Comment on "VO$_2$: Peierls or Mott-Hubbard? A View from Band Theory"

In a recent Letter [1] Wentzcovitch, Schulz, and Allen reopened the discussion on the nature of the metal-insulator transition in vanadium dioxide (VO$_2$). On the basis of LDA (local density approximation) calculations on the monoclinic M_1 structure which gave a semimetal with a very small number of carriers, they concluded that this phase is an ordinary band (Peierls) insulator and not a Mott-Hubbard insulator in which onsite Coulomb correlations dominate. The authors, however, presented results only for one of the insulating phases of VO$_2$: They and others have pointed out that all V^{4+} ions are in singlet V-V pairs which makes a clear distinction impossible. In this Comment we wish to remark that this ambiguity does not apply to the other insulating phases of VO$_2$, which are clearly of the Mott-Hubbard type.

There are two structural components to the lattice distortion from the high temperature rutile (R) phase, namely a pairing and a twisting of V-V pairs out of the rutile axis c_r. Around twenty years ago the nature of a second monoclinic insulating phase (M_2) was established [2]. The metal-insulator transition is $R \rightarrow M_2$ in V$_{1-x}$Cr$_x$O$_2$ with x very small ($x \gtrsim 3 \times 10^{-3}$) [2] or in pure VO$_2$ [3] when a small uniaxial pressure is applied along $(110)_r$. In M_2 one-half of the V chains of the R phase pairs but does not twist and the other half twists but does not pair (see Fig. 1). There are simple electrostatic reasons that the pairing on one set of V chains induces a twist in the other V chains. Thus the M_1 phase of VO$_2$ can be viewed as a simple superposition of two lattice distortions of the M_2 type.

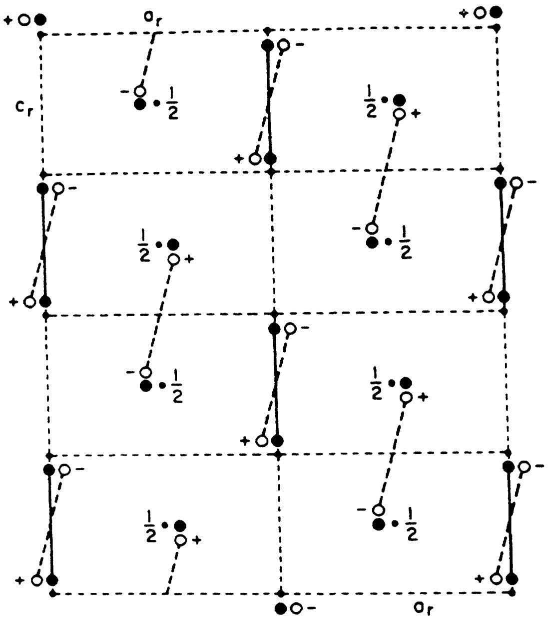

FIG. 1. Comparison of V-V pairing in the three phases (R, M_1, and M_2). In M_1 (open circles) all the vanadium atoms both pair and twist from the rutile positions. In M_2 (filled circles) one-half of the vanadium atoms pairs but does not twist and the other half forms unpaired zigzag chains. (The distortions are exaggerated by a factor of 2 for clarity.)

In M_2 one-half of the V^{4+} ions form equally spaced V chains, and NMR and EPR experiments show that they behave magnetically as $s = \frac{1}{2}$ Heisenberg chains ($J \approx 300$ K). It is clear that these V chains in M_2 are magnetic (or Mott-Hubbard) insulators. Since M_2 can be stabilized by minimal perturbations, it is also clear that M_2 is a local minimum for VO$_2$, whose free energy is only very slightly higher than that of M_1 at room temperature and pressure. Further cooling leads to a continuous $M_2 \rightarrow M_1$ transition through an intermediate insulating triclinic (T) phase where pairing (or dimerization) on one set of V chains grows continuously [4].

The M_2 phase is a Mott-Hubbard insulator and the M_1 phase is a superposition of two M_2-type lattice distortions. Further a continuous $M_2 \rightarrow M_1$ transition through the intermediate insulating T phase is observed with decreasing temperature. These experiments led us to conclude previously [2,3] that all the insulating phases of VO$_2$, (M_1, M_2, and T) were of the same type and should be classified as Mott-Hubbard and not band insulators.

T. M. Rice
Theoretische Physik,
ETH-Hönggerberg,
8093 Zürich, Switzerland

H. Launois
Laboratoire de Microstructures et de Microélectronique,
196 Avenue Henri Ravera,
92220 Bagneux, France

J. P. Pouget
Laboratoire de Physique des Solides,
Université de Paris-Sud,
Bâtiment 510, 91405 Orsay, France

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[4] Note, however, the initial transition $M_2 \rightarrow T$ is discontinuous.

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