

Orbital-Assisted Metal-Insulator Transition in VO<sub>2</sub>M. W. Haverkort,<sup>1</sup> Z. Hu,<sup>1</sup> A. Tanaka,<sup>2</sup> W. Reichelt,<sup>3</sup> S. V. Streltsov,<sup>4</sup> M. A. Korotin,<sup>4</sup> V. I. Anisimov,<sup>4</sup> H. H. Hsieh,<sup>5</sup> H.-J. Lin,<sup>6</sup> C. T. Chen,<sup>6</sup> D. I. Khomskii,<sup>1</sup> and L. H. Tjeng<sup>1</sup><sup>1</sup>*II. Physikalisches Institut, Universität zu Köln, Zùlpicher Strasse 77, D-50937 Köln, Germany*<sup>2</sup>*Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan*<sup>3</sup>*Institut für Anorganische Chemie, Technische Universität Dresden, Mommsenstrasse 13, D-01069 Dresden, Germany*<sup>4</sup>*Institute of Metal Physics, S. Kovalevskoy 18, 620219 Ekaterinburg GSP-170, Russia*<sup>5</sup>*Chung Cheng Institute of Technology, National Defense University, Taoyuan 335, Taiwan*<sup>6</sup>*National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 30077, Taiwan*

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We found direct experimental evidence for an orbital switching in the V 3*d* states across the metal-insulator transition in VO<sub>2</sub>. We have used soft-x-ray absorption spectroscopy at the V *L*<sub>2,3</sub> edges as a sensitive local probe and have determined quantitatively the orbital polarizations. These results strongly suggest that, in going from the metallic to the insulating state, the orbital occupation changes in a manner that charge fluctuations and effective bandwidths are reduced, that the system becomes more one dimensional and more susceptible to a Peierls-like transition, and that the required massive orbital switching can only be made if the system is close to a Mott insulating regime.

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The problem of metal-insulator transitions (MITs) in transition metal compounds has already attracted considerable attention for a long time. Among the best studied of such systems are the V oxides, especially V<sub>2</sub>O<sub>3</sub> and VO<sub>2</sub> [1,2]. The long-standing problem in these systems is the relative role of electron-lattice interactions and corresponding structural distortions versus electron correlations. This problem is especially acute for the MIT in VO<sub>2</sub>, which was described either as predominantly a Peierls transition [3] or as a Mott-Hubbard transition [4].

An intriguing aspect that has largely been neglected in the discussions about MITs in TM oxides is the possible role of magnetic correlations and especially the orbital structure of constituent TM ions [5]. Very recently, a theoretical model for spinels such as MgTi<sub>2</sub>O<sub>4</sub> and CuIr<sub>2</sub>S<sub>4</sub> has been proposed in which a specific orbital occupation effectively leads to the formation of one-dimensional bands, making the systems, in a natural manner, susceptible to a Peierls-like MIT [6].

The crystal and electronic structure of VO<sub>2</sub> is in this respect more intricate. The MIT in VO<sub>2</sub> is a structural transition from the high-temperature rutile (*R*) structure to a monoclinic (*M*<sub>1</sub>) structure, in which there appears simultaneous *dimerization* in each V chain along the *c* axis and a *twisting* of V-V pairs due to an antiferroelectric shift of neighboring V atoms towards the apex oxygens (lying at the axis perpendicular to the crystal *c* axis); see Fig. 1. As argued already long ago by Goodenough [7], one should discriminate between two types of orbitals and corresponding bands: *d*<sub>||</sub> orbitals and bands, formed by the *t*<sub>2*g*</sub> orbitals with strong direct overlap with the neighboring V in the chains, and  $\pi^*$  orbitals and bands, made of the two other *t*<sub>2*g*</sub> orbitals. In the *R* phase, the *d*<sub>||</sub> band overlaps with the  $\pi^*$  band, resulting in an orbitally isotropic metallic state; see Fig. 2. The twisting in the *M*<sub>1</sub> phase

increases the V-apex O hybridization and moves the  $\pi^*$  band up so that only the *d*<sub>||</sub> band is occupied. The later one then becomes split by the dimerization, leading to the insulating state.

Many theoretical *ab initio* studies were performed to test the Goodenough picture. Local-density approximation (LDA) calculations indicated indeed that the *d*<sub>||</sub> band becomes more occupied in the *M*<sub>1</sub> phase [3,8], but they failed to reproduce the insulating state. An L(S)DA + *U* approach predicted even more dramatic changes in the orbital occupations, but unfortunately it did not give the metallic solution for the *R* phase [9,10]. A change in the orbital occupation was also obtained in the exact diagonalization study for a three-band Hubbard model using finite size clusters [11]. Very recently, various LDA + DMFT meth-

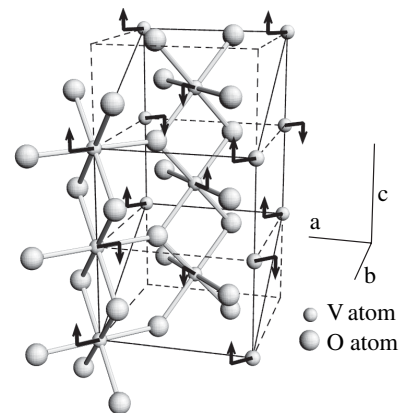


FIG. 1. Crystal structure of VO<sub>2</sub> in the metallic rutile (*R*) phase and in the insulating monoclinic (*M*<sub>1</sub>) phase. The arrows show the direction of the displacements of the V ions in the *M*<sub>1</sub> phase. The *a*, *b*, and *c* axes are defined with respect to the rutile structure.

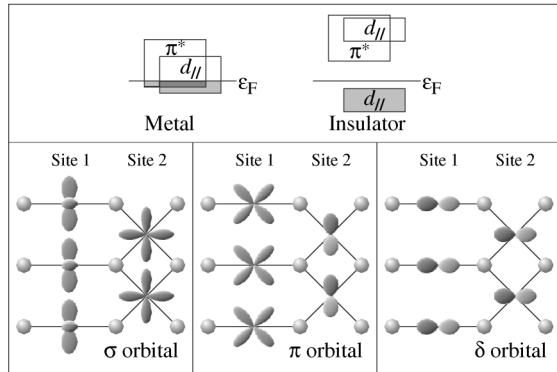


FIG. 2. Top panel: Schematic electronic structure of  $\text{VO}_2$  according to Goodenough [7]. Bottom panel: Definitions of the relevant  $\text{V } 3d t_{2g}$  orbitals used in this work, drawn in the  $(110)$  plane spanned by the  $a$ ,  $b$  and  $c$  axes of Fig. 1. Sites 1 and 2 are related by a  $90^\circ$  rotation around the  $c$  axis.

ods have been applied to explain the MITs, and also here the orbital occupations are an important issue [10,12,13]. In view of the fact that the orbital occupation and changes thereof are central to the MIT theories for  $\text{VO}_2$ , it is quite surprising that an experimental proof of it is lacking, an aspect which is also relevant for other materials [14,15].

In this Letter, we give direct experimental evidence of this orbital redistribution at the MIT in  $\text{VO}_2$ . We present a polarization-dependent x-ray absorption spectroscopy (XAS) study on  $\text{VO}_2$  single crystals at the  $\text{V } L_{2,3}$  ( $2p \rightarrow 3d$ ) edges. Here we make use of the fact that the Coulomb interaction of the  $2p$  core hole with the  $3d$  electrons is much larger than the  $3d t_{2g}$  bandwidth, so that the absorption process is strongly excitonic and therefore well understood in terms of atomiclike transitions to multiplet split final states subject to dipole selection rules. This makes the technique an extremely sensitive local probe [16–18], ideal to study the orbital character [5,19] of the ground or initial state. For our experiment on  $\text{VO}_2$ , we redefine the orbitals in terms of  $\sigma$ ,  $\pi$ , or  $\delta$  with respect to the  $\text{V}$  chain as shown in Fig. 2. The  $\sigma$  orbital is then equivalent to the  $d_{\parallel}$ , and the  $\pi$  and  $\delta$  to the  $\pi^*$ . The transition probability will strongly depend on which of the  $\sigma$ ,  $\pi$ , or  $\delta$  orbitals is occupied and on how the polarization vector  $\vec{E}$  of the light is oriented. Our measurements reveal a dramatic switching of the orbital occupation across the MIT, even more than in  $\text{V}_2\text{O}_3$  [5], indicating the crucial role of the orbitals and lattice in the correlated motion of the electrons.

Single crystals of  $\text{VO}_2$  with  $T_{\text{MIT}} = 67^\circ\text{C}$  have been grown by the vapor transport method [20]. The XAS measurements were performed at the Dragon beam line of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The spectra were recorded using the total electron yield method in a chamber with a base pressure of  $3 \times 10^{-10}$  mbar. Clean sample areas were obtained by cleaving the crystals *in situ*. The photon energy resolution at the  $\text{V } L_{2,3}$  edges ( $h\nu \approx 510\text{--}530$  eV) was set at 0.15 eV, and the degree of linear polarization was

$\approx 98\%$ . The  $\text{VO}_2$  single crystal was mounted with the  $c$  axis perpendicular to the Poynting vector of the light. By rotating the sample around this 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 allows for an optical path of the incoming beam which is independent of the polarization, guaranteeing a reliable comparison of the spectral line shapes as a function of polarization.

Figure 3 shows the  $\text{V } L_{2,3}$  XAS spectra of  $\text{VO}_2$  taken in the insulating  $M_1$  phase (top panel) and in the metallic  $R$  phase (bottom panel). The general line shape of the spectra is similar to that in earlier works, each of which reports spectra for only one particular polarization [21,22]. In our work, we have measured for each phase the spectra with two different light polarizations, namely,  $\vec{E} \parallel c$  (solid lines) and  $\vec{E} \perp c$  (dashed lines). We observe a clear polarization dependence for the insulating phase. By contrast, the polarization dependence is quite weak for the metallic phase. Figure 3 shows for each phase also the dichroic spectrum, i.e., the difference between the spectra taken with the two polarizations. One now can see that the dichroic spectrum of the insulating phase has not only a larger amplitude, but also a very different line shape than that of the metallic phase.

To extract information concerning the orbital occupation from the  $\text{V } L_{2,3}$  XAS spectra, we have performed simulations of the atomiclike  $2p^6 3d^1 \rightarrow 2p^5 3d^2$  transitions using the well-proven configuration interaction cluster model

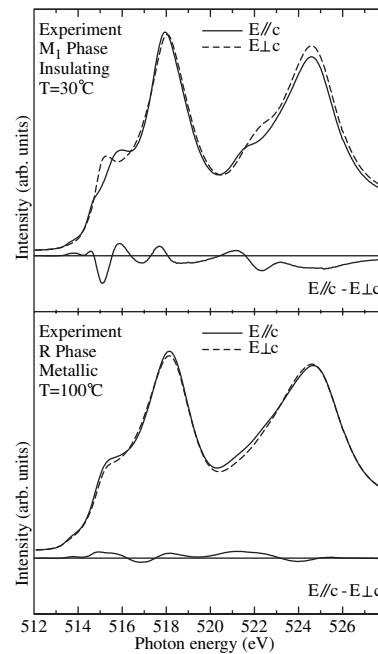


FIG. 3. Experimental  $\text{V } L_{2,3}$  XAS spectra of  $\text{VO}_2$  in the insulating  $M_1$  phase (top panel,  $T = 30^\circ\text{C}$ ) and metallic  $R$  phase (bottom panel,  $T = 100^\circ\text{C}$ ), taken with the light polarization  $\vec{E} \parallel c$  (solid lines) and  $\vec{E} \perp c$  (dashed lines). The metal-insulator transition temperature is  $67^\circ\text{C}$ .

[16–18]. The method uses a  $\text{VO}_6$  cluster which includes the full atomic multiplet theory and the local effects of the solid. It accounts for the intra-atomic  $3d$ - $3d$  and  $2p$ - $3d$  Coulomb interactions, the atomic  $2p$  and  $3d$  spin-orbit couplings, the O  $2p$ -V  $3d$  hybridization, and local crystal field parameters. Parameters for the multipole part of the Coulomb interactions were given by the Hartree-Fock values [16], while the monopole parts ( $U_{dd}$ ,  $U_{pd}$ ) as well as the O  $2p$ -V  $3d$  charge transfer energy were determined from photoemission experiments [23]. The one-electron parameters such as the O  $2p$ -V  $3d$  and O  $2p$ -O  $2p$  transfer integrals as well as the local crystal fields were extracted from the LDA band structure results [9] for the crystal structure corresponding to each of the two phases of  $\text{VO}_2$ . The simulations have been carried out using the XTLS 8.0 program [11,16,24].

Figure 4 shows the results of our theoretical simulations of the spectra. In the top part of the right panels we have simulated the insulating  $M_1$ -phase spectra for the following three scenarios: The V  $3d^1$  ion is set either in the pure  $\sigma$ -,  $\pi$ -, or  $\delta$ -orbital symmetry. One can clearly observe that the different orbital symmetries will lead to very different spectra with quite different polarization dependence. One can notice that the  $\sigma$ -orbital scenario resembles the experimental spectra the most, especially when one focuses on the most excitonic part of the spectrum, namely, between 512 and 516 eV. In a simulation with the V ion in the ground state that belongs to the true local symmetry of the  $M_1$  phase, we find even a better fit to the experimental data as shown in the left panels. The corresponding orbital symmetry, as listed in the second column of Table I, has indeed overwhelmingly the  $\sigma$  character (0.81), and only very little  $\pi$  (0.10) and  $\delta$  (0.09).

We have also simulated the spectra for the metallic  $R$  phase, again for the three scenarios in which the V ion set to have either the pure  $\sigma$ -,  $\pi$ -, or  $\delta$ -orbital symmetry. The bottom part of the right panels shows that each scenario results in quite different spectra and polarization dependence. We also note that each of the  $R$ -phase scenario gives spectra different from the corresponding  $M_1$  phase, simply

because of the differences in the local electronic structure, resulting from the different crystal structure. What is important now is that none of the three scenarios of the  $R$ -phase give good agreement with the experimental spectra. Apparently, the V ion has an orbital symmetry which is very far from a pure  $\sigma$ , or  $\pi$ , or  $\delta$ . We now approximate the initial state symmetry of the V ion by a linear combination of those three symmetries, and optimize the relative weights to obtain the best fit to the experiment, with the emphasis on the excitonic part. Figure 4 (bottom left panel) shows that this state is built up of  $0.33\sigma$ ,  $0.16\pi$ , and  $0.51\delta$  symmetries; see also the fifth column of Table I. It seems thus that in the metallic phase the V orbital occupation is almost isotropic.

In Table I we have also listed the  $3d$  orbital occupation as found from the simulations of the experimental spectra. These numbers are not identical to the symmetry occupation numbers because of the covalency, i.e., the hybridization of the V  $3d$  with the surrounding O  $2p$  ligands. We now can compare our findings directly with the numbers from our LDA and LSDA +  $U$  calculations [9]. We note that our LDA band structure is quite similar to the one published earlier [3,8], and that the occupation numbers of our LSDA +  $U$  calculations are in close agreement with the one published very recently [10]. For the insulating  $M_1$  phase, we find that the orbital occupation, which is highly ( $\sigma$ ) polarized, is well reproduced by the LSDA +  $U$  model, but not so by the standard LDA; see Table I. On the other hand, for the metallic  $R$  phase, we observe that the almost isotropic orbital occupation as experimentally determined is well reproduced by the LDA, but not so by the LSDA +  $U$  method. It seems that the LDA tends to underestimate the orbital polarization, which makes the method less suitable for the insulating phase. The LSDA +  $U$  approach, on the other hand, tends to overestimate it, which is a disadvantage for this approach for the metallic phase. These problems are likely to be related to the fact that the LDA cannot reproduce the insulating state in the  $M_1$  phase, while the LSDA +  $U$  method does not give the metallic state for the  $R$ -phase. Nevertheless, the general

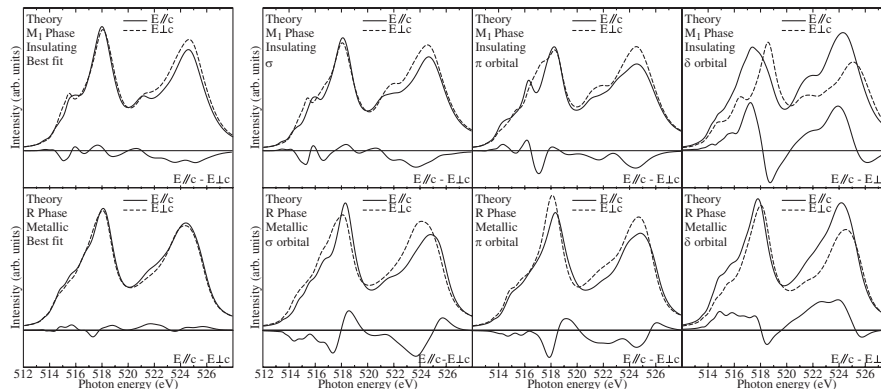


FIG. 4. Theoretical simulations for the polarization-dependent V  $L_{2,3}$  XAS spectra. Left panels: Best fit to the experimental spectra, using orbital occupations as indicated in Table I. Right panels: Simulations for the V  $3d^1$  ion assuming a pure  $\sigma$ -,  $\pi$ -, or  $\delta$ -orbital occupation. Top part of the panels: Simulations for the insulating  $M_1$  phase. Bottom part of the panels: *Idem* for the metallic  $R$  phase.

TABLE I. Symmetry and orbital occupation of the 3d shell of VO<sub>2</sub> in the M<sub>1</sub> and R phases.

	M <sub>1</sub> phase				R phase			
	Fit to exp		<i>ab initio</i>		Fit to exp		<i>ab initio</i>	
	Symmetry	<i>n</i> <sub>3d</sub>	LDA	LSDA + <i>U</i>	Symmetry	<i>n</i> <sub>3d</sub>	LDA	LSDA + <i>U</i>
$\sigma$	0.81	0.86	0.64	0.89	0.33	0.41	0.43	0.20
$\pi$	0.10	0.21	0.39	0.23	0.16	0.25	0.35	0.24
$\delta$	0.09	0.17	0.41	0.25	0.51	0.58	0.67	0.97
$e_{g1}$	0.00	0.27	0.46	0.40	0.00	0.27	0.47	0.42
$e_{g2}$	0.00	0.32	0.53	0.51	0.00	0.27	0.48	0.48
Total	1.00	1.83	2.43	2.48	1.00	1.78	2.40	2.31

trend that the orbital occupation is more  $\sigma$  polarized in the M<sub>1</sub> phase is predicted correctly in both approaches.

In comparing our experimental results with the dynamical mean-field theory (DMFT) calculations, we note that in one implementation of the standard LDA + DMFT method the change in orbital polarization is too small which has been attributed to the fact that the insulating phase cannot be reproduced [10]. Very exciting is that an LDA + cluster/DMFT study [13] has been very successful in reproducing the strong change in orbital polarization, indicating the importance of the  $k$  dependence of the self-energy correction.

The significant outcome of our experiments is that the orbital occupation changes from almost isotropic in the metallic phase to the almost completely  $\sigma$  polarized in the insulating phase, in close agreement with the three-band Hubbard model [11]. This very strong change leads to a dramatic modification of the intersite exchange interactions with large consequences for the effective Hubbard  $U$  for nearest neighbor charge fluctuations [5,11] and effective bandwidths [5]. Moreover, the orbital polarization change is such that VO<sub>2</sub> in terms of its electronic structure is effectively transformed from a three-dimensional to a one-dimensional system [6]. The V ions in the chain along the  $c$  axis are then very susceptible to a Peierls transition. In this respect, the MIT in VO<sub>2</sub> indeed has many features of a Peierls transition [3]. However, to get the dramatic change of the orbital occupation, one also need the condition that strong electron correlations bring this narrow band system close to the Mott regime [4]. The MIT in VO<sub>2</sub> may therefore be labeled as an orbital-assisted “collaborative” Mott-Peierls transition.

To conclude, we have found direct experimental evidence for an orbital switching in the V 3d states across the metal-insulator transition in VO<sub>2</sub>. The orbital occupation in the insulating state is such that the effective bandwidths are reduced and the system electronically more one dimensional and thus more susceptible to a Peierls-like transition.

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- [24] Parameters for VO<sub>6</sub> cluster (in eV):  $\Delta = 2.5$ ,  $U_{dd} = 4.5$ ,  $U_{pd} = 6.1$ ; Slater integrals 80% of Hartree-Fock values.