Orbital-Assisted Metal-Insulator Transition in VO$_2$

Beamline

11A Dragon beamline

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We found direct experimental evidence for an orbital switching in the V 3d states across the metal-insulator transition in VO$_2$. We have used the V L$_{2,3}$ XAS spectrum as a sensitive local probe and determined quantitatively the orbital polarizations. The 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 band widths are reduced, that the system becomes more 1-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.

The problem of metal-insulator transitions (MIT) in transition metal oxides attracts considerable attention for a long time. The long-standing problem in VO$_2$ 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$_2$, which was described either as predominantly a Peierls transition or as a Mott-Hubbard transition. The MIT in VO$_2$ is a structural transition from the high-temperature rutile (*R*) structure to a monoclinic (*M$_1$*) structure, in which there appears simultaneous *dimerization* in each V chain along the *c*-axis. As argued already long ago by Goodenough, one should discriminate between two types of orbitals and corresponding bands: d$_{||}$-orbitals/bands, formed by the *t$_{2g}$*-orbitals with strong direct overlap with the neighboring V in the chains, and π*-orbitals/bands, made of the two other t$_{2g}$-orbitals. In the *R*-phase, the d$_{||}$ band overlaps with the π*-band, resulting in a orbitally isotropic metallic state, see Fig. 1. In the *M$_1$*-phase the V - apex O hybridization increases and the π* band moves up, so that only the d$_{||}$ band is occupied. The later one then becomes split by the dimerization, leading to the insulating state.
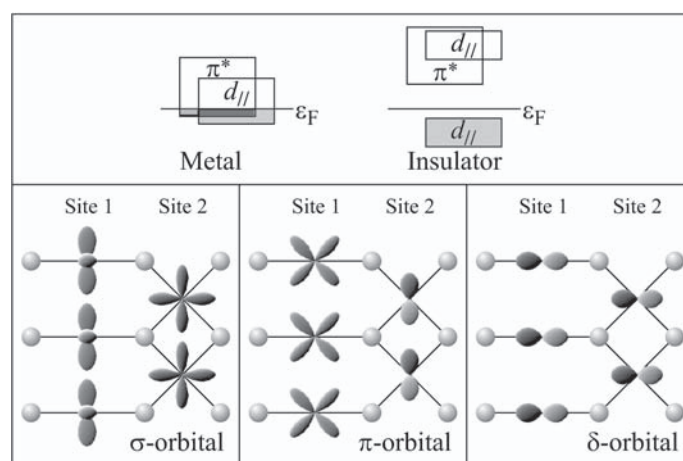

Fig. 1: Top panel: schematic electronic structure of VO$_2$ according to Goodenough [3]; bottom panel: definitions of the relevant V *3d t$_{2g}$* orbitals used in this work, drawn in the (110) plane. Site 1 and 2 are related by a 90˚ rotation around the *c*-axis.

Many theoretical *ab-initio* studies were performed to test the Goodenough picture. LDA calculations indicated indeed that the d$_\parallel$ band becomes more occupied in the *M$_1$*-phase, but they failed to reproduce the insulating state. 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. A change in the orbital occupation was also obtained in the exact diagonalization study for a three-band Hubbard model using finite size clusters. Very recently, various LDA+DMFT methods have been applied to explain the MIT, and also here the orbital occupations are an important issue. In view of the fact that the orbital occupation and changes thereof are central to the MIT theories for VO$_2$, it is quite surprising that an experimental proof of it is lacking.

In this report we give a direct experimental evidence of this orbital redistribution at the MIT in VO$_2$ using a polarization-dependent V-$L_{2,3}$ XAS spectrum on the single crystal VO$_2$. 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$_{2g}$* band width, so that the absorption process is strongly excitonic and therefore well understood in terms of atomic-like transitions to multiplet split final states. This makes the technique an extremely sensitive local probe to study the orbital character of the ground. Here, we redefine the orbitals in terms of σ, π, and δ with respect to the V chain as shown in Fig. 1. The σ orbital is then equivalent to the d$_\parallel$ and the π or δ to the π^*. The transition probability will strongly depend on which of the σ, π, and δ orbitals are occupied and on how the polarization vector **E** of the light is oriented.

Figure 2 shows the V $L_{2,3}$ XAS spectra of VO$_2$ taken in the insulating *M$_1$*-phase (top panel), and in the metallic R-phase (bottom panel). We observe a clear polarization dependence for the insulating phase and quit weak for the metallic phase. Figure 2 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 lineshape than that of the metallic phase. To extract information concerning the orbital occupation from the experimental spectra, we calculate the spectra with well-proved configuration interaction cluster model.
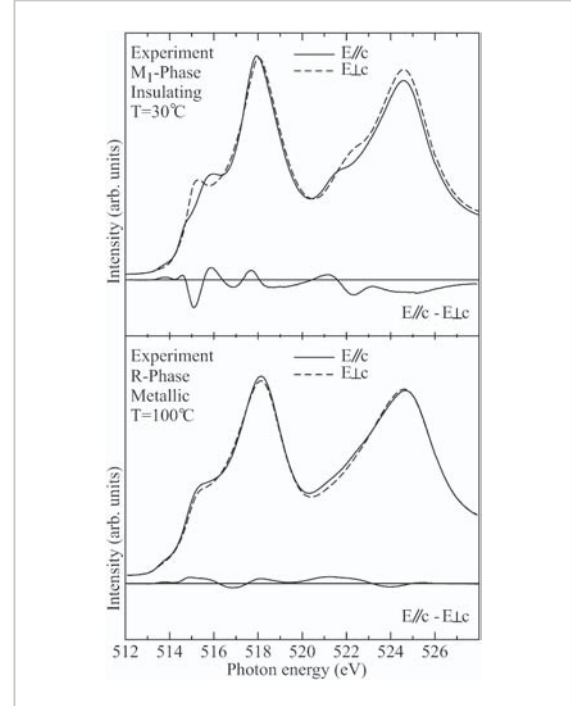

Fig. 2: Experimental V $L_{2,3}$ XAS spectra of VO$_2$ in the insulating M$_1$-phase (top panel, T=30˚C) and metallic R-phase (bottom panel, T=100˚C), taken with the light polarization **E**//c (solid lines) and **E**⊥c (dashed lines). The metal-insulator transition temperature is 67˚C.

which includes the full atomic multiplet theory and the local effects of the solid. Parameters for the multipole part of the Coulomb interactions were given by the Hartree-Fock values, while the monopole parts U_{dd}, U_{pd} as well as the O *2p* - V *3d* charge transfer energy were determined from photoemission experiments. 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.

Figure 3 shows the results of theoretical simulations. In the top part of the right panel we present theoretical spectra in the insulating *M$_1$*-phase for the following three scenarios: the V 3d^1 ion is set either in the pure σ, π, or δ-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 σ-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 agreement
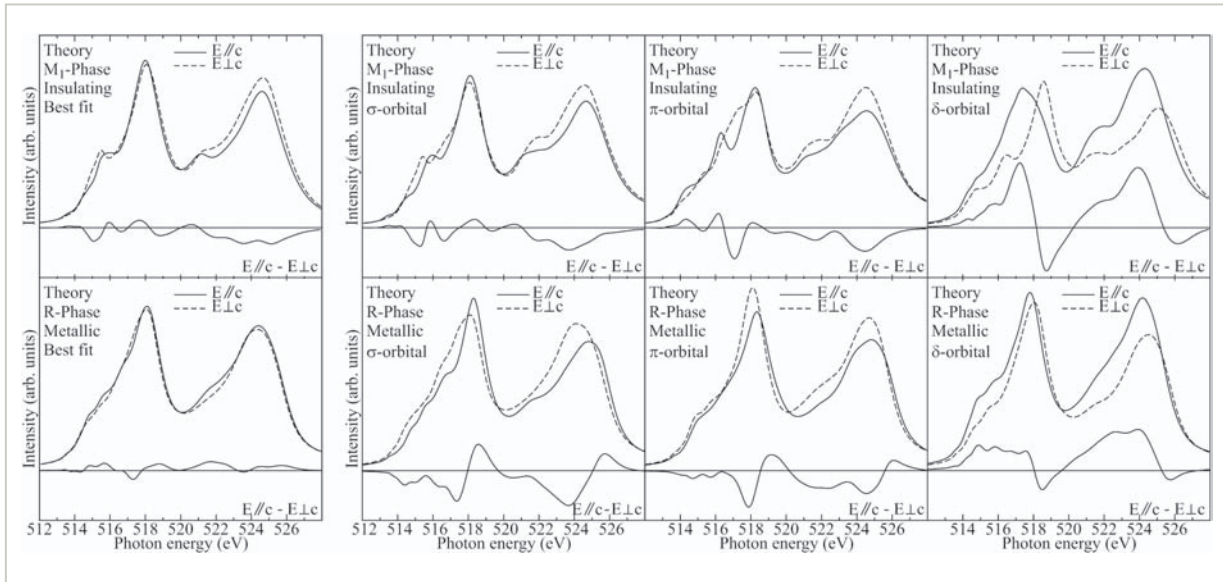
Fig. 3: Theoretical simulations for the polarization dependent V L$_{2,3}$ XAS spectra. Left panel: best fit to the experimental spectra, using orbital occupations as indicated in Table I. Right panel: simulations for the V 3d^1 ion assuming a pure σ, π, or δ orbital occupation. Top part of the panels: simulations for the insulating M$_1$-phase. Bottom part of the panels: *idem* for the metallic R-phase.

with the experimental data as shown in the left panel. The corresponding orbital symmetry, as listed in the left column of Table I, has indeed overwhelmingly the σ character (0.81), and only very little π (0.10) and δ (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 σ, π, or δ-orbital symmetry. The bottom part of the right panel 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 of crystal structure. Important is now 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 σ, π, or δ. 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 3 (bottom left panel) shows that this state is built up of 0.33 σ, 0.16 π and 0.51 δ symmetries, see also the 5th column of Table 1. It seems thus that in the metallic phase the V orbital occupation is almost isotropic.

In Table 1 we have also listed the *3d* orbital occu-

pation found from the above simulations. 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. We note that our LDA band structure is quite similar to the one published earlier, and that the occupation numbers of our LSDA+U is in close agreement with the one published very recently. For the insulating *M$_1$*-phase, we find that the orbital occupation, which is highly σ 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 deter-

Table 1: Symmetry and orbital occupation of the *3d* shell of VO$_2$ in the *M$_1$*- and *R*-phase.

| | M$_1$ phase | | | | R phase | | | |
| | fit to exp. | | ab initio | | fit to exp. | | ab initio | |
	sym	n$_{3d}$	LDA	LSDA+U	sym	n$_{3d}$	LDA	LSDA+U
σ	0.81	0.86	0.64	0.89	0.33	0.41	0.43	0.20
π	0.10	0.21	0.39	0.23	0.16	0.25	0.35	0.24
δ	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
tot	1.00	1.83	2.43	2.48	1.00	1.78	2.40	2.31

mined is well reproduced by the LDA, but not so by the LSDA+U. It seems that the LDA tends to underestimate the orbital polarization, which makes the method less suitable for the insulating phase. The LSDA+U, on the other hand, tend to overestimate it, which puts this approach in disadvantage 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 does not give the metallic state for the R-phase. Nevertheless, the general trend that the orbital occupation is more σ-polarized in the M_1-phase is predicted correctly in both approaches. In comparing our experimental results with the 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. Exciting is that an LDA+cluster/DMFT study 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 σ-polarized in the insulating phase, in close agreement with the three band Hubbard model. 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 and effective band widths. Moreover, the orbital polarization change is such that VO_2 in terms of its electronic structure is transformed from a 3-dimensional to effectively a 1-dimensional system. 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_2 indeed has many features of a Peierls transition. 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. The MIT in VO_2 may therefore be labelled 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_2. The orbital occupation in the insulating state is such that the effective band widths are reduced and the sys-tem electronically more 1-dimensional and thus more susceptible to a Peierls-like transition.

Experimental Station

XAS chamber of the Universität zu Köln, Germany

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