

Soft-x-ray-absorption studies of the electronic-structure changes through the VO₂ phase transition

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We present the O 1s and V 2p absorption edges of VO₂ at room temperature and at $T = 120^\circ\text{C}$, i.e., below and above the metal-insulator transition temperature $T_c \approx 67^\circ\text{C}$. The O 1s spectra show a clear splitting of 1 eV in the unoccupied $d_{||}$ band below T_c . Because the V 2p absorption edges are dominated by the V 2p-3d interaction in the final state, these spectra show minor changes that cannot be easily correlated with the changes in the unoccupied density of states.

I. INTRODUCTION

The site and symmetry selectivity of x-ray absorption has always been a major potential source of information. However the deep core levels probed by hard x rays are broad and only the recent improvements in the energy resolution of the soft-x-ray monochromators¹⁻³ and the development of powerful theoretical techniques to analyze the experimental results⁴⁻¹⁰ has allowed a boom in the field of soft-x-ray-absorption spectroscopy (XAS). In an effort to explore the limits of soft-XAS we are using it to study the unoccupied states in very interesting and sometimes difficult materials. In this case we present data on VO₂ which undergoes a first-order structural phase transition at $T_c \approx 67^\circ\text{C}$ which is accompanied by an abrupt change in the electric conductivity. In addition the optical properties of this material also change dramatically, even in the visible, which promises to make VO₂ a very useful component in future optical switching devices.

Here we present the O 1s and V 2p absorption edges of VO₂ at room temperature and at $T = 120^\circ\text{C}$ (i.e., below and above the transition temperature T_c , respectively). The O 1s spectrum proves to be very useful in the study of the metal-insulator transition because it maps the unoccupied states on the V 3d band due to O 2p-V 3d covalent mixing. The fact that we are not dealing with joint density of states usually makes the interpretation of the spectra much easier in comparison with the analysis of optical properties. In particular we will show that the O 1s spectrum gives directly the splitting of the unoccupied $d_{||}$ band, and that the changes across the phase tran-

sition are larger than those indicated for other states by other investigations.

The paramagnetic metallic phase of VO₂ has the tetragonal rutile (TiO₂) structure. Below T_c it undergoes a structural transition to a nonmagnetic monoclinic phase in which pairs of V atoms are brought closer to each other.¹¹ This material has been studied by means of many spectroscopic techniques such as photoemission,¹²⁻¹⁵ reflectance, and hard-x-ray absorption,¹⁶ and especially photoemission spectra showed the disappearance of the states at the Fermi level when going from the high-temperature to the low-temperature phase.¹⁵ The electronic structure of VO₂ was calculated using the band-structure approach in the metallic phase and cluster calculations in both phases.¹⁷⁻¹⁹

II. EXPERIMENTAL DETAILS

The experiments reported here were performed at the National Synchrotron Light Source in Brookhaven using the Dragon monochromator.³ The energy resolution of the monochromator in the energy range of interest (~ 500 eV) was better than 100 meV. Note that the O 1s linewidth is about 100-200 meV,²⁰ which is narrower than the energy resolution of any monochromator in this energy range up to 1988. The sample was a VO₂ single crystal grown by the chemical vapor transport method and cleaved parallel to the (110)_r plane of the rutile phase. The spectra were collected in the total electron yield mode with the polarization vector of the photons parallel to the c axis of the rutile phase.

III. RESULTS AND DISCUSSION

Figure 1 shows the O 1s absorption spectra of VO₂ taken at room temperature and $T=120^\circ\text{C}$. The sharp peaks near threshold are attributed to transition to states with mainly V 3d character which are hybridized with O 2p states. This is in agreement with the assignment of this structure in previous studies of transition-metal oxides.²¹ To understand the origin of the different peaks in the spectra we will resort to the widely used classification scheme based largely on molecular-orbital (MO) and crystal-field ideas.²²

The top panel of Fig. 2 shows schematically how the VO₆ octahedra share edges in the undistorted rutile structure and the coordinate system used in the present analysis. The V 3d_{3z²-r²} and 3d_{x²-y²} orbitals point towards the ligands and form the σ and σ^* bands with the O 2p orbitals. On the other hand, the V 3d_{xz} and 3d_{yz} orbitals point in between the ligands and form the π and π^* bands. Finally the relatively nonbonding V 3d_{xy} orbital points in between the ligands and towards the next-nearest-neighbor V site and form the d_{\parallel} band. Figure 2(a) shows the electronic structure of metallic VO₂ based on this MO analysis.^{22,23} In particular we note the formation of the partially filled d_{\parallel} band overlapping the π^* band. The complicated distortion below T_c destroys completely the symmetry of the VO₆ octahedra and forms pairs of V atoms. Figure 2(b) shows the splitting of the d_{\parallel} band due to the formation of the V-V dimers. The band splitting is partly originated by pairing effects, however, electron repulsion yields an important contribution to the splitting.^{18,24,25} The filling of the lower energy band, which corresponds to singlet pairing within the dimers, explains both the abrupt drop in the electric conductivity and the absence of magnetic order below T_c .

With this classification in mind we can now assign the

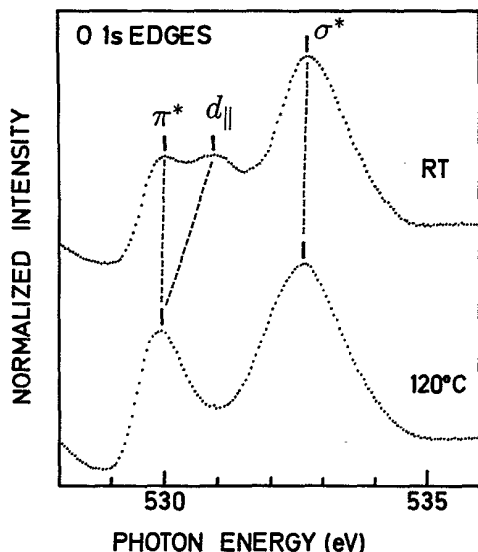


FIG. 1. O 1s absorption spectra of VO₂ taken at room temperature and $T=120^\circ\text{C}$.

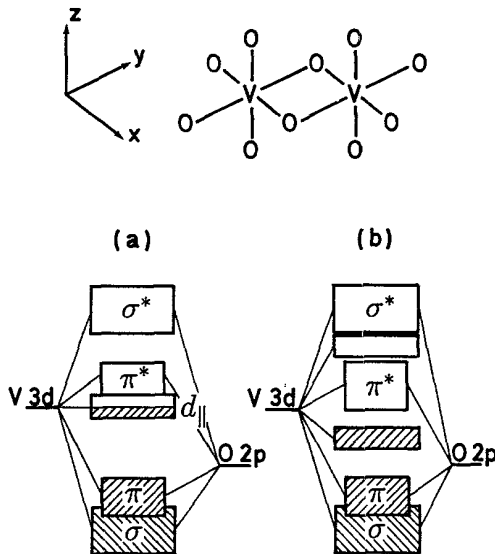


FIG. 2. Top panel: schematic representation of the VO₆ octahedra in the undistorted rutile structure. Lower panel: MO approach to the electronic structure in VO₂; (a) undistorted and (b) distorted.

peaks in the O 1s spectra. In particular we note that the localized pairing interactions, which result from the V-V dimerization below T_c , are strong enough to push the unoccupied part of the d_{\parallel} band more than 1 eV above the π^* band edge. By contrast, the weak shift of the σ^* band towards higher energies (~ 0.2 eV) reflects smaller changes in bonding and the π^* band hardly shifts at all due to its even weaker bonding properties. As optical data and photoemission spectra indicate that the gap between the occupied d_{\parallel} and the unoccupied π^* edges is ~ 0.7 eV (Ref. 15) we arrive at a splitting of more than 2 eV between the occupied and the unoccupied d_{\parallel} band edges. Thus it is worth stressing again that the main changes occur in the d_{\parallel} band and that the π^* band hardly changes.

Within the framework of the model discussed above the intensity of the different peaks in the O 1s spectra should be related to the degree of hybridization in each MO-derived band. Using this criterion one could explain the larger intensity of the σ^* band peak with respect to the weakly bonding π^* and d_{\parallel} band peaks. However, it is particularly puzzling that the relatively nonbonding d_{\parallel} band peak in the distorted phase is almost as intense as the π^* band peak. This discrepancy between simple MO theory and experiment was already noticed in the study of the O 1s spectra of transition-metal oxides²¹ and indicates the importance of solid-state effects beyond this approximation. A full qualitative discussion of the O 1s spectra would require a symmetry-projected band-structure calculation, like the one presented in the study of the O 1s spectra of CuO,⁸ the computation of independent particle matrix elements and the inclusion of core-hole effects. Unfortunately, not even a band-structure calculation of VO₂ in the distorted phase is available at the present time.

Figure 3 shows the V $2p$ absorption edge of VO_2 taken at room temperature and $T=120^\circ\text{C}$. We observe the presence of minor changes between the spectra which are not commensurate with those observed in the O $1s$ spectra and cannot be explained by an increase in the phonon contribution to the broadening either. However, the spectra have some common features whose discussion is a good starting point to understand the origin of the changes between the spectra. These features are the transfer of spectral weight away from threshold, the deviation of the intensity ratio between the spin-orbit-split $2p_{3/2}$ and $2p_{1/2}$ doublet from the ideal 2/1 ratio, and the decrease in the apparent spin-orbit splitting of the $2p$ level in the absorption spectra (~ 6.6 eV) as compared with the splitting observed in XPS (~ 7.4 eV).¹⁴ Zaanen *et al.* demonstrated that all these effects are the natural consequence of the strong interaction between the $2p$ core hole and the $3d$ electrons in the final state.⁶ These interactions are of the same order of magnitude of the V $2p$ spin-orbit splitting which causes a large redistribution of the intensity throughout the entire spectra.⁶

We also note that the structure of the V $2p$ edges does not match the density of states inferred from the O $1s$ spectra or given by *ab initio* calculations.^{17,19} We attribute this discrepancy to the strong influence of the V $2p$ - $3d$ interactions in the final state. Taking these points into account we conclude that the changes in the V $2p$ absorption spectra above and below T_c are mainly due to changes in the V $3d$ band structure, but since the atomic correlations dominate the spectra these changes are washed out.

Finally we discuss the question of whether the transition is of a Mott (electron-electron correlation) or a Peierls (electron-lattice interaction) type. This question was the subject of intense theoretical efforts based on sophisticated computation techniques.²⁶⁻²⁹ We believe that no clear-cut answer is possible because *both* effects contribute to the transition. In particular electron correlation contributes to the splitting of the $d_{||}$ band^{18,24,25} and the observation of an anomalously large Debye-Waller factor in x-ray-diffraction studies of VO_2 just above the transition indicates the importance of electron-phonon interactions.³⁰ However, we want to make a few remarks. The absence of magnetic order below T_c indicates that the transition cannot be formally considered of the Mott type and suggests the formation of a singlet within each dimer. The large splitting of the $d_{||}$ band inferred from the O $1s$ spectra, in contrast with the weak changes observed in the π^* and σ^* bands, shows clearly the importance of *localized pairing interactions* within the V-V dimer. Therefore, we think that the transition in VO_2 is basically driven by the lowering in energy of the occupied $d_{||}$ band associated with the distortion of the crystal symmetry and the concomitant enhancement of electron-electron correlation effects. We also note that if pairing

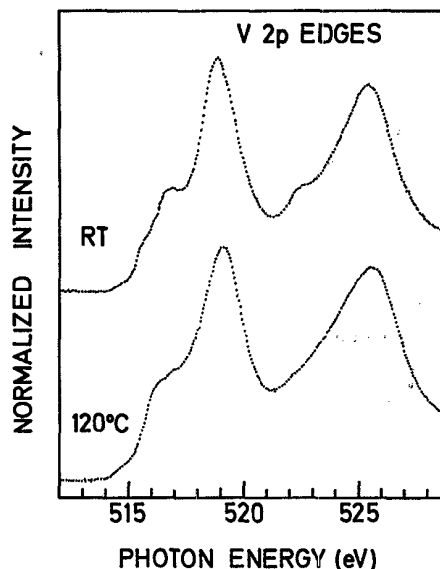


FIG. 3. V $2p$ absorption spectra of VO_2 taken at room temperature and $T=120^\circ\text{C}$.

is necessary for the formation of a given bond then each extra bond makes more likely the formation of the next bond since the hopping which stabilizes the metallic phase is made less probable; this provides the basis of the cooperative effect necessary to explain the origin of the phase transition itself.

IV. SUMMARY AND CONCLUSIONS

In summary, we have shown that XAS yields very interesting information on the metal-insulator phase transition in VO_2 . In particular the O $1s$ spectrum maps the mainly V $3d$ band character and shows directly the splitting of the unoccupied $d_{||}$ band. This observation gives further support to the theories which explain the transition in terms of *localized pairing interactions* within the V-V dimer. We think that the potential of XAS in the study of phase transitions is not limited to this particular case and deserves to be fully investigated.

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