

Direct imaging of the massive 3d orbital switching across the metal-insulator transition in VO₂

Paulius Dolmantis^{1,*}, Chun-Fu Chang¹, Martin Sundermann^{1,2}, Andrea Marino¹, Andrea Amorese^{1,†}, Hlynur Gretarsson², Marcus Schmidt¹, Thomas Christoph Koethe³, Maurits W. Haverkort⁴, and Liu Hao Tjeng^{1,‡}

¹Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany

²PETRA III, Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany

³II. Physikalisches Institut, Universität zu Köln, Zùlpicher Straße 77, 50937 Köln, Germany

⁴Institute for Theoretical Physics, Heidelberg University, Philosophenweg 19, 69120 Heidelberg, Germany



(Received 22 November 2025; accepted 18 April 2026; published 14 May 2026)

We carried out nonresonant inelastic x-ray scattering measurements at the V L_1 edge to probe the local V 3d charge density in VO₂ across the metal-insulator transition (MIT). Without relying on spectral calculations, we were able to integrate directly from the orientational dependence an image of the occupied 3d shell and extract quantitatively the orbital occupations of the V ions. We found that in the low-temperature insulating M_1 phase the V is highly polarized toward the σ configuration. The orbital occupation undergoes significant redistribution upon transition into the metallic R phase, leading to a more isotropic charge density. The massiveness of the orbital switching promotes the scenario in which electron correlations and lattice degrees of freedom are strongly coupled, so that the contribution of the lattice and the electronic part to the energetics must be treated on equal footing to model the MIT quantitatively.

DOI: [10.1103/dvsr-8ft7](https://doi.org/10.1103/dvsr-8ft7)

Transition metal oxides are a broad class of materials that exhibit a wide range of electronic properties, making them an attractive topic of research in condensed matter physics and materials science. One of the most intriguing phenomena is the occurrence of metal-insulator transitions (MITs) and here especially the case of VO₂ continues to attract intense attention. From fundamental point of view, the complexity to describe quantitatively the MIT forms a true intellectual challenge, both theoretically and experimentally; see Refs. [1–3] for recent reviews. At the same time, the MIT taking place at near ambient temperatures and also available in thin film form triggered numerous studies not only for applications [4] but also for the curiosity of exploring phenomena using various forms of stimuli, including uniaxial stress [5,6] and ultrashort light pulses with varying wavelengths [7–11].

The MIT in VO₂ occurs at $T_{\text{MIT}} \sim 340$ K with several orders of magnitude resistivity change [12]. It is accompanied by a structural phase transition, from the high-temperature metallic rutile R phase into the low-temperature insulating monoclinic M_1 structure in which twisted V-V dimers are formed along the c -axis V chains [13–15]. Moreover, two additional insulating phases can form: The triclinic T and the M_2 can be stabilized by Cr doping [16] or uniaxial pressure [15].

The presence of both electron correlations and band formation of the V 3d states leads to a complex interplay between charge, spin, orbital, and lattice degrees of freedom. Various basic models for the MIT have been proposed, such as the Peierl's instability or the Mott transition, or even a combination of both; see Refs. [1,2] for an overview. The strong and short-range response of the lattice leads also to the suggestion that the driving force may not be electronic in nature but is rather connected to inherent lattice instabilities or anharmonic lattice dynamics [3,17]. In order to shed light into this long-standing and ongoing problem, we need to determine experimentally the electron charge density of VO₂ that is relevant for the MIT. Here, it is understood that the charge density is a fundamental quantity not only for explanations based on density functional theories (DFTs) but also for the development of minimal many-body models that aim to capture the physics of the MIT. Several studies have been devoted to measure the V 3d charge density or 3d orbital occupation, e.g., by x-ray diffraction [18] or by spectroscopy [17,19–23]. Figure 1 illustrates schematically the definitions of the orbitals often used to describe the VO₂ problem. Strong changes have been observed across the MIT, but the actual distribution of the charge or orbital occupation as well as the amount of change varies significantly among the studies. Some of these discrepancies may be attributed to uncertainties about how to process the experimental data, but a major part is certainly caused by the nontrivial task of extracting physical information from the spectroscopic data. In analyzing spectra, one must use theory and calculations, but this is in fact a challenge by itself, since *ab initio* calculations hit their limits due to the many-body nature of the problem.

Here, we will utilize a recently developed experimental method that circumvents the need for involved analysis and instead provides the information as measured. With this

*Contact author: Paulius.Dolmantis@cpfs.mpg.de

†Present address: ASML Netherlands B.V., De Run 6501, 5504 DR Veldhoven, The Netherlands.

‡Contact author: Hao.Tjeng@cpfs.mpg.de

Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI. Open access publication funded by Max Planck Society.

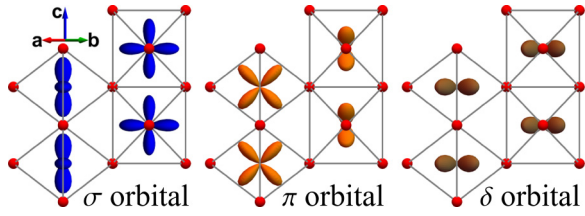


FIG. 1. Definition of t_{2g} orbitals used in this work, as viewed in (110) plane with rutile c axis pointing up: (left) σ orbital, (middle) π orbital, and (right) δ orbital.

technique, we can make a direct image of the active orbital and determine what the atomiclike object looks like in the single crystal. The method is nonresonant inelastic x-ray scattering (NIXS), using an s -core level. As has recently been shown, the angular dependence of the NIXS integrated intensity of the dipole-forbidden $3s \rightarrow 3d$ transition (M_1 edge) can directly map out the shape of the local $3d$ orbital hole density of an ion in its ground state or initial state [24–26]. The method makes use of high momentum transfers in the inelastic scattering process, in order for the dipole-forbidden terms to gain intensity. In our present work on VO_2 , we will utilize the V $2s \rightarrow 3d$ variant (L_1 edge) as will be explained below.

VO_2 single crystals were synthesized by the chemical vapor transport method. Flat and mirrorlike single-crystal surfaces were used for the measurements. The spectra were taken at the NIXS end station of the P01 beam line at PETRA III (DESY). The sample was mounted in a DynaFlow cryostat developed by van der Linden *et al.* [27], in which

the sample is directly cooled by helium gas at pressure of about 10 mbar. The cryostat provides large x-ray access of $2\Theta = 180^\circ$. The entrance windows were modified to consist of polyimide-Al composite foils in order to improve resistance against beam-induced damage [28]. The spectrometer uses a Rowland geometry and consists of a 3×4 array of 1 m radius spherically bent Si crystal analyzers, which select the 9.7 keV photons scattered from the sample using the Si(660) Bragg reflection and focus them on a 55- μm -pixel Si Medipix3 two-dimensional (2D) detector [24]. A large scattering angle of $2\Theta = 155^\circ$ was chosen to guarantee large momentum transfers $|\vec{q}| \approx (9.9 \pm 0.1 \text{ \AA}^{-1})$. The incident beam energy was scanned with a Si(111) double-crystal monochromator and the overall energy resolution was $\approx 1.5 \text{ eV}$.

The experimental geometry is schematically shown in Fig. 2(a). The sample is exposed to x-rays with momentum $\vec{k}_{\text{in}}$ and energy $\hbar\omega_{\text{in}}$, which are scattered from the sample with momentum $\vec{k}_{\text{out}}$ and energy $\hbar\omega_{\text{out}}$. The momentum transfer $\vec{q} = \vec{k}_{\text{in}} - \vec{k}_{\text{out}}$ points along the diagonal of the scattering parallelogram. The energy transfer is given by $\hbar\omega = \hbar\omega_{\text{in}} - \hbar\omega_{\text{out}}$. By rotating the crystal, spectra were collected for many different crystal orientations $[xyz]$ with respect to the fixed momentum transfer. For our VO_2 sample, the measurements were performed at angles spanning three different cuts defined by the crystal high-symmetry axes as shown in Fig. 2(b). Due to the presence of two V ions per unit cell rotated 90° around the c axis in the rutile structure, we will interpret our data in terms of sums of the charge densities of the orbitals on the two sites. These are shown in Fig. 2(c), where we also have indicated the cuts as defined in Fig. 2(b). We have included not

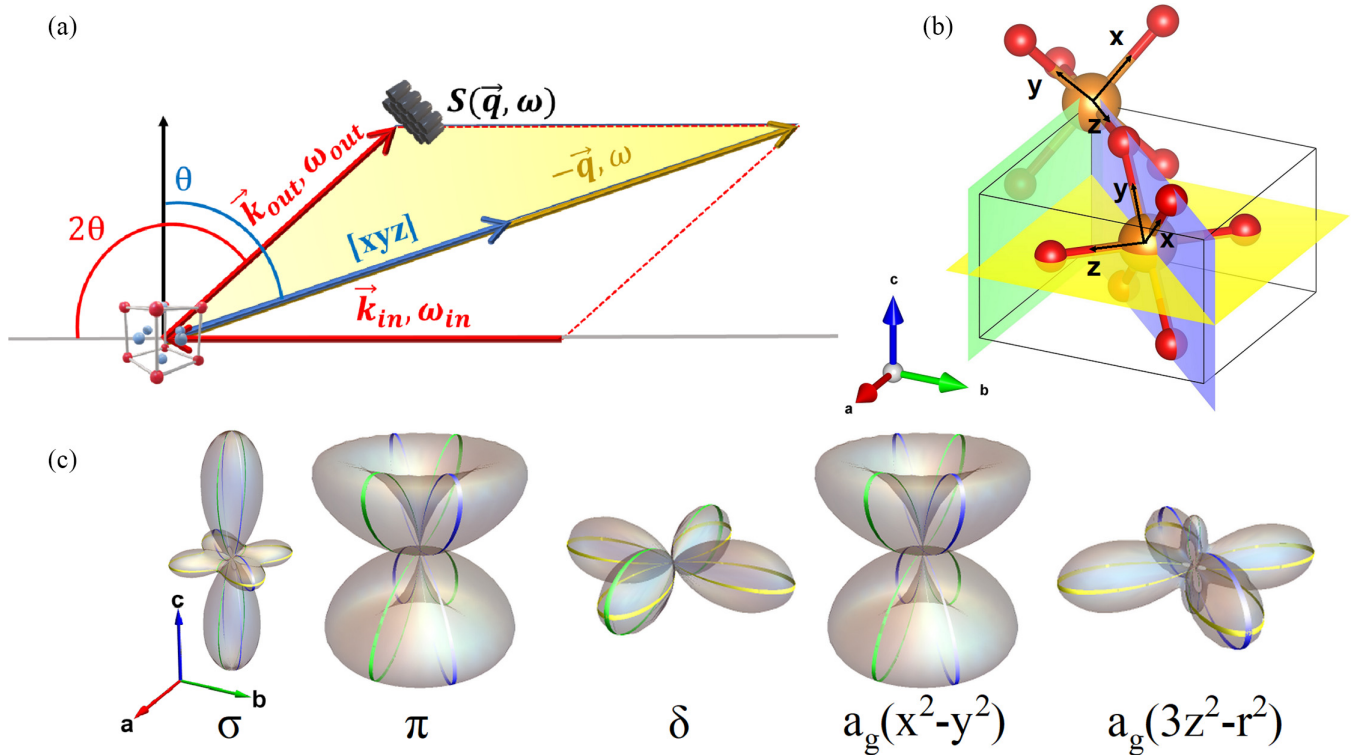


FIG. 2. (a) Scattering geometry, (b) crystal planes measured in experiment, and (c) orbitally resolved charge densities for the two V sites: Lines show the cuts in the planes colored according to panel (b).

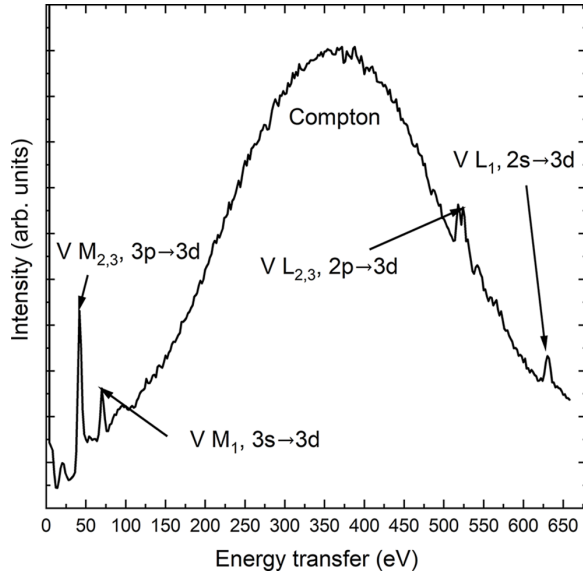


FIG. 3. Typical wide energy range NIXS scan for $2\theta = 155^\circ$.

only the standard t_{2g} orbitals, namely, σ , π , and δ , but also e_g , namely, $a_g(x^2 - y^2)$ and $a_g(3z^2 - r^2)$. The latter two orbitals must be included to describe properly the highly covalent nature of the V in VO_2 . We note that the π and $a_g(x^2 - y^2)$ orbitals for the two-site sums are indistinguishable.

A typical wide energy range scan is shown in Fig. 3. An extremely intense elastic scattering line is present at 0 eV energy transfer. Its width is mainly determined by the experimental resolution. The characteristic V $M_{2,3}$, M_1 , $L_{2,3}$, and L_1 lines can be observed on top of the broad Compton scattering profile. In this work, we will utilize the V L_1 line rather than the M_1 since the V L_1 is far away from other lines so that all the background can be attributed to the Compton scattering for which a well-defined background subtraction can be made.

Figure 4 displays the measured V L_1 NIXS spectra for a range of crystal orientations in the $c \rightarrow a$ plane with angles reaching $\vec{q} \parallel (001)$ and $\vec{q} \parallel (100)$. The spectra were normalized to the Compton profile intensities [24]. A linear background subtraction was applied to all spectra to remove the Compton scattering contribution. The blue curves are data taken at 20 K in the M_1 phase and the red curves are spectra collected at 400 K in the R phase. Data taken for crystal orientations in the $a \rightarrow b$ and $c \rightarrow a + b$ planes are presented in the Appendix.

To quantitatively discuss the data, we integrated the intensity of each L_1 spectrum and display the result in a polar plot as shown in Fig. 5 for the three sets of crystal orientations chosen in our experiment: the $c \rightarrow a$ plane (left panels), the $a \rightarrow b$ plane (middle panels), and the $c \rightarrow a + b$ plane (right panels). See also Fig. 2(b) for a three-dimensional view on these planes. The full blue and red circles are the integrated intensities of the 20 and 400 K measurements, respectively. As established earlier [24–26], the orientational dependence of the integrated L_1 intensity is directly proportional to the density of 3d holes in the direction of the momentum transfer in the NIXS experiment. In other words, the solid blue and red circles reflect directly the V 3d hole density in the M_1 and R phase, respectively. We can clearly observe that the shape of the 3d hole density changes significantly across the MIT.

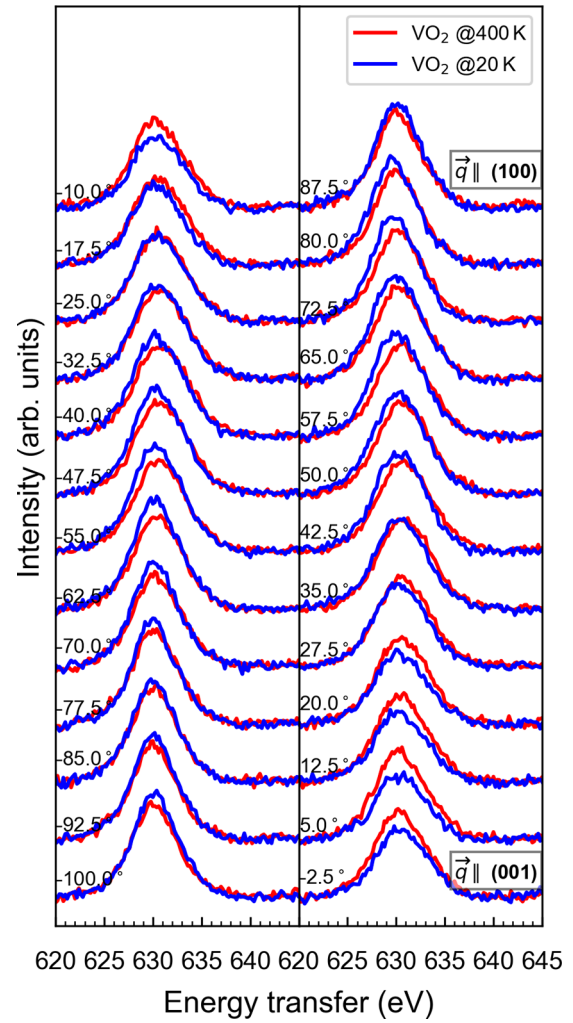


FIG. 4. V L_1 NIXS spectra measured for different orientations of the VO_2 single crystal with the experimental scattering geometry fixed. The experimental angles and high-symmetry crystal directions in the $c \rightarrow a$ plane are indicated [see also Figs. 2(a) and 2(b)]. The measurements have been carried out at 20 K in the M_1 phase (blue curves) and at 400 K in the R phase (red curves).

We first analyze the low-temperature results. Although the valence of the V ion is formally 4+, the amount of charge n_{3d} in the 3d shell is considerably higher than one electron. All DFT band structure calculations reveal that the hybridization of the V 3d with the O 2p states is strong [29–34], implying appreciable transfer of charge from the formally full O 2p shell to the V 3d. Very recent DFT plus DMFT (dynamical mean field theory) calculations demonstrated the necessity to include configuration interactions to a very high order to quantitatively explain the core level photoemission spectra of VO_2 [35]. This is related to the fact that VO_2 as an early transition metal compound contains a large number of holes in the 3d shell, resulting in a large 3d-level degeneracy within a many-body framework, which in turn leads to large effective interconfiguration transfer integrals [36]. The DFT + DMFT calculations found a 3d shell filling of about $n_{3d} = 2.1$ electrons. With this number of $n_{3d} = 2.1$ electrons, we now can extract quantitatively the orbital occupations from the NIXS

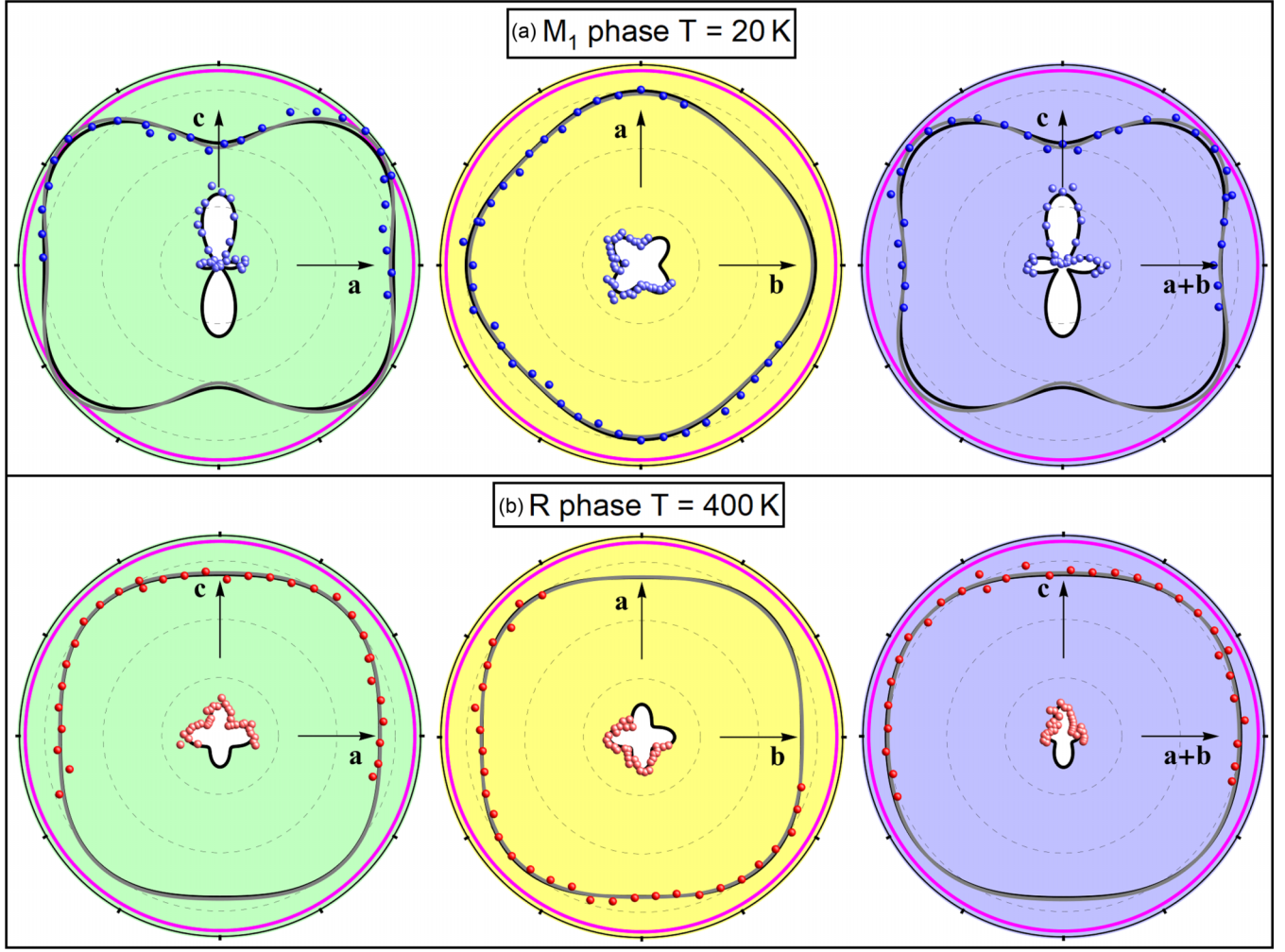


FIG. 5. Polar plot of the integrated intensity of the V L_1 edge of VO_2 , for crystal orientations in the $c \rightarrow a$ plane (left panels), $a \rightarrow b$ plane (middle panels), and $c \rightarrow a + b$ plane (right panels). See also Fig. 2(b). Filled blue circles are data taken at 20 K in the M_1 phase (top panels) and filled red circles at 400 K in the R phase (bottom panels). The solid gray line is the best fit for the V $3d$ hole charge density in a covalent model with 2.10 electrons occupying the V $3d$ shell. The outer solid black line is the best fit assuming an ionic model with 1.00 electron in the V t_{2g} subshell. The magenta line is the sphere representing the hole charge density for a completely empty V $3d$ shell, and is used in the ionic model to extract from the experiment the V $3d$ electron density, plotted as open blue circles (20 K) and open red circles (400 K) in the center of each panel, with the inner solid black lines showing the corresponding fitted electron densities. The extracted electron occupations are listed in Table I.

data from Fig. 5 by carrying out a fit using the composite orbitals as displayed in Fig. 2(c). The result is shown by the solid gray lines in the top panels of Fig. 5, which depict the $3d$ hole density of VO_2 in the M_1 phase. Table I lists a breakdown in terms of the $3d$ electron occupations. The largest charge density is in the σ orbital, but other orbitals do play a role too. In Fig. 6, we plot the three-dimensional electron charge density $\rho(r, \theta, \phi) = R^2(r) \times |\psi(\theta, \phi)|^2$ for a single V site. Here, $R(r)$ is the calculated radial wavefunction for a V^{4+} ion from the Cowan's code [37] (see inset of Fig. 6), whereas the function $|\psi(\theta, \phi)|^2$ is the shape of the composite orbital that is constructed as the incoherent sum of the orbital densities shown in Fig. 2(c) weighted with the occupation numbers listed in Table I. In making this plot, we would like to note that we have assumed that the occupation of the $a_g(x^2 - y^2)$ orbital is the same as that of the $a_g(3z^2 - r^2)$ orbital. We need to make such an assumption since the π and $a_g(x^2 - y^2)$ orbitals for

the two-site sums are indistinguishable [see Fig. 2(c)], and we have experimentally only information about their sum.

TABLE I. Electron occupations in the M_1 and R phases deduced from the orientation dependence of the integrated V L_1 intensities. The covalent model uses $n_{3d} = 2.1$ electrons for the total $3d$ occupation, while the ionic t_{2g} model has the constraint of 1 electron in the t_{2g} and 0 electron in the e_g .

	σ	$\pi + a_g(x^2 - y^2)$	δ	$a_g(3z^2 - r^2)$
M_1^a	1.18	0.39	0.30	0.24
R^a	0.59	0.68	0.55	0.29
M_1^b	0.98	0.00	0.02	—
R^b	0.43	0.22	0.35	—

^aCovalent model: constraint: $n_{3d} = 2.10$.

^bIonic t_{2g} model: constraint: $\sigma + \pi + \delta = 1$.

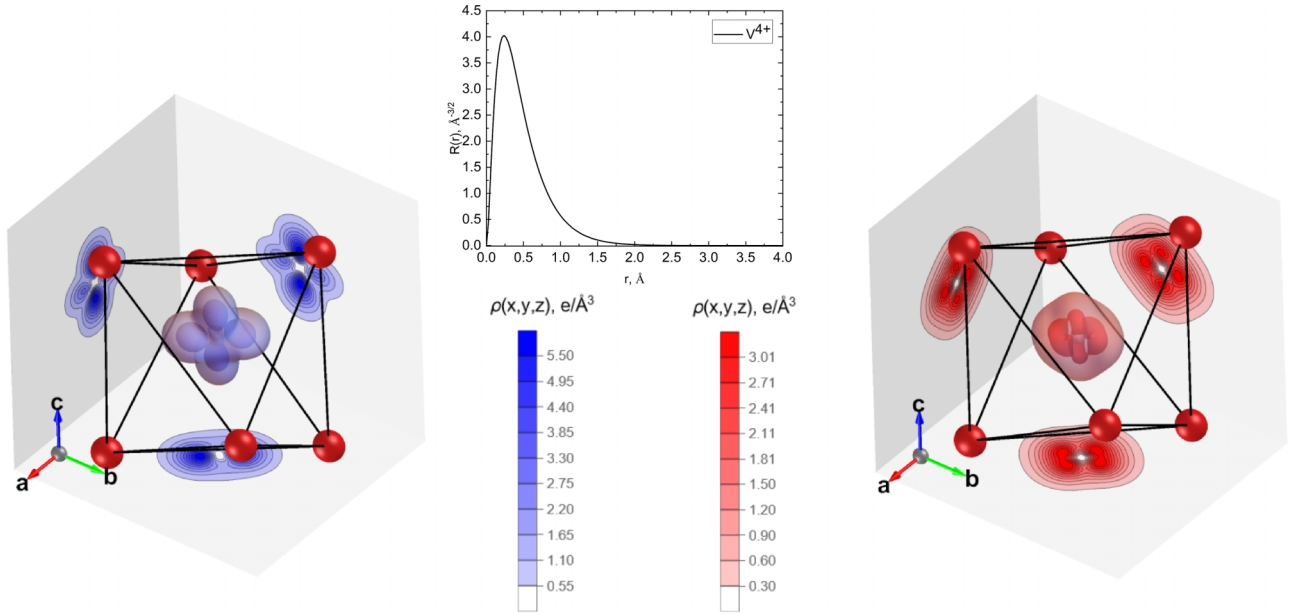


FIG. 6. Electron charge density $\rho(r, \theta, \phi)$ from the covalent model: (left) M_1 phase and (right) R phase. The 3D contours in the center part of the figures show electron isodensity surfaces of 2.1 and $1.0 \text{ e}/\text{\AA}^3$. The projections visualize cuts through the V site parallel to the respective planes. The inset shows the radial wavefunction $R(r)$ for V^{4+} .

Nevertheless, other choices will not change the finding that the actual charge density of the V ion in the M_1 phase is not coming from a pure σ character. Our finding is thus in disagreement with the suggestion from a recent x-ray diffraction study to have observed a pure σ charge density [18].

Next, we focus our attention to the high-temperature phase. Using again the number of $n_{3d} = 2.1$ electrons for the V $3d$ occupation [35], the best fit to the NIXS data is represented by the solid gray lines in the bottom panels of Fig. 5. The corresponding orbital occupations are listed in Table I. The change in the numbers with respect to the low-temperature phase is evident. In Fig. 6, we also plot the three-dimensional electron charge density $\rho(r, \theta, \phi)$ in the R phase for a single V site. In doing so, we have again taken the occupation of the $a_g(x^2 - y^2)$ orbital to be the same as that of the $a_g(3z^2 - r^2)$, as already explained above. Figure 6 best illustrates the dramatic change of the V $3d$ charge density across the MIT. It is therefore of no surprise that the lattice must react strongly to such changes. In fact, this finding implies that the contribution of the lattice to the energetics of the MIT [3,17] must be treated on equal footing as the electronic part [38–40].

While covalency is in many aspects an important quantity, the question arises whether the consideration of all five $3d$ orbitals is really needed for the many-body modeling of the electronic degrees of freedom across the MIT. As represented by Fig. 1, most existing theoretical studies and especially those that include explicitly strong electron correlations have focused on the degrees of freedom within the t_{2g} subshell only (with and without the corresponding O $2p$ states) [41–49]. Only few many-body studies include also the e_g orbitals (and all O $2p$ states) [50,51].

To possibly answer this question, we set out to reanalyze our low-temperature data using the limiting case of an ionic V^{4+} and t_{2g} -only model. Carrying out the fit under the constraint that the sum of the occupations of the σ , π , and δ

orbitals is set to 1, we have plotted as best result the solid black lines in the top panels of Fig. 5. This fit turns out to be almost as good as the above covalent fit using all five $3d$ orbitals: The deviations between the solid gray and solid black lines are marginal. The corresponding electron occupations are listed in Table I: 0.98 electrons in the σ orbital with some 0.02 electrons in the δ orbital. This electron density is shown by the solid black lines in the center of the top panels of Fig. 5. Alternatively, not using a fit but just using the ansatz that the V is in the ionic $3d^1$ state, we can draw an auxiliary sphere representing the ten-hole charge density of a V $3d^0$ ion (see the magenta lines in Fig. 5) and deduce the electron occupation by subtracting the measured V L_1 integrated intensities, given by solid blue circles, from this sphere. The result is displayed by the open blue circles in the center of the top panels of Fig. 5, which match very well the drawn electron density from the fit.

This ionic analysis suggests that, in a configuration-interaction scheme, the local state in the M_1 phase can be viewed as a predominantly $3d^1$ configuration of σ character, with coherent admixtures of $3d^{n+1}\bar{L}^n$ ligand-hole configurations, all transforming according to the same irreducible representation. The strong hybridization with the oxygen ligands increases the charge count from 1 to about 2.1 electrons with the other $3d$ orbitals gaining occupancy (plus also a redistribution due to hybridization with neighboring V ions), while preserving the irreducible representation of the low-energy manifold. These considerations would naturally lead to the notion that the lower Hubbard band in the insulating phase is spanned by the V $3d$ and O $2p$ states of the σ type and is separated in energy from all other bands.

For the high-temperature phase, we find that the ionic V^{4+} and t_{2g} -only model also yields a fit that is of comparable quality as that from the covalent model. See the solid black and gray lines in the bottom panels of Fig. 5. Table I lists that in the R phase the orbital occupations within the t_{2g} set of orbitals are

almost distributed isotropically, and thus very different from the M_1 phase with its highly polarized σ configuration. We also have taken the difference between the spherical ten-hole charge density of a V $3d^0$ ion t_{2g} electron density, drawn as magenta lines, and the measured V L_1 integrated intensities, given by the solid red circles. The difference plot is depicted by the open red circles, which match very well the drawn electron density from the fit. We thus conclude that the local state in the R phase can be viewed as an incoherent mixture of $3d^1$ configurations with a σ , π , or δ orbital occupied, each admixed with $3d^{n+1}\bar{L}^n$ ligand-hole configurations. In contrast to the M_1 phase, the local state in the R phase does not transform according to a single irreducible representation.

It is known for some time now that standard band theory fails to explain the insulating state of VO₂ in the M_1 phase [29–32]. While the band gap cannot be reproduced due to the insufficient treatment of electron correlation effects, our data shed light on this problem from a different perspective: In standard band theory, the π and δ orbitals close to the Fermi level are calculated to be partially filled, while from our experiment we find that it is essentially only the σ orbital that is occupied. It is therefore not surprising that DFT-based studies cannot reproduce the electronic structure if the calculated *charge density* is incorrect to begin with. The failure of band theory is also reflected by the fact that the calculated change of the orbital occupation across the MIT is much too small. This would require energy shifts of the various bands by a substantial fraction of the bandwidth, which cannot be produced by the calculations using the experimental crystal structures. However, taking into account electron correlations, the effective bandwidth will be strongly reduced and considerable orbital occupation changes can then be materialized. The orbital occupation changes in turn will lead to large changes in the effective Hubbard U parameter due to the strong intra-atomic multiplet interactions, as well as direction-dependent changes in the effective bandwidths [52].

The results of our ionic V⁴⁺ and t_{2g} -only model also show that those many-body studies that consider only the degrees of freedom within the $3d^1$ t_{2g} subshell [41–49] may have a good starting point to describe the electronic contribution to the energetics of the MIT. The high σ orbital polarization in the M_1 phase was generally found in these studies, and also the trend toward a more isotropic orbital occupation in the R phase came out of the calculations. Perhaps worth noting, only the exact diagonalization study [41] yielded the 100% σ polarization for the M_1 phase.

For a more quantitative theoretical understanding of the MIT, all of the V $3d$ orbitals (in addition to the O $2p$) must be included in the calculations [50,51]. However, in order to achieve realistic results, it remains difficult to determine the model parameters. There is no clear or unique procedure how to do this from an *ab initio* perspective. While it is obvious that the V $3d$ charge is not one electron but significantly larger due to hybridization with the O $2p$ bands, estimates from DFT vary considerably. A DFT + DMFT investigation [50], for example, started from $n_{3d} = 3.15$ and found that in the insulating M_1 phase two electrons occupy the t_{2g} subshell: Not only the σ contains one electron but also the π orbital. A fit to our experimental results using $n_{3d} = 3.15$ yields $n_\sigma = 1.29$, $n_\pi + n_{a_g(x^2-y^2)} = 0.87$, $n_\delta = 0.52$, and $n_{a_g(z^2)} = 0.47$; i.e., only

one orbital has an occupation higher than 1.0. The experiment thus falsifies the scenario with two electrons occupying the t_{2g} subshell. We can therefore exclude the implicitly proposed explanation in terms of an orbital-selective Mott transition. A more recent DFT + DMFT study, on the other hand, put forward a scenario that is much closer to our experimental results: In the M_1 phase, the σ band hosts essentially one electron, while the other bands, i.e., $a_g(x^2 - y^2)$ and $a_g(3z^2 - r^2)$, as well as π and δ , are also occupied but with only fractions of an electron.

To summarize, using nonresonant inelastic x-ray scattering measurements at the V L_1 edge, we were able to obtain direct images of the local V $3d$ charge density in VO₂. We found that in the low-temperature insulating M_1 phase the electron density of the V ions is primarily in the σ orbital, while the other orbitals are also occupied due to covalency and band formation. Our results deviate quantitatively from other existing experimental studies that are mostly based on spectroscopic measurements and thus require approximations of the many-body problem in order to extract the desired information from the spectra. For example, the analysis of the soft x-ray absorption data [19] relied on single-site cluster calculations, while a multisite approach would be more appropriate since the system undergoes a metal-insulator transition, which is a non-local phenomenon. Our charge densities also differ strongly from the ones found in standard band structure calculations explaining the failure of one-electron theories to produce the insulating state. An analysis based on ionic model revealed that VO₂ is effectively in a pure σ configuration, suggesting that the corresponding lower Hubbard band is split off from the other bands in the M_1 phase. The orbital occupation undergoes significant redistribution upon transition into the metallic R phase. The massiveness of the orbital switching is indicative of the presence of electron correlations and strong coupling

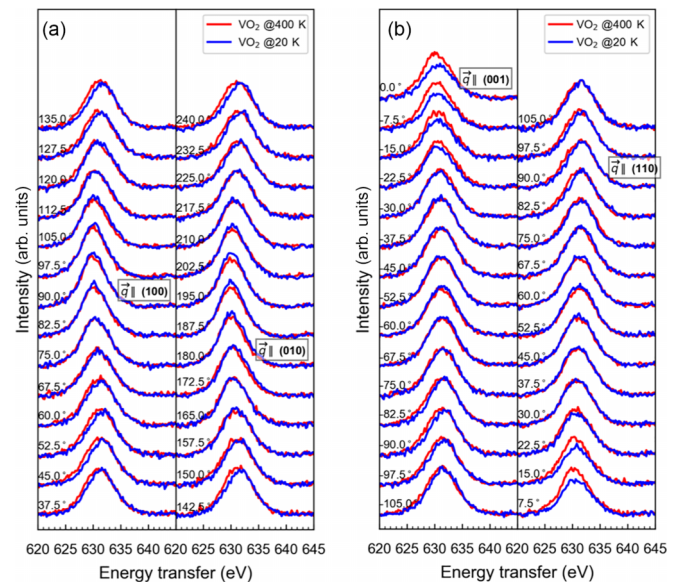


FIG. 7. s-NIXS spectra measured at different phases of VO₂. (a) $a \rightarrow b$ plane: 20 K M_1 (blue), 400 K R (red). (b) $c \rightarrow a+b$ plane: 20 K M_1 (blue), 400 K R (red). Experimental angles and high-symmetry points are indicated in boxes next to the spectra.

with the lattice. To explain the metal-insulator transition quantitatively, the contribution of the lattice and the electronic part to the energetics must be treated on equal footing.

ACKNOWLEDGMENTS

The work at the MPI-CPfS Dresden was partially supported by SFB1143 (Project No. 247310070). The NIXS experiment was performed at PETRA-III at DESY, a member of the Helmholtz Association (HGF). We thank C. Becker, K. Höfer, and T. Mende from MPI CPfS and F.-U. Dill, S. Mayer, and H.-C. Wille from PETRA-III at DESY for their skillful technical support.

DATA AVAILABILITY

The data that support the findings of this article are openly available [53].

APPENDIX: s -NIXS L_1 EDGE SPECTRA OF $a \rightarrow b$ AND $c \rightarrow a + b$ CUTS

Figures 7(a) and 7(b) show measured s -NIXS spectra for V L_1 edges for $a \rightarrow b$ and $c \rightarrow a + b$ cuts, respectively. Integrated intensities are displayed in Fig. 5.

-
- [1] J.-P. Pouget, Basic aspects of the metal–insulator transition in vanadium dioxide VO₂: A critical review, *C. R. Phys.* **22**, 37 (2021).
 - [2] F. Grandi, A. Amaricci, and M. Fabrizio, Unraveling the Mott–Peierls intrigue in vanadium dioxide, *Phys. Rev. Res.* **2**, 013298 (2020).
 - [3] Z. Hiroi, Structural instability of the rutile compounds and its relevance to the metal–insulator transition of VO₂, *Prog. Solid State Chem.* **43**, 47 (2015).
 - [4] J. del Valle, P. Salev, F. Tesler, N. M. Vargas, Y. Kalcheim, P. Wang, J. Trastoy, M.-H. Lee, G. Kassabian, J. G. Ramírez, M. J. Rozenberg, and I. K. Schuller, Subthreshold firing in Mott nanodevices, *Nature (London)* **569**, 388 (2019).
 - [5] J. H. Park, J. M. Coy, T. S. Kasirga, C. Huang, Z. Fei, S. Hunter, and D. H. Cobden, Measurement of a solid-state triple point at the metal–insulator transition in VO₂, *Nature (London)* **500**, 431 (2013).
 - [6] N. B. Aetukuri, A. X. Gray, M. Drouard, M. Cossale, L. Gao, A. H. Reid, R. Kukreja, H. Ohldag, C. A. Jenkins, E. Arenholz, K. P. Roche, H. A. Dürr, M. G. Samant, and S. S. P. Parkin, Control of the metal–insulator transition in vanadium dioxide by modifying orbital occupancy, *Nat. Phys.* **9**, 661 (2013).
 - [7] V. R. Morrison, R. P. Chatelain, K. L. Tiwari, A. Hendaoui, A. Bruhács, M. Chaker, and B. J. Siwick, A photoinduced metal-like phase of monoclinic VO₂ revealed by ultrafast electron diffraction, *Science* **346**, 445 (2014).
 - [8] S. Wall, S. Yang, L. Vidas, M. Chollet, J. M. Glowina, M. Kozina, T. Katayama, T. Henighan, M. Jiang, T. A. Miller, D. A. Reis, L. A. Boatner, O. Delaire, and M. Trigo, Ultrafast disordering of vanadium dimers in photoexcited VO₂, *Science* **362**, 572 (2018).
 - [9] J. Li, L. Wu, S. Yang, X. Jin, W. Wang, J. Tao, L. Boatner, M. Babzien, M. Fedurin, M. Palmer, W. Yin, O. Delaire, and Y. Zhu, Direct detection of V-V atom dimerization and rotation dynamic pathways upon ultrafast photoexcitation in VO₂, *Phys. Rev. X* **12**, 021032 (2022).
 - [10] H.-W. Liu, W.-H. Liu, Z.-J. Suo, Z. Wang, J.-W. Luo, S.-S. Li, and L.-W. Wang, Unifying the order and disorder dynamics in photoexcited VO₂, *Proc. Natl. Acad. Sci. USA* **119**, e2122534119 (2022).
 - [11] A. S. Johnson, D. Perez-Salinas, K. M. Siddiqui, S. Kim, S. Choi, K. Volckaert, P. E. Majchrzak, S. Ulstrup, N. Agarwal, K. Hallman, *et al.*, Ultrafast X-ray imaging of the light-induced phase transition in VO₂, *Nat. Phys.* **19**, 215 (2023).
 - [12] F. J. Morin, Oxides which show a metal-to-insulator transition at the Neel temperature, *Phys. Rev. Lett.* **3**, 34 (1959).
 - [13] R. Heckingbottom and J. W. Linnett, Structure of vanadium dioxide, *Nature (London)* **194**, 678 (1962).
 - [14] M. Marezio, D. B. McWhan, J. P. Remeika, and P. D. Dernier, Structural aspects of the metal–insulator transitions in Cr-doped VO₂, *Phys. Rev. B* **5**, 2541 (1972).
 - [15] J. P. Pouget, H. Launois, J. P. D’Haenens, P. Merenda, and T. M. Rice, Electron localization induced by uniaxial stress in pure VO₂, *Phys. Rev. Lett.* **35**, 873 (1975).
 - [16] J. P. Pouget, H. Launois, T. M. Rice, P. Dernier, A. Gossard, G. Villeneuve, and P. Hagenmuller, Dimerization of a linear Heisenberg chain in the insulating phases of V_{1-x}Cr_xO₂, *Phys. Rev. B* **10**, 1801 (1974).
 - [17] J. D. Budai, J. Hong, M. E. Manley, E. D. Specht, C. W. Li, J. Z. Tischler, D. L. Abernathy, A. H. Said, B. M. Leu, L. A. Boatner, R. J. McQueeney, and O. Delaire, Metallization of vanadium dioxide driven by large phonon entropy, *Nature (London)* **515**, 535 (2014).
 - [18] S. Kitou, A. Nakano, M. Imaizumi, Y. Nakamura, I. Terasaki, and T.-H. Arima, Molecular orbital formation and metastable short-range ordered structure in VO₂, *Phys. Rev. B* **109**, L100101 (2024).
 - [19] M. W. Haverkort, Z. Hu, A. Tanaka, W. Reichelt, S. V. Streltsov, M. A. Korotin, V. I. Anisimov, H. H. Hsieh, H.-J. Lin, C. T. Chen, D. I. Khomskii, and L. H. Tjeng, Orbital-assisted metal–insulator transition in VO₂, *Phys. Rev. Lett.* **95**, 196404 (2005).
 - [20] A. Cavalleri, M. Rini, H. H. W. Chong, S. Fourmaux, T. E. Glover, P. A. Heimann, J. C. Kieffer, and R. W. Schoenlein, Band-selective measurements of electron dynamics in VO₂ using femtosecond near-edge X-ray absorption, *Phys. Rev. Lett.* **95**, 067405 (2005).
 - [21] K. Okazaki, S. Sugai, Y. Muraoka, and Z. Hiroi, Role of electron–electron and electron–phonon interaction effects in the optical conductivity of VO₂, *Phys. Rev. B* **73**, 165116 (2006).
 - [22] M. M. Qazilbash, K. S. Burch, D. Whisler, D. Shrekenhamer, B. G. Chae, H. T. Kim, and D. N. Basov, Correlated metallic state of vanadium dioxide, *Phys. Rev. B* **74**, 205118 (2006).
 - [23] Y. Shimizu, T. Jin-no, F. Iwase, M. Itoh, and Y. Ueda, Occupation switching of d orbitals in vanadium dioxide

- probed via hyperfine interactions, *Phys. Rev. B* **101**, 245123 (2020).
- [24] H. Yavaş, M. Sundermann, K. Chen, A. Amorese, A. Severing, H. Gretarsson, M. W. Haverkort, and L. H. Tjeng, Direct imaging of orbitals in quantum materials, *Nat. Phys.* **15**, 559 (2019).
- [25] B. Leedahl, M. Sundermann, A. Amorese, A. Severing, H. Gretarsson, L. Zhang, A. C. Komarek, A. Maignan, M. W. Haverkort, and L. H. Tjeng, Origin of Ising magnetism in $\text{Ca}_3\text{Co}_2\text{O}_6$ unveiled by orbital imaging, *Nat. Commun.* **10**, 5447 (2019).
- [26] A. Amorese, B. Leedahl, M. Sundermann, H. Gretarsson, Z. Hu, H. J. Lin, C. T. Chen, M. Schmidt, H. Borrmann, Y. Grin, A. Severing, M. W. Haverkort, and L. H. Tjeng, Selective orbital imaging of excited states with X-ray spectroscopy: The example of $\alpha\text{-MnS}$, *Phys. Rev. X* **11**, 011002 (2021).
- [27] P. J. E. M. van der Linden, M. Moretti Sala, C. Henriquet, M. Rossi, K. Ohgushi, F. Fauth, L. Simonelli, C. Marini, E. Fraga, C. Murray, J. Potter, and M. Krisch, A compact and versatile dynamic flow cryostat for photon science, *Rev. Sci. Instrum.* **87**, 115103 (2016).
- [28] M. Sundermann, f -electron charge densities probed using core level non-resonant inelastic x-ray scattering, [arXiv:1911.06901](https://arxiv.org/abs/1911.06901).
- [29] M. Gupta, A. J. Freeman, and D. E. Ellis, Electronic structure and lattice instability of metallic VO_2 , *Phys. Rev. B* **16**, 3338 (1977).
- [30] R. M. Wentzcovitch, W. W. Schulz, and P. B. Allen, VO_2 : Peierls or Mott-Hubbard? A view from band theory, *Phys. Rev. Lett.* **72**, 3389 (1994).
- [31] V. Eyert, The metal-insulator transitions of VO_2 : A band theoretical approach, *Ann. Phys.* **514**, 650 (2002).
- [32] M. A. Korotin, N. A. Skorikov, and V. I. Anisimov, Variation of orbital symmetry of the localized $3d^1$ electron of the V^{4+} ion upon the metal-insulator transition in VO_2 , *Phys. Met. Metallogr.* **94**, 17 (2002).
- [33] M. Gatti, F. Bruneval, V. Olevano, and L. Reining, Understanding correlations in vanadium dioxide from first principles, *Phys. Rev. Lett.* **99**, 266402 (2007).
- [34] V. Eyert, VO_2 : A novel view from band theory, *Phys. Rev. Lett.* **107**, 016401 (2011).
- [35] T. Yamaguchi, K. Higashi, A. Regoutz, Y. Takahashi, M. Lazemi, Q. Che, F. M. F. de Groot, and A. Hariki, Atomic multiplet and charge transfer screening effects in $1s$ and $2p$ core-level x-ray photoelectron spectra of early $3d$ transition-metal oxides, *Phys. Rev. B* **109**, 205143 (2024).
- [36] O. Gunnarsson and K. Schönhammer, Electron spectroscopies for Ce compounds in the impurity model, *Phys. Rev. B* **28**, 4315 (1983).
- [37] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Oakland, CA, 1981).
- [38] E. Pavarini, E. Koch, and A. I. Lichtenstein, Mechanism for orbital ordering in KCuF_3 , *Phys. Rev. Lett.* **101**, 266405 (2008).
- [39] E. Pavarini and E. Koch, Origin of Jahn-Teller distortion and orbital order in LaMnO_3 , *Phys. Rev. Lett.* **104**, 086402 (2010).
- [40] X.-J. Zhang, E. Koch, and E. Pavarini, Origin of transitions inversion in rare-earth vanadates, *Phys. Rev. Lett.* **135**, 026508 (2025).
- [41] A. Tanaka, On the metal-insulator transitions in VO_2 and Ti_2O_3 from a unified viewpoint, *J. Phys. Soc. Jpn.* **73**, 152 (2004).
- [42] S. Biermann, A. Poteryaev, A. I. Lichtenstein, and A. Georges, Dynamical singlets and correlation-assisted Peierls transition in VO_2 , *Phys. Rev. Lett.* **94**, 026404 (2005).
- [43] A. Liebsch, H. Ishida, and G. Bihlmayer, Coulomb correlations and orbital polarization in the metal-insulator transition of VO_2 , *Phys. Rev. B* **71**, 085109 (2005).
- [44] M. S. Laad, L. Craco, and E. Müller-Hartmann, Metal-insulator transition in rutile-based VO_2 , *Phys. Rev. B* **73**, 195120 (2006).
- [45] J. M. Tomczak and S. Biermann, Effective band structure of correlated materials: The case of VO_2 , *J. Phys.: Condens. Matter* **19**, 365206 (2007).
- [46] J. M. Tomczak, F. Aryasetiawan, and S. Biermann, Effective bandstructure in the insulating phase versus strong dynamical correlations in metallic VO_2 , *Phys. Rev. B* **78**, 115103 (2008).
- [47] B. Lazarovits, K. Kim, K. Haule, and G. Kotliar, Effects of strain on the electronic structure of VO_2 , *Phys. Rev. B* **81**, 115117 (2010).
- [48] A. S. Belozerov, M. A. Korotin, V. I. Anisimov, and A. I. Poteryaev, Monoclinic M_1 phase of VO_2 : Mott-Hubbard versus band insulator, *Phys. Rev. B* **85**, 045109 (2012).
- [49] P. Milkvik, M. E. Merkel, N. A. Spaldin, and C. Ederer, Single-site DFT + DMFT for vanadium dioxide using bond-centered orbitals, *Phys. Rev. Res.* **6**, 033122 (2024).
- [50] C. Weber, D. D. O'Regan, N. D. M. Hine, M. C. Payne, G. Kotliar, and P. B. Littlewood, Vanadium dioxide: A Peierls-Mott insulator stable against disorder, *Phys. Rev. Lett.* **108**, 256402 (2012).
- [51] W. H. Brito, M. C. O. Aguiar, K. Haule, and G. Kotliar, Metal-insulator transition in VO_2 : A DFT + DMFT perspective, *Phys. Rev. Lett.* **117**, 056402 (2016).
- [52] C. F. Chang, T. C. Koethe, Z. Hu, J. Weinen, S. Agrestini, L. Zhao, J. Gegner, H. Ott, G. Panaccione, H. Wu, *et al.*, C -axis dimer and its electronic breakup: The insulator-to-metal transition in Ti_2O_3 , *Phys. Rev. X* **8**, 021004 (2018).
- [53] P. Dolmantis, s -NIXS of $\text{V } L_1$ edge data of VO_2 across phase transition, Edmond Repository (Max Planck Society), 2025, <https://doi.org/10.17617/3.LB7KTI>.