RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 17 15 JUNE 1990-I

Polaronic satellites in x-ray-absorption spectra

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(Received 2 April 1990)

Satellite structure in the $2p$ absorption spectra of early $3d$ transition-metal compounds is reported. The spectral shape depends strongly on the local symmetry of the excited atom and gives evidence that in Ti oxides the excitation on the metal is screened by an exciton transition in the oxygen band and not by a charge-transfer or Mott-Hubbard transition as in the case of narrow-band metal compounds. The relative satellite intensities can be used to assess the anisotropy of the local electronic structure and the influence of the excited electron on the screening of the core-hole potential.

Since the advent of synchrotron-radiation facilities, x-ray-absorption spectroscopy (XAS) has gained much interest as a site and symmetry selective probe to study the unoccupied density of states above the Fermi level. The dipole selection rules and the local character of the optical-transition-matrix elements involving a core state assure that only the local unoccupied states are probed. The core electron is excited into an efficient screening orbital so that the perturbation of the core-hole potential on the remaining ground-state electrons is small. Therefore, satellites due to multielectronic transitions in x-ray-absorption spectra of solids are not a common feature.[1] They have only been observed in interatomic intermediate valence systems, such as rare-earth compounds,[2] and charge-transfer semiconductors, such as Ni dihalides and NiO,[3] in combination with intense satellites in x-ray-photoelectron spectroscopy (XPS). The analysis of these absorption and photoemission spectra in a cluster or impurity model yields the values of the parameters for the local electronic structure, viz. the core-hole-$4f$ (or $3d$) Coulomb interaction, the f-f (or d-d) Coulomb interactions, and the charge-transfer energy.[2-6] The satellite separation, which is the energy difference between the excited and the relaxed final-state configuration, is mainly determined by the Coulomb interactions. The XPS satellite intensity reaches a maximum in the atomic limit and is reduced if the Coulomb interactions are decreased and/or the mixing (hybridization) between the metal and ligand valence states is increased. At the threshold of x-ray absorption, where the core-hole potential is screened by the additional d (f) electron, the satellite intensity is reduced to a few percent of the XPS value.[2,3]

In this paper we report the presence of satellite structure in the x-ray-absorption spectra of insulating compounds which have much smaller Coulomb interactions than the narrow-band Ni and Ce compounds. We observed a low-intensity satellite structure with a separation varying between 7 and 14 eV in the $2p$ absorption spectra of Ca, Ti, and V oxides and halides. For example, the Ca $2p$ satellites in CaO have an energy separation of 8 eV and a relative intensity of 0.005, whereas the Ti $2p$ satellites in TiO_2 have a separation of 13 eV and an intensity of $\sim$0.05.

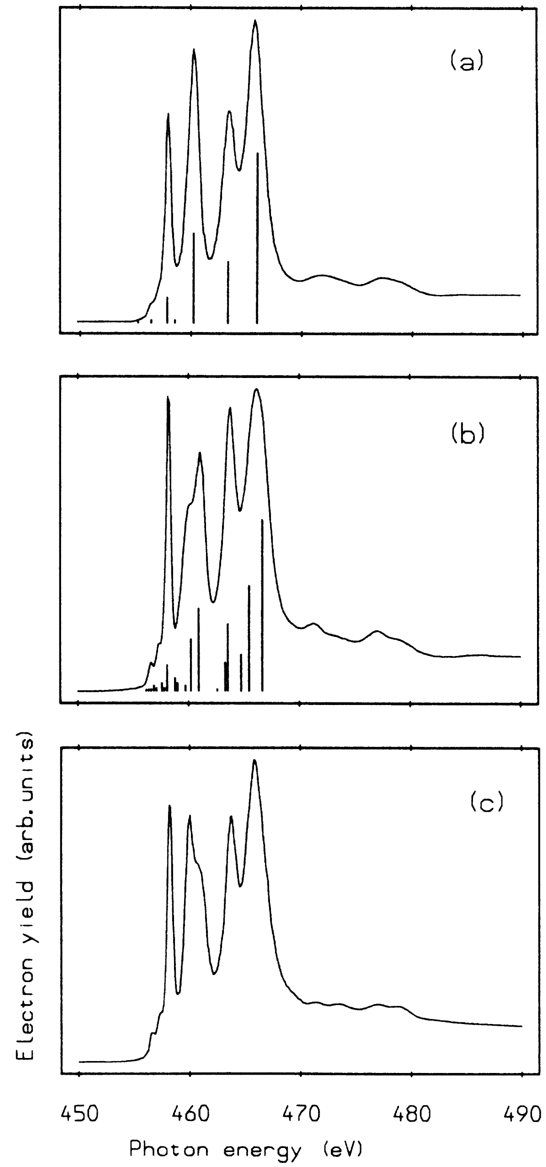

FIG. 1. The Ti $2p$ absorption spectra of (a) $SrTiO_3$, (b) TiO_2 rutile, and (c) TiO_2 anatase. The sticks give the calculated line strength of the dipole transition probability $3d^0 \rightarrow 2p^5 3d^1$ in (a) O_h and (b) D_{2h} symmetry.

Figure 1 gives the spectra of $SrTiO_3$ and TiO_2 in the anatase and rutile structure, which were measured with total electron yield in a vacuum of 10^{-10} torr. An energy resolution of ~300 meV was obtained using the spherical grating monochromator of beamline 1.1 at the Synchrotron Radiation Source in Daresbury.[7] The energy resolution and statistics are better than in earlier published electron-energy-loss[8,9] and absorption spectra.[10]

The main structure in Fig. 1 can be explained by the calculation of the dipole transition probability from a ground-state Ti $3d^0$ to a final-state $2p^5 3d^1$.[11] The core-hole spin-orbit interaction splits the spectrum into a $2p_{3/2}$ and a $2p_{1/2}$ level with a separation of 5.5 eV, which are further split by crystal-field interaction. In the octahedral site symmetry of $SrTiO_3$ the $2p_{1/2}$ manifold has two levels and the $2p_{3/2}$ manifold has five levels, of which only two have a large intensity. The four major peaks in Fig. 1 can be labeled according to their main character as $2p_{3/2}3d_\pi$, $2p_{3/2}3d_\sigma$, $2p_{1/2}3d_\pi$, and $2p_{1/2}3d_\sigma$, although none of the states is pure. The $3d_\sigma$ states (e_g levels) have orbitals which are directed towards the oxygens and, therefore, have a higher energy than the $3d_\pi$ states (t_{2g} levels). The distortion of the Ti site from octahedral to D_{2h} and D_{2d} symmetry in rutile and anatase, respectively, results in an asymmetric broadening of the $3d_\sigma$ peaks. At ~13 eV above the main structure, a low-intensity structure is found, which is redrawn in Fig. 2 with a spline subtracted from the spectrum. This structure is also split into four peaks by the $2p$ spin-orbit and the crystal-field interaction. Although, the splitting is very similar to the main multiplet structure, the peak intensities are different. In a molecular-orbital diagram the assignment of this structure would be an antibonding orbital of Ti $4sp$ and O $2p$ character.[10,12] The comparison with band-structure calculations[8,13,14] is hampered due to technical difficulties for more extended basis sets which include the Ti $4sp$ states.[15] The molecular orbitals which contain O $2p$ states can also be observed in the O $1s$ absorption spectrum, which is given in Fig. 3. The two peaks with a splitting of 2.5 eV at the O $1s$ edge of rutile and anatase can be attributed to the unoccupied O $2p_\pi$ and $2p_\sigma$ states which are covalent mixed with the Ti $3d_\pi$ and $3d_\sigma$ states, respectively. The structure between 7 and 18 eV above the edge is due to the O $2p$ states which are covalent mixed with Ti $4sp$ states.[16] It is clear that the low-intensity structure in the Ti $2p$ spectra shows hardly any relation with the structure in this O $1s$ spectrum, as would be the case for transitions to final states of mixed character. A further indication that we are not dealing with a one-electron transition is that the Ti $2p$ satellite separation in XAS is close to the satellite separation in XPS.[12,17] Therefore, the satellite must be due to an excited state, which is independent of the photon energy.

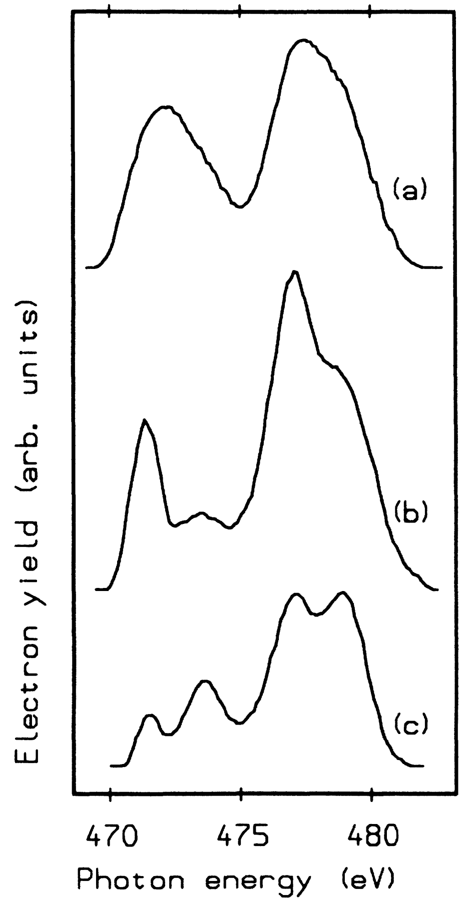

FIG. 2. The satellite structure in the Ti $2p$ absorption spectra of (a) $SrTiO_3$, (b) rutile, and (c) anatase.

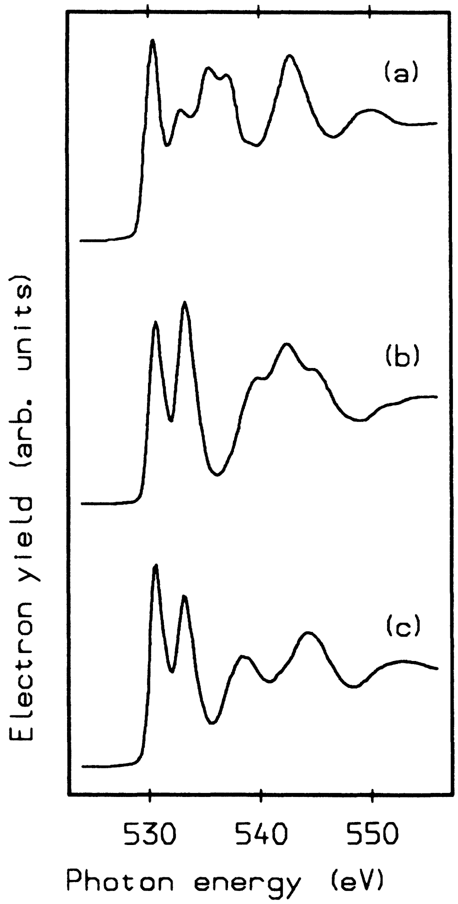

FIG. 3. The O $1s$ absorption spectra of (a) $SrTiO_3$, (b) rutile, and (c) anatase.

The satellite separation is too large for a charge-transfer or Mott-Hubbard type of transition, since the Coulomb interactions involved are only in the order of 1 eV (Ref. 18) and the optical charge-transfer gap is 3 eV.[10] However, the satellite separation is close to the optical transition of the oxygen $p \rightarrow s$ exciton at 14.1 eV.[19] de Boer, Haas, and Sawatzky[20] have proposed a model based on exciton transitions to explain the satellites in XPS. In the initial state of an insulating $3d$ transition-metal oxide the O $2p$ bonding orbitals are occupied and the $3s$ orbitals are empty. After photoemission the core-hole potential on the metal polarizes the oxygen ions. In the relaxed final state the oxygens are polarized toward the metal with $3s$ character mixed into the $2p$ wave function. The excited final state has an oxygen $3s$ electron and $2p$ hole. This exciton in the core-hole potential of the metal can be called an electronic polaron.[21] In x-ray absorption the core electron is not ejected, but excited to an unoccupied $3d$ state. The screening of the core-hole potential by the additional $3d$ electron reduces the polarization of the oxygen valence electrons. The amount of screening depends on the symmetry of the final state. If the electron distribution is directed towards the anions, then the core-hole potential is better screened and the polaronic satellite will be smaller. Table I shows that the final-state symmetries which have a large overlap with the oxygen atoms give low satellite intensities, e.g., the $3d_\sigma$ states give lower satellite intensities than the $3d_\pi$ states. In rutile and anatase the branching ratio $2p_{3/2}$:$2p_{1/2}$ for the excited state is lower than for the relaxed state. For reasons given in Ref. 22, a lower branching ratio indicates a larger $2p$-$3d$ electrostatic interaction, which is in agreement with an unscreened core hole in the excited state. In $SrTiO_3$ this effect is reduced because of a larger exciton bandwidth. The satellite intensity for the $3d_\pi$ in anatase is reduced, because the overlap between the Ti $3d_\pi$ and O $2p_\pi$ states is larger, which is clear from the larger O $2p_\pi$ peak in Fig. 2. Thus, the satellite intensities can be understood from a polaronic model.[23]

TABLE I. Satellite to main peak intensity ratios in the Ti $2p$ absorption spectra.

Main peak character	$2p_{3/2}3d_\pi$	$2p_{3/2}3d_\sigma$	$2p_{1/2}3d_\pi$	$2p_{1/2}3d_\sigma$
$SrTiO_3$	0.10	0.04	0.10	0.04
Rutile	0.07	0.03	0.12	0.05
Anatase	0.02	0.02	0.06	0.04

In summary, evidence for a polaronic transition as the origin for the Ti $2p$ satellites is obtained from the coincidence in energy of the XAS and XPS satellite separation, and also from the dependence of the XAS satellite intensities on the final-state symmetry. The Coulomb potential on the metal atom is screened by the polarization of the anions rather than by a transition which involves the transfer of an electron between the metal and the anions. It is expected that polaronic satellites are quite common in insulating transition-metal compounds, but have remained unnoticed because of the very low intensity. Brighter synchrotron radiation sources equipped with high-resolution monochromators will be an advantage to resolve these low-intensity satellites. The sensitivity of the satellite intensity for the site symmetry of the excited atom may be used to determine the anisotropy of the local electronic structure in the early transition-metal compounds.

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[1] See, e.g., G. Wendin, *Breakdown of the One-Electron Pictures in Photoelectron Spectra,* Structure and Bonding Vol. 45 (Springer-Verlag, New York, 1981), p. 1; A. Meisel, G. Leonhardt, and R. Szargan, *X-Ray Spectra and Chemical Binding,* Springer Series in Chemical Physics Vol. 37 (Springer-Verlag, New York, 1989), p. 1.

[2] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **28**, 4315 (1983).

[3] G. van der Laan, J. Zaanen, G. A. Sawatzky, R. Karnatak, and J. M. Esteva, Phys. Rev. B **33**, 4253 (1986).

[4] J. Zaanen, C. Westra, and G. A. Sawatzky, Phys. Rev. B **33**, 8060 (1986).

[5] G. van der Laan, C. Westra, C. Haas, and G. A. Sawatzky, Phys. Rev. B **23**, 4369 (1981).

[6] L. C. Davis, J. Appl. Phys. **59**, 25 (1986).

[7] H. A. Padmore, Rev. Sci. Instrum. **60**, 1608 (1989).

[8] L. A. Grunes, R. D. Leapman, C. N. Wilker, R. Hoffmann, and A. B. Kunz, Phys. Rev. B **25**, 7157 (1982); L. A. Grunes, *ibid.* **27**, 2111 (1983).

[9] R. Brydson, H. Sauer, W. Engel, J. M. Thomas, E. Zeitler, N. Kosugi, and H. Kuroda, J. Conden. Matter **1**, 797 (1989).

[10] D. W. Fisher, Phys. Rev. B **5**, 4219 (1972).

[11] B. T. Thole (unpublished).

[12] S. K. Sen, J. Riga, and J. Verbist, Chem. Phys. Lett. **39**, 560 (1976).

[13] R. V. Kasowski and R. H. Tait, Phys. Rev. B **20**, 5168 (1979).

[14] S. Munnix and M. Schmeits, Phys. Rev. B **30**, 2202 (1984).

[15] Recently, an augmented-localized-spherical-wave calculation with an extended basis set which includes also metal $4s$ and $4p$ and oxygen $3s$ and $3p$ states, has been used to calculate the O $1s$ absorption edge of CuO. See M. Grioni, M. T. Czyzyk, F. M. F. de Groot, J. C. Fuggle, and B. E. Watts, Phys. Rev. B **39**, 4886 (1989).

[16] F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, and H. Petersen, Phys. Rev. B **40**, 5715 (1989).

[17] K. S. Kim and N. Winograd, Chem. Phys. Lett. **31**, 312 (1974).

[18] T. Bandyopadhyay and D. D. Sarma, Phys. Rev. B **39**, 3517 (1989).

[19] M. Cardona and G. Harbeke, Phys. Rev. A **137**, 1467 (1965); D. W. Fischer, Phys. Rev. B **5**, 4219 (1972).

[20] D. K. G. de Boer, C. Haas, and G. A. Sawatzky, Phys. Rev. B **29**, 4401 (1984).

[21] de Boer *et al.* (Ref. 20) used the name exciton satellite which might be somewhat confusing. In XAS the title "core exciton" is in use for structure which arises from a core-hole valence-electron configuration below the interband threshold in insulators and semiconductors.

[22] B. T. Thole and G. van der Laan, Phys. Rev. B **38**, 3158 (1988).

[23] G. van der Laan, C. S. Mythen, and H. A. Padmore, Europhys. Lett. **11**, 67 (1990).