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Multiplet splitting of final-state configurations in x-ray-absorption spectrum of metal VO_2: Effect of core-hole-screening, electron correlation, and metal-insulator transition

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X-ray-absorption K-edge spectra of the V $1s$ core level in VO_2 exhibit broadening and splitting of the $1s \rightarrow t_{2g}$ core transition at the K threshold at the semiconductor-to-metal phase transition. The three components observed in the metallic phase are assigned to final-state configurations characterized by different occupation numbers of the localized $d_{\parallel}$ band at the Fermi level: $d_{\parallel}^2$, $d_{\parallel}^1$, and $d_{\parallel}^0$. In the low-temperature semiconducting phase only the $d_{\parallel}^1$ final-state configuration is present. This experiment shows the core-hole-induced relaxation in x-ray-absorption spectroscopy of a narrow-band metal, where electron correlation is not negligible.

I. INTRODUCTION

A. Core-hole induced relaxation

Recently, the use of synchrotron radiation has stimulated interest in core-level spectroscopy such as x-ray-absorption spectroscopy (XAS) because it is a probe of local spatial and electronic structure. One basic problem to be tested experimentally is that some features observed in an XAS experiment may not reflect the initial ground-state configurations directly because of the strong disturbance the core hole makes on the system, and therefore, final-state effects may be important.

The relaxation effects are expected to be relevant in the cases where a localized state is at the Fermi level on the absorber site. These effects have been measured in mixed-valent systems where a localized f level is at the Fermi level.[1,2]

As predicted by theoretical calculations[3-6] if there is an unoccupied localized valence state at the Fermi level, the excited core hole can pull down this state well below the Fermi level. Different ionization energies result from different final-state occupancies of this deeper localized level.

In the case of rare-earth compounds the electrons in the very narrow $4f$ band, of width W, are strongly correlated because $U \gg W$, where U is the Hubbard valence-electron—valence-electron Coulomb correlation parameter.[7] In this correlated limit a different type of core-hole screening appears, other than the usual screening of electrons in the conduction band at the Fermi level. One electron from a neighbor atom can fill the deeper localized level giving the so-called "shake-down" effect. This effect has been observed both in x-ray photoemission spectra (XPS) (Ref. 8) and in XAS (Ref. 2) experiments on mixed-valent systems. In agreement with theoretical analysis[6] the experiments show[2] that the shake-down effect is dependent on the width W of the localized band.

In the case of wide conduction band $U \ll W$ the core-hole-induced relaxation is expected not to be important and the final state in XAS can usually be described by the one-electron conduction-band picture.[9,10] Here I report the first study of the effects of core-hole relaxation in XAS experiments on a transition-metal oxide where $U \sim W$ in the narrow conduction band, and therefore its electronic structure, cannot be described by either the strongly correlated limit or by the one-electron itinerant model. This complex intermediate situation is characteristic of transition-metal oxides. In these systems, such as in $NaWO_3$, MoO_2, and MoO_3, multiplet splitting of final states in core-level x-ray photoemission spectra has been measured.[11-13] The final-state splitting of an XPS core line has been recently calculated by Cox[14] for a model of a single narrow band with various values of U/W showing the evolution of XPS satellites from the appearance of the shake-down peak $U/W > 1$ to the shake-up peak $U/W < 1$.

B. The electronic structure of VO_2.

VO_2 has been the object of extensive investigation[15] because single crystals of VO_2 undergo a metal-insulator transition (MIT) at 68 °C decreasing the temperature. Valence-band photoemission[16,17] shows the opening of a ~ 0.5 eV band gap in the semiconducting phase.

Recent experimental results on the temperature-dependent red shift of the plasmon energy in the metallic phase[18] and a theoretical study[19] show that the two-band model[15] of the electronic structure of VO_2 near the Fermi level is appropriate to describe the electronic behavior of VO_2. The electronic structure of the high-temperature metallic phase of VO_2 has been calculated using both band-structure and molecular approaches.[15,19–22] The Fermi level intersects the t_{2g} conduction band occupied by one electron per V atom. The t_{2g} band is formed by a manyfold of 6 bands which can be separated into a localized twofold $d_{\|}$ band and a delocalized fourfold π^* band. The interaction of the 3*d* orbitals of V ions along the *c* axis of the rutile structure (with an anomalous short V-V distance) gives rise to the narrow $d_{\|}$ band overlapped by the wide π^* band formed by antibonding vanadium 3*d* and oxygen 2*p* states. Magnetic susceptibility[15] and plasmon resonance[18] experiments, in agreement with recent calculations,[19] give a $d_{\|}^{0.7}$ $\pi^{*0.3}$ configuration for the high-temperature metallic phase.

In the low-temperature semiconductor phase the electrons become localized on the V-V dimers of the monoclinic distorted structure. The $d_{\|}$ band is split by crystal distortion and intra-atomic correlation effects.[19,22] One $d_{\|}$ band, completely filled by one electron, is lowered below E_F forming a band gap of about 0.6 eV between its top and the bottom of the π^* band. The ground state of the semiconductor is described by the $d_{\|}^{1}\pi^{*0}$ frozen configuration with integral occupation numbers.

In this paper we report a study of VO_2 by high-resolution x-ray-absorption edge spectroscopy. In edge spectroscopy one studies the electronic transitions from a core atomic level to unoccupied conduction states above the Fermi energy. At the *K* edge of vanadium in the "edge" energy region ~ 8 eV above the absorption threshold, the first two absorption peaks arise from one-electron t_{2g} and e_g final states.[9,10,23] Although transitions from the V 1*s* level to t_{2g} and e_g bands are forbidden to zeroth-order dipole approximation they become allowed in the first-order perturbation theory mainly due both to a small admixture of the 4*p* antibonding states and to quadrupole transitions.

II. EXPERIMENTAL

The high-resolution x-ray-absorption edge spectra were measured using the synchrotron radiation emitted by the storage ring ADONE at the Frascati facility Progetto per l'Utilizzazione della Luce di Sincrotrone. The storage ring was operated at 1.5 GeV and 60 mA. The x rays were monochromatized by a Si(220) *a* channel-cut single crystal at 17 m from the source. The energy resolution at the V *K* edge was $\Delta E/E \sim 10^{-4}$. The data acquisition and analysis was made by an on-line computer. The sample was a powder of VO_2 obtained *in situ* from a VO_2 single crystal characterized by x-ray diffraction, which exhibits the MIT at 68 °C. The sample was kept in a small aluminum box transparent to x rays in order to obtain a homogeneous sample temperature. Many spectra above and below the phase-transition temperature were recorded. The use of synchrotron radiation allows us to collect x-ray-absorption edge spectra with higher resolution and signal-to-noise ratio than was previously possible with standard x-ray sources.

III. RESULTS

Figure 1 shows the x-ray-absorption spectra of VO_2 and V_2O_5 over the energy range of the "edge region" ~ 8 eV and of the "x-ray-absorption near-edge structure (XANES) region."[9,23] In the edge region the first peaks are assigned to molecular empty orbitals while in the XANES region the peaks are due to multiple-scattering resonances in the continuum. We have focused our attention on the edge region where the main feature *A* is due to the t_{2g} band originated by the molecular orbital,

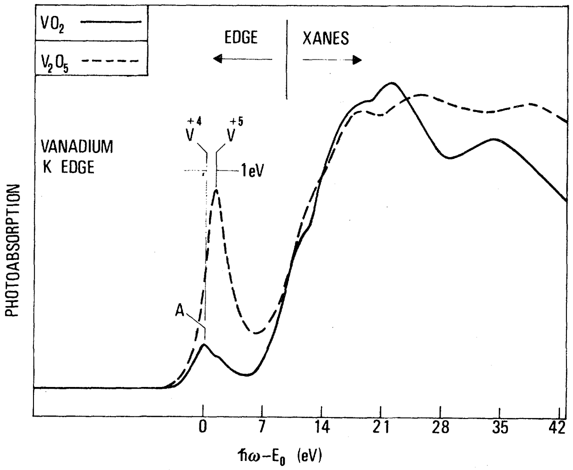

FIG. 1. Edge and XANES spectra of VO_2 and V_2O_5 at the V *K* edge.

mostly d-like, of the VO_6 microscopic cluster. In V_2O_5 the first peak is due to the t_2 mostly-p-like orbital of the VO_5 cluster which therefore appears as strong as a dipole-allowed transition. The chemical shift between the first peak in the edge region going from VO_2 to V_2O_5 is 1 ∓ 0.1 eV with the same chemical shift of the V $2p$ core levels measured by XPS spectroscopy.[17,24]

Figure 2 shows the broadening effect of the metal-insulator transition on the x-ray-absorption edge and near-edge spectrum (XANES) of VO_2. Figure 3 shows the correlation between the first feature at the K threshold and the density of states of the conduction band t_{2g} and e_g from Ref. 21. Also the valence-band XPS spectrum probing the filled valence band is plotted (dashed line). It is clear that the first main peak A_1 at the K threshold of the absorption spectrum is due to the $1s \rightarrow t_{2g}$ transition.

Figure 4 shows the K-edge absorption spectra of metal VO_2 above the transition temperature, at about 420 K, and of the semiconductor VO_2 at room temperature. In the lower part the first-derivative spectra are plotted. The MIT phase transition induces, at the transition temperature $T_t = 68\,^{\circ}C$, a discontinuous change of the shape of the spectra, as is expected in a first-order transition.

Figure 5 shows the variation of the intensity of peak A_1 in Fig. 4 as a function of the temperature. Clearly, a discontinuous decrease of the peak height appears at the metal-insulator-transition temperature.

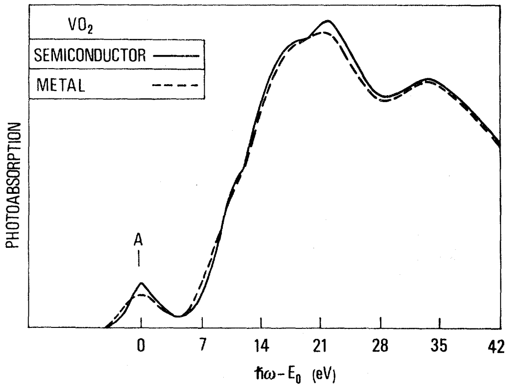

FIG. 2. XANES of VO_2 before (semiconducting phase $T = 273$ K) and after (metallic phase $T = 373$ K) the phase transition.

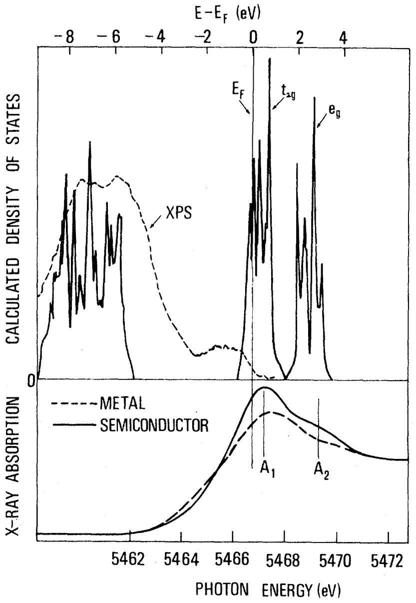

FIG. 3. Comparison of the edge structure with the calculated density of states of the conduction band of metallic VO_2 (Ref. 21).

IV. DISCUSSION

A. Single final-state configuration in the semiconductor

Let us first discuss the semiconductor edge. Figure 6 shows the results of the spectra analysis by a curve-fitting program using a single Lorentzi-

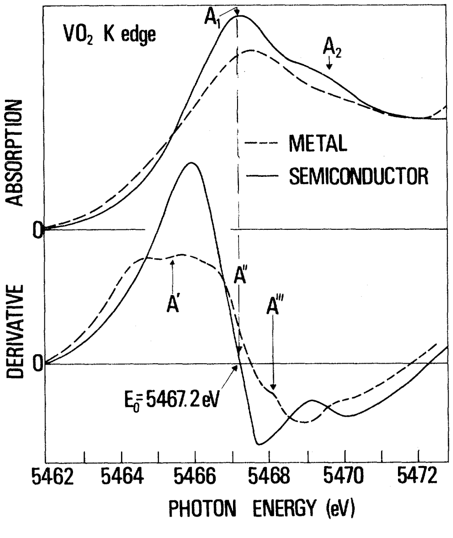

FIG. 4. Absorption edges and their derivatives of VO_2 in the metal and semiconductor phases.

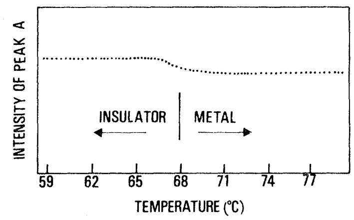

FIG. 5. Temperature dependence of the maximum of peak A.

an for the A_1 peak and an arctan for the $1s$ continuum transitions with the same linewidth. This very simple fitting, used to reduce to a minimum the number of parameters, gives a good fit of the semiconductor spectrum with the same linewidth for both spectra, $2\Gamma = 3.6$ eV full width at half maximum.

On the basis of the calculated electronic structure of VO$_2$ the K edge of the semiconductor is therefore explained. The single peak A corresponds to excitation from the ground state $1s^2 d_\parallel^1 \pi^{*0}$ to the excited final-state $1s^1 d_\parallel^1 \pi^{*1}$ configuration. Core-hole-induced relaxation can be disregarded in the insulator phase of VO$_2$ because the localized $d_\parallel$ is fully occupied and the conduction band is the empty delocalized π^* band where $U \ll W$.

B. Multiple final-state configurations in the metal

Above the transition temperature *a discontinuous change of the shape of the A_1 peak appears, increasing the crystal temperature.* The derivative spectrum in Fig. 4 shows directly that this peak in the metal phase is split into three components. In fact, two additional features labeled A' and A''' *were needed* to fit the measured spectrum shown in Fig. 6. A' is shifted to lower energy by -0.9 ± 0.3 eV with respect to A_1, and the other A''' is shifted to higher energy by $+0.9 \pm 0.3$ eV. The combined intensity of the three peaks A', A'' (at the same energy as A_1), and A''', and the intensity of single peak A_1 in semiconductor VO$_2$, are equal within a few percent. The intensity ratio between the corresponding peaks A''/A_1 is 0.55.

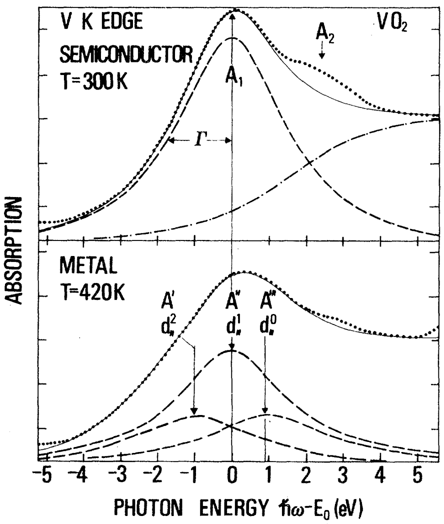

FIG. 6. Fitting of the absorption-edge spectra with Lorentzians and arctan curves.

The hypothesis that the splitting in the metal is due to the splitting of an unoccupied t_{2g} band (the final state of the core transition) has been rejected because we have observed the same broadening effect on all the other peaks at higher energies, in the XANES region, and the same broadening and splitting has been observed in the $2p$ core line of the XPS spectrum[17] which is not sensitive to unoccupied valence bands. Moreover, one would expect a broadening and splitting of the t_{2g} band at the MIT in the opposite direction going from the rutile metal phase to the distorted monoclinic semiconductor phase.

The structures A', A'', and A''' should be assigned to final-state splitting of the core transition in the metal phase. We identify the peaks labeled A', A'', and A''' in Fig. 6 as formal $\bar{d}_\parallel^2$, $\bar{d}_\parallel^1$, and $\bar{d}_\parallel^0$ configurations in the final excited state of the V ion after photoabsorption.

The ground state of metallic VO$_2$ $2p^6\, d_\parallel^{0.7} \pi^{*0.3}$ can be described by the overlap of two *virtually degenerate* configurations, $d_\parallel^1 \pi^{*0}$ and $d_\parallel^0 \pi^{*1}$. In the excited state where the core hole is switched on, three possible excited states as shown in Fig. 7 can appear,

$$2p^5 \bar{d}_\parallel^0 \pi^{*2} \leftrightarrow A''' ,$$

$$2p^5 \bar{d}_\parallel^1 \pi^{*1} \leftrightarrow A'' ,$$

$$2p^5 \bar{d}_\parallel^2 \pi^{*0} \leftrightarrow A' ,$$

characterized by the different occupation number of the relaxed $\bar{d}_\parallel$ localized band. In the excited state the three configurations will have different energies mainly due to the Coulomb attractive interaction between the $2p$ hole and the electrons in the localized $d_\parallel$ band Q_{hd}.

The value of Q_{hd} can be estimated if the value of the one-site valence-$d_\parallel$-electron—valence-$d_\parallel$-electron correlation parameter U_{dd} is known. From theoretical calculations[19,22] $U_{dd} = 1.1$ eV in

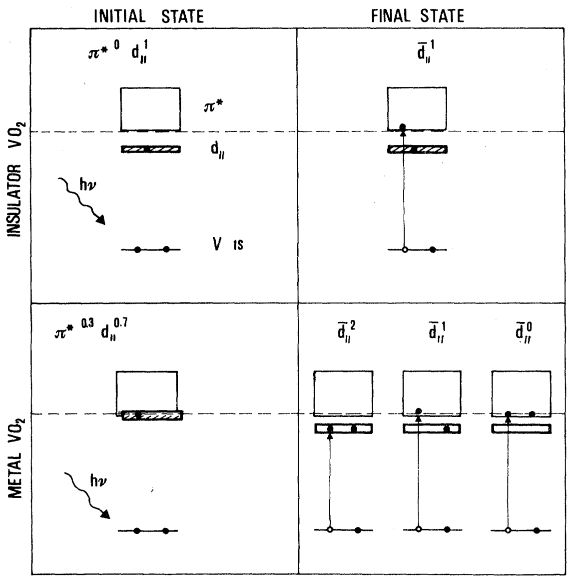

FIG. 7. Schematic picture of initial- and final-state configurations in metal and insulator VO_2.

VO_2. Because both Q_{hd} and U_{dd} are one-center Coulomb integrals and because Q_{hd} is expected to be somewhat larger than U_{dd}, a reasonable value of their ratio U/Q for a transition-metal oxide is 0.7.[14] Therefore, $Q_{hd} = 1.5$ eV, which is close to the exciton shift for the VO_4 K edge estimated by Curelau and Wendin.[25] Because $U_{dd}/W_d \sim 1$ and $Q_{hd}/W_d \sim 1.5$, where $W_d = 1$ eV is the $d_{||}$ bandwidth, the core-hole-induced relaxation is in the complex intermediate situation, described by Cox,[14] typical of transition-metal oxides. In this intermediate situation there is a strong final-state interconfigurations interaction[26,14] and strong satellites appear in core-level spectra.

C. XPS spectra of VO_2 and V_2O_3

The broadening and splitting of the V $2p$ core line in the XPS spectrum of VO_2 going from the semiconductor-to-metal phase increasing the sample temperature has been observed by Sawatzy and Post.[17] These authors have also observed the broadening and splitting in three components of the V $3p$ line of V_2O_3 at its metal-insulator-transition temperature. The presence of XPS core-line splitting confirms the present interpretation of the multiplet splitting of the XAS core transition near the K threshold as due to final-state effects for the core-hole-induced relaxation.

V. DIFFERENT REGIMES FOR CORE-HOLE-INDUCED RELAXATION

The electronic structure of VO_2 and V_2O_3 cannot be treated in either the one-electron band limit or in the strongly correlated limit. In fact, the calculated valence-electron—valence-electron interaction $U_{dd} \sim 1.1$ eV is comparable with the $d_{||}$ one-electron bandwidth $W \sim 1$ eV. In this case we are not in the one-electron band-structure approximation $U \ll W$ nor in the case of a strongly correlated Hubbard model $U \gg W$.

The electron-electron correlation effect is very important for electron in the $d_{||}$ (Ref. 18) and it seems to be the driving mechanism for the metal-insulator transition in VO_2.[19] The other characteristic aspect of the electronic structure of VO_2 is that the Fermi level is crossing the two lowest conduction bands and the single electron per vanadium atom is distributed over the localized narrow $d_{||}$ band and the wider π band.

Because final-state effects are expected in the presence of a narrow localized conduction band[3–6] it is interesting to compare the case of VO_2 with that of different systems which can be described by an itinerant picture of the conduction band or by a localized picture. An extreme example of narrow-band metals is given by rare-earth compounds where the $4f$ band should be described by the localized picture due to the strong Hubbard correlation $U_{ff} \gg W_f$. In these systems final-state effects appear to be very important mainly in the case of Ce compounds where the $4f$ band is hybridized with the $5d$ band and can be as large as 1 eV. In the case of $CePd_3$, multiplet splitting of final-state configurations, described as $4f^0$, $4f^1$, and $4f^2$ states, appears in XAS spectroscopy.[2] The observed multiplet splitting at the L_3 edge is due to the core-hole-induced relaxation in a mixed-valence system where the Hubbard parameter for the $4f$ band is $U_{ff} \approx 6$ eV and $W_f \approx 1$ eV, and the core-hole $4f$-electron attraction is $Q_{hf} \approx 9.5$ eV. In fact, $CePd_3$ is believed to fluctuate in the ground state between the $4f^0 5d^1$ and the $4f^1 5d^0$ configurations. In this case the $4f^2$ final-state configuration can be called a "shake-down" satellite appearing at the low photon-energy side of the absorption threshold.

At the other side are wide conduction-band metals which can be well described by the itinerant electron model. In this delocalized limit $U \ll W$ and $Q \ll W$ weak final-state effects appear at the core threshold of XAS spectra, the Mahan-Noziéres infrared singularity in metals at the $L_{2,3}$

edges,[27] and a small shift between the binding energy of a single asymmetric-symmetric XPS line and the XAS threshold can appear.[10]

In the case of a single narrow band with no valence-electron correlation $U \ll W$ and $Q \gg W$ three peaks appear with comparable intensity, the physical significance being that ionization can occur from the three valence-electron configurations (two, one, or zero electrons) possible for each atom.[14,17,28] Sawatzky has assigned the multiplet splitting of the XPS line of VO_2 to this core-hole-relaxation regime, where the XPS spectrum of a noncorrelated narrow-band metal appears similar to that of a mixed-valent system. However, the situation of VO_2 is more complex because of the presence of the degenerate delocalized π^* band and the fact that the correlation parameter U_{dd} cannot be disregarded.

In the case of VO_2, $U \simeq Q \simeq W$, this experiment shows that final-state effects are important and can give an apparent mixed-valence state for VO_2 in agreement with XPS data and the model calculations of Cox.[14] The satellites are quite strong and the final-state interconfigurations interaction is large. Therefore, the mixing of valence-band degenerate configurations in the ground state, i.e., covalency, is expected to be different in the excited final states.[26] In this complex situation final-state intensities are not simply related with occupation probabilities of ground-state configurations.

VI. BROADENING OF V *K* EDGE OF V_2O_3 AT THE METAL-INSULATOR TRANSITION

The broadening of the vanadium *K* edge in the XAS spectrum of V_2O_3 has also been observed at the metal-insulator transition.[29] Figure 8 shows the V *K* edge below and above the transition temperature. A clear broadening of the absorption peaks in the "edge" region appears in the metal. In V_2O_3 there are two electrons per V atom in the conduction band, and the density of states of the t_{2g} band shows many features, therefore, the interpretation and analysis is more complex than in VO_2. However, also in this system, similar to VO_2, the excited state in the metal shows a broadening effect in comparison with the semiconductor, indicating many final-state configurations in the metal phase.

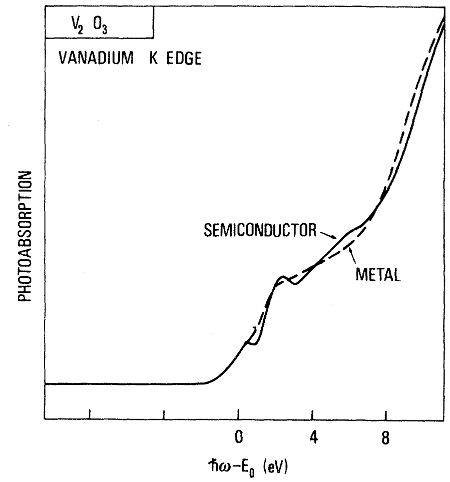

FIG. 8. Effect of metal-insulator phase transition on x-ray absorption *K*-edge spectrum of V_2O_3 (Ref. 31).

VII. CONCLUSION

From the comparison of the x-ray-absorption edge spectra of VO_2 in the metal and in the semiconductor phase the presence of multiple final-state configurations in the metal phase have been identified. This result shows that in the presence of the localized state of a bandwidth $W \sim U \sim 1$ eV final-state effects are important in XAS spectroscopy. This experiment should stimulate theoretical research on the core-hole-relaxation effects on the x-ray-absorption transitions at the core threshold of systems where electron correlation cannot be disregarded.

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