

Transfer of Spectral Weight and Symmetry across the Metal-Insulator Transition in VO₂

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We present a detailed study of the valence and conduction bands of VO₂ across the metal-insulator transition using bulk-sensitive photoelectron and O *K* x-ray absorption spectroscopies. We observe a giant transfer of spectral weight with distinct features that require an explanation which goes beyond the Peierls transition model as well as the standard single-band Hubbard model. Analysis of the symmetry and energies of the bands reveals the decisive role of the V *3d* orbital degrees of freedom. Comparison to recent realistic many body calculations shows that much of the *k* dependence of the self-energy correction can be cast within a dimer model.

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The metal-insulator transition (MIT) in VO₂ [1] has been a subject of debate for several decades and forms an important benchmark problem for theoretical solid state physics [2–4]. The formation of V dimers in the low temperature phase, for example, has led to the proposition that the MIT is Peierls-like [5,6], but this was countered by the claim that electron correlation effects are expected to be so strongly present that the MIT should be regarded as essentially a Mott transition [7,8]. Very recently, a twist to this debate was provided by a new study using cluster dynamical mean field theory (CDMFT) [9] asserting that both the singlet pairing and the strong Coulomb interactions are needed to open the gap.

One of the most direct methods to critically test the validity of the different models is to determine the excitation spectrum associated with the introduction of an extra particle into the system [10]. Several direct-photoemission (PES) experiments have been reported in the literature [11–15], but, surprisingly, none of the available spectra provides a satisfactory match with the calculated density of states [6,16–18] or imaginary part of the Green's function [9,18,19]. The question arises whether the proper experimental spectrum still has to be collected, or whether none of the theories was able to catch the physics essential for the MIT of VO₂.

In this Letter, we present a bulk-sensitive valence band PES study on VO₂ single crystals across the MIT, i.e., going from the low temperature insulating *M*₁ phase to the high temperature metallic *R* phase. We also investigate the conduction band using O *K* x-ray absorption spectroscopy (XAS). Our measurements reveal a giant transfer of spectral weight, even more than that in V₂O₃ [20]. Important is that this is accompanied with particular spectral features which signal that the transition is not of the standard Peierls nor single-band Mott-Hubbard type. The

symmetry and energies of the bands are discussed in connection to the recently determined orbital occupation [21] and to the importance of the *k* dependence of the self-energy correction [9].

Single crystals of VO₂ with *T*_{MIT} = 340 K have been grown by the vapor transport method [22]. The PES experiments were performed at the ID08 beam line of the ESRF in Grenoble. The crystals were cleaved *in situ* exposing a (110) surface with an area of ≈ 3 × 2 mm². The probing depth is maximized by measuring at normal emission. The photon energy was set to 700 eV, sufficiently high to ensure bulk sensitivity [23–25]. The overall energy resolution was set to 0.16 eV, and the Fermi level *E*_{*F*} was calibrated using a polycrystalline Ag reference sample. The angular acceptance of the Scienta SES 2002 electron energy analyzer is about ±7°, which covers more than one Brillouin zone at 700 eV kinetic energy, thereby yielding essentially angle-integrated spectra. The XAS measurements were carried out at the Dragon beam line of the NSRRC in Taiwan, with a photon energy resolution of 0.15 eV for the O *K* edge and a degree of linear polarization of ≈ 98%. VO₂ single crystals were mounted with the *c* axis perpendicular to the Poynting vector of the light. By rotating the samples around the Poynting vector, the polarization of the electric field vector can be varied continuously from $\vec{E} \parallel c$ to $\vec{E} \perp c$. This measurement geometry ensures that the optical path of the incoming beam is independent of the polarization, guaranteeing a reliable comparison of the spectral line shapes as a function of polarization. Bulk representative spectra were collected by using the total electron yield method on *in situ* cleaved single crystals.

Figure 1 shows the valence band PES spectra of VO₂ taken at 300 and 348 K, i.e., below and above *T*_{MIT}. It can be clearly seen that the low temperature *M*₁ phase is an insulator with negligible spectral weight at *E*_{*F*} and that the

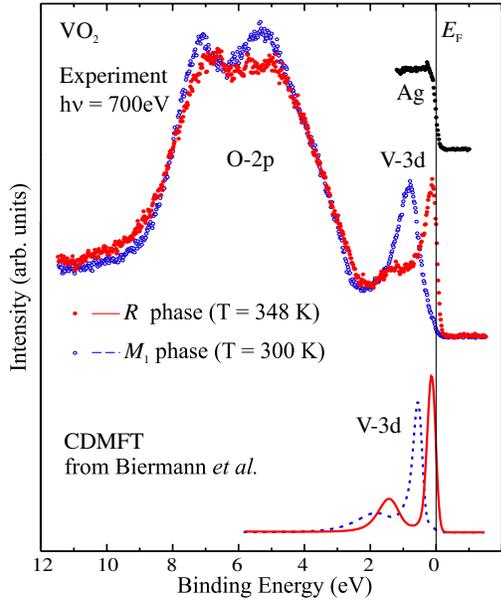


FIG. 1 (color online). Top: Valence band photoemission spectra of VO_2 taken at 300 K (insulating M_1 phase) and 348 K (metallic R phase) with 700 eV photons, together with the Ag Fermi level E_F reference. Bottom: CDMFT results for the $V 3d(t_{2g})$ spectral weights from Biermann *et al.* [9].

high temperature R phase, by contrast, is a metal with an extremely high spectral weight at E_F . These spectra are quantitatively and qualitatively different from the ones published so far. Not only is the $V 3d$ vs $O 2p$ spectral weight ratio larger than previously observed, thereby giving a clearer view on the most relevant states, but also the $V 3d$ peak at 0.9 eV of the insulator is more resolved from the $O 2p$ band [11–15].

Most important is, however, the exceptionally high peak at E_F of the metal together with the presence of a small but distinguishable satellite at 1.3 eV. This line shape has not been observed before [11–15]. It is also quantitatively different from the one taken under the $V 2p \rightarrow 3d$ resonance conditions reported recently [26]. We notice that also our resonant PES spectra (not shown here) have a smaller main peak to satellite ratio and larger widths than the *direct* PES spectrum of Fig. 1. This effect can be attributed to incoherent Auger emission accompanying resonant PES [27].

We also would like to point out that the satellite of the metal has a *different* energy than the main peak of the insulator. This shows that our samples are free from poor quality surfaces which could remain insulating above T_{MIT} . This, in turn, demonstrates that our spectra are indeed representative for the bulk [25].

In comparing the PES spectra with band structure calculations using the local density approximation (LDA) [6,16,17], we can see obvious discrepancies: These calculations always produce a metal, i.e., not only for the R but also for the M_1 phase. In addition, the gap between the $V 3d$ and $O 2p$ bands in the calculated density of states is not

present in the experimental spectra. These aspects are direct indications for strong electron correlation effects in the material. Using the LDA + U approach [17,18], the gap between the $V 3d$ and $O 2p$ bands disappears, and the spectral line shape of the M_1 phase becomes reasonably reproduced, but at the price that not only the M_1 but also the R phase are calculated to be insulators. Resorting to the LDA + DMFT method, one still finds unsatisfactorily metallic solutions for both phases if one assumes a realistic value of 4 eV for U [18]. It is nevertheless interesting to note that the satellites in the calculated R and M_1 spectra have energies close to those of the satellite in the experimental R phase and the main peak of the M_1 phase, respectively. This at least suggests that the parameters which define the energy positions are reasonably estimated and that the problem rather lies in how to transfer the spectral weight more rapidly across the MIT [18].

To resolve this theoretical problem, Biermann *et al.* [9] attempted to include the k dependence of the self-energy correction by implementing the CDMFT approach, in which the V dimer is taken as the cluster. The underlying idea is that the essential part of the k dependence can be found within these V dimers when the material enters the insulating M_1 phase. We have reproduced their results [9] in Fig. 1 after multiplication with the Fermi function for 300 and 348 K, respectively, and convolution with the experimental overall resolution of 0.16 eV. Comparison with our experimental spectra yields very good agreement. The extremely high spectral weight at E_F as well as the satellite at 1.3 eV in the metallic R phase are well reproduced. Moreover, the insulating nature of the M_1 phase is now also well explained. The calculated position of the M_1 main peak is somewhat off from the experimental one, but this may be a matter of fine-tuning the parameters. The small satellite in the CDMFT is not visible in the experimental spectrum as this is probably hidden by the intense $O 2p$ band.

Important for the physics of the MIT in VO_2 is the finding that the insulator peak has a lower binding energy than the satellite of the metal. This suggests directly that the MIT cannot be described within the often-used single-band Hubbard model, in which the satellite of the metal develops into the lower Hubbard band at equal or slightly higher energies when increased correlation effects turn the metal into an insulator [4]. This suggestion is further supported by the CDMFT, which shows that the imaginary part of the self-energy does not diverge towards zero frequency. These findings strongly point out that another degree of freedom must play an important role. Very recently, polarization-dependent XAS experiments on the $V-L_{2,3}$ edges revealed that, in going from the metallic to the insulating state, the orbital occupation changes in a manner such that the material switches its electronic structure from three-dimensional to effectively one-dimensional [21]. This makes the system more susceptible to a Peierls-like transition. This orbital switching

could also have a massive influence on the intersite exchange interactions with large consequences for the effective Hubbard U for nearest neighbor charge fluctuations [28,29] and effective band widths [28].

To check these ideas, we carried out polarization-dependent XAS measurements at the O K edge. This technique is complementary to PES, since by probing the “unoccupied” O $2p$ partial density of states we, in fact, study the conduction band. Figure 2 depicts the spectra taken with the polarization vector $\vec{E} \parallel c$ and $\vec{E} \perp c$ at 300 and 373 K, respectively, i.e., both below and above the MIT. The spectra show a very strong polarization dependence (solid vs dashed lines) and for each polarization also a clear temperature dependence (thick blue vs thin red lines). In going to the metallic phase, one observes, in particular, a shift of about 0.2 eV towards lower energies for the leading edge of the spectra. Together with the shift of roughly 0.4 eV in the opposite direction for the leading edge of the PES valence band spectra shown in Fig. 1, we thus find that the MIT involves the closing of a band gap of about 0.6 eV [30]. This is an anomalously large energy if one compares it to the energy scale of T_{MIT} , which is of order 30 meV. Such a discrepancy in energy scales has also been recognized for the V_2O_3 system [28], and this forms, in fact, yet another indication that the MIT cannot be described within the framework of the single-band Hubbard model.

To address specifically the possible role of the orbital degrees of freedom, we now focus on the polarization dependence of the O K XAS spectra. For the $\vec{E} \parallel c$ spectra (solid lines), we observe that the peak labeled as d_{\parallel} in Fig. 2 disappears in going from the insulating (thick blue line) to the metallic (thin red line) phase. The inset in Fig. 2

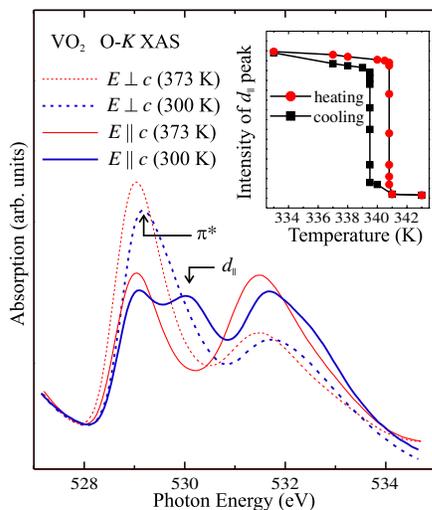


FIG. 2 (color online). O K XAS of VO_2 taken with the polarization vector $\vec{E} \parallel c$ (solid lines) and $\vec{E} \perp c$ (dashed lines) at 300 K (thick blue lines, insulating M_1 phase) and 373 K (thin red lines, metallic R phase). The inset shows the temperature dependence of the d_{\parallel} peak across the metal-insulator transition at 340 K.

shows in detail the temperature dependence of the intensity of this peak. The sharp hysteresis across the MIT at 340 K confirms not only the high quality of the samples but also that the occurrence of this peak is intimately linked to the MIT. The O K structures are due to transitions from the O $1s$ to the O $2p$ orbitals that are mixed into the unoccupied V $3d$ t_{2g} and e_g states [31]. Following the proposal by Abbate *et al.* [32], the first peak at 529.1 eV can be assigned to the $t_{2g}-\pi^*$ orbital and the second at 530.1 eV to the $t_{2g}-d_{\parallel}$. These assignments can now be confirmed by our polarization dependence data: The d_{\parallel} peak can be seen with $\vec{E} \parallel c$ polarization only, since mainly the O $2p$ orbitals with z symmetry (with z along c) have sufficient hybridization with the d_{\parallel} state which, as we will discuss below, is made up of the antibonding state of pairs of d_{\parallel} orbitals [2].

The observation of the d_{\parallel} peak as a main characteristic for the MIT strongly supports the conclusions of the recent orbital occupation study mentioned above [21]. There it was found that the orbital occupation is almost isotropic in the metallic phase but that it becomes essentially pure d_{\parallel} in the insulating phase. It is then quite natural to expect that this electronically one-dimensional chain undergoes a Peierls transition and forms bonding/antibonding states of pairs of d_{\parallel} orbitals. Important is the assertion that such a change in orbital occupation can be made only if the system is so strongly correlated that, in fact, it is already close to a Mott transition [21]. This can now be quantified from the spectra of Figs. 1 and 2. The energy separation between the bonding and antibonding d_{\parallel} peaks can be estimated from the energy position of the insulator peak in the PES spectrum plus that of the d_{\parallel} peak with respect to the onset of the XAS spectrum. This totals to roughly 2.5–2.8 eV. In a pure one-electron approximation, the energy separation equals $2t$, where t is the intradimer hopping integral. Using the LDA estimate of $t \approx 0.7$ eV [9], the separation would be 1.4 eV, a value which is clearly too small and which partially illustrates why LDA does not reproduce the insulating state of VO_2 . Using instead the simple hydrogen-molecule model [33] to include explicitly correlation effects, the energy separation is given by $\sqrt{U^2 + 16t^2} - 2t$. Using $U \approx 4$ eV [9], we obtain a value of about 3.0 eV, which is satisfactorily close to the experiment.

The band gap itself of VO_2 is not determined by the d_{\parallel} bonding/antibonding separation. While the first ionization state is given by the d_{\parallel} bonding state, the first affinity state is in the simplest approximation set mainly by the π^* state, which lies about 1 eV lower in energy than the d_{\parallel} antibonding state as can be seen from Fig. 2. This is also the general finding from the CDMFT study [9]: The π^* band dominates the lower part of the conduction band, while the d_{\parallel} band centers at higher energies. Nevertheless, details in the band structure may lead to some fine tuning: The CDMFT predicts that there is some amount of d_{\parallel} at the very onset of the conduction band. This is shown in Fig. 3, where we have replotted the CDMFT curves [9] after

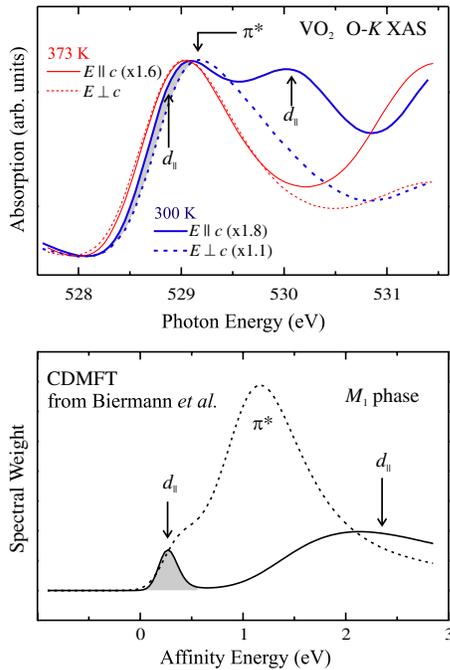


FIG. 3 (color online). Top: O K XAS of VO₂ from Fig. 2, rescaled to the maximum of the first peak. Bottom: CDMFT results for the V $3d(t_{2g})$ spectral weights as reproduced from Biermann *et al.* [9].

multiplication with the Fermi function for 300 K and convolution with the experimental resolution of 0.16 eV. To address this issue experimentally, we have also replotted in Fig. 3 the XAS spectra but now rescaled to the height of the first peak. In the metallic phase, the first peak for the $\vec{E} \parallel c$ spectrum (thin red solid line) falls on top of that of the $\vec{E} \perp c$ (thin red dashed line), confirming that the orbitals have similar energies and are similarly occupied [21]. For the insulating phase, on the other hand, we can clearly see that the top of the first peak of the $\vec{E} \parallel c$ spectrum (thick blue solid line) lies ≈ 0.1 eV lower than that of the $\vec{E} \perp c$ (thick blue dashed line), indicating that the former is not of pure π^* character as the latter is. This, in turn, strongly suggests that there must be a state of different symmetry, i.e., $d_{||}$, making up the low energy side of the peak, precisely as predicted by the CDMFT. It would be interesting to find out whether this sharp low lying state could represent a heavy quasiparticle if one dopes VO₂ in the M_1 phase with electrons.

To summarize, using bulk-sensitive spectroscopies we have been able to observe dramatic changes in the valence and conduction bands across the metal-insulator transition of VO₂. These changes require an explanation which goes beyond both the standard Peierls transition and single-band Hubbard models. Analysis of the symmetry and energies of the bands reveals that the V $3d$ orbital switching is the key for opening a band gap that is much larger than the energy scale of the transition temperature. Dynamical mean field theories using a two-site cluster provide a good starting

point to capture much of the k dependence of the self-energy correction for VO₂.

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