Ab Initio phonon calculations in metallic and insulating VO_2

Christopher Hendriks, Eric J. Walter, Henry Krakauer
Department of Physics, College of William and Mary, Williamsburg, VA 23187, USA

Vanadium dioxide (VO_2) undergoes a first-order metal-insulator transition (MIT) from the high temperature rutile phase (R) to an insulating, low temperature monoclinic phase (M1). Several competing insulating phases exist, with phase boundaries in a narrow temperature and strain range close to the MIT [1, 2]. Recently, novel IR and Raman measurements of micro- and nano-structured VO_2 samples have become increasingly available; this allows the phases to be studied while avoiding many difficulties with bulk samples, such as twinning and cracking on cycling through the MIT. Theoretical calculations of vibrational properties can assist in the interpretation of such experiments [3].

We will present first-principles calculations of phonon frequencies for the various phases and compare these to available measurements for the R, M1, M2 and T phases. All calculations were done with the Vienna Ab-initio Simulation Package (VASP) [6]. Phonon frequencies were obtained through computation of force constants via density functional perturbation theory and subsequent analysis using PHONOPY [7]. To describe correlation effects within the V 3d bands, we used the DFT+U extension of standard DFT (= GGA). Calculated results can depend sensitively on the numerical value of the effective on-site electronic interaction parameter, the Hubbard U. A common approach is to tune the value of U in a semi-empirical way, seeking agreement with available experimental measurements of certain properties. One can then use the so determined value to make predictions on other aspects of the behavior of the system of interest. We adopt this approach here.

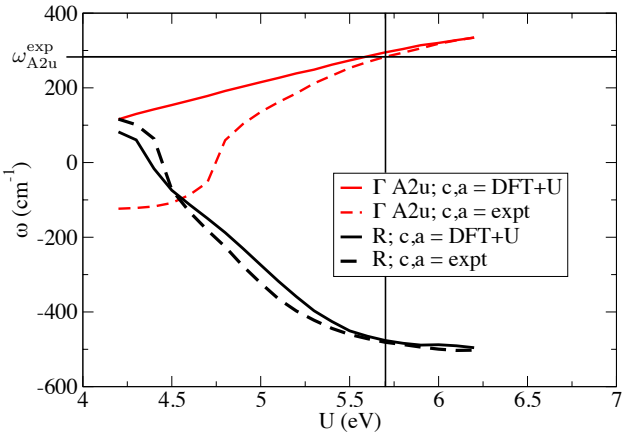

Figure 1: Rutile phonon frequencies vs Hubbard U (J was fixed at 0.8 eV). Calculations were performed using experimental and DFT+U optimized lattice parameters. Vertical line shows $U = 5.7$ eV; horizontal line shows experimental A2u frequency.

Experiment	Theory
–	126
201	211
227	232
293	304
340	413
434	446
451	500
648	643
–	667
829	834

Table 1: Comparison of Ag Raman frequencies for M2. Values are in cm^{-1}.

Since the metalic R phase is the parent compound of the various insulating phases that we are interested in studying, we focus on its calculated phonon frequencies and structural instabilities. For example, the M1, M2 and related phases can be traced to harmonically unstable R-point modes. We find the unstable R mode (two-fold degenerate) and the A2u Γ-mode to be most sensitive to the value of U. Figure 1 shows the variation of these phonon modes in rutile VO_2 as a function of the Hubbard parameter U. With $U = 0$ eV, i.e. regular DFT, there is no R-point instability. Adjusting U so that the calculated Γ-point A2u mode frequency agrees with experiment yields $U = 5.7$ eV. Previously, IR phonon calculations in the M1 phase have been reported using a slightly different value of U [3]; the current work yields similarly good agreement with experiment for the R and M1 phase. In addition, our comparison of calculated M2 Raman Ag frequencies with experimental measurement also show good agreement, as shown in Table 1.

Increasingly measurements are being made on micro- and nano-structured VO_2. Such samples facilitate experimental control of applied stress and external

fields to study the properties of the various phases. For example, recent measurements of M1 to M2 phase changes have been reported for VO_2 nano-rods under applied uniaxial strain, showing changes in Raman active phonon frequencies [2]. Theoretical calculations can help interpret these experiments. We will report strain dependent phonon frequencies on the different phases.

Acknowledgments: This work was supported by ONR grant N00014-12-1-1042. Calculations were performed on the SciClone cluster at the College of William and Mary.

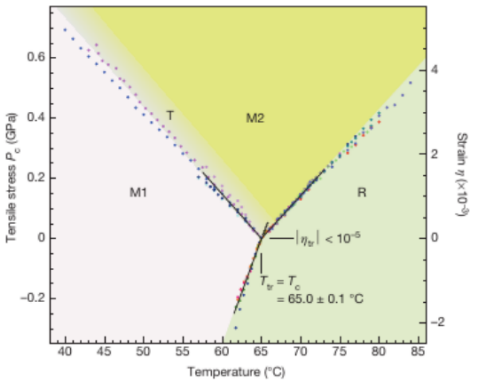

Figure 2: Strain-temperature phase diagram showing the VO_2 triple point.[1]

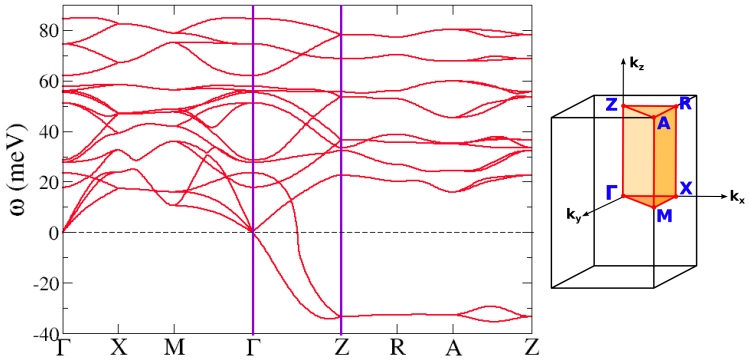

Figure 3: Dispersion curve of rutile VO_2 ($U = 4.2$ eV).

References

[1] J. H. Park, J.M. Coy, T.S. Kasirga, C. Huang, Z. Fei, S. Hunter and D.H. Cobden, *Nature* **500**, 431 (2013).

[2] J. M. Atkin, S. Berweger, E. Chavez, M.B. Raschke, *Phys. Rev. B* **85**, 020101 (2012).

[3] T. J. Huffman, P. Xu, M.M. Qazilbash, E.J. Walter, H. Krakauer, J. Wei, D.H. Cobden, H.A. Becthel, M.C. Martin, G.L. Carr and D.N. Basov, *Phys. Rev. B* **87**, 115121 (2013).

[4] P. Schilbe and D. Maurer, *Mat. Sci. and Eng. A* **370**, 449-452 (2004).

[5] C. Marini, E. Arcangeletti, D. Di Castro, L. Baldassare, A. Perucchi, S. Lupi, L. Malavasi, L. Boeri, E. Pomjakushina, K.Conder and P. Postorino, *Phys. Rev. B* **77**, 235111 (2008).

[6] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

[7] A. Togo, F. Oba, and I. Tanaka, *Phys. Rev. B* **78**, 134106 (2008).