Resonant Auger spectroscopy at the O *K* edge of NiO

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We have measured the photon-energy dependence of the O $1s2s2s$ and O $1s2s2p$ resonant Auger lines at the O *K* edge of NiO. The transition from the Raman-like regime, where these features are observed at constant binding energy, to the Auger regime, where they appear at constant kinetic energy, is found for a photon energy ~0.8 eV lower than the absorption maximum at threshold, usually assigned to O $2p$ states hybridized with the Ni $3d$ orbitals. We interpret this behavior as a consequence of the fact that the intermediate states of the resonant Auger process also have Ni $4sp$ character. At the photon energy where the Raman- to Auger-like regime transition takes place, the constant kinetic energy of the Auger features is ~1.8 eV higher with respect to off-resonance excitation. Analysis of the photon-energy dependence of the kinetic energy of the Auger peaks across the transition from the Raman-like to the Auger-like regime allows us to determine the onset of the Ni $4sp$ continuum in the O *K* edge absorption spectrum. [S0163-1829(99)03031-3]

INTRODUCTION

With the availability of tunable photon-energy sources offered by synchrotron radiation facilities, resonant spectroscopy has become a powerful technique to study the electronic properties of condensed matter. For this reason, the understanding of the core-hole recombination processes (Auger, x-ray emission) for resonance spectroscopy has become a very crucial topic.

The two-step model of the Auger or x-ray emission process often fails if the energy of the excitation is close to an absorption threshold. The creation of a core hole and its radiative or nonradiative decay can no longer be considered as distinct independent processes, but they have to be viewed in a one-step model, described by a Kramers-Heisenberg-type matrix element.[1] This case is characterized by the fact that the absorbing atom can be left in the same final state (FS) while the excess energy of the incoming photon is transferred completely to the outgoing electron (Auger) or photon (x-ray emission). Thus, the energy position of the features in the Auger (x-ray emission) spectrum follows the incoming photon energy. This behavior is often addressed as the resonant radiationless (emission of an Auger electron) or radiative (emission of a photon) Raman regime. This is the typical situation obtained when the photon energy is set before threshold or across a resonance in the absorption spectrum due to a well-localized intermediate state. If the energy of the final state of the absorbing atom can vary over a continuum of values, for instance when the photoelectron is excited into a band, then the normal Auger (fluorescence) case might be retrieved. In this case, the electrons (photons), produced by the recombination of the core hole, are detected at constant kinetic (photon) energy. The transition between Raman- and Auger-like behaviors can also be induced by the possibility of the electron excited in the intermediate state (IS) relaxing and losing energy faster than the lifetime of the initial core hole.

Resonant Auger (RAES) and resonant x-ray emission (RXES) spectroscopy have become important techniques to study the electronic properties of condensed matter. In solid-state physics they have been widely employed in the investigation of core-excited states and of decay processes. A recent example is the observation of resonant Auger dichroism, induced by the one-step recombination of a spin-polarized core hole excited with circularly polarized light.[2] Concerning RXES, a recent finding is, for instance, that the crystal momentum can be conserved.[3] This suggests the use of RXES as new band-structure probe. For these reasons, a better understanding of the relaxation processes of the intermediate state in RAES and RXES is particularly important, since relaxation might invalidate the applicability of the one-step model and destroy the conservation of momentum. As an example, the relaxation of the intermediate state in insulators has been recently investigated in $L_{2,3}$-edge resonant x-ray scattering studies in MnO (Ref. 4) and NiO,[5] that found evidence of d-d transitions and electron-hole pair excitation.

Recently, we have performed an experiment on NiO where we studied the Ni $2p3s3p$ and Ni $2p3p3p$ Auger lines at the Ni L_3 resonance.[6] We investigated the transition from Raman to Auger behavior of these lines induced by transitions to delocalized intermediate states or by the participation of inelastic processes in the recombination of the core hole. There is some indication that these processes involve energies much smaller than the NiO band gap, suggesting that the intermediate state can relax by other means than d-d transitions. In the present paper, we describe the behavior of the O $1s2s2s$ and O $1s2s2p$ resonant Auger lines when the excitation energy is varied around the O *K* absorption edge.

In NiO, resonant Auger spectroscopy at the O *K* and at the Ni $L_{2,3}$ edges are quite different cases.[7] The intermediate state of the RAES process reached after absorption of a photon at the Ni $L_{2,3}$ edge has mostly Ni $3d$ character and is usually considered as well localized. In fact, the onset of the transitions to the continuum of the valence band formed by sp state is found ~11 eV above the maximum of the L_3 white line. On the other hand, at the O *K* edge, an O $1s$ hole is created and the core electron is promoted into one of the empty O $2p$ states. These are strongly hybridized and form a wide band. This picture has recently been confirmed by reso-

nant valence-band photoemission.[8,9] In this context, it should be recalled that in a system such as Ni metal, where the intermediate state is characterized by the presence of an electron in a delocalized band, the transition between Raman and Auger-like regimes is observed as soon as the excitation reaches the threshold.[10] This is a consequence, as anticipated above, of the delocalization into the solid of the excited electron, which no longer participates to the recombination of the core hole. Similar effects have also been observed for the Pd, Rh,[11] and Ag (Ref. 12) $L_3M_{4,5}M_{4,5}$ Auger lines.

EXPERIMENT

A NiO single crystal was cleaved *in situ* to obtain a clean (100) surface. The base pressure of the apparatus was better than 5×10^{-10} mbar. C $1s$ core-level photoemission was used to check for possible carbon contamination. Between successive cleaves, the amount of carbon on the surface of the sample remained below the detection limit.

The resonant Auger data were collected at the dragon beam line ID12B at the European Synchrotron Radiation Facility,[13] using the circularly polarized light emitted by the helical undulator Helios I.[14] The photon energy resolution was ~0.2 eV. The energy distribution of the photoelectrons was measured at normal emission using a commercial hemispherical analyzer (PHI Model 3057, mean diameter 279.4 mm) with multichannel detection. The bandwidth of the analyzer was set to ~0.3 eV, while its acceptance angle was ±20°. The light incidence angle on the sample was 60° with respect to the surface normal, while the (010) crystallographic axis of the sample was parallel to the plane containing the photon wave vector and the sample normal. All data were collected at room temperature.

Particular care has been dedicated to the absolute photon-energy calibration. This was obtained by measuring the difference between the kinetic-energy positions of the Ni $2p$ peaks due to the first and second order of the monochromator. Then the position of the Ni $3p$ core levels and of the O $1s$ line in second order have been monitored to correct possible shifts of the photon energy and kinetic-energy axis due to monochromator drifts and/or sample charging. The analyzer work function ϕ has been determined by measuring the Fermi level of sputtered Cu(100) using the first and second order of the monochromator.

RESULTS AND DISCUSSION

In Fig. 1(a) we present the absorption spectrum of NiO at the O K edge. The peak at $h\nu = 531.5$ eV corresponds to absorption due to empty O $2p$ states hybridized with Ni $3d$ orbitals. The structures at higher photon energies ($h\nu > 534$ eV) are attributed to $2p$ weight in states of predominantly Ni $4sp$ character.[15] The general line shape can also be reproduced by multiple scattering calculations as discussed previously.[9,16] The spectrum is also very similar to the electron-energy loss spectra and comparable to the high energy inverse photoemission spectra.[17] In early $3d$ transition-metal oxides, the absorption spectrum shows a doublet near the O K threshold. This is due to the octahedral crystal field and to the exchange interaction, which split the $3d$ orbitals
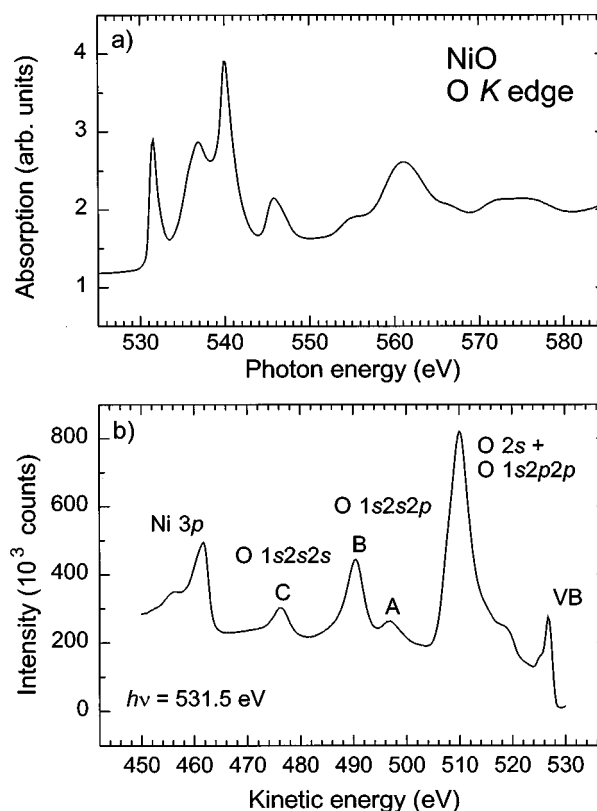

FIG. 1. (a) O K edge absorption spectrum of NiO. (b) Photoemission spectrum of NiO obtained at $h\nu = 531.5$ eV.

into spin-up and spin-down states of t_{2g} or e_g symmetry. In the case of NiO, only the minority spin e_g states are partially empty and one single peak is observed, corresponding to transition between an O $1s$ core level and an O $2p$ state hybridized with an e_g orbital.[15]

Figure 1(b) shows the photoemission spectrum of NiO obtained at $h\nu = 531.5$ eV. This is the photon energy that corresponds to the position of the maximum absorption at threshold. Three RAES peaks are visible, labeled in Fig. 1(b) as A, B, and C. Peak C corresponds to the O $1s2s2s$ Auger transition while peaks A and B belong to the O $1s2s2p$ manifold. At the O K edge, the O $1s2p2p$ Auger process resonates with the photoemission from the O $1s$ core level. In the present paper, we will focus our attention only on the O $1s2s2p$ and O $1s2s2s$ Auger lines, since these transitions do not involve interference effects with photoemission peaks such as the ones giving rise to Fano profiles.

In Fig. 2 the kinetic-energy (KE) position of peaks A, B, and C is plotted as a function of the incoming photon energy. Well below the O K edge, peaks B and C appear at constant binding energy (peak A is too weak in this photon-energy range for its position to be determined accurately). As explained above, this behavior is typical of the nonradiative Raman regime, where the absorption of a photon and the emission of an Auger electron have to be viewed as a onestep process. The constant binding energy (BE) regime seems to be dominant for photon energies up to $h\nu = 530.7(\pm 0.2)$ eV. Around this value, the kinetic energy of the RAES lines reaches a maximum that is ~1.8 eV higher than the KE value characteristic of the off-resonance Auger.
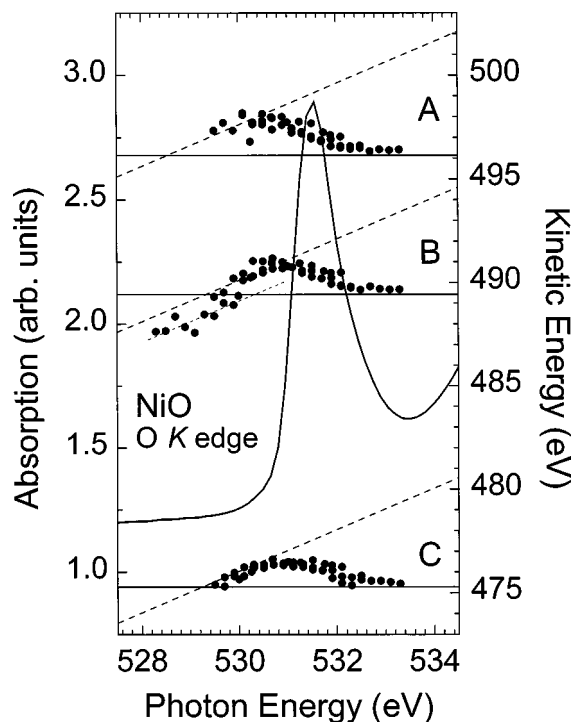
FIG. 2. Kinetic-energy position of peaks A, B, and C of Fig. 1(b) as a function of the photon energy. The dashed lines represent points at constant binding energy, while the horizontal solid lines correspond to the values of the kinetic-energy positions of the peaks at $h\nu = 545.8$ eV.

At higher photon energies, the position of the RAES peaks gradually moves towards lower KE values and eventually reaches (at $h\nu \sim 533$ eV) the kinetic energy of the off-resonant Auger spectra. We would like to stress that the deviation from the Raman-like behavior takes place 0.8 ± 0.2 eV before the O K edge, where the absorption cross section is at least five times lower than at threshold. From such a consideration, we exclude the presence of experimental artifacts due to the finite resolution of the monochromator such as the ones described in Refs. 6 and 18. These artifacts consist in the apparent constant kinetic energy of the RAES peaks position that is observed when $h\nu$ is scanned across one of the IS resonances (observed, say, at $h\bar{\nu}$). Since the photon-energy resolution $\Delta h\nu$ is finite, the photon energy $h\bar{\nu}$ will always be available to excite the same resonant intermediate state as long as $h\nu$ varies in an interval of the order of $\Delta h\nu$ around the resonance. If the RAES peak position is plotted as a function of the mean excitation energy, a constant kinetic energy is observed (i.e., Auger behavior). Excitation energies for which $h\bar{\nu}$ lies (significantly) below or above the resolution window will show the expected peak at constant binding energy (i.e., Raman behavior) if the IS is not delocalized or relaxed. Since in our case the deviation from the Raman regime takes place at a photon energy below the absorption threshold much lower than the monochromator bandpass (0.2 eV), we can exclude the intervention of such artifacts. Note that the energy resolution of the electron analyzer has no influence on the observed KE position of the RAES peaks.

The Raman and the off-resonance Auger lines cross at an energy much lower than the absorption maximum. As a consequence of energy conservation, this means that the intermediate states that give constant kinetic-energy Auger peaks when the photon energy is well above threshold are not the same ones that contribute to the absorption peak at $h\nu = 531.5$ eV. A similar behavior has been observed for Cu L_3 RAES in Cu_2O,[19] where the intermediate state is represented by the combination of a $2p_{3/2}$ hole with a $4sp$ electron in strong interaction with the O $2sp$ valence band. In this case, the crossing between the Raman and the off-resonance Auger lines occurs at about 1.5 eV below the L_3 maximum. On the contrary, in CuO, where the L_3 edge corresponds to a single line resonance well separated from the excitations to continuum states since in the IS the Cu $3d$ shell is completely filled and the $4sp$ band is empty, this crossing is observed much closer to threshold, at about 0.6 eV below the L_3 maximum.[19]

We have already noticed that the presence of overlapping distinct intermediate and final states can lead to a very complex photon energy dependence of the KE position of the RAES peaks.[6] If the energy separation between the corresponding FS's is smaller than the lifetime broadening, they will appear as a single RAES peak. However, tuning the excitation from one (relaxed or unrelaxed) IS to a different one would transfer spectral weight across the peak, which would not follow a simple constant binding (Raman) or kinetic (Auger) energy behavior.[6] Moreover, under the conditions described above, interference effects in the intermediate or in the final state are also likely to become important, increasing the complexity of the RAES process. The observation that the behavior of the KE position of the RAES peaks drastically changes below threshold means that, even if their contribution to the XAS spectrum is very small, there are intermediate states more bound than the ones giving the absorption maximum at $h\nu = 531.5$ eV.

Assuming the absence of interference between different intermediate states involved in the recombination of the core hole, the resulting RAES spectra should correspond to the superposition of their respective independent contributions.[1] This suggest a possible interpretation of the KE dependence of the RAES peaks shown in Fig. 2. These peaks might in fact result from transitions to the states responsible for the absorption peak at $h\nu = 531.5$ eV and giving rise to a Raman behavior (constant BE), superposed on to the constant KE peaks, which are due to excitations into more bound delocalized or relaxed intermediate states. The superposition of these two components would in fact result in a dependence of the peak position similar to the one shown in Fig. 2, with a maximum KE for $h\nu \sim 531.5$ eV. The RAES peaks should also be broadened since they would be the superposition of two different contributions with a different photon-energy dependence. However, within the error bars of our experiment, such a broadening is not observed. An alternative explanation of the RAES peaks position might be that the interference between intermediate states is not negligible. In this case, the separation into a Raman and an Auger component would not be possible in the photon-energy region corresponding to the absorption prepeak. This would also explain the lowering of the KE maximum below the photon energy corresponding to the resonance maximum. Note that the asymmetry of the absorption prepeak is an indication of

the presence of interference between spatially localized and extended IS's (see below).

If the final states derived from the distinct IS's are at the same energy, when $h\nu$ is set well below the excitation threshold of all the possible IS, the RAES peaks will be observed at constant BE, representative of the binding energy of the final state. Under this assumption, an estimation of the upper limit of the BE of the most bound IS can be obtained. It will be given by the intersection of the Raman line interpolating the constant BE points below $h\nu=531$ eV and the Auger line corresponding to the KE of the RAES peaks above threshold (see Fig. 2). Comparing the behavior of peaks B and C, we find that the most bound IS's cannot lie more than ~2.3 eV below the absorption peak in Fig. 2 (before threshold, peak A is very weak and its BE is not well defined).

Concerning the nature of the IS's excited below $h\nu=531.5$ eV, a possible interpretation could be that they are gap states. If this was the case, the transition towards a constant kinetic-energy regime of the RAES peaks would be induced by the relaxation of these gap states before the recombination of the core hole. Actually, we have already observed in the case of Ni L_3 RAES that relaxation might take place for intermediate states if the photon energy is tuned just a few hundred meV above the value necessary to excite them, even if they are well localized.[6] In Li$_x$Ni$_{1-x}$O, the Li$^+$ impurities induce extra holes of O $2p$ character, increasing the number of gap states participating to the O K edge absorption and allowing for a determination of their energy distribution (in the presence of a core hole).[20,21] The O K XAS spectra of Li-doped NiO show an extra peak centered at ~3 eV below the absorption prepeak in undoped NiO. This energy difference appears to be too large compared to the value of ~2.3 eV reported above.

A second possibility could be that the IS's excited well below $h\nu=531.5$ eV contain some Ni $4sp$ character. In other words, the continuum states containing Ni $4sp$ and O $2p$ weight responsible for the large absorption coefficient for $h\nu>534$ eV might have a tail extending below the peak at threshold. This is a very well-known case in atomic physics, where it has been demonstrated that transitions to the continuum can dominate the absorption spectra for photon energies well below threshold.[22] Even in systems with strong discrete resonances below threshold the effects due to Auger or fluorescence emission from the continuum might be important. An example is represented by the resonant $L\alpha_{1,2}$ fluorescence following photoexcitation of Xe over a range containing the L_3 edge.[23] Well below the ionization threshold, states belonging to the Rydberg series are excited and give intense Raman peaks that are strongly asymmetric because of the contribution of threshold fluorescence.[23]

In our case, the asymmetry of the XAS peak in Fig. 2 confirms its interaction with the continuum, which will be formed mostly from the Ni $4sp$ band. Since IS's of Ni $4sp$ character are also responsible for the constant KE RAES above threshold, on the basis of what was discussed above and assuming no interference effects we can state that the tail of the valence band in the O K edge extends down to ~529.2 eV. This conclusion is also supported by our determination of the O $1s$ binding energy (528.6 eV) in NiO.

Neglecting any screening effect, to excite an O $1s$ electron into the conduction band at the O K edge the photon needs an energy equal to the O $1s$ binding energy plus the energy difference between the Fermi level and the conduction-band minimum. Assuming a band gap of about 4 eV, and a valence-band maximum ~0.3 eV lower than the Fermi level,[24] it turns out that the transitions to the O $2p$/Ni $4sp$ valence band are excited for photon energies greater than or equal to $h\nu=532.3$ eV. This is already quite close to the absorption prepeak of O $2p$/Ni $3d$ character, and screening might further reduce this value. Considering the fact that the tail of continuum states can extend to lower photon energies than the tail of sharp resonances,[22,23,25] this is consistent with the observation of the Raman to Auger transition starting ~0.8 eV before the prepeak. It should also be noted that the kinetic energy of the Auger lines have essentially converged at their high-energy limit by $h\nu=532.5$ eV.

We will now relax the condition that the FS's obtained as a consequence of excitation into distinct IS's are degenerate. Suppose that $h\nu$ is set well below the excitation threshold of all the accessible IS. Then the RAES peaks will be observed at a constant BE corresponding to the binding energy of the FS resulting from the transition into the tail of the Ni $4sp$ derived IS's, which extends to lower photon energies than the Ni $3d$ derived IS's. This FS contains two holes, namely O $2s^2$ (peak C in Fig. 1) or O $2s2p$ (peaks A and B), screened by an electron in the Ni $4sp$ band. As the photon energy is increased, the intermediate state is more and more dominated by the Ni $3d$/O $2p$ resonance at $h\nu=531.5$ eV, which has a high cross section. As a consequence, the BF of the RAES peaks will be representative of the BE of the final state with two holes ($2s^2$ or $2s2p$) screened by an O $2p$ electron hybridized with the Ni $3d$ orbitals. Now notice that the position of peak B in Fig. 2 does not seem to follow exactly a constant BE line. From $h\nu=528.5$ to $h\nu=529.5$ eV, it follows a constant BE line that is ~1 eV below the line followed from $h\nu=529.5$ to $h\nu=530.5$ eV. In this photon energy region the error bars are quite large because of the small intensity of the RAES features, which are also superposed on a high background. However, in principle in this way we can obtain an estimate of the value of the different screening of a O $2s$ core hole by an electron excited into O $2p$ states hybridized with Ni $4sp$ or Ni $3d$ orbitals, respectively.

CONCLUSIONS

To conclude, the O $1s2s2s$ and O $1s2s2p$ resonant Auger lines have been studied as the energy of the exciting photons was scanned across the at the O K edge. The position of the RAES peaks reveals a transition from a constant binding energy (Raman) behavior, to a constant kinetic-energy (Auger) regime. This transition is observed for a photon energy ~0.8 eV lower than the absorption maximum at threshold and is interpreted in terms of relaxation of the intermediate state of the resonant Auger process when an O $1s$ core electron is excited into gap states. At the Raman-Augertrade off, the kinetic energy of the RAES peaks

reaches a maximum that is ~ 1.8 eV higher than the off-resonance excitation case. This complex dependence of the kinetic energy of the RAES peaks is interpreted as due to overlapping distinct intermediate states with Ni $3d$ or Ni $4sp$ character. Valuable information about the energy position of the onset of the continuum of O $2p$ states hybridized with the Ni $4sp$ band can be extracted from this dependence.

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