Ultrafast response of photoexcited carriers in VO₂ at high-pressure

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Abstract

We utilize near-infrared pump—mid-infrared probe spectroscopy to investigate the ultrafast electronic response of pressurized VO₂. A clear anomaly in the linear mid-infrared response as well as in the fluence dependence of the pump–probe signal is observed around 8 GPa indicating a pressure-induced phase transition. Distinct pump–probe signals and a pumping threshold behavior typical for the insulating VO₂ phase persist also in the high-pressure phase. Thus, in contrast to the temperature-induced rutile metallic state of VO₂, the pressure-induced monoclinic phase preserves the energy gap. However, our results indicate the appearance and a gradual growth of additional intragap states upon increasing pressure above 8 GPa. These observations can be interpreted in terms of a bandwidth-controlled Mott–Hubbard transition.

1. Introduction

At ambient pressure vanadium dioxide (VO₂) exhibits a sharp insulator-to-metal transition (IMT) accompanied by a transformation from the monoclinic to rutile crystal structure above a critical temperature Tc = 340 K [1]. Such strong coupling between electronic and lattice subsystems during the phase transition has attracted continuing interest for more than a half century [2–4]. The dimerized vanadium chains of the monoclinic phase suggest that a Peierls distortion underlies the insulating state, but electronic correlation leading to the carrier localization typical of a Mott insulator is also observed [5–9]. Numerous studies of the IMT in VO₂ under the influence of temperature [6, 10–12], strain [13–15], chemical substitution [16, 17] and ultrafast photoexcitation [11, 18–30] have been performed during recent years. Some of them show that the electronic and structural phase transitions are separable within certain temperature ranges, pointing to a primary role for electron correlation as the driving mechanism for the IMT [11, 13, 31]. Moreover, time-resolved photoemission spectroscopy [26] and ultrafast electron diffraction [27] have demonstrated that a transient monoclinic but metallic phase can be induced via photoexcitation.

Application of external pressure offers an attractive way to distinguish the influence of the structural instability from the correlation effects on the IMT in VO₂. At a critical pressure between 10 and 16 GPa at room temperature VO₂ undergoes an isostructural transformation which preserves the dimerized monoclinic structure [32–36]. In addition, infrared spectroscopy suggests band gap filling above 10 GPa [32]. Thus, the pressure-driven phase transition should be dominated by changes in the electronic band structure which are necessarily different from that of the temperature-induced IMT. Therefore, it is highly desirable to ascertain how the band structure of the monoclinic phase VO₂ changes under high-pressure. Unfortunately, in a high-pressure diamond anvil cell (DAC), conventional photoemission spectroscopy cannot be used. On the other hand, x-ray absorption spectroscopy can be used for direct probing of the changes in the band structure caused by the application of high-pressure although a detailed view of intragap states is difficult due to limited energy resolution [37]. In this situation an additional experimental technique such as pump–probe spectroscopy...
providing indirect information about the character of electronic states can be useful for understanding the high-pressure properties of VO₂. A recent theoretical study of coherent electronic states in a Mott–Peierls insulator points out that ultrafast pump–probe spectroscopy which can selectively excite and probe coherent and incoherent electronic states is well suited for the testing of theoretical predictions when the electronic interactions are tuned by pressure [38]. Here we utilize ultrafast near-infrared pump—mid-infrared probe spectroscopy in a high-pressure DAC to investigate the non-equilibrium dynamics of electronic response in VO₂. Our results provide evidence that near-infrared pumping induces additional long-lived charge carriers—even in the new phase above the critical pressure. The method of non-degenerate nonlinear spectroscopy enables us to trace the evolution of localized, weakly localized and/or fully delocalized electronic states in VO₂ across the pressure-driven phase transition. Based on our results and other experimental studies we propose a possible scenario for the observed pressure-induced phase transition.

2. Experiments

The single crystals of VO₂ were grown by thermal decomposition of V₂O₅ at the Oak Ridge National Laboratory [12]. For pressure-dependent measurements small pieces of VO₂ crystals were mounted inside an Almax Plate DAC. The pressure inside the DAC was monitored via a standard ruby fluorescence method [39].

For the time-resolved measurements the samples were polished to thicknesses of 20–30 μm and cut into pieces about 100 μm in diameter. Cesium iodide powder was used as a pressure transmitting medium in order to ensure direct contact between the sample surface and the front diamond anvil. The pump–probe setup is based on a Ti:sapphire laser amplifier system (Coherent RegA), providing 55 fs long pulses centered at λ ≈ 800 nm with a repetition rate of 250 kHz. A portion of the beam was used for the pumping branch, whereas the remaining part was utilized to generate probe pulses at λ ≈ 10 μm (0.12 eV or 30 THz) using difference frequency mixing between signal and idler pulses from a parametric amplifier. The pump and probe beams were focused non-collinearly down to a spot size of 30–50 μm on a single crystal of VO₂ inside the DAC.

Raman measurements at high pressures were performed on a tiny, 10 μm thick single VO₂ crystal with 4:1 methanol–ethanol mixture as a pressure transmitting medium. Unpolarized Raman spectra excited at a wavelength of 532 nm were collected using a Jobin-Yvon LabRAM HR 800 spectrometer equipped with a cryogenically cooled silicon CCD camera.

3. Results

3.1. Near-infrared pump—mid-infrared probe measurements

In the pump–probe experiment we measure the change in reflectivity ΔR of a photoexcited (pump photon energy 1.55 eV) VO₂ single crystal inside a DAC normalized to the reflectivity R in the unexcited state. The small probe photon energy of 0.12 eV (well below the band gap energy Eₔ = 0.6 eV of VO₂ at ambient conditions) ensures that the pump–probe signal is dominated by the response of free charge carriers and/or localized intragap electronic states [22, 23].

Figure 1(a) shows the change of the pump–probe signal of VO₂ at 2.1 GPa measured for different pump fluences. All of the curves show a quasi-instantaneous increase of the reflectivity—limited only by the durations of the pump and the probe pulses. The onset is followed by a fast relaxation with a time constant of approximately 0.15 ps. A previous study demonstrated similar values of the decay time [22]. As will be apparent from figure 2(a), the relaxation rate is constant up to 16 GPa. The slight drop of the relaxation time at higher pressures observed for two samples may be an artifact caused by a decreased signal-to-noise ratio for the data taken at the highest pressures where the signal amplitude becomes very low.

At low-fluence (blue trace), the pump–probe signal vanishes after about 1 ps indicating a complete recombination of the photoexcited charge carriers. At pump fluences above a threshold Φₜh, a persistent enhanced reflectivity reveals the creation of a metastable metallic phase (orange and red trace in figure 1(a)). All of these observations are fully consistent with the results for ambient conditions published previously [22, 24, 25]. The threshold fluence Φₜh corresponds to the photoinjection of a critical density of free charge carriers that screen the Coulomb interaction, and thus induce the collapse of the energy gap leading to the metastable metallic state [22, 26].

Remarkably, in contrast to the low-pressure regime, at elevated pressures the long-lived excited state is already observed at pump fluences below the threshold as shown, for example, in figure 1(b). This becomes obvious when we plot pump–probe signals averaged at around 1 ps (where the relaxation process is already completed) as a function of the pump fluence. Figures 1(c) and (d) show such plots for the same pressures as for figures 1(a) and (b), respectively. The threshold behavior is clearly seen in both cases. However, in contrast to
previous studies at ambient pressure [22–24], at sufficiently high pressures the pump–probe signal of VO2 does not vanish after 1 ps even in the low-fluence regime (see figures 1(b) and (d)). Therefore, we define the threshold fluence \( \Phi_{th} \) as a crossing point (marked by red arrows) of the two asymptotes (dashed gray lines) illustrated in figures 1(c) and (d).

In order to determine \( \Phi_{th} \) for each applied pressure we fit the fluence dependence of the pump–probe signal at the delay time of 1 ps using a phenomenological fitting function with bi-asymptotic behavior:
\[
\frac{\Delta R(\Phi)}{R} = c \ln [ae^{a\Phi} + (1 - a)e^{-a\Phi}],
\]

(1)

where \(c, a, s_1\), and \(s_2\) are independent positive fitting parameters. In the limit of very large or very small fluences one of the exponential terms in equation (1) dominates and the fitting function demonstrates a nearly linear fluence dependence. The crossing point of these two asymptotes can be derived from the equality of both exponential terms in equation (1) giving the threshold fluence

\[
\Phi_{th} = \frac{1}{s_2 - s_1} \ln \left( \frac{a}{1 - a} \right).
\]

(2)

The width of the transition region between the low- and high-fluence asymptotes \(\Delta \Phi_{th}\), can be determined from the full width at half maximum of the second derivative of equation (1) which constitutes a peak with the maximum at \(\Phi_{th}\). One can show that the ratio \(\Delta \Phi_{th}/\Phi_{th}\) characterizing the smearing of the threshold is

\[
\frac{\Delta \Phi_{th}}{\Phi_{th}} = \frac{2 \ln (\sqrt{2} + 1)}{\ln \left( \frac{a}{1 - a} \right)}.
\]

(3)

Figure 2(b) shows how the threshold smearing changes with pressure. Between 6 and 8 GPa \(\Delta \Phi_{th}/\Phi_{th}\) experiences an increase related to the onset of a finite slope in the fluence dependence of the pump–probe signal (see figure 1(d)) and to a drop in the threshold fluence. In the following we address this anomalous behavior in detail. Overall the threshold behavior remains well-defined in the whole studied pressure range.

The analysis of pump–probe traces at different pump fluences and various pressures reveals two main parameters that exhibit anomalous pressure behavior: (i) threshold fluence \(\Phi_{th}\) and (ii) slope of the low-fluence asymptote \(m_1 = cs_1\). Figure 3 shows the pressure dependence of these key parameters together with the linear (unexcited) transmissivity and reflectivity of the sample at the probe photon energy. Starting from ambient pressure, the threshold fluence \(\Phi_{th}\) monotonically increases up to a critical pressure \(p_c\) of \(\approx 8\) GPa as shown in figure 3(a). A higher threshold fluence signifies that more free carriers have to be photo-induced to overcome the correlations and to induce the metastable metallic state. This trend contrasts with the behavior of the thermally driven IMT where a noticeable decrease of the threshold fluence on approaching \(T_c\) has been reported [23, 24]. Most probably this difference is related to the stiffening of the dimerized lattice structure under pressure [32, 35]; that makes the vanadium dimers even more stable, and thus raises the energy barrier to the metallic rutile phase. The observed increase of \(\Phi_{th}\) with pressure is consistent with the recently reported growth of \(T_c\) in VO2 under pressure and the estimations of the corresponding increase in the latent heat of the IMT [36].

Around the critical pressure \(p_c\) we observe an anomalous drop of \(\Phi_{th}\). Remarkably, it coincides with the vanishing of the linear transmissivity (figure 3(c)), the start of the increase in the reflectivity (figure 3(d)) as well as the onset of a finite slope \(m_1\) of the low-fluence asymptote (figure 3(b)) that corresponds to switching of the pump–probe response character from the situation in figures 1(a) and (c) to that of figures 1(b) and (d). This effect is highly reproducible and has been observed in independent measurements on three different VO2 samples as presented in figure 3.

The same anomaly in the linear mid-infrared response was reported by Arcangeletti et al. who observed a noticeable transfer of the spectral weight below the band gap energy [32]. They interpreted it in terms of pressure-induced metallization in VO2. The sharper drop in our transmissivity-versus-pressure data can be explained by the larger thickness of our sample. Although a truly metallic behavior can be confirmed only by the extrapolation of the optical conductivity to zero frequency which is not possible in our measurements, the increasing reflectivity and the vanishing transmittance for \(p > p_c\) imply the progressive buildup of (localized or delocalized) intragap electronic states [32].

### 3.2. Raman spectroscopy

In order to study the impact of pressure on the crystal structure of VO2 we have performed a complementary high-pressure Raman measurement. Figures 4(a) and (b) depict two Raman spectra at selected pressures: one below and one above \(p_c\), respectively. In both spectra we observe the same set of phonon peaks indicating that the monoclinic structure is preserved. This behavior contrasts to the temperature-driven IMT, where the sharp Raman peaks disappear in the rutile metallic phase [40].

Figure 4(c) shows the frequencies of Raman modes as a function of pressure. The kinks around 12 GPa indicating an isostructural phase transition to a monoclinic M1′ phase [33, 35] are in agreement with previous Raman studies [32, 35, 36], where transition pressures of 10–16 GPa are reported. Thus, our Raman results clearly indicate that VO2 preserves monoclinic structure up to the highest pressure applied in our experiments. On the other hand, it is not possible to make an unequivocal conclusion about the separation of the structural anomaly at 12 GPa observed in Raman and the transition at \(p_c\) of \(\approx 8\) GPa revealed by the optical spectroscopy.
due to the different experimental conditions: While the Raman experiment was performed under nearly hydrostatic conditions, the pump–probe measurements may be affected by an anisotropic compression due to the solid pressure transmitting medium [41] and relatively thick VO$_2$ samples (see section 2).

4. Discussion

The pressure-independent relaxation time of the photoexcited carriers in VO$_2$ observed in our experiment (figure 2(a)) is rather surprising in the view of the notable variation experienced by other parameters around the critical pressure (figure 3). A theoretical modeling for a Mott insulator predicts an acceleration of the holon–doublon recombination process upon an increase of the bandwidth $t$ and the inter-site repulsion energy $V$ caused by external pressure which has been confirmed for a quasi-one-dimensional organic system ET-F$_2$TCNQ [42]. However, one has to point out that the interaction parameters $t$, $U$ and $V$ in ET-F$_2$TCNQ [42] are smaller than those in VO$_2$ [43] by about an order of magnitude and may demonstrate a quantitatively different variation under external pressure. Possibly this difference in the energy scales leads to a much weaker pressure dependence of the relaxation time in VO$_2$.

Let us now discuss the nonlinear response of VO$_2$ above the critical pressure $p_c$. The photo-induced change in the mid-infrared reflectivity remains similar to that in the insulating state (see figures 1(a) and (b)). This fact indicates that the majority of vanadium d-electrons stays localized even in the high-pressure phase so that photoexcitation is still able to induce a phase with higher conductivity. This behavior is clearly different from the photoexcitation of normal metals where the total number of free carriers is preserved and the pump–probe response is determined solely by the increase in electronic temperature [44]. The observed drop of $\Phi_{th}$ for $p > p_c$ can be related to the reduction of the energy barrier between the equilibrium and the transient photoexcited lattice structures of VO$_2$. In addition to the structural aspect, the appearance of the intragap states and the corresponding depletion of the states in the Hubbard bands may additionally affect the reduction of $\Phi_{th}$. As a result, fewer photoinjected carriers are required to achieve the critical concentration that closes the band gap.

Figure 3. Pressure dependence of (a) threshold fluence $\Phi_{th}$ and (b) slope $m_1$ of the low-fluence asymptote obtained from the fitting using equation (1) for three different VO$_2$ crystals. (c) Normalized linear transmissivity and (d) reflectivity of VO$_2$ in the DAC as a function of pressure. Color coding for different samples corresponds to that of figure 2.
The pressure-induced transition also leads to the onset of a non-vanishing slope $m_1$ of the low-fluence asymptote (see figure 1(d)). This means that for $p > p_c$ even pumping well below a threshold fluence can induce a metastable metallic phase with enhanced reflectivity, as illustrated in figure 1(b). In other words, a certain amount of long-lived free charge carriers directly proportional to the number of pump photons can be added without reaching the critical concentration for a band gap collapse. Thus, the appearance of a finite $m_1$ is expected to be a non-cooperative phenomenon related to the photoexcitation of weakly localized states (WLS) located near the Fermi level.

The observed behavior of the pump–probe response across the pressure-driven phase transition can be understood on the basis of the schematic band diagrams depicted in figures 5(a)–(c). Figure 5(a) shows the band structure of VO$_2$ at ambient conditions established in previous studies $[2, 5, 10]$. The $t_{2g}$ vanadium orbitals overlapping along the $a_M$ axis $[45]$ form two relatively narrow bands usually denoted as $d_{1||}$. The low- and the high-energy bands correspond to bonding and antibonding states on a vanadium dimer. Due to the on-site Coulomb repulsion $U$ of $t_{2g}$ electrons, the lower and upper Hubbard bands are formed on the lower and upper $d_{1||}$ bands, respectively $[5]$. In our qualitative band diagrams, we present both bands as somewhat broader $d_{1||}$ bands. Photoexcitation promotes the localized electrons from the $d_{1||}$ band into the high-energy delocalized states (red arrow in figure 5(a)) leading to the transient increase of reflectivity.

In our measurements, we observe photo-induced free charge carriers typical of the insulating VO$_2$ phase well above the pressure-induced phase transition—in stark contrast to the temperature-induced transition. This difference becomes clear by comparing the pump–probe signals measured on our VO$_2$ samples using the same excitation fluence for different pressures (figure 5(d)) and for different temperatures (figure 5(e)). For temperatures above $T_c$, the metallic VO$_2$ phase possesses the rutile crystal structure without the dimerization $[2]$. Thus, $d_{1||}$ bands become degenerate and cross the Fermi level together with other $t_{2g}$ bands (see figure 5(c)) resulting in a complete delocalization of all 3$d$ electrons of vanadium ions $[2, 10]$. Therefore, photoexcitation

\[\text{Figure 4. Raman spectra of VO}_2\text{ at 5.5 (a) and 16.9 GPa (b). Arrows mark the positions of the phonon modes. (c) Pressure dependence of selected Raman modes. The open symbol corresponds to a Raman spectrum that was captured after the release of pressure. Color coding corresponds to the arrow markers in panels (a) and (b). The vertical dashed line marks the pressure of 12 GPa.} \]
increases the electronic temperature, but it does not lead to an increase in the total number of free charge carriers. Correspondingly we observe a very weak negative change in $\Delta R/R$ for $T > T_c$ as shown by the red trace in figure 5(e). In contrast to this, the high-pressure phase of VO$_2$ is monoclinic suggesting that the $d_{||}$ bands remain split. The sizable pump-induced change $\Delta R/R$ for $p > p_c$ shown in figure 5(d) indicates that a large part of the $3d$ electrons are localized, i.e., they occupy states in a band which does not cross the Fermi level. This assumption is supported by x-ray absorption measurements [37] which show that the spectral weight transfer for the pressure-induced phase transition is much smaller than for the temperature-driven transition to the rutile phase.

Overall our experimental results suggest a schematic band diagram shown in figure 5(b). It assumes that the band splitting is preserved above the pressure-induced transition, and the possible weak metallic conductivity originates from a spectral weight transfer to a narrow intragap quasiparticle peak (QP) at the Fermi level. Part of its spectral weight can be transferred to a low-energy satellite representing the WLS [46]. At elevated pressures well above $p_c$, the QP and/or the WLS gain more spectral weight leading to the observed increase in reflectivity (figure 3(d)). At the same time, the pump–probe signal $\Delta R/R$ and the slope $m_1$ become smaller since the photo-induced relative change in the density of free charge carriers decreases for a given pump fluence (see the decrease from orange to red trace in figure 5(d)). Finally, $m_1$ almost vanishes at high pressures (figure 3(b)) indicating that the WLS merge with the QP.
We emphasize that the proposed band diagram not only explains our experimental observations, but is also consistent with recent resistivity measurements that demonstrate the thermally activated character of the conductivity below $T_c$ for pressures up to 20 GPa \cite{36, 47}. The resistivity behavior implies only the existence of an energy gap leading to the decrease in the number of thermally activated charge carriers upon cooling. The relatively small number of free electrons in the QP with a high effective mass caused by correlation effects can give only a small (almost temperature-independent) additional contribution to the conductivity of the sample. Thus, the thermally activated charge carriers are expected to dominate the resistivity around room temperature resembling a typical insulating behavior. The presence of the free charge carriers in the QP should be prominent only at low temperatures when thermal activation becomes inefficient. If electronic states in the QP remain delocalized, the low-temperature resistivity will saturate at a finite value. A signature of such behavior was observed in recent high-pressure resistivity measurements down to 90 K \cite{47}.

We now discuss the scenario of the pressure-induced transition in VO$_2$ via the suggested band diagram. Our data confirm that the dimerized monoclinic structure is preserved and even becomes more stable under an initial pressure increase. Thus, the intimate coupling between the electronic and lattice subsystems characteristic of the temperature-driven IMT does not take place for the pressure-induced transition which should have a predominantly electronic origin. The simplest scenario in this case is an IMT in the non-degenerate Hubbard model \cite{48}. Single-site dynamical mean-field theory (DMFT) calculations for such a model show that an increasing portion of spectral weight is transferred from the lower and upper Hubbard bands to a QP at the Fermi level when the effective correlation drops below a critical value, while the Hubbard bands persist \cite{48, 49}. The onset of the QP and the redistribution of spectral weight are governed by the ratio of the Coulomb repulsion $U$ and the hopping bandwidth $t$ \cite{48}. Recent material specific modeling of VO$_2$ based on cluster-DMFT calculations has demonstrated very similar results and confirmed the dominating role of the Mott mechanism \cite{9, 38}.

Application of pressure improves the overlap between the orbitals leading to increased bandwidth $t$ and reduced effective correlation $U/t$ that eventually results in a bandwidth-controlled Mott–Hubbard transition. This simple model is capable of explaining the existence of the band gap in the high-pressure phase of VO$_2$ as suggested by our present study (figure 5(b)). The only discrepancy is related to the existence of the WLS that are absent for the bandwidth-controlled IMT in the standard non-degenerate Hubbard model in single-site DMFT \cite{48, 49}.

We expect two possible reasons for the appearance of WLS: (i) The WLS may be caused by lattice defects in the VO$_2$ crystal. Possibly their density increases substantially due to the high strain imposed by external pressure \cite{29}. Initially delocalized electrons in the narrow QP are known to possess a high effective mass due to strong correlation effects \cite{6, 48}, and thus may be localized and bound to lattice defects. As increasing pressure weakens the correlation, the effective mass should strongly decrease such that the binding energy of the localized states may drop below the energy of thermal fluctuations at room temperature. As a result, the bound states would be ionized and the WLS peak would merge with the QP. (ii) The WLS may be an intrinsic feature of a realistic Hubbard model which goes beyond the single-site approximation and includes all relevant bands in VO$_2$ and must be solved using contemporary calculation techniques \cite{5, 43, 50}. Since the recent cluster-DMFT calculations for a dimerized Mott–Peierls insulator do not reveal localized intragap states \cite{38}, the defect-related origin of the WLS seem to be more probable. In particular, DMFT results of Weber \textit{et al} show that oxygen vacancies can produce localized intragap states in the monoclinic VO$_2$ \cite{7}.

5. Conclusion

Our pump–probe and linear mid-infrared measurements suggest a qualitatively novel view on the pressure-induced phase transition in VO$_2$ above a critical pressure of $\approx$8 GPa. The remnant threshold behavior indicates the preserved band gap while linear mid-infrared response shows the presence of intragap states. These signatures agree well with the scenario of a bandwidth-controlled Mott–Hubbard transition, which is characterized by spectral weight transfer from the Hubbard bands to delocalized and/or weakly localized intragap states. Owing to the stability of the dimerized monoclinic structure, our observations indicate the predominantly electronic character of the pressure-induced phase transition in VO$_2$. Our findings provide a benchmark for material specific theoretical modeling of VO$_2$ under high pressures and may be applicable for understanding similar phenomena in other strongly correlated systems with lattice instabilities.

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