We investigate far-infrared properties of strain engineered vanadium dioxide nanosheets through epitaxial growth on a (100)\textsubscript{R} TiO\textsubscript{2} substrate. The nanosheets exhibit large uniaxial strain leading to highly uniform and oriented cracks along the rutile c-axis. Dramatic anisotropy arises for both the metal-insulator transition temperature, which is different from the structural transition temperature along the c\textsubscript{R} axis, and the metallic state conductivity. Detailed analysis reveals a Mott-Hubbard like behavior along the rutile c\textsubscript{R} axis.

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I. INTRODUCTION

During the past five decades, vanadates have been intensely investigated from the point of view of clarifying the physics of metal-insulator transitions (MIT). Vanadium dioxide (VO$_2$) is particularly intriguing, exhibiting a MIT with a conductivity decrease of over five orders of magnitude\cite{8}. This is accompanied by a transition from a high temperature metallic rutile structure to an insulating monoclinic structure below the transition temperature. In bulk, the structural transition temperature, $T_{S\text{t}b\text{ulk}}$, equals the metal-insulator transition temperature, $T_{MI\text{bulk}}$, i.e. $T_{S\text{t}b\text{ulk}} \approx T_{MI\text{bulk}} \approx 340\text{K}$\cite{2}. However, VO$_2$ is not yet fully understood regarding the Mott-Hubbard or Peierls like nature of its MIT, though it is now generally accepted that a complete description requires explicit consideration of electron-electron correlations\cite{5,4}. This is motivated in particular by the observed difference between the MIT and the structural transition temperatures, which provides significant evidence that the correlated conductivity behavior is independent of the structural phase\cite{5,4}. Additionally, recent experimental studies highlight the multifunctional potential of VO$_2$ including current or photoinduced phase changes (with the commensurate large tuning of the dielectric function) as well as integration with other technologies for applications including light detection and memory-based metamaterials\cite{5,4,11,12,13}.

Strain engineering enables an additional degree of control of technologically relevant properties and provides a discriminatory capability towards obtaining fundamental insight into the microscopic origin of the macroscopic characteristics. Strain has been used to modify the MIT temperature in VO$_2$ through direct application\cite{12,13} or substrate-dependent application\cite{22,13} of stress. For the present measurements, we utilize highly strained epitaxial (100)$_R$ VO$_2$ thin films. The far-infrared conductivity is measured using non-contact polarization sensitive terahertz time-domain spectroscopy (THz-TDS) providing direct access to the coherent quasiparticle response along b$_R$ or c$_R$ by simply changing the sample orientation. Subsequent analysis indicates that the strain engineered tuning of vanadium $a_{1g}$ and $e^\pi_g$ orbitals controls the MIT transition temperature along c$_R$, which is different from the structural transition temperature. The origin of the observed conductivity anisotropy is also discussed, along with the potential for a technological application of strain engineered VO$_2$ thin films as temperature switched far-infrared polarizers.

II. EXPERIMENTS

The $\sim 100\text{nm}$ and $\sim 250\text{nm}$ thick VO$_2$ films we investigated were deposited on rutile (100)$_R$ TiO$_2$ substrates by temperature optimized sputtering from a vanadium target, using the reactive bias target ion beam deposition technique in an Ar+O$_2$ gas mixture; details of the growth conditions can be found elsewhere\cite{22}. The samples morphology was characterized by optical, atomic force (AFM) and scanning electron microscopies (SEM), and the film microstructure was analyzed by temperature dependent X-ray diffraction (XRD).

THz-TDS is a non-contact method to measure far-infrared conductivity. The conductivity anisotropy is easily determined from transmission of THz pulses for different sample orientations. In our case the output of a 1kHz 35fs Ti:Sapphire amplifier is used to generate nearly single-cycle THz pulses via optical rectification in a ZnTe crystal. We then employ a standard THz Time Domain Spectroscopy (THz-TDS) setup to measure the transmission in the THz frequency range $\sim 0.2 - 2.0\text{THz}\text{[13]}$. By changing the sample orientation with respect to the THz pulse polarization we are able to monitor the transmission along different crystal axes.

(100)$_R$ TiO$_2$ has a large refractive index anisotropy in the THz range, partly caused by its characteristic rutile structure. Such an anisotropy in the (100)$_R$ TiO$_2$ substrate makes it easy to distinguish transmitted THz signals with polarization parallel to c$_R$ from THz signals with polarization perpendicular to b$_R$ (Fig. 1[a]). Temperature dependent experimental characterization of the TiO$_2$ substrate in the THz range, using our THz TDS setup, led to values of

$$n_c \approx 12.4 - 6 \times 10^{-4}\Delta T + 1.2i$$

$$n_\sigma \approx 9.1 - 3 \times 10^{-4}\Delta T + 0.4i$$

for the refractive index along c$_R$ and b$_R$, respectively, in accordance with previous results\cite{23}. Here, $\Delta T$ stands for the temperature deviation with respect to room temperature. This approximation to the TiO$_2$ complex refractive index holds between room temperature and 400K; it does not take into account the temperature dependence of the imaginary part, which is negligible for our purposes.

The conductivity of the VO$_2$ film is extracted using the Fresnel equations, after experimental determination of the ratio of the THz transmission of the film to the THz transmission of a bare TiO$_2$ substrate, used as a reference. THz TDS is thus a non-contact conductivity measurement, which allows one to quickly characterize the conductivity anisotropy in many samples with different thicknesses and substrates.

III. RESULTS

A. Characterization of the VO$_2$ nanosheets
Figure 2(a) is an AFM phase image of the 250 nm film, showing periodic buckling and cracking of the film parallel to \(c_R\), with inter-crack spacings on the order of 1 \(\mu\)m. The depth profile reveals nanosized ridges, \(~15\) nm high, near the cracks. The SEM image in Fig. 2(b) confirms the \(~250\) nm thickness of the film. It shows that the cracks’ depth matches the film thickness and it gives an estimate of about 30 \(\mu\)m for their width. Such nanocracks were not detected by the AFM due to lack of tip sensitivity.

The optical images of the 100 nm (Fig. 3(a)) and the 250 nm (Fig. 3(b)) films confirm the \(~1\) \(\mu\)m period spacing of the cracks along \(c_R\). Also, the observed uniformity in the distribution of cracks is an indication that our films are strained in a highly homogeneous and oriented fashion. This crack distribution enables a comparison of our results with those of VO\(_2\) nanobeams, aligned along \(c_R\) [17], although the dimensionality of our nanosheets gives access to the properties of strained VO\(_2\) along more than one axis. Such cracking uniformity was achieved by optimizing the growth conditions of the samples, in particular the growth temperature. In the case of our \((100)_R\) VO\(_2\) films the growth temperature was set to \(~500^\circ\)C. Films grown at \(~450^\circ\)C show cracking along different directions, which makes the characterization of the films along \(c_R\) less straightforward. All subsequent analysis is analogous for both the 100 nm and the 250 nm thick films. Unless otherwise specified the results will refer to the 100 nm thick sample.

Detailed room temperature XRD of the VO\(_2\) film confirms the single crystal nature of the sample and yields the lattice parameters of the material (Fig. 4(a)). Comparing these values with those in the rutile phase of bulk VO\(_2\) [21] yields mismatches of \(\sim0.83\%\) along \(a_R\), \(\sim2.17\%\) along \(b_R\), and \(1.41\%\) along \(c_R\), indicative of a compressive strain along \(a_R\) and \(b_R\), as opposed to a tensile strain along \(c_R\). Such strain values along \(c_R\) are comparable to those achieved in one-dimensional VO\(_2\) nanobeams [17]. Bulk rutile TiO\(_2\) has larger lattice constants than bulk rutile VO\(_2\) along all directions so one would expect that both \(b_R\) and \(c_R\) would expand in \((100)_R\) VO\(_2\) films grown on a \((100)_R\) TiO\(_2\) substrate. However, our nanosheets show that the expansion along \(c_R\) surpasses the substrate clamping effect due to the \(b_R\)-axis, leading to a compressive strain in the \((ab)_R\)-plane. This behavior is also observed in the 250 nm thick film, with mismatches of \(\sim0.68\%\) along \(a_R\), \(\sim1.94\%\) along \(b_R\), and \(0.86\%\) along \(c_R\).

Temperature dependent XRD results (Fig. 3(c)) show that a small \(a_R\)-axis expansion, \(\sim0.1\%\), occurs during the film’s structural transition. This transition occurs at a temperature \(T_{St}^{film} \sim 340 K \sim T_{bulk}^{St}\), the same as in bulk, and shows the expected hysteric behavior. (From here on \(T_{St}\) will refer to both bulk and film structural transition temperatures.) The \(a_R\)-axis expansion in our strained sheet can be compared to that in bulk VO\(_2\), estimated as \(a_R^{strain}/a_R^{bulk} \sim 0.6 - 0.8\%[22,23]\), where \(a_R^{bulk}\) is the equivalent of \(a_R\) in the bulk monoclinic insulating structure. The order of magnitude difference between the lattice parameter variation in the film and that in bulk stems from the clamping effect of the rutile TiO\(_2\) substrate. This is consistent with the large strain observed in room temperature XRD, caused by the strong substrate clamping effect. The structural change exhibited at 340 K by our strained VO\(_2\) nanosheets is thus smaller than the change observed in bulk VO\(_2\). Since VO\(_2\) shares the TiO\(_2\) rutile structure at high temperatures, the reduced structural change is expected to have an impact mainly on the low temperature VO\(_2\) film’s structure. The temperature dependent \((200)_R\) 2\(\theta\) plots from which the data in Fig. 3(c) were extracted are presented in Fig. 4(b). These raw data provide further support to our observation that the clamping effect due to the substrate is very strong, thereby preventing the development of significantly different structural phases in the strained VO\(_2\) film.

B. THz Time Domain Spectroscopy

As shown in Fig. 1 upon increasing the temperature from the insulating to the metallic phase the THz peak transmission in the 100 nm \((100)_R\) VO\(_2\) film drops by \(~70\%) along the \(c_R\)-axis and by \(~15\%) along the \(b_R\)-axis, and the THz peak transmission in the 250 nm \((100)_R\) VO\(_2\) film drops by \(~85\%) along the \(c_R\)-axis and by \(~15\%) along the \(b_R\)-axis. Figure 4(b) shows the transmission anisotropy in our 250 nm VO\(_2\) sample, normalized to its low temperature value along each axis (\(b_R\) and \(c_R\)). This representation highlights the dramatic difference between the low temperature transmission along \(b_R\) and that along \(c_R\), thereby illustrating the potential of strained VO\(_2\) films as temperature tunable THz polarizing beamsplitters.

Figure 5(a) shows the temperature dependent far infrared conductivity, obtained from the transmission data, for the 100 nm \((100)_R\) VO\(_2\) nanosheet. The conductivity along \(c_R\) shows a clear transition from the insulating to the metallic state with a narrow hysteresis, which is indicative of the high quality of the film. In the metallic state the conductivity is \(\sigma_{c_R} \sim 5650(\Omega cm)^{-1}\), comparable to bulk single crystal values [4]. The MIT along \(c_R\) occurs at a temperature \(T_{M1}^{c_R} \sim 365^\circ\)K. \(T_{M1}^{c_R}\) is significantly larger than both the structural transition temperature and the bulk MIT temperature, \(T_{St} \sim T_{M1}^{bulk} \sim 340^\circ\)K. Our VO\(_2\) films therefore exhibit, along \(c_R\), a \(\sim 25^\circ\)K temperature difference between the structural and the metal-insulator transition temperatures. The combination of the quasi three dimensionality of our nanosheets, which enables a direct measurement of the strain along the three crystal axes through XRD analysis, with the polarization sensitivity of THz spectroscopy is the key to identifying this distinction between the two transition temperatures.

The conductivity along \(b_R\) also exhibits a transition (see inset of Fig. 5(a)), which occurs at \(T_{M1}^{b_R} \sim 340^\circ\)K. Along this direction we therefore observe that the structural and metal-insulator transition temperatures are the same, \(T_{M1}^{c_R} \sim T_{St} \sim T_{M1}^{bulk}\). However, the conductivity along \(b_R\) reaches a high temperature value about 30 times smaller...
than the high temperature conductivity along \( c_R \). This strong conductivity anisotropy will be addressed later in the text.

THz TDS results for the 250nm thick sample (Fig. 6) indicate that its transport properties are similar to that of the 100nm sample. In particular, the high temperature conductivity along \( c_R \) remains as good as in bulk VO\(_2\) single crystal\([13]\) while \( T^{\text{b}}_{\text{MI}} \approx 365K > T^{\text{bulk}}_{\text{MI}} \). The high temperature conductivity along \( b_R \) is very low, \(< 100(\Omega cm)^{-1}\), and the transition temperature can only be estimated at \( T^{\text{b}}_{\text{MI}} \approx 340K \), consistent with \( T^{\text{bulk}}_{\text{MI}} \) and \( T_{\text{St}} \) and in line with what is observed in the 100nm sample (Fig. 5(a)).

### IV. DISCUSSION

Understanding the contribution of the V\(_3d\) orbitals to the electronic properties is crucial in order to explain the large material anisotropy in \( T_{\text{MI}} \).\([23]\) A splitting of the 5-fold degenerate 3d states occurs due to the octahedral coordination of the V atoms, resulting in a higher energy doubly degenerate \( e_g \) level and a lower energy triply degenerate \( t_{2g} \) level. Trigonal distortion further splits the \( t_{2g} \) levels leading to an upshifted doubly degenerate \( e_g^\pi \) state, responsible for conduction in the \( ab_R \)-plane, while downshifting a non-degenerate \( c_R \)-oriented \( a_{1g} \) state (Fig. 3(b)). Recent cluster Dynamical Mean Field Theory (cDMFT) calculations\([3] \) which include the effect of a \( \pm 2\% \) strain along \( c_R \), have demonstrated that a tensile strain along \( c_R \) narrows the \( a_{1g} \) derived band and leads to a compressive strain in the \( ab_R \)-plane, which uplifts the \( e_g^\pi \) band (Fig. 5(c)). In the Mott picture the energy increase of \( e_g^\pi \) electrons reduces the screening of electrons residing in the \( a_{1g} \) band, thereby enhancing the effect of correlations (i.e. increasing the screened Hubbard \( U \)). This results in an increase of the insulating band gap which opens, below \( T_{\text{MI}} \), between the bonding \( a_{1g} \) and the anti-bonding \( e_g^\pi \) levels, therefore leading to an increased \( T_{\text{MI}} \) along \( c_R \).\([23,24]\)

The epitaxial strain in our film can be decomposed into a uniaxial tensile strain along \( c_R \) and a uniaxial compressive strain along \( b_R \). Along \( c_R \), \( T^{\text{c}}_{\text{MI}} \approx 365K > T^{\text{bulk}}_{\text{MI}} \), in line with previous experimental results\([31]\) while \( \sigma_{cR} \) remains comparable to the best single crystal value\([4]\). These results agree with the Mott picture above, where the increased lattice spacing along \( c_R \) further increases the ratio of Coulomb repulsion to the inter-atomic hopping integral, thereby destabilizing the metallic phase and increasing \( T^{\text{c}}_{\text{MI}} \). The Peierls picture predicts a decrease in \( T^{\text{b}}_{\text{MI}} \) with tensile strain along \( c_R \), thus failing to describe our results along that axis.\([31]\) Also contrary to the Peierls-driven MIT scenario along \( c_R \) is the fact that the structural transition occurs at a temperature \( T_{\text{St}} \approx 340K, 25K \) lower than \( T^{\text{c}}_{\text{MI}} \): in a Peierls picture both transitions would be expected to occur at the same temperature. In contrast to what happens along \( c_R \), the results along \( b_R \), where \( T^{\text{b}}_{\text{MI}} = T_{\text{St}} \), are compatible with a Peierls-driven MIT scenario.

As mentioned above, our samples are cracked along \( c_R \). The occurrence of such cracks is common in VO\(_2\), in both bulk and strained samples\([20,27]\), and this has prevented accurate measurements of the DC conductivity in this material in the direction perpendicular to \( c_R \). Hindered quasiparticle motion along \( b_R \) due to the presence of \( c_R \) oriented cracks is the most likely explanation for the reduced value of \( \sigma_{bR} \) in our films. However, a different scenario could arise in the THz range. Due to the small value of the far-infrared carrier mean free path (\(~1\text{ps}\)) compared to DC, the \(~1\text{ps}\) long THz field should be able to couple to the material along \( b_R \) despite the cracks along \( c_R \). According to this picture, the uniaxial compressive strain along \( b_R \) would play a significant role in reducing \( \sigma_{bR} \), compared to \( \sigma_{cR} \), while keeping \( T^{\text{b}}_{\text{MI}} = T^{\text{bulk}}_{\text{MI}} = T_{\text{St}} \). Given the orbitals orientation, conductivity in the \( ab_R \)-plane is mediated by the \( e_g^\pi \) orbitals whose energy is controlled by the overlap between O\(_2p\) and V\(_3d\) orbitals\([22]\). Low conductivity behavior in the compressed \( ab_R \)-plane for \( T > T^{\text{c}}_{\text{MI}} \) would then arise from the \( e_g^\pi \) states being higher in energy than in the unstrained case, which reduces their overlap with the Fermi level (Fig. 5(c)). VO\(_2\) nanosheets that remain uncracked while maintaining a high level of strain along \( b_R \) must be investigated in order to clarify the role of the \( e_g^\pi \) orbitals on the high temperature value of \( \sigma_{bR} \), thereby also clarifying the nature of the MIT along that axis.

Our strained VO\(_2\) films on a TiO\(_2\) substrate have been shown to enable the separation of the far-infrared signal’s polarization components both in time and intensity. The temperature dependent THz conductivity of strained VO\(_2\) nanosheets (Figs. 5(a) and 7) shows that incident light polarized parallel to \( b_R \) is transmitted through VO\(_2\) at both low and high temperatures, whereas incident light polarized parallel to \( c_R \) is transmitted through VO\(_2\) at low temperatures but reflected at high temperatures. Our strained VO\(_2\) single crystal nanosheets can thus be thought of as temperature switchable far-infrared polarizing beamsplitters.

### V. PHASE DIAGRAM

Finally, it is interesting to map the strain of our film onto the VO\(_2\) phase diagram in Fig. 7, constructed based on past studies of VO\(_2\) as a function of temperature, pressure\([17,23]\) and doping\([30,33]\). In general, it is not trivial to map the effect of doping onto that of pressure. This was initiated by Pouget et al., who found a one-to-one correspondence between Cr-doping and the application of uniaxial stress along [110].\([20,24]\) Other doping experiments tend to indicate that doping ions with radii smaller than V\(^{4+}\) lead to an increase in \( T_{\text{MI}} \) whereas those with larger radii have the opposite effect.\([34]\) This is similar to what happens in V\(_2\)O\(_3\), a canonical Mott insulator.\([35]\)
Although we cannot distinguish between the two. M1, M2 and M3/T are all structurally too far from rutile and monoclinic structures. As for the low temperature structure, M4 or rutile seem to be the most likely candidates, indicative of a more complex behavior of VO$_2$ to lead to the results shown in Fig. 3C, and they are located in different regions of the phase diagram, as seen in Fig. 5–7. Independence of the conductivity behavior from the structural phase has been reported before.

R$_{Ga, Ge, Sn, Mn, Co, etc.}$ with formal charges of +3 or +4. Stress along [001]$_R$ in $\sim 0.3$% mismatch along (110)$_R$, all the information in the diagram refers to stress along [001]$_R$. The white oval indicates the phase space characteristic of our (100)$_R$ VO$_2$ samples. The uniaxial stress on our films along (110)$_R$ has been estimated, respectively for the 100nm and the 250nm samples, to $\sim 20.9$kbar and $\sim 18.5$kbar, based on the measured $-2.32$% and $-2.06$% mismatch along (110)$_R$ and on a Young modulus of $\sim 900$kbar. These uniaxial stress values are higher than ever reported, to our knowledge, for uniaxial stress on VO$_2$.

The dependence of $T_{MI}$ on doping, studied in V$_{1-x}$M$_x$O$_2$ compounds, can be approximately mapped onto its dependence on applied pressure. Reduction of V$^{4+}$ is achieved using M = Nb, Mo, W, Ta, Re, Ir, F, Ti, Os, Ru, Tc, etc., with formal charges of +4, +5 or +6. The effect on $T_{MI}$ is similar to that of negative (compressive) stress along [001]$_R$, yielding $dT_{MI}/dx = -0.3 \sim -28$K/at.%. Oxidation of V$^{4+}$ is achieved using M = Cr, Al, Fe, Ga, Ge, Sn, Mn, Co, etc., with formal charges of +3 or +2. The effect on $T_{MI}$ is similar to that of positive (tensile) stress along [001]$_R$, yielding $dT_{MI}/dx = 0 \sim 13$K/at.%. Our results, indicated by the white oval in the phase diagram of Fig. 7 are comparable to those of Everhart et al., where an anisotropy of about two orders of magnitude is observed in the metallic phase of bulk VO$_2$ single crystals doped with iron at 0.076%.$^{32}$ Our estimate of the stress puts our samples in a region of the phase diagram where $T_{MI}$ increases with stress, and where a two phase behavior is expected above $T_{MI}$. This is consistent with our observation of both insulating ($T < T_{MI}^R$) and metallic ($T > T_{MI}^R$) values of $\sigma_{cr}$ in the same rutile structure, above $T_{St}$. The independence of the conductivity behavior from the structural phase has been reported before,$^{32}$ though relative to monoclinic structures. As for the low temperature structure, M4 or rutile seem to be the most likely candidates, although we cannot distinguish between the two. M1, M2 and M3/T are all structurally too far from rutile$^{20,30,31}$ to lead to the results shown in Fig. 3C, and they are located in different regions of the phase diagram, as seen in Fig. 7. These observations, along with the strong conductivity anisotropy exhibited by our strained nanosheets, are indicative of a more complex behavior of VO$_2$, beyond the currently accepted doping and strain dependence of its structural and transport properties (Fig. 7).

Coming back to the conductivity measured in our strained nanosheets, it is important to point out that its anisotropy is unexpectedly large compared to previous experimental observations and theoretical calculations on VO$_2$ samples.$^{22,28}$ The anisotropy in the DC conductivity, $\sigma_{cr}$ or $\sigma_{st}$, in undoped VO$_2$ samples is generally $\geq 1$ for $T < T_{MI}$ but can take many different values for $T > T_{MI}$ (Table I). Differences in sample quality and stoichiometry as well as in conductivity measurement techniques surely affect the results, but variations in geometry and internal strain / cracking are likely to also have an effect on the anisotropy of metallic VO$_2$.

Table I and II present a complete and up to date review, to our knowledge, of the experimental and theoretical data on conductivity anisotropy in VO$_2$, including the effect of externally applied stress. Table I includes several results for the strain induced variation of $T_{MI}$ and of the conductivity in VO$_2$, for situations where hydrostatic or uniaxial pressure is applied to the samples.$^{17,18,27,30,34,38,49,60}$ Table II presents several results for the strain-induced variation of $T_{MI}$ and of the conductivity in VO$_2$, for situations where hydrostatic or uniaxial pressure is applied to the samples.$^{26,32,33,40,41,65}$

As seen in Tables I and II in most situations where uniaxial pressure is applied the conductivity is measured along $c_R$, the only axis along which it is well defined due to geometry constraints of the samples or to cracking. Few studies determine the conductivity along $a_R$ or $b_R$ as a function of applied pressure. In general, it is agreed that (i) an applied uniaxial compressive (tensile) stress along the $c_R$-axis leads to an increased (decreased) conductivity at $T > T_{MI}$; (ii) an applied uniaxial compressive (tensile) stress along the $c_R$-axis leads to a decreased (increased) $T_{MI}$ (the axis along which $T_{MI}$ is measured is not always specified); (iii) a small uniaxial stress applied along the [110]$_R$ direction has no significant effect on the conductivity nor $T_{MI}$ along $c_R$ but it promotes a phase transition between different monoclinic structures (M1, M2, T/M3, M4), in the insulating phase.$^{20,31}$ Further experiments are needed in order to systematically measure the conductivity along $a_R$ or $b_R$. Under (i) an applied uniaxial stress along $a_R$ or $b_R$; (ii) an applied uniaxial stress along $c_R$; (iii) hydrostatic pressure. Also, clear criteria for distinguishing $T_{MI}$ from $T_{St}$ would be extremely valuable to help draw a more accurate and complete phase diagram, in line with what has been attempted in previous studies.$^{26}$ The highly oriented strain across a quasi three dimensional structure, achieved in epitaxially grown VO$_2$ nanosheets, offers an extraordinary versatility and potential for investigation of these issues.

Theoretically, several pictures have been suggested to explain the anisotropy in (unstrained) VO$_2$: (1) a two band
model description of 3d electrons, within the framework of the Goodenough model, predicts a non conducting abR-plane for $T > T_{MI}$, any residual conductivity in that plane being due to the overlap of O2p and V3d orbitals $^{[23,24]}$. 

LDA calculations by Allen’s group predict the structural distortion to be the main force driving the MIT in VO$_2$, followed by a simple Peierls picture $^{[25]}$. (3) a three-band Hubbard model, suggested by Tanaka et al., predicts a one dimensional conducting phase along c$_R$ for $T < T_{MI}$ and an isotropically conducting phase for $T > T_{MI}$ $^{[26]}$. (4) LDA+cDMFT calculations by Biermann et al. suggest that electron correlations within the $e_g^\sigma$ levels are weaker than those along the a$_{1g}$ ones $^{[27]}$. (5) subsequent LDA+cDMFT calculations by Kotliar’s group, which include a moderate degree of uniaxial strain, suggest that electronic correlations are the main driving force in the MIT, and that the rutile phase itself should be able to support both metallic and insulating electronic behavior $^{[28]}$. (6) Liebsch et al. compared the development of the insulating gap below $T_{MI}$ $^{[29]}$. Nonetheless, most of the calculations based on unstrained VO$_2$ samples agree that (i) a$_{1g}$ and e$_g^\pi$ states can be regarded as nearly independent; (ii) the conductivity is expected to be of predominantly a$_{1g}$ behavior for $T < T_{MI}$ and nearly isotropic for $T > T_{MI}$; (iii) electron correlations should be included in the model, mainly in the c$_R$ oriented a$_{1g}$ levels. Our results agree with (i) and (iii), while strain induced cracking prevents the accurate description of the effect mentioned in (ii). Further theoretical investigations should take into account not only strain $^{[30]}$ but also the oxygen degrees of freedom, in order to provide a more accurate description of the O2p and V3d orbitals overlap, most relevant for describing the conductivity in the ab$_R$-plane, and of the subsequent cracking along c$_R$. Such estimates would be adequate for a quantitative, rather than merely qualitative, comparison with our experimental data.

VI. CONCLUSION

In summary, we have observed a large anisotropy of the properties of strained 100nm and 250nm thick VO$_2$ nanosheets. The increased value of $T_{MI}^{c_R}$ compared to $T_{SI}$ is a clear signature of a Mott- rather than Peierls-driven MIT along c$_R$. An $e_g^\pi$ orbital tuning picture is proposed to explain the reduced value of the high temperature $\sigma_{br}$, although a crack induced conductivity decrease cannot be conclusively ruled out. Additional experiments are needed in order to clarify the mechanism of the phase transition in strained VO$_2$, mainly in the direction perpendicular to c$_R$. This would allow the development of a more comprehensive phase diagram for this material. In general, epitaxial strain engineering is a powerful tool which has the potential to enable careful tuning of the metal-insulator transition in numerous other correlated electron materials, thereby providing a viable route towards technologically relevant multifunctionality and increased understanding of the microscopic origin of the MIT.

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FIG. 1. (a) THz transmission along $c_R$ and $b_R$ (vertically offset) in the 100$\text{nm}$ (100)$_R$ VO$_2$ sample (solid) and in the TiO$_2$ reference substrate (dashed), below (blue) and above (red) $T_{MI}$. The large refractive index anisotropy of the TiO$_2$ substrate leads to a slower propagation of the laser pulse along $c_R$ than along $b_R$, which enables the distinction of the two signals, and thus the orientation of the sample with respect to the incident field polarization. (b) THz transmission along $c_R$ and $b_R$ in the 250$\text{nm}$ (100)$_R$ VO$_2$ sample, below (blue) and above (red) $T_{MI}$, normalized to the high temperature value. The relative low temperature transmission along $b_R$ ($\sim 85\%$) is dramatically different from that along $c_R$ ($\sim 15\%$).

FIG. 2. Characterization of the 250$\text{nm}$ thick (100)$_R$ VO$_2$ film. (a) AFM phase image (0$^\circ$-5$^\circ$ scale) and corresponding height profile: the 250$\text{nm}$ sample shows buckling induced ridges along $c_R$ (height indicated by the arrows: $\Delta z = 14.307\text{nm}$). (b) SEM image of a section of the sample (seen from the edge, the surface and the cross section being located as labeled) showing a $\sim 30\text{nm}$ wide crack.
FIG. 3. Characterization of VO₂ thin films on a (100)_{R} TiO₂ substrate. Optical images of the (a) 250 nm and (b) 100 nm films: the samples show buckling induced ridges along c_{R}, spaced by \sim 1 \mu m. (c) Temperature dependence (for increasing and decreasing temperature) of the a-axis lattice spacing, deduced from XRD data: a \sim 0.1\% increase is observed along a_{R}, in the 100 nm thick VO₂ sample, across the structural transition which occurs at T_{St} = 340 K. The expected linear increase of the a_{R}-axis lattice spacing of TiO₂ with temperature is also observed.
FIG. 4. (a) Room temperature XRD of the 100nm thick VO₂ thin film, along three different directions: (200)₉₀, (110)₉₀, (101)₉₀. The lattice parameters can be estimated as 4.52 Å along a₉₀, 4.46 Å along b₉₀ and 2.89 Å along c₉₀, yielding mismatches of -0.83% along a₉₀, -2.17% along b₉₀ and 1.41% along c₉₀. (b) Temperature dependent XRD of the 100nm thick VO₂ thin film. Both the TiO₂ and the VO₂ (200)₉₀ peaks are seen to shift as a function of temperature. There is no evidence of the development of any additional structural phase.

FIG. 5. (a) Temperature dependence of the far infrared conductivity in 100nm (100)₉₀ VO₂: σ₉₀ ≃ 30σ₉₀ above the MIT temperature; T₉₀¹₉₀ = 365K while T₉₀¹₉₀ = 340K = T₉₀¹°. (b) The VO₂ rutile unit cell, following Eyert. (c) Effect of tensile strain along c₉₀ on the electronic structure of metallic VO₂: antibonding e₉₀ bands are shifted upwards while the a₁g band is narrowed.
FIG. 6. Temperature dependence of the far-infrared conductivity in 250nm (100) \(R\) VO\(_2\): \(\sigma_{cR} \approx 5250(\Omega \text{cm})^{-1}\) for \(T > T_{MI}^{cR} \approx 365K\); \(\sigma_{bR} < 100(\Omega \text{cm})^{-1}\) and \(T_{MI}^{bR}\) can only be estimated as \(T_{MI}^{bR} \approx 340K\).

FIG. 7. Phase diagram of VO\(_2\) for stress applied mostly along [110]. The black solid line indicates \(T_{MI}\); the white oval defines the phase space of our samples; uniaxial stress results are presented in the region delimited by the dashed white lines; doping \((V_{1-x}M_xO_2)\) leading to reduction \((M=\text{Nb}^{5+})\) or oxidation \((M=\text{Cr}^{3+})\) of V\(^{4+}\) is specified on the top horizontal axis (refer to the main text for more details).
| publication        | sample type                                      | method               | anisotropy below $T_{MI}$ | anisotropy above $T_{MI}$ |
|--------------------|--------------------------------------------------|----------------------|---------------------------|---------------------------|
| Bongers et al.     | bulk single crystal (needle along $c_R$, 6x0.3x0.15mm) | two-probe            | 2                         | 2.5                       |
| (1965)             |                                                  |                      |                           |                           |
| Barker et al.      | bulk polycrystal (well defined $c_R$)             | Hall voltage         | 0.7-0.8                   | 1.1-2                     |
| (1966)             |                                                  |                      |                           |                           |
| Kosuge et al.      | bulk single crystal                              | two-probe            | 1.14                      | 0.58                      |
| (1967)             |                                                  |                      |                           |                           |
| Koide et al.       | single crystal film on rutile substrate           | two probe            | 2                         | 0.001-0.1                 |
| (1967)             | bulk single crystal (needle along $c_R$, 3x0.8x0.07mm) | two-probe            | < 1.2                     | 0.33                      |
| Everhart et al.    | bulk single crystal (4-7x1-4x1-4mm)               | four-probe           | 2-10                      | 7.5                       |
| (1968)             |                                                  |                      |                           |                           |
| Verleur et al.     | bulk single crystal                              | reflectivity         | 0.28-1.4                  | 0.79-2                    |
| (1968)             | (0.25-5eV)                                       |                      |                           |                           |
| Continenza et al.  | (calculations)                                    | model GW             | 3-6.7                     | N/A                       |
| (1999)             | (0-10eV)                                         |                      |                           |                           |
| Mossanek et al.    | (calculations)                                    | LDA (0-12eV)         | 0.6-3                     | 0.7-3.3                   |
| (2007)             |                                                  |                      |                           |                           |
| Lysenko et al.     | 30nm film on (012) Al₂O₃                         | optical (400nm)      | 1.05                      | 1                         |
| (2007)             | diffraction                                      |                      |                           |                           |
| Lu et al.          | 40nm film on (011)R TiO₂                          | star-shaped electrodes | 5.14                     | 1                         |
| (2008)             |                                                  |                      |                           |                           |
| Tomczak et al.     | (calculations)                                    | LDA+CDMFT (0-5eV)    | 0.73-1.67                 | 0.96-1.14                 |
| (2009)             |                                                  |                      |                           |                           |
| our results        | 100nm film on (100)R TiO₂                         | THz TDS              | N/A                       | ~30                       |
| (2010)             | (far infrared)                                   |                      |                           |                           |

**TABLE I.** Compilation of previous experimental and theoretical results for the conductivity (DC, unless otherwise specified) anisotropy, $\frac{\sigma_{cR}}{\sigma_{bR}}$ or $\frac{\sigma_{cR}}{\sigma_{aR}}$, in VO₂, above and below $T_{MI}$, when no external stress is applied. [12,36–39,60–64]
| publication            | sample type | applied pressure | conductivity vs. pressure | conductivity along... | $dT_{MI}/dP$ [K/kbar] | $dT_{MI}/dP$ along... |
|------------------------|-------------|------------------|--------------------------|-----------------------|-----------------------|-----------------------|
| Minomura et al. (1964)| bulk        | uniaxial         | not specified            | not specified         | -0.46                 | not specified         |
| Neuman et al. (1964)  | single crystal | hydrostatic     | increases                | not specified         | no significant change | not specified         |
|                       | powder      | hydrostatic      | increases                | not specified         | no significant change | not specified         |
| Berglund et al. (1969)| bulk single crystal | hydrostatic     | increases; saturates above $T_{MI}$, at 15-20kbar | $c_R$ | 0.082 | $c_R$ |
| Ladd et al. (1969)   | bulk single crystal | hydrostatic     | increases (up to 30kbar, at $T_{room}$) | $c_R$ | 0.06 | $c_R$ |
|                       |             |                  | along $a_R$ or $b_R$     | $c_R$ | no significant change | $c_R$ |
|                       |             |                  | along $c_R$ (up to 0.5kbar) | $c_R$ | -1.2 | $c_R$ |
| Pouget et al. (1975) | bulk single crystal | hydrostatic     | no significant change    | $c_R$ | no significant change | $c_R$ |
| Gregg et al. (1997)  | thin films on Al$_2$O$_3$(012) | in-plane | increases below $T_{MI}$ | not specified | N/A | N/A |
| Muraoka et al. (2002)| 10-15nm thick single crystal thin films on (001)$_R$ | along $c_R$ | increases (epitaxial: 0.3% for [001]$_R$, 1.2% for [110]$_R$) | not specified | $<0$ | $a_R$ or $b_R$ for [001]$_R$; not specified for $[110]_R$ |
|                       | 10-15nm thick single crystal thin films on (110)$_R$ TiO$_2$ | along $c_R$ | increases (epitaxial: 0.3% for [001]$_R$, 1.2% for [110]$_R$) | not specified | $<0$ | $a_R$ or $b_R$ for [001]$_R$; not specified for $[110]_R$ |
| Arcangeletti et al. (2007)| single crystal (5µm thick slab) | uniaxial (diamond a. c., up to 140kbar) | increases below $T_{MI}$ (750-6000cm$^{-1}$) | not specified | N/A | N/A |
| Lu et al. (2008)      | single crystal thin film on (011)$_R$ TiO$_2$ | in-plane (epitaxial: 1.2%//[011]$_R$, 0.4%//[001]$_R$) | N/A | $a_R$ or $b_R$ | $<0$ | $a_R$ or $b_R$ |
| Sakai (2008)          | polycrystalline thin film on metallic Ti (a$_R$ in plane) | in-plane (point contact, up to 255kbar) | increases | not specified | $>0$ | not specified |
| Cao et al. (2009)     | single crystal thin film on (0.5-2x0.5-2x100 nm, along $c_R$) | along $c_R$ (3-point bend, up to 12kbar) | increases (optical) | $c_R$ | $<0$ | $c_R$ |
| our results (2010)    | single crystal thin film on (100)$_R$ TiO$_2$ | in-plane (epitaxial: 5.4%//[001]$_R$, -2.3%//[101]$_R$) | no significant change (far IR)) | $b_R$ | no significant change | $b_R$ |

TABLE II. Compilation of previous experimental and theoretical results for the variation of $T_{MI}$ and of the conductivity (DC, unless otherwise specified) in VO$_2$, under applied hydrostatic or uniaxial pressures. We assume $\Delta P > 0$ for compression and $\Delta P < 0$ for expansion.