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**Anisotropic infrared response of vanadium dioxide microcrystals**

T. J. Huffman  
*William & Mary*

Peng Xu  
*William & Mary*

M. M. Qazilbash  
*William & Mary*, mmqazilbash@wm.edu

E. J. Walter  
*William & Mary*, ejwalt@wm.edu

H. Krakauer  
*William & Mary*

*See next page for additional authors*

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Authors
T. J. Huffman, Peng Xu, M. M. Qazilbash, E. J. Walter, H. Krakauer, Jiang Wei, D. H. Cobden, and H. A. Bechtel

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Anisotropic infrared response of vanadium dioxide microcrystals


1Department of Physics, College of William and Mary, Williamsburg, Virginia 23187-8795, USA
2Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana 70118, USA
3Department of Physics, University of Washington, Seattle, Washington 98195, USA
4Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
5Photon Sciences, Brookhaven National Laboratory, Upton, New York 11973, USA
6Department 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 M1 phase and a conducting rutile phase. Accurate measurements of possible anisotropy of the electronic properties and phonon features of VO2 in the insulating monoclinic M1 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 M1 and metallic rutile phases. We have also performed \textit{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. 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. 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. 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 \( \sim 0.6 \) eV. 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. On the other hand, several researchers, including Mott, have emphasized the role of electronic correlations.

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. 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. 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. 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. Evidence for this scenario has been provided by x-ray diffuse scattering experiments.

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 \( e_g^2 \) orbitals across the phase transition.
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.\cite{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.\cite{24} Domains approximately 40 micrometers in size result, the difference between the two types of domains being the orientation of the $b_m$ axis.\cite{23} A macroscopic infrared measurement averages over these domains.\cite{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.\cite{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.\cite{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.\cite{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.\cite{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 technical details about our experiment and data analysis for the experts in Supplemental Material.\cite{29}

II. METHODS

A. Experimental methods

The single domain microcrystals used in this experiment were grown by vapor transport on oxidized silicon substrate.\cite{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. 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 \( \text{VO}_2 \) microcrystal was determined by rotating the polarizer until the \( A_u \) phonon around 600 cm\(^{-1}\) was absent in the spectrum. Then, the polarizer was oriented perpendicular to the \( a_m \) axis. 

As the resulting spectrum for \( \hat{E} \perp a_m \) contains none of the \( B_m \) phonons seen in the \( \hat{E} \parallel a_m \) 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., \( \hat{E} \perp a_m \) is in fact \( \hat{E} \parallel b_m \).

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.

Kramers-Kronig consistent oscillators were used to model the normalized transmission spectra and extract \( \varepsilon_1 \) and \( \varepsilon_2 \), 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:

\[
\varepsilon(\omega) = \sum_{i=1}^{n} \frac{s_i}{1 - \omega^2 \gamma_i^2 - i \omega \omega_i},
\]

where \( \omega_i \) is the center frequency of the \( i \)th phonon in units of inverse wavelength, \( s_i \) is the oscillator strength parameter, and \( \gamma_i \) 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 ESPRESSO\(^{32} \) computational package, using the DFT + \( U \)\(^{33} \) extension, in order to describe strong \( V \) \( d-d \) orbital correlations. The PBE\(^{34} \) version of the generalized gradient approximation (GGA) was used for all calculations and only nonmagnetic ground states were considered throughout this work. The rotationally invariant\(^{35} \) 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 rutile\(^{36} \) 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 (≈0.03 eV Å\(^{-1}\)). Ultrasoft pseudopotentials\(^{38} \) were obtained from the QUANTUM ESPRESSO website for vanadium and oxygen.\(^{39} \) Tests showed that a wave function plane-wave cutoff of \( E_{\text{cut}} = 50 \) 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 \( 4 \times 4 \times 4 \) Monkhorst-Pack\(^{40} \) \( k \)-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 PHONOPY\(^{41} \) program, and Born effective charge tensors \( Z^* \) and \( \varepsilon_{\infty} \) 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 \( P2_1/c \).\(^{3} \) 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 \( A_u \) 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 (\( \hat{E} \)) of the incident light is parallel to \( a_m \) (\( B_u \)), and seven distinct features when \( \hat{E} \) 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 \( \approx 600 \) 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 \( \sim 600 \) cm\(^{-1}\) could be due to two-phonon processes arising from phonons near \( \sim 300 \) cm\(^{-1}\).

FIG. 2. The experimentally derived imaginary part of the complex dielectric function for monoclinic (\( M_1 \)) \( \text{VO}_2 \) at \( T = 295 \) K for (a) \( \hat{E} \parallel b_m \) (\( A_u \)) and (b) \( \hat{E} \parallel a_m \) (\( B_u \)) in the phonon spectral region.
TABLE I. Lorentz oscillator fit parameters for monoclinic (M1) VO2 zone-center infrared active phonons.

<table>
<thead>
<tr>
<th>Mode no.</th>
<th>( \omega_i ) (cm(^{-1}))</th>
<th>( s_i )</th>
<th>( \gamma_i )</th>
<th>( \omega_i ) (cm(^{-1}))</th>
<th>( s_i )</th>
<th>( \gamma_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>189</td>
<td>0.54</td>
<td>0.012</td>
<td>505</td>
<td>0.062</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>281</td>
<td>4.53</td>
<td>0.074</td>
<td>324</td>
<td>3.49</td>
<td>0.038</td>
</tr>
<tr>
<td>3</td>
<td>310</td>
<td>6.69</td>
<td>0.055</td>
<td>351</td>
<td>1.67</td>
<td>0.441</td>
</tr>
<tr>
<td>4</td>
<td>336</td>
<td>0.49</td>
<td>0.023</td>
<td>367</td>
<td>1.88</td>
<td>0.044</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>0.77</td>
<td>0.060</td>
<td>500</td>
<td>0.99</td>
<td>0.038</td>
</tr>
<tr>
<td>6</td>
<td>521</td>
<td>1.34</td>
<td>0.047</td>
<td>392</td>
<td>1.08</td>
<td>0.110</td>
</tr>
<tr>
<td>7</td>
<td>607</td>
<td>3.42</td>
<td>0.040</td>
<td>519</td>
<td>1.08</td>
<td>0.110</td>
</tr>
<tr>
<td>8</td>
<td>720</td>
<td>0.15</td>
<td>0.056</td>
<td>709</td>
<td>0.25</td>
<td>0.071</td>
</tr>
</tbody>
</table>

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 \( \sim 7.5 \) 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 \( B_u \) (\( E \parallel a_m \)) 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 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 \( \sim 1.0 \) eV which is in line with the experimentally determined band gap of \( \sim 0.6 \) eV. 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 \( \epsilon_{\infty} \) as well as the Born effective charge tensors \( Z^* \). Due to technical complications in calculating \( \epsilon_{\infty} \) and \( Z^* \) with GGA + \( U \), we used the

FIG. 3. (Color online) Comparison of VO2 monoclinic (M1) center frequencies of \( A_u \) and \( B_u \) phonon modes from our experiment and Ref. 23.

FIG. 4. (Color online) (a) The \( a_r \) and \( c_r \) axes infrared conductivity (\( \sigma_1 \)) of rutile VO2 at \( T = 400 \) K. The plots are consistent with the \( c_r \) axis dc conductivity constraint explained in Supplemental Material. The known dc conductivity along \( c_r \) is shown by the red circle in (a). Lifting this constraint produces the error bars shown in (b) and (c). These error bars arise from systematic uncertainties explained in Supplemental Material; the systematic uncertainties affect the conductivity (\( \sigma_1 \)) of both axes in a similar manner.
Experimental values 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 $Z^*_{\alpha\beta}(V) = +5\epsilon_{\alpha\beta}$ and $Z^*_{\alpha\beta}(O) = -2.5\epsilon_{\alpha\beta}$ [$Z^*_{\alpha\beta}(O)$ 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 $\Gamma$ to $Y$ direction in the Brillouin zone), so only the $B_u$ frequencies depend on $\varepsilon_\infty$ and $Z^*$.\textsuperscript{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 $P4_2/mnm$.\textsuperscript{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.\textsuperscript{28} 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$_2$.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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 $c_r$ axis is due to the rutile phase.

### Notes:

1. $A_u$ 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).

### 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.

<table>
<thead>
<tr>
<th>Mode no.</th>
<th>$A_u$ mode center frequencies (cm$^{-1}$)</th>
<th>$B_u$ mode center frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>Theory</td>
</tr>
<tr>
<td>1</td>
<td>(189)</td>
<td>149</td>
</tr>
<tr>
<td>2</td>
<td>281</td>
<td>246</td>
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<td>3</td>
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<tr>
<td>7</td>
<td>607</td>
<td>512</td>
</tr>
<tr>
<td>8</td>
<td>720</td>
<td>720</td>
</tr>
</tbody>
</table>

MAD 45 cm$^{-1}$

MAD 39 (36) cm$^{-1}$

<table>
<thead>
<tr>
<th>Mode no.</th>
<th>$A_{2u}$ mode</th>
<th>$E_u$ modes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\omega_1$ (cm$^{-1}$)</td>
<td>$s_1$</td>
</tr>
<tr>
<td>1</td>
<td>284</td>
<td>8.33</td>
</tr>
<tr>
<td>2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

TABLE III. Lorentz oscillator fit parameters for rutile VO$_2$ zone center infrared active phonons.
axis compared to the \( a \) axis persists down to these frequencies. This is consistent with dc resistivity measurements made on single crystal VO\(_2\).\(^{47}\) However, the degree of anisotropy was much greater than that seen in our experiment, as the dc conductivities parallel and perpendicular to \( c \) were reported to be 2500 and 333 \( \Omega^{-1}\) cm\(^{-1}\), respectively.\(^{47}\) An even greater degree of anisotropy is seen in highly strained VO\(_2\) thin films on TiO\(_2\) substrates, where the dc conductivity is measured to be 41.5 times greater along \( c \) than along \( a \). These films are under a 1.92% tensile strain along \( c \), and a 0.93% compressive strain along \( a \).\(^{48}\) 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 \( (\sigma_1)\), around 1500 cm\(^{-1}\) in both polarizations is within the experimental uncertainty. A similar peak in \( \sigma_1 \) has been seen previously in nanoscale metallic “puddles” of VO\(_2\) near the phase transition.\(^{49,50}\) However, a feature has not been seen in previous macroscopic experiments on polycrystalline thin films of VO\(_2\).\(^{12,14}\)

The agreement between experiment and theory for the phonon frequencies of the rutile structure is on par with the \( M \) 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 \( \omega^2 \)) until \( U \) is increased to about 5 eV. In rutile TiO\(_2\), 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 VO\(_2\), the same ferroelectric-like instability incorrectly appears at the experimental volume. Note that in VO\(_2\), 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 \( a \) axis. To examine strain effects, we recomputed the phonon frequencies in the presence of \( \sim 1\% \) strain along the \( c \) axis, relaxing the in-plane axes. Differences between calculated and measured phonon frequencies changed by less than \( \sim 9 \) 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 VO\(_2\) 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 VO\(_2\) have been measured and identified for the first time.\(^{29}\) The electronic part of the infrared conductivity of metallic rutile VO\(_2\) is weakly anisotropic and is measured to be higher along the \( c \) axis as compared to the \( a \) axis. The oscillator parameters of 14 of the 15 zone center infrared active phonon modes of the monoclinic \( M_1 \) phase of untwinned VO\(_2\) have been measured for the first time. In addition, we have solved an \( A_u \) mode near 500 cm\(^{-1}\) and observe a distinct \( B_{1g} \) 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 VO\(_2\). Our calculated results agree well with our measured frequencies.

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