Photoemission evidence for crossover from Peierls-like to Mott-like transition in highly strained VO$_2$

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We present a spectroscopic study that reveals that the metal-insulator transition of strained VO$_2$ thin films may be driven towards a purely electronic transition, which does not rely on the Peierls dimerization, by the application of mechanical strain. Comparison with a moderately strained system, which does involve the lattice, demonstrates the crossover from Peierls- to Mott-like transitions.

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The metal-insulator transition (MIT) in VO$_2$ is of both fundamental and technical interest, the former due to lingering important questions about its origins,[1,2] and the latter due to possible applications in electronic devices such as ultrafast optical switches and field effect transistors.[3,4] In bulk VO$_2$, a large structural distortion accompanies the transition from the metallic rutile to the insulating monoclinic phase, which is known to impose a significant bottleneck on the time scale of the photo-induced transition.[5] Recently, the possibility of tailoring the transition temperature of the MIT in VO$_2$ through doping and/or nanoscale engineering[6–8] has heralded renewed interest in the potential application of VO$_2$ as a novel functional material. Whereas the mechanism of the MIT in bulk VO$_2$ is now reasonably well understood as an orbital-assisted collaborative Mott-Peierls transition (or associated variants),[9,10] i.e., the MIT involves *both* the lattice and electron-correlation effects, the situation is less clear under large applied strain to the lattice. For example, the introduction of Nb as an isoelectronic dopant to V leads to an expansion of the c/a constant, and eventually (for $\geqslant 15\%$ Nb) an insulating rutile phase is observed[11] (i.e., without any structural distortion).

The crucial aspects of the electronic structure of VO$_2$ center around the behavior of the V a_{1g} orbital, which is oriented along the rutile c axis (c_R axis), and is also labeled as $d_\parallel$ for this reason. In the Peierls-type model, this orbital becomes split in the insulating monoclinic phase due to the dimerization of V atoms in the c_R axis, and the associated twisting of the VO$_6$ octahedra pushes the e_g^π bands upwards in energy, deoccupying them.[1] On the other hand, the correlation-driven mechanism[2] proposes that the strong correlations in the a_{1g} orbital are screened by the e_g^π band in the metallic phase. In the insulating phase, the e_g^π states are empty and the unscreened correlations open the gap. In the past, it has been difficult to distinguish between these two models, owing to the large structural distortion that accompanies the transition. However, a growing body of experimental and theoretical evidence supports that both are important in driving the MIT of bulk VO$_2$. For example, the local density approximation (LDA) fails to reproduce the MIT (Ref. 12) without recourse to hybrid functionals beyond the LDA,[13] and dynamical

mean-field theory (DMFT) calculations[14,15] (that explicitly include dynamical electron correlations) are required to explain a good deal of the experimental data (for example, Refs. 6, 9, 11, and 16). We report here a photoemission spectroscopy (PES) study of strained VO$_2$ thin films in which we show that the MIT may be driven towards a purely electronic transition, which does not rely on the Peierls dimerization, by the application of mechanical strain.

High-quality thin films ($\sim$40 nm) of VO$_2$ were grown on rutile TiO$_2$(110)- and TiO$_2$(100)-oriented substrates by reactive bias target ion-beam deposition.[7] X-ray diffraction measurements confirm the epitaxy of VO$_2$ with the substrate and establish the expanded c_R-axis lattice parameter of VO$_2$ compared with the bulk.[17] This tensive strain is found to be approximately twice as large for VO$_2$/TiO$_2$(100) [hereafter referred to as VO$_2$(100)] at +3.7%, whereas the c_R-axis strain of VO$_2$/TiO$_2$(110) [referred to as VO$_2$(110)] is +1.7%. Atomic force microscopy measurements[17] suggest a very low root-mean-square roughness of $\sim$0.3–0.4 nm. Both samples display MITs above room temperature, at 345 K and 340 K for VO$_2$(110) and VO$_2$(100), respectively. Note that the MIT temperature of our VO$_2$(110) film is lower than that observed in Ref. 6. PES measurements were carried out at beamline I3 (MAX III) of MAX-lab, Lund University, Sweden, using a Scienta R-4000 analyzer set to an energy resolution of 12 meV, with pressures in the analysis chamber of better than 5×10^{-10} torr between room temperature and 150 °C. The binding energy of the PES spectra were referenced to polycrystalline gold in electrical contact with the samples. The samples were prepared for ultra-high vacuum measurements by several (one to three) repetitions of annealing in a partial O$_2$ environment ($\sim$450 °C, 1×10^{-6} torr O$_2$, 30 min). This procedure has been carefully developed to remove contaminant surface species from the samples without modifying the chemical environment of VO$_2$. Samples were aligned using low-energy electron diffraction and Laue x-ray diffraction. Soft x-ray spectroscopy measurements were performed at beamline X1B of the National Synchrotron Light Source (NSLS), Brookhaven. X-ray absorption spectroscopy (XAS) measurements were made in total electron yield mode with a beamline resolution of 0.2 eV, and the photon energy was
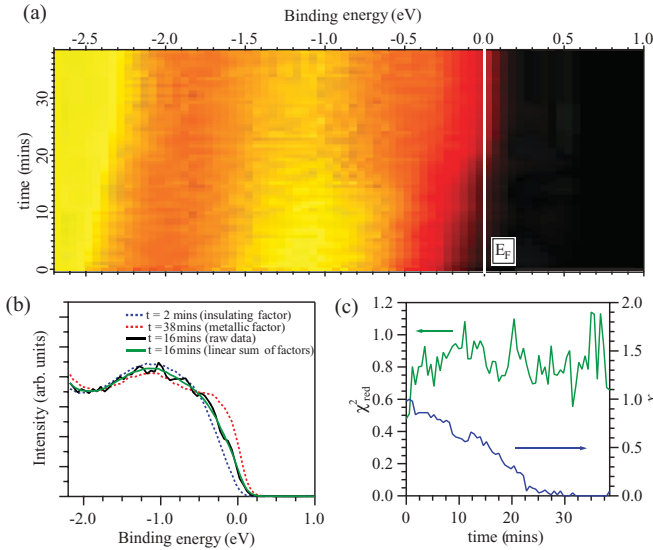
FIG. 1. (Color online) V $3d$ PES spectra of $VO_2(110)$ during a heating cycle through the MIT. (a) A two-dimensional map of the evolution of the V $3d$ states with time. (b) Spectrum recorded halfway through the heating cycle compared with a linear sum of the insulating and metallic factors. (c) The goodness-of-fit parameter χ^2 between the time-dependent data and its fit to the two end members of the series. Also shown is the evolution of the fraction x of the insulating spectrum used to describe the data.

FIG. 2. (Color online) PES spectra of the O $2p$ and V $3d$ states across the MIT of strained VO_2, recorded at 30 eV and with $E \parallel c_R$. The insets show an enlargement near E_F.

calibrated with reference to TiO_2 spectra. Resonant x-ray emission spectroscopy (RXES) measurements were recorded with a Nordgren-type grating spectrometer[18] set to an energy resolution of 0.7 eV, and the instrument was calibrated using a Zn reference spectrum.

For *moderately strained* $VO_2(110)$, angle-integrated PES spectra of the V $3d$ states near E_F are shown in Fig. 1(a) as a function of time during a slow heating cycle through the MIT. The evolution of the V $3d$ states is characterized by a transfer in spectral weight from $\sim$1 eV binding energy towards E_F, associated with the shift in the quasiparticle peak energy that becomes gapped out below the MIT.[14] The small remnant weight near 1 eV in the metallic phase represents the lower Hubbard band (LHB) of the rutile metallic phase and is slightly shifted towards higher binding energies, in agreement with cluster DMFT (cDMFT) results.[14] These results are in excellent agreement with previous PES measurements of both bulk and thin-film VO_2.[16,19,20] In Fig. 1(b), a comparison of the metallic and insulating spectra (end members of the heating cycle) is made with a spectrum recorded midway through the series. A linear superposition of the two end members is also shown, supporting real-space measurements of bulk VO_2 that find no evidence of an intermediate phase in the transition.[21] Indeed, the spectra throughout the heating cycle have been carefully analyzed using a factor analysis approach, and we find only two factors are required to reproduce the spectra for all energies and temperatures measured [Fig. 1(c)].

In Fig. 2, angle-integrated PES spectra of the O $2p$ and V $3d$ states of moderately strained $VO_2(110)$ and $VO_2(100)$ are shown across the MIT. In $VO_2(110)$, a large gap develops in the insulating (room-temperature) spectra, the magnitude of which is $\sim$300 meV (measured from extrema in the first
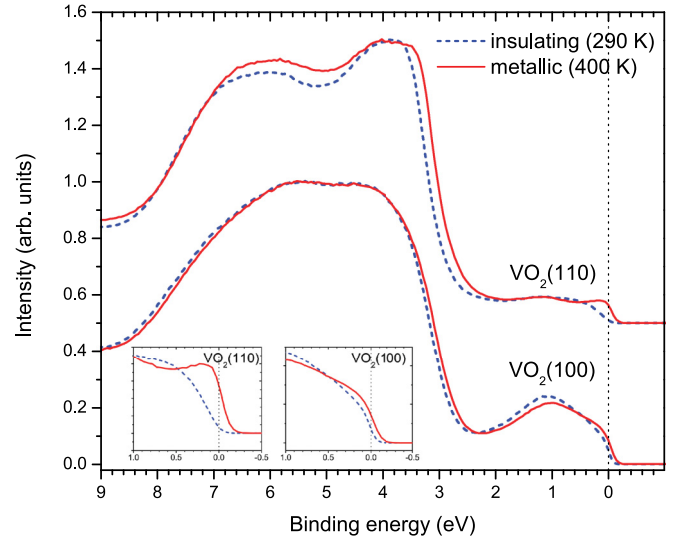
derivative). However, for the *highly strained* $VO_2(100)$ system [Fig. 2(b)], the magnitude of the insulating gap is much smaller, at $\lesssim$50 meV, with only a weak shift in the O $2p$ band. Here, the strong double-peaked structure in the O $2p$ manifold is less prominent; rather, the spectra exhibit broad, asymmetric peaks, similar to earlier PES studies of VO_2.[19] The weak opening of the insulating gap in films under high strain compared to moderate strain constitutes our first clue that the physics of the MIT may be different for highly strained $VO_2(100)$.

In order to understand in more detail the behavior of the two systems across the MIT, we now focus on the dependence of the V $3d$ states with photon polarization. By rotating the polarization vector of the incident photons, it is possible to couple to different symmetry orbitals, providing orbital resolution to PES measurements. In particular, for $E \parallel c_R$, the matrix elements that couple the PES process of the V $3d$ states are maximized for the a_{1g} states. In Fig. 3(a), high-resolution, angle-integrated spectra above and below the MIT are shown for $E \parallel c_R$ and $E \perp c_R$ for $VO_2(110)$, normalized to the intensity between 1.0 and 1.2 eV. It is clear from Fig. 3(a) that there is a substantial change in the shape of the spectra across the transition, and even in the relative energies of features between different polarizations. In Fig. 3(b), the polarization anisotropy, $I_{\parallel} - I_{\perp}$, is shown for the spectra from metallic and insulating phases, representing approximate experimental PES spectra of the a_{1g} orbital. In the metallic phase, the quasiparticle peak is centered at E_F, with the LHB at $\sim$1.5 eV. The quasiparticle peak shifts down to $\sim$0.4 eV in the insulating spectra, accompanied by a shift of the LHB to $\sim$1.8 eV. These results are in remarkable agreement with the cDMFT calculations of the a_{1g} orbital of Biermann *et al.*,[14] which are reproduced by the dotted lines in Fig. 3(b). In the M_1 insulating phase of VO_2, the a_{1g} state is overwhelmingly the most occupied of the V t_{2g} orbitals (contributing $\sim$80% to the total occupied density of states), whereas these orbitals are almost evenly populated in the metallic rutile phase. Further evidence of this interpretation is provided by parameter-free
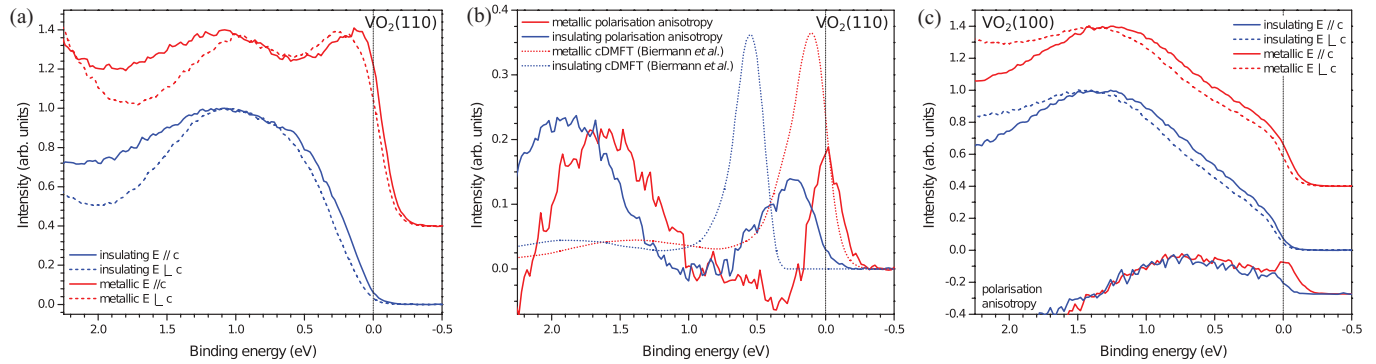
FIG. 3. (Color online) High-resolution V $3d$ PES spectra across the MIT of the VO_2 thin films at 30 eV. (a) Spectra of moderately strained $VO_2(110)$ for two different incident photon polarizations: $E \parallel c_R$ and $E \perp c_R$. (b) Polarization anisotropy of $VO_2(110)$ in the insulating and metallic phases compared with cDMFT calculations of Biermann *et al.*[14] (c) Polarization-dependent spectra of highly strained $VO_2(100)$. Shown at the bottom of the figure is the weak polarization anisotropy for this system.

analysis of the insulating spectra. For $E \perp c_R$, the extremum of the first derivative is located ∼300 meV below E_F, but is much smaller for $E \parallel c_R$ at ∼150 meV (the associated error in determining this quantity is ∼10 meV), supporting the cDMFT results that show the a_{1g} orbital lies closer to E_F than the e_g^π states.

In Fig. 3(c), high-resolution spectra of highly strained $VO_2(100)$ are shown alongside their polarization anisotropy. These spectra show much weaker anisotropy, with very similar shapes both above and below the transition: a very small quasiparticle "peak" shifts to deeper energies (and diminishes in intensity) in the insulating phase. Examination of the first derivative of both photon polarizations in the insulating phase reveal both extrema lie ∼50 meV below E_F, demonstrating the relative isotropy of the gap for $VO_2(100)$. The similarity of the polarization anisotropy across the MIT suggests that the population of orbitals is approximately the same in the insulating and metallic phases, inconsistent with the structural distortion that preferentially occupies the a_{1g} orbitals. DMFT calculations of the rutile phase with varying on-site Hubbard U have demonstrated that an *insulating rutile* phase (i.e., without structural distortion) may be stabilized for large values of U.[15] Bulk rutile VO_2 is believed to lie close to (but on the metallic side of) the crossover region (in which both metallic and insulating phases are stable). However, the nature of the insulating rutile phase is very different from the insulating M_1 phase of bulk VO_2, characterized by a very small insulating gap and almost even population of t_{2g} orbitals (similar to the metallic phase). Our PES measurements of highly strained $VO_2(100)$ are consistent with such a scenario, in which we observe both a very small insulating gap ($\lesssim$50 meV) *and* similar populations of the t_{2g} orbitals across the transition, in contrast to our results of the moderately strained $VO_2(110)$ system. It is suggested that the large tensive strain of $VO_2(100)$ leads to a narrowing of the bandwidth W of the t_{2g} bands, and the accompanying increase in the relative importance of electron correlations, characterized by U/W. In this simple model (schematically depicted in Fig. 4), $U/W_{bulk} < U/W_{(110)} < U/W_{(100)}$, and the system may be pushed into the coexistence region of the phase diagram, with a crossover from the traditional lattice-electronic mechanism of the bulk system to an electronic one for the highly strained system.

For Nb-doped VO_2, an insulating rutile phase has already been observed, for which the mechanism was interpreted as electronic in origin, assisted by the disorder.[11] Here, we show that such an electronic-driven transition can also be stabilized for pure VO_2 at ambient pressures by introducing large tensive strain to the system. These findings are in agreement with a recent optical study of similar VO_2 thin films, in which the decoupling of the structural and electronic components of the MIT was reported.[22] One can then circumvent the well-known structural bottleneck in the time scale of the transition,[5] of substantial value for applications that are envisaged to exploit the ultrafast nature of the MIT of VO_2.[3,23] Furthermore, this observation that the electronic-driven transition in highly strained VO_2 is quite different to that in moderately strained VO_2 (in agreement with DMFT) supplies additional weight to the argument that *both* the Peierls-type and Mott-type mechanisms are important in stabilizing the M_1 phase of bulk VO_2.
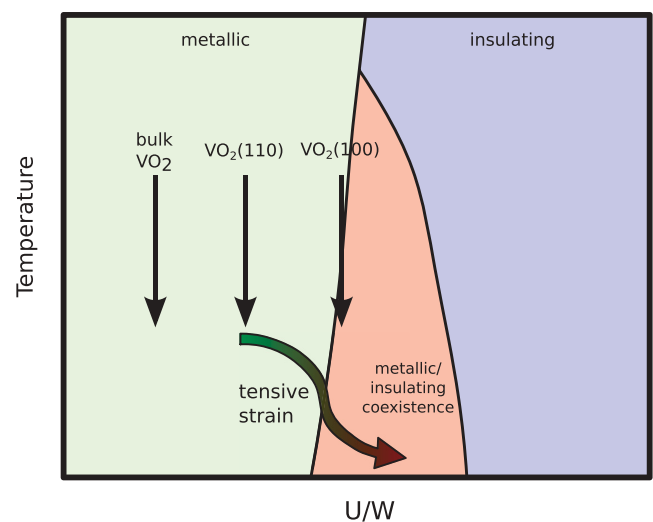

FIG. 4. (Color online) Schematic representation of the impact of tensive c_R-axis strain on the phase diagram of VO_2. Tensive strain expands the c_R axis, narrowing the bandwidth W, and leading to an increase in the relative importance of electron correlations, U/W. The phase diagram is based on the DMFT results of Ref. [15].
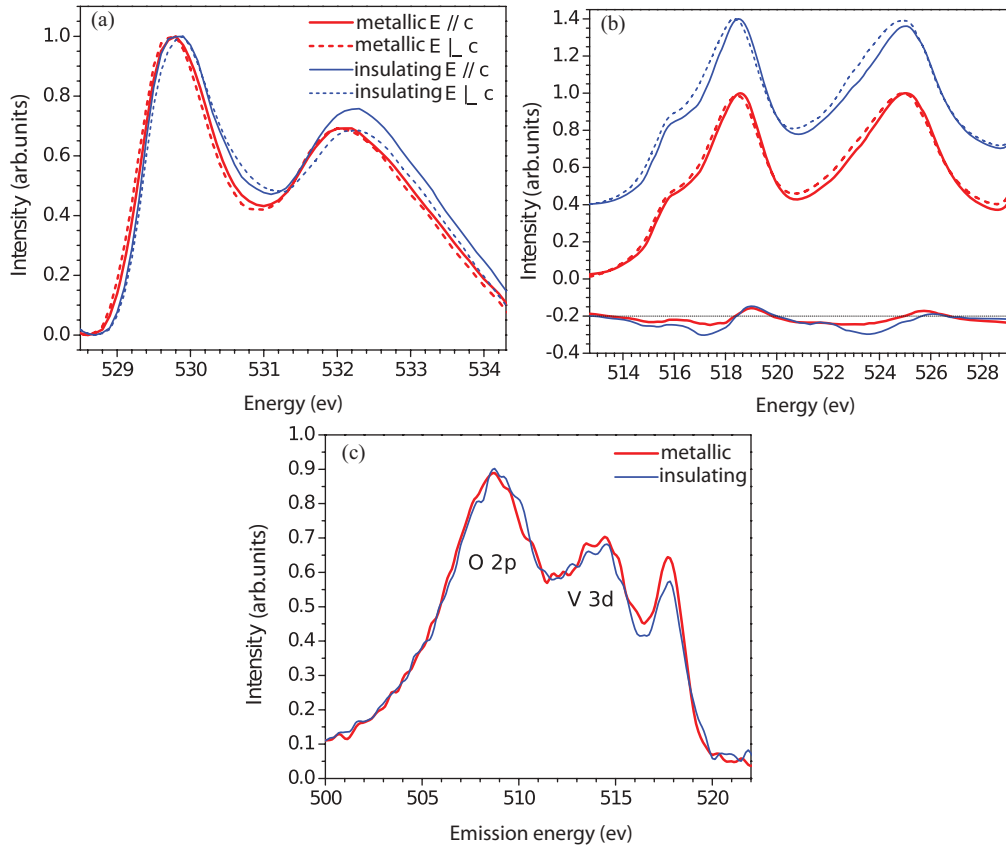
FIG. 5. (Color online) Soft x-ray measurements on VO_2(100) through the MIT. (a) Polarization-dependent O K-edge XAS. (b) Polarization-dependent V $L_{3,2}$-edge XAS. At the bottom of the figure, the anisotropy between $E \parallel c_R$ and $E \perp c_R$ are shown. (c) RXES spectra, recorded at the V L_3-edge peak.

In order to reinforce our PES results, soft x-ray XAS and RXES measurements have also been performed and are shown in Fig. 5. It is well known that XAS of the O K-edge[16,24] and V $L_{3,2}$-edge[9] are sensitive to changes in the population of the t_{2g} orbitals across the MIT, and we have previously demonstrated that RXES at the V L_3-edge is a sensitive probe of the structural distortion associated with the MIT in moderately strained VO_2.[25,26] For VO_2(100), we find our XAS spectra from films in the metallic phase at the V $L_{3,2}$- and O K-edges [Figs. 5(a) and 5(b)] are in good agreement with other such measurements of the metallic phase of bulk and moderately strained VO_2.[9,16,25] However, the spectra from insulating films are almost identical to those from the metallic films, with only a weak shift in the O K-edge threshold (of $\lesssim 0.1$ eV, which is the accuracy of these measurements), indicating the very small insulating gap. In particular, the a_{1g} ($d_\parallel$) peak, a signature of V-V dimerization in the distorted monoclinic phase, is absent at low temperature. Similarly, RXES measurements of VO_2(100) are not found to exhibit any temperature dependence across the MIT [Fig. 5(c)]. For moderately strained VO_2(110), a large change in the relative intensity of the V $3d$ feature at $\sim$515 eV is related to the different bonding environments of V-O induced by the structural distortion of the VO_6 octahedra at the MIT.[25] Here, we find this ratio is the same for the insulating and metallic spectra of VO_2(100), indicating the twisting of

the VO_6 octahedra is absent in this sample. Both of these observations are consistent with the PES evidence described above and together suggest a rutilelike structure exists in both metallic and insulating phases. Moreover, recent temperature-dependent x-ray diffraction measurements on similar thin films[22] suggest that the change in lattice spacing at the MIT is very weak (by an order of magnitude) for their highly strained VO_2(100) films compared with the bulk, and is decoupled from the electronic transition. For our VO_2(100) samples, we find a similar suppression of the lattice spacing component of the transition compared with VO_2(110),[17] emphasizing the weaker role of the lattice in the MIT of VO_2(100).

In summary, we have observed a crossover from a Mott-Peierls–like transition to a Mott-like transition with an increase in tensive strain along the c_R axis in VO_2 through several different spectroscopic techniques. XAS and RXES were used to demonstrate the absence of the large structural distortion at the MIT that characterizes bulk and moderately strained VO_2. PES measurements revealed a weak insulating gap as well as the suppression of orbital redistribution across the transition. We further showed that by exploiting the relative polarization of the incident photons, PES can probe changes in the orbital occupation across electronic phase transitions. Our observations have important implications for novel functional material engineering of VO_2, suggesting a route towards

circumventing the structural bottleneck in the ultrafast time scale of the MIT.

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