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Anisotropic infrared response of vanadium dioxide microcrystalsT. J. Huffman,¹ Peng Xu,¹ M. M. Qazilbash,^{1,*} E. J. Walter,¹ H. Krakauer,¹ Jiang Wei,² D. H. Cobden,³ H. A. Bechtel,⁴ M. C. Martin,⁴ G. L. Carr,⁵ and D. N. Basov⁶¹*Department of Physics, College of William and Mary, Williamsburg, Virginia 23187-8795, USA*²*Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana 70118, USA*³*Department of Physics, University of Washington, Seattle, Washington 98195, USA*⁴*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*⁵*Photon Sciences, Brookhaven National Laboratory, Upton, New York 11973, USA*⁶*Department of Physics, University of California, San Diego, La Jolla, California 92093, USA*

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Vanadium dioxide (VO₂) undergoes a phase transition at a temperature of 340 K between an insulating monoclinic M_1 phase and a conducting rutile phase. Accurate measurements of possible anisotropy of the electronic properties and phonon features of VO₂ in the insulating monoclinic M_1 and metallic rutile phases are a prerequisite for understanding the phase transition in this correlated system. Recently, it has become possible to grow single domain untwinned VO₂ microcrystals, which makes it possible to investigate the true anisotropy of VO₂. We performed polarized transmission infrared micro-spectroscopy on these untwinned microcrystals in the spectral range between 200 cm⁻¹ and 6000 cm⁻¹ and have obtained the anisotropic phonon parameters and low frequency electronic properties in the insulating monoclinic M_1 and metallic rutile phases. We have also performed *ab initio* GGA + U total energy calculations of phonon frequencies for both phases. We find our measurements and calculations to be in good agreement.

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I. INTRODUCTION

Correlated electron systems often possess multiple interacting degrees of freedom such as electronic, lattice, magnetic, and orbital. Small changes in these degrees of freedom can lead to dramatically different emergent properties such as high-temperature superconductivity, colossal magnetoresistance, metal-insulator transitions, and multiferroicity.¹⁻⁴ This leads to extraordinarily rich phase diagrams as functions of external parameters such as strain, chemical doping, applied fields, and temperature. Precise understanding and control of emergent properties can lead to a number of applications. However, a complete understanding of how and why these phase changes occur in complex, correlated systems has proved elusive. Experimental measurements provide constraints based on the observed behavior of complex systems, thus contributing to our understanding of these materials.

Vanadium dioxide (VO₂) is one such material.⁵⁻⁸ VO₂ undergoes a metal insulator transition (MIT) at $T_c = 340$ K between an insulating phase below T_c and a conducting phase above T_c . The MIT is accompanied by a structural transition such that the monoclinic M_1 lattice of the insulating phase transforms into the rutile lattice of the metallic phase. This system is particularly attractive for the investigation of strongly interacting degrees of freedom because of its relatively simple unit cell and because no chemical doping is required for the phase transition to occur. Moreover, VO₂ shares a common structural element, a transition metal inside an oxygen octahedron, with other strongly correlated systems such as the colossal magnetoresistive manganites and the high-temperature superconducting cuprates. The vanadium ions are in the 4+ valence state, with one electron in the d orbitals.^{9,10} Although partially filled d orbitals would suggest metallic behavior for VO₂, it instead exhibits an MIT such that the low-temperature ground state is an insulator with an

energy gap of ~ 0.6 eV.¹¹⁻¹⁵ The driving mechanism of this MIT is not well understood. There are competing explanations for the MIT in VO₂, broadly divided into two categories: the Peierls distortion and the Mott transition. The models based on the Peierls distortion tend to explain the MIT purely in terms of lattice instability, unit-cell doubling, and vanadium-vanadium pairing.^{9,16} On the other hand, several researchers, including Mott, have emphasized the role of electronic correlations.¹⁷⁻²⁰

There are actually three different insulating phases of VO₂ (M_1 , M_2 , and T). In each of these structures, the displacements of the vanadium atoms from their rutile positions are very different. This indicates that the Peierls distortion may not be sufficient to explain the MIT.¹⁷ Moreover, shifts in optical spectral weight over energy scales of several electron volts between the monoclinic M_1 and rutile phases indicate that correlation effects are indeed important.¹⁴ However, the precise role of the M_1 unit cell doubling, whether it is the ultimate cause of the transition or driven by electronic correlations, remains unclear.^{9,10} Since the unit cell doubling accompanies the MIT, any explanation of the phase transition in VO₂ must account for the structural change. The structural transition may be caused by a softening of an acoustic phonon at the R point.²¹ Evidence for this scenario has been provided by x-ray diffuse scattering experiments.²²

The anisotropy of the monoclinic M_1 and rutile lattice structures of VO₂, along with the inherent anisotropy of the electronic p and d orbitals, may be expected to lead to anisotropy in the electronic and phonon properties. The directional dependence of these properties could play a major role in the MIT. Evidence for the relevance of anisotropy is provided by photoemission and x-ray absorption experiments that have documented the changes in occupation of the a_{1g} and e_g^π orbitals across the phase transition.¹³ Accurate

measurements of the anisotropy of the lattice dynamics and the infrared electronic properties in the monoclinic M_1 and the rutile phases are therefore important in the investigation of the cause(s) of the MIT.

Previous infrared spectroscopy experiments on polycrystalline thin films or bulk crystals have been limited in their ability to investigate the anisotropy of VO_2 due to the nature of their samples.^{12,14,23,24} For example, as large VO_2 single crystals go through the structural transition, they exhibit twinning because the symmetry of the rutile (tetragonal) structure is broken in the monoclinic M_1 structure. The rutile c_r axis always becomes the monoclinic a_m axis, but only one of the rutile a_r axes can transform to the monoclinic b_m axis leading to two possible orientations of the b_m axis differing by a 90 degree rotation about the c_r axis.²⁴ Domains approximately 40 micrometers in size result, the difference between the two types of domains being the orientation of the b_m axis.²³ A macroscopic infrared measurement averages over these domains.²³ Therefore twinning is a problem for measuring the anisotropy of charge dynamics of VO_2 . Moreover, multidomain crystals also tend to crack or break as they go through the MIT.²³ As the cracks may introduce new reflection planes, extracting the optical properties from such a crystal is fraught with difficulties. Polycrystalline thin films typically have grains with different orientations. Therefore in both types of samples, assignment of phonon symmetries and parameters is difficult. Thus either a single domain crystal or an epitaxial, untwinned film is required to make meaningful, specific measurements of the anisotropy of the electronic properties and phonon parameters.

Recently, it has become possible to grow untwinned single domain VO_2 microcrystals on oxidized silicon substrates by the vapor transport method.^{25,26} Single domain crystals are less likely to crack as they go through the MIT. At room temperature, the a_m axis of the monoclinic M_1 phase of the microcrystal is parallel to the plane of the substrate.²⁷ Previously, infrared spectroscopy has been performed on VO_2 microcrystals in the spectral range between 1000 and 7000 cm^{-1} . However, these experiments did not consider the anisotropic nature of the VO_2 microcrystal and could not measure the infrared active phonons.²⁸ Broadband infrared microspectroscopy with polarized light allows us to measure a single-domain sample to obtain the true anisotropy of the optical constants. In this work, we report the center frequencies, oscillator strengths, and broadenings of 14 of the 15 infrared (IR) active phonons in monoclinic M_1 VO_2 and all four infrared active phonons in rutile VO_2 , and assign them their proper group theory labels. We compare our results to previous work done on twinned bulk crystals in Ref. 23 and to zone-center frequencies calculated with first-principles theory. We also report the directional dependence of the low-frequency optical conductivity of metallic rutile VO_2 between 200 and 6000 cm^{-1} .

The paper is organized as follows: in the next section, we present the salient aspects of the experimental methods and data analysis followed by an account of the theoretical methods. Next, we discuss the experimental and theoretical results for the monoclinic phase and then the rutile phase. We conclude by reviewing our main results. Finally, we present

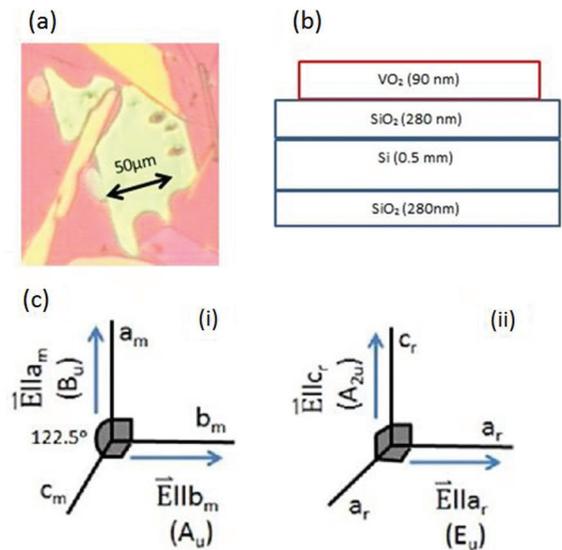


FIG. 1. (Color online) (a) Optical image of the VO_2 microcrystal studied. The double-ended arrow indicates the size of the crystal. (b) Schematic cross-sectional view of the microcrystal and substrate. The substrate is oxidized silicon. The thicknesses of the various layers are given in parentheses. (c) Diagram of the polarizations used with respect to the crystallographic axes in (i) the monoclinic (M_1) phase and (ii) the rutile phase.

technical details about our experiment and data analysis for the experts in Supplemental Material.²⁹

II. METHODS

A. Experimental methods

The single domain microcrystals used in this experiment were grown by vapor transport on oxidized silicon substrate.²⁶ Most of these crystals grow in long, thin rods that are not particularly suitable for infrared microspectroscopy because their narrow dimension tends to be smaller than the diffraction limit. However, there are a few large microcrystals with low aspect ratios among the ensemble, and we chose one of the largest crystals for our experiment [see Fig. 1(a)]. The thickness of the VO_2 microcrystal was directly measured by an atomic force microscope. Layer thicknesses used in the modeling are shown in Fig. 1(b). As the substrate is transparent in the infrared spectral range, it is possible to make transmission measurements for obtaining the frequency-dependent complex dielectric function of VO_2 microcrystals.

Preliminary characterization of the VO_2 microcrystals with infrared microscopy at frequencies greater than 800 cm^{-1} was carried out at the Advanced Light Source at Lawrence Berkeley National Laboratory. To extend our spectral range into the phonon region, we later performed broadband infrared microspectroscopy between 200 and 6000 cm^{-1} on the VO_2 microcrystal at the U12IR beam line at National Synchrotron Light Source (Brookhaven National Laboratory). A Fourier transform infrared (FTIR) spectrometer was used to measure the broadband infrared transmission of the VO_2 microcrystal and substrate normalized to the transmission of the substrate between 200 and 6000 cm^{-1} . A 15X 0.58 NA Schwarzschild microscope objective focused the FTIR

beam onto the microcrystal.³⁰ A wire-grid on KRS-5 substrate polarizer was used to orient the electric field of the incident light both perpendicular and parallel to the a_m axis of the M_1 phase [see Fig. 1(c)]. The orientation of the a_m axis in the VO_2 microcrystal was determined by rotating the polarizer until the A_u phonon around 600 cm^{-1} was absent in the spectrum.²³ Then, the polarizer was oriented perpendicular to the a_m axis. As the resulting spectrum for $\vec{E} \perp a_m$ contains none of the B_u phonons seen in the $\vec{E} \parallel a_m$ spectrum, it can be concluded that the crystal is oriented such that both the a_m and b_m axes are in the plane of the crystal, i.e., $\vec{E} \perp a_m$ is in fact $\vec{E} \parallel b_m$. In the rutile phase, the incident light was polarized parallel to the a_r and c_r axes [see Fig. 1(c)]. Normalized, broadband transmission spectra were taken at 295 K for the monoclinic M_1 phase, and at 400 K for the rutile phase. The absolute transmission of the substrate was also measured at both these temperatures.²⁹

Kramers-Kronig consistent oscillators were used to model the normalized transmission spectra and extract ε_1 and ε_2 , the real and imaginary parts of the complex dielectric function. Phonon features in the normalized transmission spectra were modeled with Lorentz oscillators of the following form:

$$\varepsilon(\omega) = \sum_{i=1}^n \frac{S_i}{1 - \frac{\omega^2}{\omega_i^2} - \frac{i\gamma_i\omega}{\omega_i}},$$

where ω_i is the center frequency of the i th phonon in units of inverse wavelength, S_i is the oscillator strength parameter, and γ_i is the broadening parameter. The electronic response of the rutile metal was modeled with Lorentz, Tauc-Lorentz, and Drude functions.

B. Theoretical methods

First-principles density functional theory (DFT)³¹ calculations were performed using the QUANTUM ESPRESSO³² computational package, using the DFT + U ³³ extension, in order to describe strong V d - d orbital correlations. The PBE³⁴ version of the generalized gradient approximation (GGA) was used for all calculations and only nonmagnetic ground states were considered throughout this work. The rotationally invariant³⁵ form of the GGA + U approach is used to apply the Hubbard U correction. For all systems, we investigated a range of U corrections ranging from 0–7 eV. A Hubbard U value of 5 eV was found to give good agreement for both structures, as discussed further below. Lattice parameters for rutile³⁶ and monoclinic M_1 ³⁷ structures were fixed at values obtained from x-ray diffraction measurements. All internal atomic coordinates were relaxed until the calculated forces were less than 1 mRy/Bohr ($\sim 0.03 \text{ eV \AA}^{-1}$). Ultrasoft pseudopotentials³⁸ were obtained from the QUANTUM ESPRESSO website for vanadium and oxygen.³⁹ Tests showed that a wave function plane-wave cutoff of $E_{\text{cut}} = 50 \text{ Ry}$ and a charge density cutoff of 300 Ry was sufficient to yield converged total energies and forces. Brillouin zone integrations were performed using $6 \times 6 \times 8$ and a $4 \times 4 \times 4$ Monkhorst-Pack⁴⁰ k -point meshes for the rutile and monoclinic structures, respectively; a small Fermi-Dirac type temperature broadening of 0.05 eV was also used in the metallic rutile phase. Zone center phonons were calculated using the method of small displacements and analyzed using the PHONOPY⁴¹ program, and Born effective

charge tensors Z^* and ε_∞ were used to include nonanalytic contributions to the dynamical matrix.

III. RESULTS AND DISCUSSION

A. Monoclinic M_1 phase

There are 12 atoms in the unit cell of monoclinic $M_1 \text{VO}_2$ of space group $P2_1/c$.⁹ Group theory then demands that there will be 36 phonon modes of which three are acoustic, 18 are Raman active, and 15 are IR active. The longitudinal or transverse character of a particular IR active mode depends upon the direction of the phonon wave vector q . When q is along the b_m axis, the eight A_u IR modes have purely longitudinal character, while the seven B_u IR modes have purely transverse character.⁴² That is to say that the net dipole moments are along b_m for the A_u modes and perpendicular to b_m for the B_u modes. Along other wave vectors, the phonons will have mixed transverse/longitudinal character due to the low symmetry of the M_1 phase. In the present experiment, the wave vector is perpendicular to the a_m - b_m plane so all 15 IR modes are expected to be seen: eight A_u modes when the light is polarized along b_m and the seven B_u modes when the light is polarized along a_m (perpendicular to b_m).

Experimentally, we see seven distinct phonon features when the electric field (\vec{E}) of the incident light is parallel to a_m (B_u), and seven distinct features when \vec{E} is parallel to b_m (A_u) (see Fig. 2). The eighth A_u feature, which has been seen by Barker *et al.*²³ at 189 cm^{-1} in a bulk, twinned crystal, is outside of our spectral range. All eight A_u modes are thus accounted for. Table I tabulates the measured phonon parameters. The A_u peak near $\sim 600 \text{ cm}^{-1}$ in Fig. 2 is asymmetric and required two Lorentz oscillators, $\omega = 607$ and 637 cm^{-1} , to fit, as shown in Table I. We speculate that the apparent asymmetry observed near $\sim 600 \text{ cm}^{-1}$ could be due to two-phonon processes arising from phonons near $\sim 300 \text{ cm}^{-1}$.

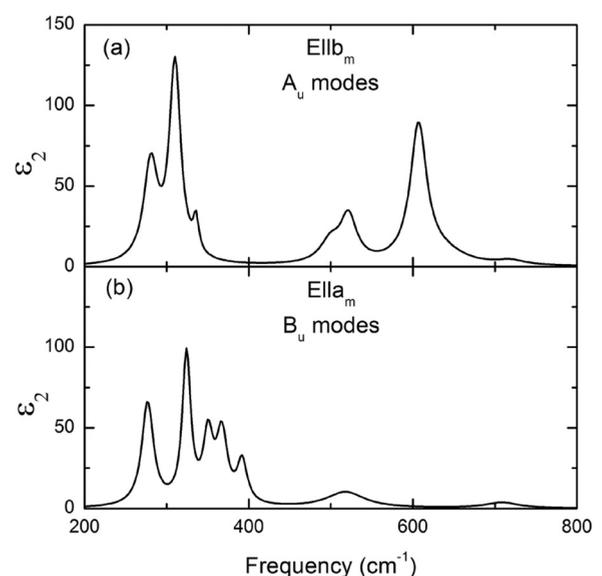


FIG. 2. The experimentally derived imaginary part of the complex dielectric function for monoclinic (M_1) VO_2 at $T = 295 \text{ K}$ for (a) $\vec{E} \parallel b_m$ (A_u) and (b) $\vec{E} \parallel a_m$ (B_u) in the phonon spectral region.

TABLE I. Lorentz oscillator fit parameters for monoclinic (M_1) VO₂ zone-center infrared active phonons.

Mode no.	A_u modes			B_u modes		
	ω_i (cm ⁻¹)	s_i	γ_i	ω_i	s_i	γ_i
(1)	(189)	(0.54)	(0.012)	277	4.01	0.062
2	281	4.53	0.074	324	3.49	0.038
3	310	6.69	0.055	351	1.67	0.041
4	336	0.49	0.023	367	1.88	0.044
5	500	0.77	0.060	392	0.99	0.038
6	521	1.34	0.047	519	1.08	0.110
7	607	3.42	0.040	709	0.25	0.071
	637	0.67	0.100	—	—	—
8	720	0.15	0.056	—	—	—

Notes: A_u mode 1 is from Ref. 23 as it falls just outside our spectral range. A_u mode 7 is asymmetric and requires two oscillators for a proper fit.

In general, our A_u center frequencies are in good agreement with Ref. 23 (see Fig. 3). Whereas Ref. 23 only identifies one mode at 505 cm⁻¹, our increased spectral resolution of 2 cm⁻¹, as opposed to the ~ 7.5 cm⁻¹ resolution of Ref. 23, allows us to resolve two distinct features at 500 and 521 cm⁻¹, so that we see seven IR active A_u modes within our measured spectral range. The broadenings of the A_u modes are within 10% of those measured by Ref. 23 for comparable modes. It should be noted that the A_u parameters in Ref. 23, measured as $E \perp a_m$, were extracted from a spectrum with all 15 IR active phonons due to the twinning of the bulk crystal. Our B_u ($\vec{E} \parallel a_m$) mode center frequencies largely agree with Ref. 23. However, we resolve two distinct modes at 351 and 367 cm⁻¹ whereas Ref. 23 reports a single mode at 355 cm⁻¹. With the inclusion of this mode, all seven B_u modes are accounted for in our data. Reference 23 also reports very weak modes at 227.5 and 478 cm⁻¹, which do not appear in our data. For comparable modes, the broadenings for the B_u modes agree reasonably well with those of Ref. 23, with the exception of B_u mode 6, which is nearly twice as broad in the present work. It should be noted that this discrepancy is due in part to the “extra” mode used in Ref. 23 at 478 cm⁻¹. Moreover, the larger broadening of B_u mode 6 could be due to contribution

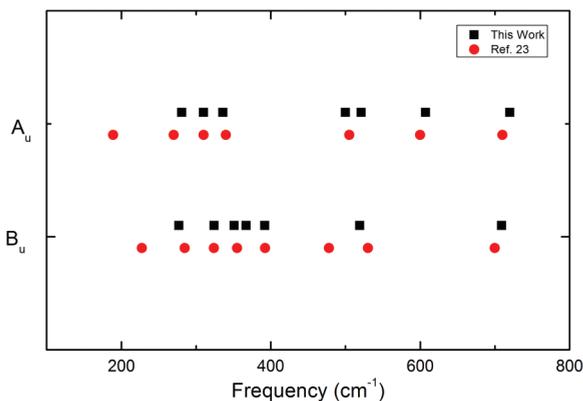


FIG. 3. (Color online) Comparison of VO₂ monoclinic (M_1) center frequencies of A_u and B_u phonon modes from our experiment and Ref. 23.

from two phonon processes associated with B_u mode 1. Even though the a_m axis is in the same direction for all the domains in Ref. 23’s twinned crystal, the phonon parameters, particularly the oscillator strengths, will depend on the orientation of the wave vector of the incident light relative to the b_m and c_m axes. Thus the oscillator strengths between our measurements on an untwinned crystal and those of Ref. 23 cannot be directly compared.

The phonon center frequencies at the gamma point have been calculated using GGA + U calculations. A Hubbard $U = 5$ eV yields good agreement with our experimental frequencies for both structures as seen in Table II. Furthermore, this value yields a band gap of ~ 1.0 eV which is in line with the experimentally determined band gap of ~ 0.6 eV.^{11–15} In general, there will be a frequency shift in the IR modes due to LO/TO-type splitting. These require knowledge of the high-frequency dielectric constant ϵ_∞ as well as the Born effective charge tensors Z^* . Due to technical complications in calculating ϵ_∞ and Z^* with GGA + U , we used the

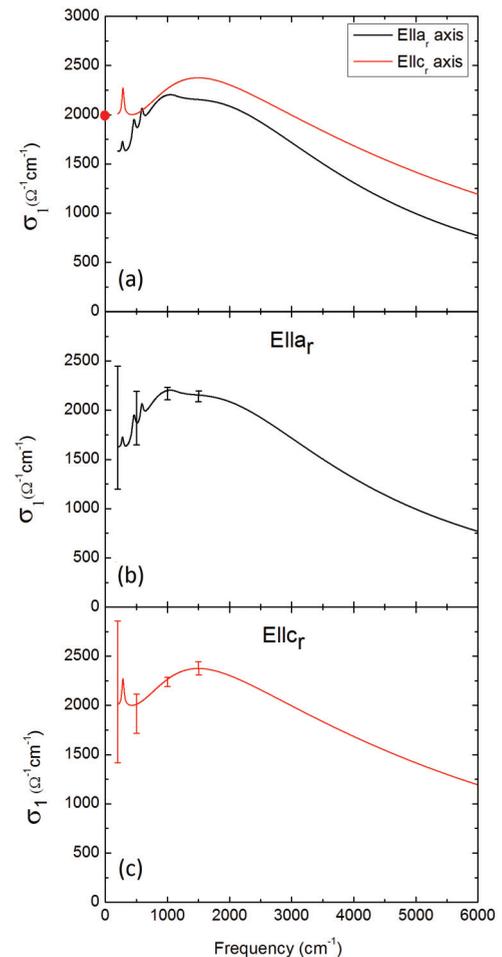


FIG. 4. (Color online) (a) The a_r and c_r axes infrared conductivity (σ_1) of rutile VO₂ at $T = 400$ K. The plots are consistent with the c_r axis dc conductivity constraint explained in Supplemental Material.²⁹ The known dc conductivity along c_r is shown by the red circle in (a).²⁶ Lifting this constraint produces the error bars shown in (b) and (c). These error bars arise from systematic uncertainties explained in Supplemental Material;²⁹ the systematic uncertainties affect the conductivity (σ_1) of both axes in a similar manner.

TABLE II. Comparison of experimental and theoretical phonon frequencies for monoclinic (M_1) VO_2 . The mean absolute difference (MAD) between the theory and experiment is given for both phonon symmetries. For the B_u theory values, the nonanalytic correction includes ZrO_2 Born effective charges (see text), whereas the frequencies in parentheses used nominal charges for V and O.

Mode no.	A_u mode center frequencies (cm^{-1})			B_u mode center frequencies (cm^{-1})		
	Experiment	Theory	Difference	Experiment	Theory	Difference
1	(189)	149	40	277	218 (227)	59 (50)
2	281	246	35	324	292 (292)	32 (32)
3	310	275	35	351	370 (370)	-19 (-19)
4	336	355	-19	367	403 (402)	-36 (-35)
5	500	417	83	392	466 (434)	-74 (-42)
6	521	466	55	519	544 (551)	-25 (-32)
7	607	512	95	709	738 (754)	-29 (-45)
8	720	720	0	-	-	-
			MAD			MAD
			45 cm^{-1}			39 (36) cm^{-1}

Notes: A_u mode 1 is from Ref. 23. To compare with theory, 607 cm^{-1} is used as the center frequency for A_u mode 7, as it is the center frequency of the stronger of the two oscillators used to model A_u mode 7 (See Table I). B_u theoretical values are for Z^* taken from ZrO_2 in Ref. 42, while values in parenthesis are for nominal Z^* values (see text).

experimentally determined value $\varepsilon_\infty \sim 12$ from the present work; two sets of Z^* tensors were used, the first from monoclinic ZrO_2 from Ref. 42 and, for comparison, the second using nominal diagonal values $Z_{\alpha\beta}^*(\text{V}) = +5e\delta_{\alpha\beta}$ and $Z_{\alpha\beta}^*(\text{O}) = -2.5e\delta_{\alpha\beta}$ [$Z_{\alpha\beta}^*(\text{O})$ were simply fixed using the acoustic sum rule]. For the sample geometry, photon wave vectors are perpendicular to the a_m - b_m plane (the Γ to Y direction in the Brillouin zone), so only the B_u frequencies depend on ε_∞ and Z^* .⁴²

As seen in Table II, the agreement between experiment and theory is slightly better for the B_u modes than for the A_u modes. The computed mean absolute deviation (MAD) for the A_u modes is 45 cm^{-1} , while for the B_u modes it is 39 or 35 cm^{-1} depending on the choice of Born tensors: values in parenthesis are for the nominal Z^* discussed above. The agreement between our measured and computed frequencies (and the band gap) can be improved by decreasing the Hubbard U correction to 3–4 eV. However, this greatly increases the discrepancy for rutile (see next section).

B. Rutile phase

The rutile structure is a simple tetragonal unit cell containing 6 atoms with space group $P4_2/mnm$.^{36,43} Group theory predicts that there will be 18 rutile VO_2 phonons: three acoustic, three silent, five Raman active, and seven infrared active modes. Of the seven infrared active phonons, three are doubly degenerate. Thus we expect to see one A_{2u} mode when $\vec{E} \parallel c_r$, and three E_u modes when $\vec{E} \parallel a_r$. Experimentally, all four rutile infrared active phonons of VO_2 are seen for the first time.²⁹ The measured phonon parameters and the low frequency optical conductivity are shown in Table III and Fig. 4, respectively. The rutile VO_2 phonons are roughly three times as broad as those of the monoclinic M_1 phase and insulating rutile TiO_2 .⁴⁴ This broadening implies a decrease in phonon lifetime possibly due to electron-phonon coupling.

Phase coexistence in the form of a stripe pattern with alternating insulating and metallic regions in the microcrystals

was observed through an optical microscope in the MIT regime. Similar stripe patterns have previously been observed in VO_2 nanorods. These stripes have been shown to be phase domains that form due to stress in the microcrystals caused by mismatch of thermal expansion between the oxidized silicon substrate and the VO_2 microcrystal.^{26,45} As the microcrystals are grown at 1273 K, the mismatch between the coefficients of thermal expansion results in a $\sim 0.7\%$ in-plane isotropic tensile strain on the rutile structure near the phase transition temperature. The M_1 structure then expands by $\sim 1.1\%$ along the a_m axis during the phase transition from rutile to monoclinic, whereas there is little change along the b_m axis. Thus the monoclinic phase is under a $\sim 0.4\%$ compressive strain along the a_m axis, and $\sim 0.7\%$ tensile strain along the b_m axis.^{26,45,46} This leads to a monoclinic M_1 unit cell volume that is only slightly larger than that of bulk VO_2 . In this way, it is possible that the effects of strain on the monoclinic M_1 phase are minimized, as our center frequencies are in good agreement with those obtained by Ref. 23 on bulk VO_2 . Strain effects could play a larger role in the rutile phase properties.

The overall shape of the electronic conductivity between 2000 and 6000 cm^{-1} for the rutile metal (Fig. 4) is consistent with previous reports.^{12,14,24} The overall higher conductivity along the rutile c_r axis compared to the a_r axis is consistent with Ref. 24. Optical conductivity below 2000 cm^{-1} along the a_r and c_r axes of the rutile phase has not been previously reported in the literature. Our data, which extend down to 200 cm^{-1} , suggest that the higher conductivity along the c_r

TABLE III. Lorentz oscillator fit parameters for rutile VO_2 zone center infrared active phonons.

Mode no.	A_{2u} mode			E_u modes		
	ω_i (cm^{-1})	s_i	γ_i	ω_i	s_i	γ_i
1	284	8.33	0.141	277	4.12	0.148
2	-	-	-	460	4.65	0.152
3	-	-	-	588	1.88	0.103

TABLE IV. Comparison of experimental and theoretical phonon frequencies for rutile VO₂. The mean absolute difference (MAD) between theory and experiment is given for all rutile phonons.

Mode no.	A_{2u} mode center frequency (cm ⁻¹)			E_u modes center frequencies (cm ⁻¹)		
	Experiment	Theory	Difference	Experiment	Theory	Difference
1	284	269	15	277	215	62
2	–	–	–	460	398	62
3	–	–	–	588	563	25
			MAD			
			41cm ⁻¹			

axis compared to the a_r axis persists down to these frequencies. This is consistent with dc resistivity measurements made on single crystal VO₂.⁴⁷ However, the degree of anisotropy was much greater than that seen in our experiment, as the dc conductivities parallel and perpendicular to c_r were reported to be 2500 and 333 $\Omega^{-1}\text{cm}^{-1}$, respectively.⁴⁷ An even greater degree of anisotropy is seen in highly strained VO₂ thin films on TiO₂ substrates, where the dc conductivity is measured to be 41.5 times greater along c_r than along a_r . These films are under a 1.92% tensile strain along c_r and a 0.93% compressive strain along a_r .⁴⁸ Thus the anisotropy of the conductivity at low frequencies is very sensitive to strain. Below 1000 cm⁻¹, there is uncertainty in our conductivity data due to the incident spot being larger than the sample. The uncertainty, discussed in greater detail in Supplemental Material,²⁹ is large enough to preclude definitive statements about the frequency dependence of the electronic response at low frequencies. The possibility of localization of the conduction electrons, as evidenced by a peak in the conductivity (σ_1), around 1500 cm⁻¹ in both polarizations is within the experimental uncertainty. A similar peak in σ_1 has been seen previously in nanoscale metallic “puddles” of VO₂ near the phase transition.^{49,50} However, such a feature has not been seen in previous macroscopic experiments on polycrystalline thin films of VO₂.^{12,14}

The agreement between experiment and theory for the phonon frequencies of the rutile structure is on par with the M_1 results (see Table IV). The MAD for the rutile modes is 41 cm⁻¹. Interestingly, three E_u modes are still in good agreement for $U = 3$ eV (their errors are 17, 59, and 61 cm⁻¹), however, the A_{2u} mode is unstable (large negative ω^2) until U is increased to about 5 eV. In rutile TiO₂, this mode is associated with an incipient ferroelectric phase; under negative pressure, calculations show that it softens, resulting in a ferroelectric phase transition.⁵¹ For values of U smaller than about 5 eV in rutile VO₂, the same ferroelectric-like instability incorrectly appears at the experimental volume. Note that in VO₂, it is not a true ferroelectric state, since the system remains metallic when the crystal is allowed to distort according to this mode.

As mentioned, microcrystals in the rutile phase are under $\sim 0.7\%$ tensile strain along the a_r axis. To examine strain effects, we recomputed the phonon frequencies in the presence

of -1% strain along the c_r axis, relaxing the in-plane axes. Differences between calculated and measured phonon frequencies changed by less than ~ 9 cm⁻¹, except for the second highest E_u mode, which increased by 22 cm⁻¹. Strain effects of this magnitude are thus not likely to be responsible for the differences between theory and experiment.

IV. CONCLUSIONS

Polarized infrared microspectroscopy of untwinned single domain VO₂ crystals was performed. Single domain samples allow for the measurement of the true anisotropy of the phonons and the electronic response. The four zone-center infrared active phonons of metallic rutile VO₂ have been measured and identified for the first time.²⁹ The electronic part of the infrared conductivity of metallic rutile VO₂ is weakly anisotropic and is measured to be higher along the c_r axis as compared to the a_r axis. The oscillator parameters of 14 of the 15 zone center infrared active phonon modes of the monoclinic M_1 phase of untwinned VO₂ have been measured for the first time. In addition, we have resolved an A_u mode near 500 cm⁻¹ and observe a distinct B_u mode at 367 cm⁻¹ not seen in previous measurements reported in Ref. 23. From our measurements together with the lowest frequency A_u mode seen in Ref. 23, all 15 monoclinic M_1 infrared active phonons are now accounted for. Using first-principles GGA + U calculations, we have computed the zone-center phonon frequencies for monoclinic and rutile VO₂. Our calculated results agree well with our measured frequencies.

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