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Energy Bands of VO[†]

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A tight-binding calculation of the energy bands of VO has been performed for several different atomic configurations using all the valence and core orbitals from vanadium and oxygen as bases. All tight-binding integrals are accurately evaluated and all sums carried to convergence. Energy bands are found to be sensitive to the particular core states included and to the degree of ionicity assumed. Results for the band structure indicate that *d* bands are about 7 eV wide, lying below the vanadium 4*s* band, so that conductivity in VO is attributed primarily to *d* electrons. The Fermi energy falls in the *d* bands at a large peak in the density of states.

I. INTRODUCTION

We report in this paper a calculation of the electronic energy bands in VO, a transition-metal compound with the NaCl crystal structure. The purpose of the calculation was twofold: first, to make a full scale application of the tight-binding method to a transition-metal compound, and second, to make an investigation into the nature of the energy bands of perfect crystals of VO.

Transition-metal compounds in general, and transition-metal oxides especially, have received considerable attention in the past few years. The wide range of electric, magnetic, and optical properties exhibited by these compounds offers a real challenge to the energy-band theory, which often fails outright in its simplest form. An excellent review of the current understanding of these compounds has been given by Adler.[1]

Some oxides of transition metals are metallic, such as TiO and VO. Others are insulators, such as NiO and CoO, while some higher oxides of titanium and vanadium undergo metal-to-insulator transitions at some critical temperature. Yet most of these compounds are predicted to be metals from the point of view of simple band theory, since they are expected to have partially filled *d* bands. Generally one might expect the *d* bands to narrow considerably as they are filled in moving across the Periodic Table in the transition series, and a completely localized model might be more appropriate to the latter elements in the series, especially when forming compounds. Conversely, the early elements in the series exhibit several valence states when forming compounds and often crystalize with large amounts of defects. They also seem to have larger bandwidths and perhaps lie closer to the band limit. VO belongs to this class and for this reason, in addition to its structural simplicity, was chosen for this study.

II. THEORETICAL SITUATION

Until the last five or six years the theory of transition-metal compounds has been left to quantum chemists, who use crystal-field theory and ligand-field or molecular-orbital theory to describe *d* electrons in solids.[2] The extent to which *d* electrons in transition-metal compounds may be treated as completely localized or completely bandlike is not yet clear, but examples of compounds may be found which seem to illustrate both limits. It thus seems worthwhile to test the methods of band theory more fully. This has not been done in the past because of calculational difficulties. All of these compounds have at least two different atoms (one molecule) in a unit cell, and many have more. Although a number have the NaCl structure, many have lower symmetries, and the methods of group theory are not so fruitful. In addition, there are magnetic properties for which some account must be made. Most band theoretical investigations which have been done to date concentrated on the NaCl-type compounds or on compounds which are metallic and give some hope in advance that band theory will yield reasonable results.

Two methods of energy-band theory have been used for determining energy bands in transition-metal compounds: the augmented-plane-wave (APW) method[3] and the tight-binding or linear-combination-of-atomic-orbitals (LCAO) method.[4] Both of these methods are suitable for narrow *d* bands found in transition-metal compounds, but the latter had been used primarily as an interpolation or empirical scheme until the work of Lafon and Lin[5] established it as an accurate quantitative method when properly applied. While the APW and LCAO methods have their own special advantages and disadvantages, the application of either in the usual way is not adequate for the transition-metal compounds.

A number of band calculations have been completed for transition-metal compounds with the NaCl structure using these two methods. The metals TiC, TiN, and TiO have been studied with detailed APW calculations[6] and also[7,8] with the Slater-Koster form[9] of the LCAO method. Yamashita[10] performed modified tight-binding calculations for TiO, and Schoen and Denker have used an APW virtual-crystal approximation[11] to study properties of both perfect crystal and defective TiO.[12] NiO and αMnS have also been examined theoretically by LCAO calculations, the former by Yamashita[10] and the latter by Bartling,[13] but without success in either case. Switendick[14] performed a paramagnetic APW calculation for NiO and proposed model antiferromagnetic bands to account for the insulating behavior. Recently, Wilson has made spin-polarized APW calculations for the magnetic insulators NiO, MnO, and αMnS.[15]

A few studies have been made for transition-metal compounds with other crystal structures. The most complete calculation was done by Mattheiss[16] for ReO_3 (which is a good metal) using the APW and Slater-Koster methods to obtain detailed agreement with both optical and Fermi-surface data. The LCAO formalism was also worked out for ReO_3 by Honig *et al.*[17] who pointed out the connection with molecular-orbital theory, but performed no numerical calculations. Kahn and Leyendecker[18] estimated the band structure of semiconducting $SrTiO_3$ (perovskite structure) using the Slater-Koster method, and Tyler and Fry[19] have used the LCAO method to obtain energy bands of metallic NiS (hexagonal NiAs structure). Finally, Nebenzahl and Weger[20] have attempted to understand the metal-to-insulator transition (corundum-to-monoclinic structure change) in V_2O_3 in terms of a model tight-binding energy-band calculation.

Although most of the band calculations mentioned above are either incomplete, inaccurate, or simply wrong, at least the APW calculations are accurate to within the approximations necessitated by the APW method, since that method has been thoroughly studied by many investigators for a number of years. This is not true of the tight-binding method, and, since it has certain inherent advantages over other methods, we have made it our purpose in this calculation to test a more rigorous application of the tight-binding method to a transition-metal compound, and in the process obtain energy band information for perfect VO.

III. EXPERIMENTAL INFORMATION FOR VO

VO has the NaCl structure at room temperature, but little else seems certain about it. The experimental situation is confusing at present because of conflicting reports of properties of "pure" VO. For example, as noted by Adler,[1] the conductivities reported for VO at 100 °K by Kawano *et al.*[21] differ from the conductivity measured by Austin[22] at the same temperature by a factor of 10^9. Stoichiometric VO is defective with a large percentage of vacancies (about 15%) on both cation and anion sublattices, and, in fact, exactly stoichiometric VO may be difficult to obtain since compositions in a wide range from $VO_{0.89}$ to $VO_{1.20}$ are stable.[23] Properties of VO appear to vary rapidly with changing stoichiometry, and conflicting reports may be due to inaccurate estimates of stiochiometry for the samples used, or even due to different sample preparation techniques. Some investigations have suggested that VO consists of mixed phases, either alternating regions of V_2O_3 and pure vanadium,[24] or at low temperatures a mixture of body-centered tetragonal V_3O[25] and a bcc[26] or body-centered tetragonal phase[23] of V_3O_4; others[27] dispute existence of these mixed phases. There are very striking similarities between properties of VO and V_2O_3 which make one speculate that some of the measurements reported for VO may be due to samples containing V_2O_3, perhaps in filamentary form.

Conductivity measurements made on VO[28] and $VO_{0.9}$[22] show sharp metal-to-semiconductor transitions with a jump in conductivity by a factor of 10^6, but magnetic susceptibility measurements[21] on VO_x showed an antiferromagnetic transition for samples with $x = 1.14$ and 1.25 (at 4.6 and 7 °K) but not for $x = 0.9$, 0.97, or 1.06. Conductivity measurements gave no indication of a semiconductor-to-metal transition for any of the samples: They were all semiconducting at the temperatures observed. Later, Warren *et al.*[29] reported a discontinuity of 10^4 in conductivity of VO at about the same temperature as the transition reported by Morin[28] (125 °K). Current reports[30] maintain that there is no metal-to-semiconductor transition for stoichiometric VO.

Additional experimental information is discussed by Adler[1] and Stringer.[31] In this paper, the only experimental information which we have relied upon is the lattice constant of VO in the NaCl phase, which we take to be 4.062 Å, and the fact that VO shows metallic conductivity above 125 °K.

IV. DETAILS OF CALCULATION

A. Method

In this band calculation we have used a version of the tight-binding method which is due to Lafon and Lin.[5] This version has been shown to be an accurate method of band calculation even for a good metal, lithium, provided that (a) all integrals, including three-center ones, be accurately evaluated, and (b) all sums over neighbors be carried to convergence. Usefulness of the method depends upon the ability to evaluate three-center integrals and perform sums over neighbors efficiently. If analytic atomic wave functions in the form of Slater-type orbitals are used, it is possible to do three-center integrals by a technique of Gaussian transformation if a Fourier series expression for the crystal potential is used.

We have extended the method of Lafon and Lin to treat *d* electrons and obtained energy bands for nickel[32] and nickel sulfide.[19] Three-center integral formulas and lattice sums for *d* electrons are described in Ref. 32, while application of the method to transition-metal compounds is discussed adequately in Ref. 19, so the reader is directed to those papers for details of the method. For reference in this paper we present only the basic formulas of the tight-binding method.

For a lattice with a basis, the tight-binding basis functions are given by the Bloch sum

$$b_{nlm}(\vec{k},\vec{r},\vec{\tau}_i)=(1/\sqrt{N})\sum_\nu e^{i\vec{k}\cdot(\vec{R}_\nu+\vec{\tau}_i)} \times \psi_{nlm}(\vec{r}-\vec{R}_\nu-\vec{\tau}_i)\ , \tag{1}$$

where N is the number of sites in the crystal and the summation is carried out over all N of these sites $\vec{R}_\nu$. $\vec{\tau}_i$ is the position in the cell at the origin of the ith type of atom with electronic wave function ψ_{nlm}, where nlm are the usual atomic quantum numbers. It is convenient to form linear combinations of these ψ_{nlm} which have special transformation properties under the group of the wave vector $\vec{k}$ before performing the Bloch sum in Eq. (1). Energy bands are obtained by taking matrix elements of the one-electron Hamiltonian between these functions and solving the secular equation

$$|H_{ij}(\vec{k})-ES_{ij}(\vec{k})|=0\ , \tag{2}$$

where i stands for the labels nlm and $\vec{\tau}_i$ and

$$H=-\nabla^2+V(\vec{r})\ .$$

The overlap, kinetic-energy, and potential-energy matrix elements are given by

$$\begin{aligned} S_{ij}(\vec{k})&=e^{i\vec{k}\cdot(\vec{\tau}_j-\vec{\tau}_i)}\sum_\nu e^{i\vec{k}\cdot\vec{R}_\nu} \times\langle\psi_{nlm}(\vec{\tau}_i)|\psi_{n'l'm'}(\vec{R}_\nu+\vec{\tau}_j)\rangle\ ,\\ T_{ij}(\vec{k})&=e^{i\vec{k}\cdot(\vec{\tau}_j-\vec{\tau}_i)}\sum_\nu e^{i\vec{k}\cdot\vec{R}_\nu} \times\langle\psi_{nlm}(\vec{\tau}_i)|-\nabla^2|\psi_{n'l'm'}(\vec{R}_\nu+\vec{\tau}_j)\rangle,\\ V_{ij}(\vec{k})&=e^{i\vec{k}\cdot(\vec{\tau}_j-\vec{\tau}_i)}\sum_\nu e^{i\vec{k}\cdot\vec{R}_\nu} \times\langle\psi_{nlm}(\vec{\tau}_i)|V(\vec{r})|\psi_{n'l'm'}(\vec{R}_\nu+\vec{\tau}_j)\rangle\ . \end{aligned} \tag{3}$$

B. Crystal Potential

While VO does not seem to exhibit the high conductivity of ReO_3, possibly because of defect-limited conductivity, it has been reported to show metallic conductivity comparable with TiO. If VO were a good metal, we would expect a neutral-atom crystal potential, such as the one used for ReO_3,[16] to be appropriate. It is likely that there will be some degree of ionicity, but we believe the correct configuration for VO is closer to the neutral-atom configuration than to the doubly ionized one. We performed our first calculations for VO using a neutral atom configuration, but later obtained energy bands for several other configurations, which will be discussed in Sec. V of this paper. In this section we focus our attention on the neutral configuration which we believe to be more nearly correct.

The same method of constructing the crystal potential has been used for all configurations: The potential is constructed as a linear combination of atomic potentials. Since we need only Fourier coefficients of the crystal potential to obtain three-center integrals, we do not encounter difficulties with the Madelung potential in the ionic configurations.[19] For the doubly ionized configuration, the atomic potentials are spherically symmetric, but even for the neutral case we use a spherically averaged atomic potential, which greatly simplifies calculation of Fourier coefficients. Atomic potentials were constructed using analytic atomic wave functions given by Clementi[33] for vanadium ($3d^34s^2$) and oxygen ($2p^4$). Since wave functions for the ions were not available ($O^=$ does not even exist in free-ion form), these same wave functions were used for all configurations both to construct ionic potentials by arbitrarily changing occupation numbers and to construct tight-binding basis functions. This fact must be kept in mind when considering results of band calculations presented in Sec. V. With Clementi's analytic atomic wave functions it is possible to obtain analytic expressions for the Fourier coefficients of the crystal potential,[32] which is a major simplification, especially for spherically symmetric atomic potentials.

Exchange has been treated by a local potential approximation, Slater's $\rho^{1/3}$ potential.[34] To use this approximation we obtained the crystalline charge density by summing contributions from the atomic charges and making a cubic harmonic expansion of $\rho^{1/3}$. In practice we retained only the spherical term in the expansion and obtained Fourier coefficients of the exchange potential by treating it as a muffin-tin potential with muffin-tin radii chosen as half the nearest-neighbor distance. An adjustable parameter λ was introduced when constructing matrix elements.

C. Basis Functions

In constructing the tight-binding basis functions given by Eq. (1) we have used the atomic wave functions from a calculation given by Clementi[33] for vanadium ($3d^3 4s^2$) and oxygen ($2p^4$). The full set of Slater-type-orbital (STO) basis functions used for the atomic variational calculations were used in the expansion of atomic wave functions for this calculation. An earlier study[5] used only a limited STO basis set and adjusted parameters variationally. In this calculation we initially tried linear combinations of these STO basis functions to represent only vanadium $3d$ and $4s$ and oxygen $2p$ orbitals and obtained matrix elements for Eq. (2) accordingly. Results presented below prompted us to include the entire valence and core orbitals of vanadium ($1s$, $2s$, $3s$, $4s$, $2p$, $3p$, $3d$) and oxygen ($1s$, $2s$, $2p$). In principle we could use the entire STO basis set of Clementi for the tight-binding calculation instead of these linear combinations to obtain better results at the expense of a larger determinant. Probably the addition of plane-wave basis states would be a better investment.

D. Integrals

Since this tight-binding calculation is more rigorous than other ones which have been attempted for transition-metal compounds, we believe it worthwhile to present some of the results for integrals used in the matrix elements. These are useful as guidelines for estimating integrals in other transition-metal compounds.

The crystal potential $V(\vec{r})$ appearing in Eq. (3) is expressed as a Fourier series in the reciprocal lattice, so there are in fact two sums which must be done for potential-energy matrix elements. Both of the sums were carried to enough terms to yield at least 0.01-Ry accuracy in the energy bands. For some basis functions this required summing a large number of terms. The sum on the reciprocal-lattice vectors was carried to 28 neighbors for p and d functions and 53 neighbors for s functions. For deep core functions, convergence of the reciprocal sum was poor, especially for the crystal-field integrals, which occur when the two orbitals in the integral are at the same site. In this case a straightforward summing of the Fourier series was not feasible for the deep core functions, and it was necessary to replace crystal-field integrals by the atomic Hartree-Fock energies. Since there is almost no overlap between these deep core states, we estimate that this introduces negligible errors.[35]

TABLE I. Crystal-field integrals for neutral VO potential. Energies measured in Rydbergs.

	Hartree-Fock atomic energy (Ry)	Potential +KE (Ry)	Exchange (Ry)
$1s$-$1s$(V)	−403.004		
$2s$-$2s$(V)	−47.7485		
$3s$-$3s$(V)	−6.36626		
$2p_x$-$2p_x$(V)	−40.0441		
$1s$-$1s$(O)	−41.3864		
$3p_x$-$3px$(V)		−0.66111	−3.0408
$3d_{xy}$-$3d_{xy}$(V)		1.9921	−2.38687
$3d_{x^2-y^2}$-$3d_{x^2-y^2}$(V)		1.9340	−2.4687
$4s$-$4s$(V)		−0.73614	−0.85674
$2s$-$2s$(O)		−0.45890	−1.940
$2p_x$-$2p_x$(O)		−0.3096	

In Tables I–IV we present some of the tight-binding integrals for a neutral atom crystal potential with configuration V($3d^4 4s^1$) and O($2p^4$), which is not the configuration for which our atomic basis functions were generated, but is what we believe to more accurately reflect the solid-state configuration (cf. nickel potential of Ref. 32). Table I lists the crystal-field integrals used for all the basis functions in this calculation. Table II lists vanadium $3d$-$3d$ integrals out to fourth neighbors in the direct lattice, Table III gives oxygen $2p$-$2p$ integrals to fourth neighbors, and Table IV shows vanadium $4s$-$4s$ integrals out to 32 neighbors. In each of these tables only the independent integrals are listed. Others may be obtained by applying operations of the cubic group.[32] All direct lattice sums in this calculation were carried to at least eight neighbors, although it was necessary to include the first 32 neighbors for $4s$-$4s$ matrix elements. The four neighbors shown in Tables II and III are adequate for an accuracy of about 0.01 Ry in energy eigenvalues.

E. Core Effects

Energy bands were first obtained for d basis functions only, using the neutral atom potential described above with exchange parameter $\lambda = 1$, with results shown in Fig. 1(a), which are typical of fcc d bands except that the bandwidth is rather large, 9.7 eV. When vanadium $4s$ and oxygen $2p$ orbitals were included, energy bands shown in Fig. 1(b) were obtained. The vanadium $4s$ Δ_1 band starts at −2.14 Ry, would rise through the d bands, were it not for hybridization, to a maximum along the Δ axis, and falls back to −2.37 Ry at the point X. The level labeled X_1, which appears in Fig. 1(b) is primarily d-like, and the $2p$ bands lie below at −1.59 Ry with a width of about 1 eV. In view of this unusual s-band behavior, we decided

TABLE II. Three-center integrals of the type $3d$-$3d$ on vanadium. Energies measured in Rydbergs.

Integral	Neighbor	Potential + KE (Ry)	Exchange (Ry)	Overlap
xy, xy	110	−0.013 533	−0.018 263	0.028 805
xz, xz	110	0.014 814	0.005 532 2	−0.110 41
yz, xz	110	0.022 171	0.010 374	−0.017 641
x^2-y^2, x^2-y^2	110	0.054 771	0.032 921	−0.286 83
$3z^2-r^2, 3z^2-r^2$	110	−0.014 825	−0.145 72	0.140 01
$xy, 2z^2-r^2$	110	0.005 007 3	0.010 396	−0.128 20
xy, xy	002	0.000 858 7	−0.000 416 4	0.000 762 8
xz, xz	002	0.056 684	0.003 528 8	−0.004 765 3
x^2-y^2, x^2-y^2	002	−0.001 650 0	−0.000 825 2	0.762 83
$3z^2-r^2, 3z^2-r^2$	002	−0.016 694	−0.011 154	0.008 686 7
xy, xy	112	−0.000 164 3	−0.000 027 4	0.000 070 08
xz, xz	112	−0.000 631 4	−0.000 264 6	0.000 494 7
xy, xz	112	−0.000 309 1	−0.000 156 9	0.000 283 1
yz, xz	112	−0.001 814 3	−0.000 951 8	0.001 231 4
x^2-y^2, x^2-y^2	112	0.000 536 5	0.000 337 4	−0.000 293 2
$3z^2-r^2, 3z^2-r^2$	112	−0.000 044 5	0.000 112 0	−0.000 090 4
$xy, 3z^2-r^2$	112	−0.001 337 9	−0.000 881 0	0.000 885 3
$yz, 3z^2-r^2$	112	−0.001 607 6	−0.000 991 1	0.001 002 4
$xz, 3z^2-r^2$	112	0.000 776 2	0.000 462 8	−0.000 443 5
xy, xy	220	−0.001 514 9	−0.000 672 7	0.000 745 3
xz, xz	220	0.000 122 8	0.000 107 9	−0.000 157 7
yz, xz	220	0.000 193 5	0.000 138 8	−0.000 195 8
x^2-y^2, x^2-y^2	220	0.000 443 9	0.000 349 8	−0.000 353 5
$3z^2-r^2, 3z^2-r^2$	220	−0.000 625 8	−0.000 307 0	0.000 273 8
$xy, 3z^2-r^2$	220	0.000 919 4	0.000 442 8	−0.000 408 3

it was necessary to add additional core functions to the basis, since it appeared that the $4s$ level was converging to one of the core levels. Figure 2 shows the result of adding all core orbitals except for oxygen $1s$ and $2s$. Now the $4s$-X_1 level lies well above the Fermi energy and d bands, and s-d hybridization similar to that found in nickel is observed. Vanadium-vanadium interactions have a pronounced effect at the point X, but not Γ. Finally we included the full core of both vanadium and oxygen and discovered that the $4s$ Δ_1 band was lifted completely above the d bands by interaction with the core levels. The largest effect of oxygen s levels on the vanadium $4s$ band occurs at Γ, with only a small shift occurring at X just enough to remove the dip visible in the highest Δ_1 band near X in Fig. 2. The d bands now lie in a gap between the vanadium $4s$ and oxygen $2p$ bands, as shown in Fig. 3.

The effects of core functions which have been demonstrated in Figs. 1–3 are quite large, indeed, much larger than might have been anticipated. Not even the relative positions of VO bands are given correctly without including at least the vana-

TABLE III. Three-center integrals of the type $2p$-$2p$ on oxygen. Energies measured in Rydbergs.

Integral	Neighbor	Potential + KE (Ry)	Exchange (Ry)	Overlap
$2p_x\,2p_x$	110	0.020 731	0.015 933	−0.020 321
$2p_z\,2p_z$	110	−0.017 555	−0.009 218 5	0.012 889
$2p_y\,2p_x$	110	0.051 565	0.031 263	−0.033 211
$2p_x\,2p_x$	002	−0.002 572 8	−0.001 236 7	0.001 551 7
$2p_z\,2p_z$	002	0.019 164	0.011 193	−0.009 561 5
$2p_x\,2p_x$	112	−0.000 169 94	0.000 080 54	−0.000 140 3
$2p_z\,2p_z$	112	0.001 639 7	0.001 346 2	−0.001 500 2
$2p_y\,2p_x$	112	0.000 460 09	0.000 371 8	−0.000 453 3
$2p_y\,2p_z$	112	0.001 028 6	0.000 759 8	−0.000 906 6
$2p_x\,2p_x$	220	0.000 302 85	0.000 295 8	−0.000 327 5
$2p_z\,2p_z$	220	−0.000 153 90	−0.000 064 15	0.000 081 74
$2p_y\,2p_x$	220	0.000 514 99	0.000 383 6	−0.000 409 3

TABLE IV. Three-center integrals of the type 4s-4s on vanadium.

Neighbor	Potential + KE (Ry)	Exchange (Ry)	Overlap
110	−0.520 91	−0.335 17	0.455 95
002	−0.334 92	−0.193 96	0.233 05
112	−0.192 70	−0.104 88	0.122 11
220	−0.112 10	−0.058 653	0.066 344
310	−0.064 740	−0.033 453	0.037 266
222	−0.038 270	−0.019 375	0.021 560
321	−0.023 260	−0.011 616	0.012 807
004	−0.014 292	−0.007 080 3	0.007 789 7
114	−0.008 959 8	−0.004 402 8	0.004 841 2
330	−0.009 009 4	−0.004 413 6	0.004 841 2
420	−0.005 723 6	−0.002 803 3	0.003 068 5
332	−0.003 713 5	−0.001 807 8	0.001 980 4
224	−0.002 447 5	−0.001 186 9	0.001 299 5
431	−0.001 639 9	−0.000 792 8	0.000 865 9
510	−0.001 638 1	−0.000 793 5	0.000 865 9
521	−0.000 762 3	−0.000 367 5	0.000 400 8
440	−0.000 529 8	−0.000 254 6	0.000 277 8
334	−0.000 371 3	−0.000 178 4	0.000 194 7
530	−0.000 371 7	−0.000 178 6	0.000 194 7
442	−0.000 263 5	−0.000 126 5	0.000 137 9
006	−0.000 263 2	−0.000 126 5	0.000 137 9
532	−0.000 188 8	−0.000 090 5	0.000 098 6
116	−0.000 188 4	−0.000 090 5	0.000 098 6
026	−0.000 136 2	−0.000 065 3	0.000 071 2
541	−0.000 099 3	−0.000 047 6	0.000 051 8
226	−0.000 072 7	−0.000 034 9	0.000 038 0
631	−0.000 053 8	−0.000 025 8	0.000 028 0
444	−0.000 040 0	−0.000 019 2	0.000 020 9
710	−0.000 030 0	−0.000 014 4	0.000 015 6
543	−0.000 030 0	−0.000 014 3	0.000 015 6
550	−0.000 030 0	−0.000 014 3	0.000 015 6
640	−0.000 022 6	−0.000 010 8	0.000 011 8

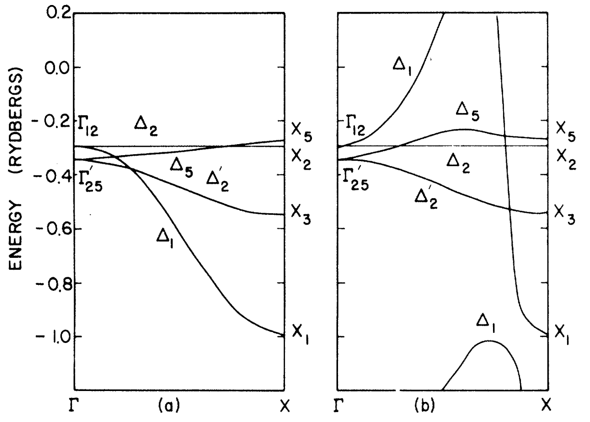

FIG. 1. (a) 3d energy bands for VO using neutral atoms and including only d basis functions. (b) Same as (a), but including 4s vanadium and 2p oxygen basis functions. Although 4s and 3$d\,\Delta_1$ bands mix, the lower one is primarily 4s.

dium 3s and oxygen 2s core basis functions, and an accurate calculation must include most of the core. The only alternative is to orthogonalize to the core states of the crystal Hamiltonian. But these states must also be accurately known or convergence difficulties may still occur, and even if they are known, an orthogonalized tight-binding function cannot be handled by the procedures used here. We conclude that core states must either be included in the variational calculation or be handled with great caution in transition-metal compounds. This behavior is probably not limited to transition-metal compounds, although it may be more pronounced there because of presence of d bands. We believe that convergence difficulties encountered in the application of the combined tight-binding and orthogonalized-plane-wave method used in alkali halides can be traced to inadequate treatment of the tight-binding portion of the calculation, both valence and core parts.[36]

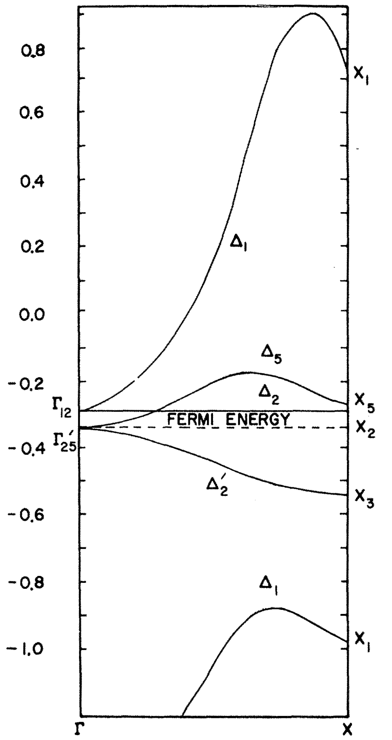

FIG. 2. Same as Fig. 1, but now including all core and valence basis functions except 1*s* and 2*s* oxygen. Energy is measured in Rydbergs.

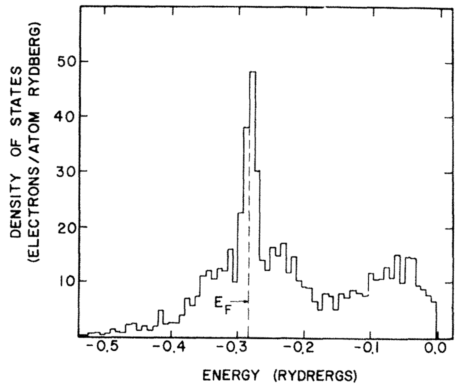

FIG. 4. Density of states for VO energy bands of Fig. 3.

V. ENERGY BANDS

A. Neutral Configurations

Energy bands obtained from the neutral-atom configuration $V(3d^4 4s^1)$ and $O(2p^4)$ using all core and valence electrons from both vanadium and oxygen are given in Fig. 3. The exchange potential described above was used with the parameter $\lambda = 1$, corresponding to the usual Slater exchange. A value of $\lambda = 0.85$ was also tried, but discarded when it gave a positive Fermi energy. Only bands in the vicinity of the Fermi energy, −0.283 Ry, are shown in Fig. 3. These arise primarily from the 3*d* levels of vanadium. For example, at the maximum of the Δ_1 band the wave function is 30% *s* and 10% *p*, the rest being 3*d*; at the maximum of the Δ_5 band the wave function is about 15% *p* and 85% 3*d*. A band arising from the 4*s* level of vanadium appears in the vicinity of Γ but quickly rises above the 3*d* bands. The oxygen 2*p* band lies at −1.56 Ry at Γ and has a width of about 2.6 eV. The maximum width of the *d* bands is about 7.3 eV, the minimum occurring at X_3 and the maximum halfway along the upper Q_1 band between *W* and *L*. Since energy bands along the Δ axis lie substantially lower than those along other symmetry axes, the Fermi level lies above both Γ_{12} and Γ'_{25}, although there are only three 3*d* electrons per cation according to this calculation. The Fermi surface is seen to be fairly complicated.

The density of states for energy bands shown in Fig. 4 was calculated using a sample of 505 points in $\frac{1}{48}$ of the Brillouin zone and an energy grid of 0.008 Ry. The broad peak at higher energies corresponds to the 4*s* band, which begins

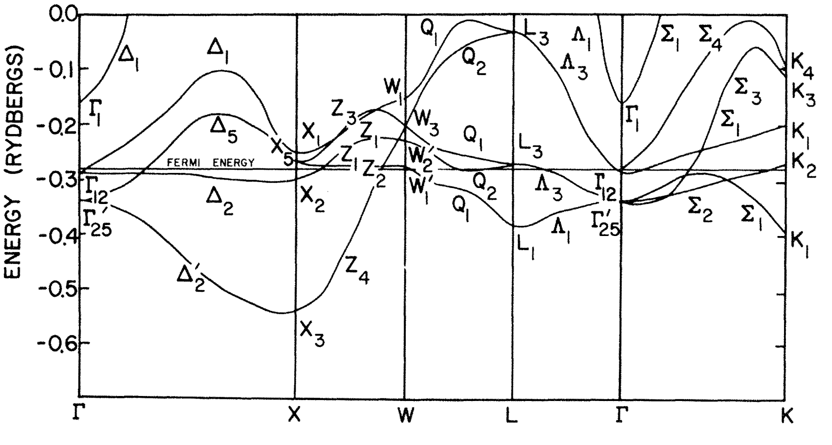

FIG. 3. Energy bands of VO using a neutral atom potential and all valence and core orbitals.

about -0.16 Ry. The sharp peak occurring at the Fermi energy may easily be traced to the very flat Δ_2 and Z_2 bands, which seem to be characteristic of fcc $3d$ transition metals or transition-metal compounds. A strong peak occurring in the density of states at the Fermi energy suggests that this paramagnetic band structure may satisfy a criterion for ferromagnetism.[37] On the other hand, with slightly more crystal-field splitting of the Γ_{12} and Γ'_{15} levels this density of states would exhibit two strong peaks with the Fermi energy falling in a minimum between them, in which case antiferromagnetism might be favored.[38]

We have also computed the band structure for another neutral configuration $\mathrm{V}(3d^3 4s^2)\,\mathrm{O}(2p^4)$, which is the one belonging to our basis functions. The Fermi energy in this case was -1.15 Ry, which was slightly above the d levels at Γ. The order of all d levels remained the same throughout the zone, and the $4s$ band appeared at the same energy as in the previous calculation, so that s and d levels were more separated.

For both neutral configuration potentials the apparent configuration obtained after the calculation for the solid was $\mathrm{V}(3d^3 4s^0)\,\mathrm{O}(2p^6)$, which corresponds to doubly ionized atoms. We therefore decided to recompute the band structure with ionized atoms.

B. Ionic Configurations

When computing three-center integrals with the Fourier series expression for the crystal potential we stored all integrals of $e^{(i\vec{k}_n \cdot \vec{r})}$ on magnetic tape for future use in a self-consistent calculation. If basis functions are kept the same at each step in a self-consistent calculation, only the Fourier coefficients of the crystal potential need be recalculated. The basic integrals are computed only once (a very time consuming process) and summed with the new Fourier coefficients each time. Although we have not yet developed computer routines for an iterative self-consistent procedure, we have been able to generate band structures rapidly for several different starting configurations in this way. Thus, using the same basis functions as for the neutral atom, we have computed band structures based on doubly ionized and partially ionized configurations.

Energy bands for the doubly ionized configuration are shown in Fig. 5 along the Δ and Z axes. The characteristically flat Δ_2 and Z_2 bands are present, but the $2p$ bands now fall *above*[39] the $3d$ bands, while the $4s$ band is well out of the picture above. The d bands now contain nine electrons and the apparent configuration is $\mathrm{V}(3d^9)\,\mathrm{O}(2p^0)$. By adjusting the exchange potential coefficient λ to a value of $\frac{2}{3}$, we were able to move the d bands relative to the p bands, but in that case the Fermi energy turned out positive. For $\lambda = 1$ the d bandwidth is about 9 eV. Clearly these results, where we assumed six $2p$ electrons and got none, are even more inconsistent than were the neutral atom configurations where we assumed four $2p$ electrons and got six.

To obtain some idea of the sensitivity of relative positions of s, p, and d bands in VO we computed the band structure for one more ionic configuration: $\mathrm{V}(3d^{3.3} 4s^0)\,\mathrm{O}(2p^{5.7})$, in which we estimated in advance the p bands should fall just above the d bands. This was in fact the case, with the Γ_{15} p level falling just above the Γ_{12} d level. Strong mixing occurred between p and d bands for this band structure, and it was difficult to make accurate assignments of relative positions of p and d bands. Pronounced effects were observed for the Δ_1 and Δ_5 bands which interact strongly when p and d bands are brought together by charge transfer: There is a bulging apart of these bands along the Δ axis. By examining eigenvectors we estimate that the p bands still lie mainly above the d bands.

C. Discussion

The band structures presented above demonstrate that relative positions of s, p, and d levels in VO are strongly dependent upon the choice of crystalline potential. In every case, however, the $4s$ band lies above the $3d$ and $2p$ bands. Comparison of effective configurations of the bands suggests that a potential constructed from neutral atoms is probably closer to the self-consistent result than is a doubly ionized version, but the question can only be resolved by a fully self-consistent calculation. It is difficult to make direct comparisons of atomic configurations and effective configurations for the solid due to overlap effects.

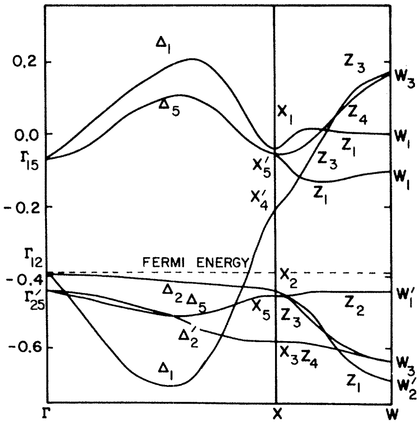

FIG. 5. Energy bands of VO using a potential constructed from doubly ionized atoms. Energy in Rydbergs.

This was demonstrated[6] for TiO where a singly ionized set of atomic potentials gave a filled oxygen $2p$ band in the crystal, instead of partially filled, but the charge densities calculated inside the oxygen APW spheres showed close agreement, indicating at least some degree of self-consistency. However, it is probably not accurate to rely simply upon approximate agreement of initial and final charge densities until a self-consistent calculation is performed to demonstrate conclusively how sensitive the band structure is to small changes in charge density.

There have been no other band calculations for VO, but there have been three studies of TiO mentioned in Sec. II of this paper. Since Ti and V are adjacent in the Periodic Table, we expect that there should be similarities in the band structures of TiO and VO. This is evidently the case if we assume the same ionicity for both. For an ionicity of one or less we obtain band structures very similar to the two APW calculations[6,12] reported for TiO.

The band structures exhibit bandwidths which are similar. The $3d$ bandwidth is about 9 eV for TiO (singly ionized) compared with about 7 eV for VO (neutral), and the relative positions of s, p, and d bands are the same, although separations are different. Ern and Switendick[6] report a gap at X of about 0.2 Ry between $2p$ and $3d$ bands, while we obtain 0.9 Ry. However, we estimate 0.2 Ry would be obtained for a singly ionized configuration. Differences in crystal-field splitting of the d levels may also be accounted for by ionicity, but the $3d$-$4s$ gap at Γ cannot be explained in this manner. Our doubly ionized configuration shows an increase in this gap with increasing ionicity. While this difference may be a real one between band structures of TiO and VO, it could also be due to the fact that we have included an insufficient number of basis functions for the higher conduction bands and should add $3s$ oxygen and $4p$ vanadium functions or plane waves to our basis set. These could cause important changes (lowering) of the $4s$ band, but probably would not alter the $3d$ bands appreciably.

VI. CONCLUSION

We have obtained band structures of VO for several atomic configurations, with results comparable to energy bands of TiO. Our principal conclusions are the following: (a) It is feasible to perform tight-binding calculations for a transition-metal compound using all core and valence electron orbitals; (b) core effects are important in first-principles tight-binding calculations; (c) $3d$ bands in VO lie below the $4s$ band, so that conductivity in VO is due primarily to d electrons; (d) the $3d$ bandwidth of VO is about the same as TiO for the same ionicity; (e) energy bands in VO are very sensitive to the degree of ionicity assumed, so that either experimental data should be used to determine the correct ionicity, or the band calculations must be done self-consistently for reliable results; (f) the density of states at the Fermi energy is very large, suggesting that VO might exhibit some sort of magnetism.

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Far-Infrared Properties of Lattice Resonant Modes. IV. Paraelectric Impurities[*]

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We have studied the three paraelectric defect systems KCl: Li^+, RbCl: Ag^+, and NaCl: OH^- through the temperature dependence and electric field dependence of their far-infrared absorption spectra. It is found that the motional energy states for the defects in these three systems have many properties in common. In each case the impurity ion has an associated electric dipole moment and low-lying tunneling energy levels. The defects also have higher energy levels which can be attributed, at least in part, to c.m. resonant-mode motion. The KCl: Li^+ tunneling levels are found to be well described by the model of Gomez, Bowen, and Krumhansl, assuming a Li^+ dipole moment of $1.14 \pm 0.05\ e\text{Å}$ for both Li^6 and Li^7. The most surprising feature of the KCl: Li^+ higher-lying energy levels is that they show a negative isotope shift [i.e., $\bar{\omega}(\mathrm{Li}^6) < \bar{\omega}(\mathrm{Li}^7)$]. The three observed absorption lines in RbCl: Ag^+, as well as their dependence on an external electric field, are shown to be consistent with a [110] off-center position for the Ag^+ ions. The far-infrared absorption spectrum of NaCl: OH^- is complicated, with at least eight absorption lines between 2 and 22 cm^{-1}. Considerable agreement is found between the experimental results and a model which incorporates both librational tunneling of the OH^- ion and c.m. vibrational motion.

I. INTRODUCTION

The first three papers of this series[1–3] have been concerned with various properties of lattice resonant modes of monatomic impurities in alkali halides. Each defect-lattice system studied in these earlier works has been confirmed to be of the on-center type, where the impurity ion substitutes for a host ion at the normal lattice site. In this paper, we wish to discuss the properties of the far-infrared absorption spectra due to paraelectric impurities in alkali halides, with particular emphasis on the motional energy states which can arise from c.m. resonant-mode motion. As will be seen, the far-infrared properties of paraelectric defect systems can be strikingly different than those of on-center impurities.

Paraelectric defects may be divided into two classes. Historically, the first class consists of dipolar diatomic impurities such as OH^- and CN^-. In these cases, the impurity molecule has several equivalent preferred directions of dipolar align-