VO_2: Peierls or Mott-Hubbard? A View from Band Theory

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The electronic and structural properties of VO_2 across its metal-insulator transition are studied using the local-density approximation. Band theory finds a monoclinic distorted ground state in good agreement with experiment, and an almost open gap to charge excitations. Although rigid criteria for distinguishing correlated from band insulators are not available, these findings suggest that VO_2 may be more bandlike than correlated.

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A series of oxides of vanadium exhibit metal-insulator transitions [1]. Of these, the end-member compounds V_2O_3 ($T_{MI} = 150$ K) and VO_2 ($T_{MI} = 340$ K) are the best studied. V_2O_3 is antiferromagnetic in its low T phase, and is commonly classified as a Mott-Hubbard insulator, whereas VO_2 is nonmagnetic, and variously classified as Mott-Hubbard [2], "spin-Peierls" [3], or an ordinary band (Peierls) [4,5] insulator. There is a significant crystallographic component to the VO_2 transition, with pairing of V atoms, cell doubling, and charge ordering. The issue is whether the one-electron or correlated-electron aspects are primary.

In contrast to previous band calculations [6–8] we address the relative energetic stability of both phases across the transition. The complexity of the low T monoclinic ($M1$) structure has previously inhibited *ab initio* investigation of this phase. While the high T rutile (R) structure has two molecules per cell, the low T structure results from a monoclinic distortion which doubles the cell size through V-V pairing and brings the number of structural degrees of freedom to 13 (see Fig. 1). We approach the stability question by performing unconstrained structural searches for the ground state within the 13-dimensional parameter space of the low T phase. Our ability to relax all parameters simultaneously relies on the efficiency of an *ab initio* molecular dynamics (MD) scheme with variable cell shape (VCS) [9]. This scheme combines two others: (1) a modified version of the Parrinello-Rahman VCS algorithm [10], with a symmetric Lagrangian which automatically keeps structural trajectories within ensembles of preselected space groups [11] and (2) a plane-wave based *ab initio* MD which, although inspired by the Car-Parrinello method [12], differs [13] in converging the electronic structure calculation before moving atoms, allowing a longer MD time step. Reliable total energy differences are obtained as the cell shape changes by fixing the plane-wave cutoff.

Our results indicate that local-density approximation (LDA) [14] not only gets the structure right, but also reasonably accurately accounts for the metal-insulator transition. We believe that this is one of the most challenging tests yet made of the correctness of the LDA total energy approach, and its success suggests that the Mott-Hubbard and spin-Peierls pictures are less appropriate than the charge-ordering picture.

We computed the electronic structure and total energy of the $M1$ and R phases of VO_2 within LDA with the Ceperley-Alder exchange-correlation potential [15]. We used soft [16] and separable [17] pseudopotentials and a plane-wave cutoff of 64 Ry, corresponding to ≈ 1750 plane waves per molecule. When the cutoff was increased to 81 Ry, absolute energies decreased ≈ 10 meV/molecule, and energy differences changed less than 1 meV/molecule. Self-consistent charge densities were computed using corresponding sets [18] of 8 and 6 **k** points in the irreducible Brillouin zone (IBZ) of $M1$ and R, respectively. By sampling **k** points consistently in both IBZ's it is

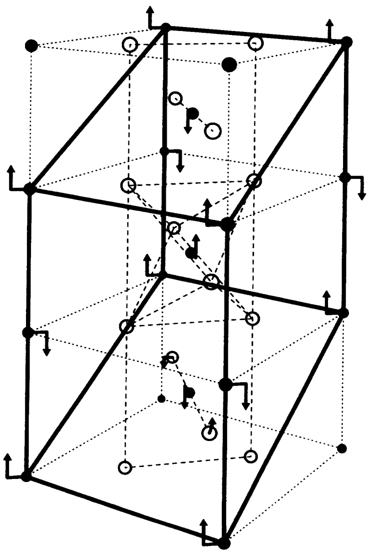

FIG. 1. Crystal structures of VO_2. Full (open) circles denote V (O) atoms. Indicated are the monoclinic ($M1$) unit cell (solid line) and the rutile (R) tetragonal cell (dotted line). The arrows indicate the distortions that lead from R to $M1$. Displacements of O atoms are given only for two inequivalent O's.

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TABLE I. Experimental and theoretical lattice parameters of the rutile (R) and monoclinic ($M1$) phases. Theoretical numbers labeled (R,6) are calculated using 6 **k** points, whereas the next column (with error margins) shows results using up to 40 **k** points. Experimental values are from Ref. [24] (R), and from Ref. [23] ($M1$). Their respective lattice vectors are $\mathbf{a}_r = a\hat{\mathbf{x}}$, $\mathbf{b}_r = a\hat{\mathbf{y}}$, $\mathbf{c}_r = c\hat{\mathbf{z}}$, and $\mathbf{a}_m = a'\hat{\mathbf{x}}$, $\mathbf{b}_m = b'\sin\alpha\hat{\mathbf{y}} + b'\cos\alpha\hat{\mathbf{z}}$, $\mathbf{c}_m = c'\hat{\mathbf{z}}$. The $M1$ phase V_4O_8 has its atoms located at $\pm(X_a, X_b, X_c)$ and at $\pm(\frac{1}{2}+X_a, \frac{1}{2}-X_b, X_c)$ where X stands for V, O^1, or O^2. The R phase V_2O_4 has V's located at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and O's at $\pm(u,u,0)$ and $(\frac{1}{2}\pm u, \frac{1}{2}\mp u, \frac{1}{2})$. For comparison, the R phase is described in terms of an $M1$ supercell (see third column). Lengths for the lattice constants are in Å, and α is in degrees.

	Theor. ($M1$)	Expt. ($M1$)	Expt. (R)
a'	4.657	4.517	4.5546
b'	5.375	5.375	5.3734
c'	5.629	5.743	5.7023
α	121.56	122.61	122.046
V_a	0.024	0.025	0.000
V_b	0.021	0.025	0.000
V_c	0.233	0.242	0.250
O_a^1	0.288	0.290	0.300
O_b^1	0.272	0.300	0.300
O_c^1	−0.118	−0.100	−0.100
O_a^2	0.315	0.310	0.300
O_b^2	0.293	0.290	0.300
O_c^2	0.399	0.390	0.400
	Theor. (R,6)	Theor. (R)	Expt. (R)
a	4.634	4.58 ± 0.03	4.5546
c/a	0.605	0.610 ± 0.005	0.6260
u	0.296	0.300 ± 0.004	0.3000

possible to calculate total energy differences without resorting to large sets. Convergence of the **k** sampling has been tested in the R phase by trying up to 40 points. As is usual for metals, convergence is slow. However, the fluctuations are small. Results are shown in Table I.

This plane-wave pseudopotential method has already been successfully applied to describe the properties of isostructural TiO_2 [19,20]. Our results for the R phase of VO_2 agree except in minor detail with the recent full potential linearized augmented plane-wave calculation by Nikolaev, Kostrubov, and Andreev [8]. There is no previous calculation of the total energy to compare our results with. The ability of the pseudopotential method to achieve comparable accuracy to all electron methods was demonstrated on a system with d electrons of even greater difficulty, ZnS, by Martins, Troullier, and Wei [21].

The R phase has six oxygens surrounding each V atom in orthorhombically distorted octahedral coordination. The octahedra stack in an arrangement that shares edges to form chains along the c direction; the c-axis chains are coupled to each other by corner sharing. The closest V-V distance is 2.85 Å in chains along the c direction. In the $M1$ phase, vanadium atoms pair along the chains, causing a unit cell doubling. In addition, V atoms have a staggered transverse displacement, and the oxygen octahedra distort and twist. These displacements are indicated in Fig. 1. There is also a monoclinic distortion of the cell vectors.

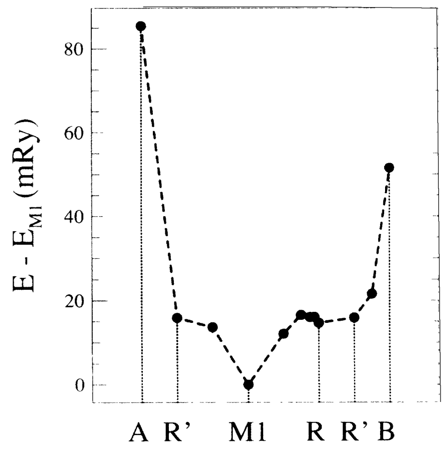

FIG. 2. Energy per unit cell (4 molecules) of VO_2 along various paths between the rutile (R) and monoclinic ($M1$) phases. R' is R but with the full $M1$ strain. A is R' but with the V atoms distorted as in $M1$; B is R' with the O atoms distorted. Points between the end points of a given path are linear interpolations of the end points.

To locate the ground state crystal structure predicted by LDA theory, we started with a self-consistent calculation of VO_2 in a structure intermediate between the R and $M1$ experimental structures. Then a damped downhill dynamics was run using the calculated forces on atoms and stresses on cell shape. To find the minimum energy requires fewer than 20 steps (each fully converged) and used about 20 h on a Cray YMP. Figure 2 shows the total energies of the $M1$ phase, the R phase, and several distortions. When the deviation from the R structure was small, the calculation returned to rutile symmetry; the R structure appears to be marginally metastable. Starting halfway between R and $M1$, the structure evolved to an $M1$ phase whose parameters are given in Table I. The total energy difference $E(R) - E(M1)$ is 4 mRy = 54 meV = 630 K per molecule. This squares well with the measured latent heat of 44 meV/molecule [22] and $T_{MI} = 340$ K.

Our theoretical distortion is somewhat larger than quoted experimentally, although not necessarily outside the uncertainties of Ref. [23] which predates modern crystallographic technology. The c-axis V-V spacing changes from uniform 2.85 Å to alternations of (2.52 Å, 3.14 Å). The corresponding experimental distances are (2.65 Å, 3.12 Å). Our optimized rutile parameters, shown at the bottom of Table I, agree within typical LDA accuracy with the accurate 360 K data of McWhan *et al.* [24]. This is an impressive confirmation of the ac-

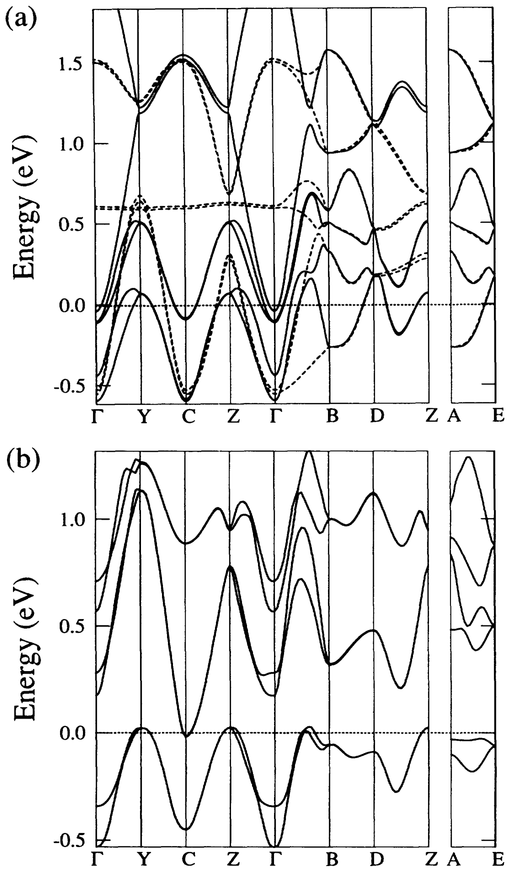

FIG. 3. The band structure of the rutile phase (a) after folding into the monoclinic BZ and the band structure of the monoclinic phase (b). In (a), the solid lines are the bands originating from the Γ point [$\mathbf{k}=(0,0,0)$]; the dashed lines show the bands from the R point [$\mathbf{k}=(0,\pi,\pi)$]. The dotted line is the Fermi level.

curacy of LDA in a complicated oxide, and of the efficacy of the VCS algorithm.

We also tested the effects of pure V-atom and pure O-atom displacements (points A and B in Fig. 2). Both caused large energy increases. However, a pure strain of cell vectors (path $R \rightarrow R'$ in Fig. 2) was relatively inexpensive in energy.

The band structure of the high-T R phase, shown in Fig. 3(a), confirms the nominal $V^{4+}(d^1)$ assignment. There are two half-filled vanadium d bands at the Fermi level, with filled oxygen p bands (not shown) 4 eV lower in energy. As reported in our previous study of the R phase [25], the density of states at the Fermi level is quite high, 4.18 states/eV molecule (both spins). Comparison with the specific heat γ measured on a metallic sample of $V_{0.86}W_{0.14}O_2$ [26] suggests that the experimental density of states may be enhanced by 3.4 indicating strong correlations. We attempted [25] to use transport measurements to determine whether the high-T R phase of VO_2 was a conventional band Fermi liquid. The results were ambiguous with the possibility that it is an unconventional metal.

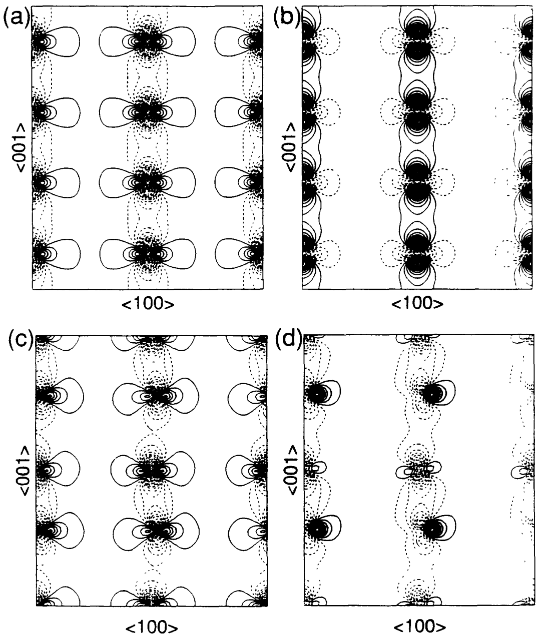

FIG. 4. Wave functions of the lowest [(a) and (c)] and next higher [(b) and (d)] vanadium d states at the Γ point of the Brillouin zone. In the rutile phase [(a) and (b)] both states are bonding along the vanadium c-axis chains. In the $M1$ phase [(c) and (d)] both states form enhanced vanadium-vanadium pair bonds.

As seen in Fig. 3(b), the energy bands near the Fermi level of the low-T stable structure have been greatly altered by the distortion. There are now four VO_2 molecules per cell, and two almost fully occupied vanadium d bands accommodate the outermost electrons, leaving only a very small band overlap with the next higher d levels. The origin of the "pseudogap" in LDA theory is metal-metal bonding, as shown in Fig. 4. This is consistent with the picture originally proposed by Goodenough [5] and with the identification of a nesting vector in the rutile-phase energy bands by Gupta, Freeman, and Ellis [7]. The structural distortion permits an enhancement of the bonds between neighboring V atoms, just as expected from a simple Peierls picture. The experimental optical gap is about 0.6 eV [27], contradicting our calculation which has a gap of ≈ -0.04 eV. The typical failure of LDA theory to give band gaps correctly is well known [28]. A similar error is made for the gap of germanium. The higher degree of correlation expected in VO_2 seems not to enhance this error.

Our calculation leaves little doubt that there is enough energy gain to account for the metal-insulator transition through strengthening the vanadium d-d bonds (reorganizing states near the Fermi level); i.e., it is appropriate to denote VO_2 as a band insulator. However, the obvious [1] relation of VO_2 to the Mott insulator V_2O_3 forces us to ask whether the categories Mott *versus* band insulator can be rigorously distinguished. Naively, dimerization is most naturally connected to the band picture, although it is also a possible way for electrons to solve the correlation problem [3,29], forming local Heitler-London singlet bonds. The correlated Heitler-London picture and the uncorrelated Hund-Mullikan (molecular orbital) picture are about equally successful in describing the H_2 molecule, for example. Arguments about the relative importance of one-electron *versus* correlation effects have arisen for other cases of dimerization [30]. LDA band theory attempts to include correlation energies correctly even though using one-electron wave functions which provide an independent-electron model of charge ordering. Ultimately, experiment should determine how we classify materials. If VO_2 is a Mott insulator, there should be spin excitations below the charge-excitation gap of 0.6 eV. Probably these would be similar to singlet to triplet excitations on vanadium dimers, or deeply bound triplet excitons. Observation of such states would strengthen the Mott-Hubbard interpretation.

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