV.4), (V.2)–(V.4), (VI.1), and (VI.2), for which the  $p_c$  orbitals serve as basis functions. The new determinants now comprise only the elements within the broken bars of Tables IV–VI. This restricts the analysis to the construction of  $s$ - and  $p$ -like bands of primarily anionic character and to  $s$ - and  $d$ -like bands of primarily cationic type. These 10 bands are characterized by 24 transfer integrals listed in parts (1) and (2) of Table VII.

The transfer integrals were determined by an optimization procedure developed by Marquardt (20). This method interpolates optimally between Taylor's series and the method of steepest descent. The numerical technique was employed to adjust the parameters in the truncated secular determinantal equations of Tables IV–VI, until an optimal fit was obtained for the eigenvalues

$A(\mathbf{k}, p_m)$  to the eigenvalues  $\lambda(\mathbf{k})$  cited by Ern and Switendick at the points  $T$ ,  $\Delta$ ,  $X$ ,  $L$ , and  $\Sigma$  in reciprocal space. In the above, the  $p_m$  represent new labels ( $m = 1, \dots, 24$ ) for the distinct transfer integrals in Table VII. These  $p_m$  were adjusted iteratively so as to minimize the quantity

$$\Phi \equiv \sum_b \sum_n [A_b(k_n; p_m) - \lambda_b(k_n)]^2 \quad (4)$$

The requisite eigenvalues were then determined by solving the subdeterminants of Table IV–VI using a procedure developed at MIT (21). The optimized  $p_m$  values are listed in Table VII.

Repeated tests showed that the numerical results were sensibly independent of the choice of initial values, as long as all  $E_{l_j l_j}(000)$  parameters were assigned initial values which in sign and magnitude corresponded to appropriate  $\lambda_b(0)$  values, and as long as the remaining parameters were assigned initial values in the range  $10^{-1} \geq p_m \geq 10^{-2} ry$ . Some of the end results were also checked independently by hand calculations as follows: numerical values for  $a$ ,  $c$ ,  $e$  were obtained from Eq. (IV.1) for the  $t_{2g}$

TABLE V

SECULAR DETERMINANTAL EQUATION FOR TiO ALONG THE  $\langle 110 \rangle$  DIRECTION IN RECIPROCAL SPACE<sup>a</sup>

$$a + 4cC + 4eC(1 + C) + 4gS^2 - \lambda = 0 \quad (\Sigma_2) \quad (V.1)$$

( $p_c$ )	( $p_a$ )	( $t_{2g}$ )	
$D + 8EC + 4FC^2 - \lambda$	$2H + 4IC$	$8iKS + 8iLSC$	= 0
	$p + 8rC$	$-4ivS$	
	$+ 4tC^2 - \lambda$	$2a + 8cC$	= 0
		$+ 8eC(1 + C)$	
		$- 8gS^2 - 2\lambda$	( $\Sigma_3$ )

( $p_c$ )	( $e_g$ )	( $p_a$ )	
$2D + 8EC(1 + C)$	$4\sqrt{3}iAS(1 + C)$	$4HC + 4I(1 + C)$	= 0
$+ 8FC + 8MS^2 - 2\lambda$	$- 4iNS(1 - C)$		
	$\alpha + 6\beta C$	$2\sqrt{3}i\xi S$	= 0
	$+ 4\gamma C(\frac{1}{2} + C) - \lambda$	$2p + 8rC(1 + C)$	
		$+ 8tC + 8zS^2 - 2\lambda$	( $\Sigma_4$ ) (V.3)

( $p_c$ )	( $s_c$ )	( $e_g$ )	( $t_{2g}$ )	( $p_a$ )	( $s_a$ )	
$2D + 8EC(1 + C)$	$- 8iBS(1 + C)$	$- 4iAS(1 + C)$	$8iKSC$	$4HC$	$4iGS$	= 0
$+ 8FC - 8MS^2$		$- 4\sqrt{3}iNS(1 - C)$	$+ 8iLS$	$+ 4I(1 + C)$		
$- 2\lambda$	$\eta + 4\zeta C(2 + C)$	$- 4\delta C(1 - C)$	$- 4\mu S^2$	$4i\sigma S$	$2\rho(1 + 2C)$	= 0
	$- \lambda$	$\alpha + 4\beta C(\frac{1}{2} + C)$	$- 4\tau S^2$	$- 2i\xi S$	$2\epsilon(1 - C)$	
		$+ 6\gamma C - \lambda$	$a + 4cC^2$	$4ivS$	$0$	= 0
			$+ 8eC - \lambda$	$2p + 8rC(1 + C)$	$- 8imS(1 + C)$	
				$+ 8tC - 8zS^2$	$- 2\lambda$	(V.4)
					$\kappa + 4tC(2 + C)$	= 0
					$- \lambda$	

<sup>a</sup>  $k_x = k_y \equiv k; k_z = 0; S \equiv \sin(ka/2); C \equiv \cos(ka/2)$ .

band along the  $\langle 100 \rangle$  direction;  $v$  was found for  $S = 1$  from Eq. (IV.3);  $p, r, t$  were calculated by combining (IV.3) with (IV.4). Similarly Eqs. (V.1) and (VI.1) were employed to determine  $\kappa$  and  $g$ . Attempts to determine  $\alpha, \beta$ , and  $\gamma$  through available  $\lambda$  values for Eq. (IV.2) led to redundancies. However on the provisional assumption that  $z = 0$ , it was possible to determine  $\alpha, \beta$ , and  $\gamma$  solely from Eqs. (V.3) and (VI.2). Comparison with the results provided in Table VII showed that the hand calculations, based on a very limited number of specified  $\lambda$ 's, agreed to within 10% with the machine calculations based on the entire set of available  $\lambda$  values. It is thus plausible

that the remaining 11 transfer integrals are also correctly determined.

### Numerical Results

Numerical results displayed in Table VII are listed in rydbergs and refer to a zero of energy at  $\epsilon_0 = -1.345$  ry relative to vacuum. The off-diagonal transfer integrals are independent of this choice since for orthogonal  $|l_j\rangle, \langle l'_j|H - \epsilon_0|l_j\rangle = \langle l'_j|H|l_j\rangle$ . The diagonal elements are all of the form  $\langle l_j|H - \lambda|l_j\rangle$ , which shows that the  $\langle l_j|H|l_j\rangle$  refer to the same  $\epsilon_0$  values as  $\lambda$  does.

For TiO, the transfer integrals range in absolute

TABLE VI  
 SECULAR DETERMINANTAL EQUATION FOR TiO ALONG THE  $\langle 111 \rangle$  DIRECTION IN RECIPROCAL SPACE<sup>a</sup>

$(p_c)$	$(s_c)$	$(t_{2g})$	$(p_a)$	$(s_a)$		
$3D + 24EC^2$ $+ 12FC^2 - 24MS^2$ $- 3\lambda$	$- 24iBSC$	$24iKSC$ $+ 24iLSC$	$6HC$ $+ 12IC$	$6iGS$	$\left. \begin{array}{l} \\ \\ \\ \\ \end{array} \right\} = 0$	
	$\eta + 12\zeta C^2$ $-\lambda$	$- 12\mu S^2$	$6i\sigma S$	$6\rho C$		$(\lambda_1)$
		$3a + 12cC^2$ $+ 24eC^2 - 24gS^2$ $- 3\lambda$	$12ivS$	$0$		$(VI.1)$
			$3p + 24rC^2$ $+ 12tC^2 - 24zS^2$ $- 3\lambda$	$- 24imSC$		
				$\kappa + 12IC^2$ $-\lambda$		
$(p_c)$	$(t_{2g})$	$(e_g)$	$(p_a)$			
$2D + 16EC^2$ $+ 8FC^2 + 8MS^2$ $- 2\lambda$	$- 8iKSC$ $- 8iLSC$	$8\sqrt{3}iASC$	$4HC + 8IC$		$\left. \begin{array}{l} \\ \\ \\ \\ \end{array} \right\} = 0$	
	$2a + 8cC^2$ $+ 16eC^2$ $+ 8gS^2 - 2\lambda$	$- 4\sqrt{3}\tau S^2$	$- 4ivS$			$(\lambda_3)$
		$\alpha + 6\beta C^2$ $+ 6\gamma C^2 - \lambda$	$2\sqrt{3}i\xi S$			$(VI.2)$
			$2p + 16rC^2$ $+ 8tC^2 + 8zS^2$ $- 2\lambda$			

<sup>a</sup>  $k_x = k_y = k_z \equiv k$ ; Eq. (VI.2) is doubly degenerate;  $S \equiv \sin(ka/2)$ ;  $C \equiv \cos(ka/2)$ .

value from 0.941 to 0.00168 *ry*. Relative to  $\epsilon_0 = -1.345$  *ry*, the integrals  $E_{i,j}(000)$  tend to exceed all others in magnitude. The absolute values of the  $\sigma$ -type and  $\pi$ -type integrals for cation-anion interactions tend to be comparable; they generally fall above the range of values encountered for  $\delta$ -type interactions, or for cation-cation or for anion-anion transfer integrals in which  $\langle 110 \rangle$ -type interactions are involved. These general conclusions are quite reasonable; however, the smaller numerical differences among members in each class are more difficult to interpret for two reasons: First, where the lobe of a rather diffuse wave function significantly overlaps with two lobes of opposite sign of another wave function, a cancellation effect may make the corresponding transfer integrals numerically smaller than a smaller degree of overlap would. Second, we are dealing with sets of orthogonalized atomic orbitals, which themselves are appropriate linear combinations of the true atomic

wave functions. The resulting delocalization is difficult to picture; the attempt to obtain detailed correlations between numerical values of the  $p_m$  and pictures based on atomic wave functions is thus problematical. This matter is discussed in more detail by Mattheiss (22).

The numerical values of the off-diagonal transfer integrals, relative to the differences in the values of diagonal elements they connect, furnish a rough measure of interaction between the two states. Two sets of calculations were carried out to obtain an indication of the extent of interaction. We first determined the dimensionless ratios  $|\langle l'_j | H | l_j \rangle| / |\langle l'_j | H | l'_j \rangle - \langle l_j | H | l_j \rangle|$  at the points  $T$ ,  $L$ ,  $A(1/2\ 00)$ , and  $\Sigma(1/2\ 1/2\ 0)$  for all off-diagonal elements. These ratios ranged in value from 0.071 to 0.66; they are not small enough to permit any of the off-diagonal elements to be neglected. As a second criterion we considered the ratio  $R_M \equiv |E_{l'_j l_j}(\mathbf{q}) S_{l'_j l_j}(\mathbf{q}, \mathbf{k})|^2 / |\lambda_{l'_j}(\mathbf{k}) - \lambda_{l_j}(\mathbf{k})|$  suggested by second order

TABLE VII

LISTING, NUMERICAL VALUES, AND DEFINITIONS FOR TRANSFER INTEGRALS

Designation	$p_m$	Energy (Rydbergs)	
1. Cation-cation interactions or anion-anion interactions not involving Ti 4 <i>p</i> states			
$E_{z_2z_2}(000)$	$\alpha$	0.888	
$E_{z_2z_2}(110)$	$\beta$	0.00168	
$E_{x_2-y_2,x_2-y_2}(110)$	$\gamma$	-0.0344	
$E_{s_2s_2}(110)$	$\delta$	0.0110	
$E_{s_2s_2}(000)$	$\eta$	0.749	
$E_{s_2s_2}(110)$	$\zeta$	-0.0206	
$E_{xy,xz}(110)$	$\tau$	-0.0113	
$E_{s_2s_2}(110)$	$\mu$	0.0175	
$E_{xy,xy}(000)$	$a$	0.643	
$E_{xy,xy}(110)$	$c$	-0.0537	
$E_{xy,xy}(011)$	$e$	0.0156	
$E_{xy,xz}(011)$	$g$	0.0145	
$E_{s_2s_2}(000)$	$\kappa$	-0.941	
$E_{s_2s_2}(110)$	$l$	0.00575	
$E_{s_2s_2}(110)$	$m$	0.0129	
$E_{x_2x_2}(000)$	$p$	0.107	
$E_{x_2x_2}(110)$	$r$	0.0134	
$E_{x_2x_2}(011)$	$t$	-0.0104	
$E_{x_2x_2}(110)$	$z$	0.00538	
2. Cation-anion interactions not involving Ti 4 <i>p</i> states			
$E_{z_2s_2}(001)$	$\epsilon$	0.0653	
$E_{z_2s_2}(001)$	$\xi$	-0.108	
$E_{s_2s_2}(100)$	$\rho$	-0.0941	
$E_{s_2s_2}(100)$	$\sigma$	-0.0764	
$E_{xy,x_2}(010)$	$v$	-0.0745	
3. Interactions involving Ti 4 <i>p</i> states			
$E_{x_2z_2}(011)$	$A$	$E_{x_2x_2}(100)$	$H$
$E_{s_2s_2}(110)$	$B$	$E_{y_2y_2}(100)$	$I$
$E_{x_2x_2}(000)$	$D$	$E_{x_2,xy}(110)$	$K$
$E_{x_2x_2}(110)$	$E$	$E_{x_2,xy}(011)$	$L$
$E_{x_2x_2}(011)$	$F$	$E_{x_2y_2}(110)$	$M$
$E_{x_2s_2}(100)$	$G$	$E_{z_2,x_2-y_2}(011)$	$N$

perturbation theory. To obtain approximate values of this ratio we substituted for the  $\lambda$ 's the values at  $\mathbf{k} = 0$  ( $\Gamma$  point in reciprocal space), and for the  $S$ 's, the maximum possible values of the structure factors. Examination shows that in all but two cases this ratio remained in the range  $0.336 \geq R_M \geq 0.0113$ ; we verified that one may not neglect any of the listed off-diagonal elements, except possibly  $\tau$  and  $\mu$ , for which  $R_M$  lies in the

$10^{-3} \geq R_M \geq 10^{-4}$  range. Spot checks also revealed that it is not generally permissible to use second order perturbation theory for approximate diagonalization of the secular determinants. For, we are attempting not just to duplicate specific eigenvalues, but also to reproduce reasonably accurately the more delicate variations of  $\lambda$  with  $k$  within a given band.

Using the optimized transfer integrals shown in Table VII, the band structure of TiO was now calculated from the secular determinantal equations of Tables IV-VI along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  directions. Results are depicted in Fig. 1 and are labeled in the standard group theoretic notation.

Comparison with the original APW calculation by Ern and Switendick shows generally satisfactory agreement. There are two sets of differences that are noteworthy: The uppermost  $\lambda_1$  and  $\Delta_1$  curves for the  $\langle 111 \rangle$  and  $\langle 100 \rangle$  directions in Fig. 1 terminate at points labeled  $L_2'$  and  $X_1$ , respectively; whereas in Ern and Switendick's numerical work these two termini were found to have the symmetry  $L_1$  and  $X_4'$  corresponding to atomic Ti 4*p* states. The discrepancy arises because of our deliberate neglect of the 4*p* wave functions. Second, in regions enclosed by rectangular frames A and B, the energy bands differ significantly from those determined numerically in Ref. (13); the latter are indicated by broken lines. For region B the difference is in all probability attributable to our neglect of the Ti 4*p* wave functions. For region A deviations from the APW calculations are not understood but will be important because of the proximity of the Fermi level. Predictions of transport properties based on the APW and the present energy band structure schemes are thus likely to differ, and probably cannot be brought into better accord, unless one were to reduce the number of drastic approximations in the tight-binding approach. Since the results were fitted to the calculations by Ern and Switendick it comes as no surprise that the two sets of band structures are quite similar, except as noted. By the same token, as was implicit in the work of Ern and Switendick but is more clearly brought out in Table VII, the conclusions differ significantly, even in the qualitative sense from earlier results (23-26) based on much cruder models and methods of approach. In particular, two earlier viewpoints seem untenable: At least for the case of TiO it is not possible to break down the general  $10 \times 10$  secular determinantal equation into smaller subunits: on the basis of the criteria set



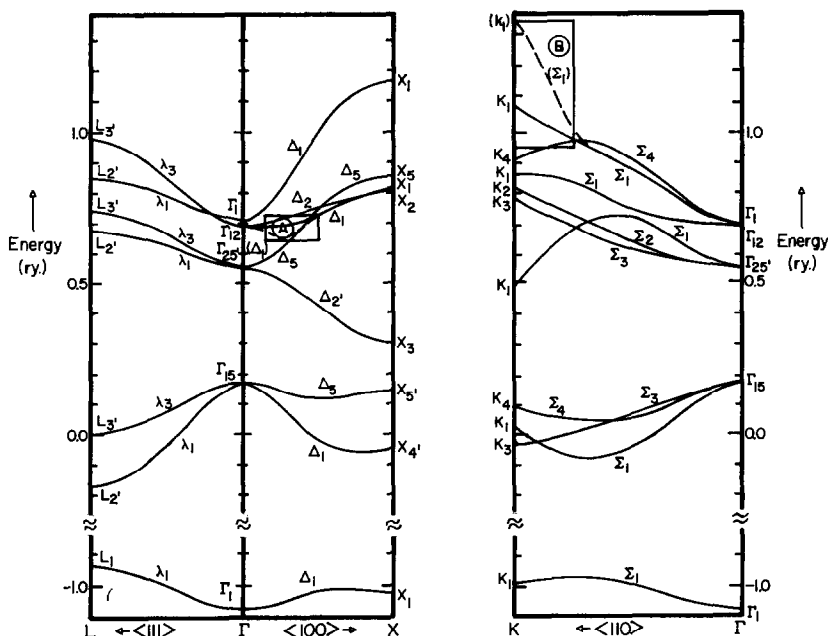


FIG. 1. Band structure of TiO as determined by the tight-binding approximation; parameters optimized for best fit to numerical data cited in Ref. (13).

forth earlier, all off-diagonal elements are too large to permit such a step to be taken. In particular, it is necessary to regard the next-nearest neighbor cation-cation or anion-anion interactions as being competitive with the nearest neighbor cation-anion bonding. Both sets are required for a proper account of the band structures depicted in Fig. 1. Second, it is clearly not permissible to describe the band structure in terms of "d-bands" in this oxide: it is true that bands originating from the point  $\Gamma_{25'}$  belong to the  $t_{2g}$  representation at  $\mathbf{k} = 0$ ; moreover, as is shown in Tables IV-VI, the  $\Gamma_{25'} - \Delta_2 - X_3$  and  $\Gamma_{25'} - \Sigma_2 - K_2$  branches do retain this  $t_{2g}$  identity along the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  directions respectively. However, the others are mixed with  $p_c, s_c,$  or  $e_g$  orbitals; also, along general directions of reciprocal space the  $t_{2g}$  (d-type) band becomes inextricably mixed with other types of orbitals of compatible symmetry.

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