L_2L_3V Coster-Kronig decay in nickel: The near-edge region

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(Received 17 September 1998)

The probability of the L_2L_3V Coster-Kronig (CK) decay process in Ni following the creation of a $2p_{1/2}$ core hole has been measured by photoemission spectroscopy using synchrotron radiation. The branching ratio between CK and L_2VV Auger decay has been determined as a function of the photon energy in the proximity of the L_2 edge (870–890 eV). It is found to become independent upon the photon energy range already a few eV above threshold. The direct low-energy (about 7 eV) CK emission spectrum has also been observed. [S0163-1829(99)03915-6]

INTRODUCTION

Electron correlation plays a fundamental role in the excitation and deexcitation processes related to the interaction between radiation and matter and, in turn, on the results of a spectroscopic analysis of these processes. This is the case, for instance, in solids with a narrow d band, of which transition metals (TM) are the most relevant example.[1,2] For these systems, the independent particle picture is no longer sufficient to describe the photoionization process and many body effects have to be included to explain the features of photoemission from core levels. Spectroscopy of the $2p$ level in $3d$ TM is a subset of this field that has been recently exploited in order to obtain information about the electronic and magnetic properties in the ground state.[3]

In this paper we will deal in particular with the relaxation of the $2p$ core hole in Ni via LVV Auger decay, a very specific aspect in itself, though contributing a piece of information for a more general understanding of charge redistribution in the final states of both primary photoemission and following deexcitation. The LVV Auger process is a nonradiative decay through which the $2p$ core hole state autoionizes towards a double vacancy valence state with one electron promoted in the continuum. The spin orbit splitting associated with the $2p^{-1}$ state is usually large enough to yield two separate multiplet spectra of Auger transitions, generally termed L_3VV and L_2VV for the $2p_{3/2}$ and $2p_{1/2}$ hole states, respectively. The $2p_{3/2}$ hole states, only contributes to the L_3VV part of the Auger spectrum here considered. On the contrary, for the $2p_{1/2}$ hole state, the cascade process

$$h\nu+2p^6 3d^8 4s^2 \rightarrow 2p_{1/2}{}^5 3d^{10}+e_{ph} \rightarrow 2p_{3/2}{}^5 3d^9+e_{ph}+e_{\mathrm{CK}} \rightarrow 2p^6 3d^7+e_{ph}+e_{\mathrm{CK}}+e_A \quad (1)$$

competes, whenever energy is allowed, with the direct L_2VV deexcitation and leaves the system in a triple vacancy state. The second step of the cascade is a Coster-Kronig (CK) transition whose probability is governed by the overlap amplitude of the $2p_{1/2}$ and $2p_{3/2}$ wave functions in the excited state. In Eq. (1), which has been written in an atomic notation, e_{ph} is the $2p_{1/2}$ photoelectron, e_{CK} is the L_2L_3V CK electron, and e_A is an $L_3'VVV$ Auger electron.

CK transitions are known to be the most relevant decay channel for the L_2 hole in TM.[4,5] This cascade channel has been the object of many experimental studies as well as of some debate dealing with the physical origin of the satellites in TM L_3VV spectra.[6–11] The analysis of the Auger process and the measure of the branching ratio β between L_2VV and $L_2L_3V \rightarrow L_3'VVV$ has been carried out mainly by high-energy photoemission experiments, either by standard photoemission[6–8,12,13] or by coincidence spectroscopy (APECS).[14–17] The latter in particular gave very detailed information on β by analyzing the correlated emission of the elastic $2p_{1/2}$ photoelectron and the L_3VV Auger spectra, with the underlying assumption that only the $L_3'VVV$ intensity can be correlated in time with the creation of the $2p_{1/2}$ core hole. In solid Ni, these experiments have measured $\beta=(0.78\pm 12)\%$ at the Al $K\alpha$ emission wavelength.[15] In this system the spectator hole is expected to be rapidly screened by the valence electrons, the screening process resulting in a very small energy shift of the $L_3'VVV$ transition (which can be thus named $L_3'VV$) with respect to the L_3VV transition.[13,17]

In spite of the sizable number of papers published on this specific topic, not much is known about the threshold regime, where electron correlation effects are expected to be quite important. In this regime the photoelectron is very active in screening the core hole, so the β value for the subsequent decay channels might be very different with respect to the high-energy regime. A couple of experiments performed on solid targets[18,19] have shown that at threshold the two-step mechanism is too crude of a model to describe the photoexcitation-Auger event. Indeed, a two-step mechanism is unable to account for the coherence between the photoabsorption and the decay processes that they have found when looking at the event with high resolution.

CK processes in the near edge region absorption spectra cause the L_2 part of the $2p$ absorption edge to be much broader than its spin orbit partner L_3.[5] In spite of evidence for CK relevance, neither β nor the direct CK emission spectrum have been measured until now in the near edge region.

The aim of our contribution to the experimental study of this CK process is twofold. On the one hand we measure β throughout the Ni L_2 near edge region as a function of the tunable energy of monochromatic photons from a synchrotron radiation source. On the other hand we directly measure the L_2L_3V CK spectrum in the solid state, an experiment which presents some difficulties because of the poor signal to background ratio since the CK kinetic energy is low and falls in the region of very intense background of secondary electrons.

EXPERIMENT

The experiment was performed on the SA-8 beam line of the storage ring Super ACO of LURE (Orsay), using a Beryl double crystal monochromator that delivers approximately a photon flux of about 5×10^7 photon/sec mm^2 at the sample position with an energy resolution of 0.4 eV over the energy range 800–900 eV. The sample was a nickel single crystal (110) surface prepared in ultrahigh vacuum following standard cleaning procedures.[20] Photoemission spectra have been measured by a wide angle acceptance spectrometer.[21] Absorption spectra have been measured in total electron yield mode (TEY), detecting with a channeltron the total current of negative particles ejected from the sample surface as a function of the photon energy. The incident photon flux I_0 was monitored by measuring both the current driven by a metal grid located before the monochromator (picoammeter reading) and the current of negative particles ejected from an Al thin foil located after the monochromator (channeltron count rate).

RESULTS AND DISCUSSION

Differential absorption spectra

With the aim of selecting the intermediate excited state preceding the Auger decay,[8,13,22,23] we have measured the full Ni LVV Auger spectrum for fixed photon energies across the region of the $2p$ thresholds. Figure 1 displays the Auger spectra after normalization to the same I_0, as measured for a number of photon energies, indicated at the right end side of the y axis. The correspondent TEY absorption spectrum is reported in Fig. 2 (circles). The Ni L_3 and L_2 resonances occur at 854.3 and 871.9 eV in our photon energy scale.

The photoelectron intensity in the 825–848 eV kinetic energy range ($I_{3/2}$) can be almost entirely assigned to the $2p$ hole decay. Nevertheless, some spurious contributions, which cannot be physically discriminated from the L_3VV spectrum, generate a systematic error in the measure of $I_{3/2}$.

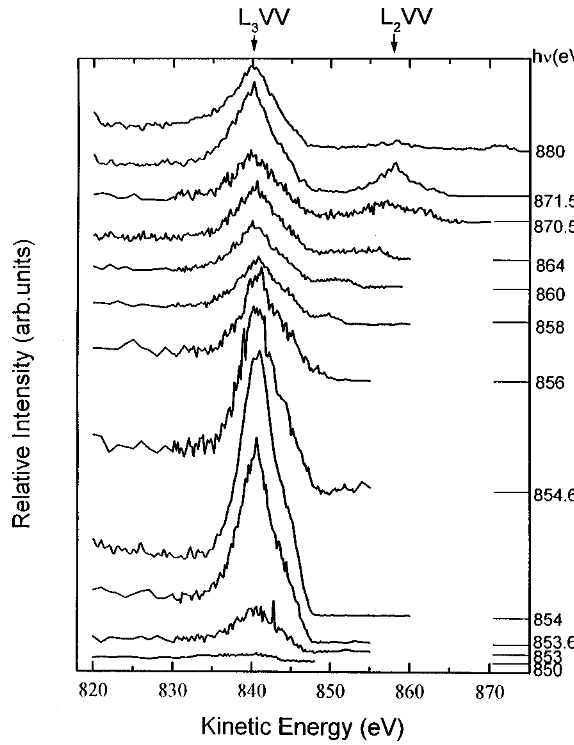

FIG. 1. Ni $L_{2,3}VV$ Auger spectra as measured as a function of the photon energy (right end side of y scale) across the $2p$ x-ray absorption edges. Intensities are normalized to the same incident photon flux.

At photon energies below the L_2 threshold and near the L_3 threshold, the valence band photoemission and its associated inelastic background is the main spurious contribution to $I_{3/2}$. Above the L_2 threshold, both the L_2VV emission low-energy tail and the valence band contributions have to be considered as sources of systematic error for $I_{3/2}$.

The relevance of the systematic error associated to these spurious contributions can be evaluated by extrapolation. The valence band photoemission intensity is measured below the L_3 threshold and assumed constant in underneath the Auger spectrum measured at $h\nu=854$ eV (very close to the L_3 resonance). We can then estimate that it contributes for less than 2% to the $I_{3/2}$ maximum (840 eV of kinetic energy).

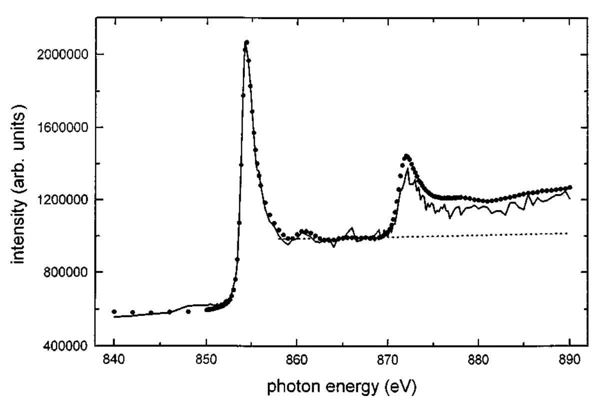

FIG. 2. Ni $2p$ edges x-ray absorption spectra in total electron yield mode (close circles) and in partial yield mode at the L_3VV maximum (continuous line) normalized to the L_3 edge. The dotted line is a linear extrapolation (see text).

With similar arguments, we estimate that its contribution does not exceed 6% in all the other Auger spectra measured for photon energies below the L_2 threshold.

For photon energies above the L_2 threshold, the low-energy tail of the L_2VV and the valence band emission are present and their contribution can be evaluated by assuming it to be constant and equal to the photoemission intensity measured at 848 eV, where the L_3VV emission should be zero. In the spectrum at $h\nu = 880$ eV, we estimate an overall spurious contribution to $I_{3/2}$ that does not exceed 6%.

$I_{3/2}$ is expected to decrease in going from 854 to 867 eV photon energy, reflecting the change of the $2p_{3/2}$ photoionization cross section (see Fig. 2). The increase in $I_{3/2}$ observed at 871.5 eV, i.e., when the $2p_{1/2}$ channel is open, can be explained only by a $2p_{1/2} \rightarrow 2p_{3/2}$ core hole transition, as described in Eq. (1).

The relevance of the cascade process is highlighted by the partial electron yield spectrum (PEY) reported in Fig. 2 (continuous line). It has been obtained by setting the electron analyzer at the L_3VV maximum (kinetic energy of about 840 eV) with a 3 eV energy band pass, and scanning the photon energy through the Ni $L_{2,3}$ edges. The main Auger line and the CK satellite[13,17] are not resolved with the present energy resolution. This measurement has been taken simultaneously with the TEY spectrum reported in Fig. 2.

It is known[13,17] that the energy shift between the L_3VV and the $L_3'VVV$ transitions is negligible with respect to the energy band pass chosen for the PEY spectrum, hence the direct L_3VV process and the cascade one will contribute on identical footing to the measured intensity.

Apart from a minor contribution coming from a continuum background, the TEY spectrum is proportional to the sum of the probability of creating a $2p_{1/2}$ or a $2p_{3/2}$ core hole, $\alpha_{1/2}(h\nu)$ and $\alpha_{3/2}(h\nu)$, respectively. The PEY spectrum is proportional to $[\alpha_{3/2}(h\nu) + \beta(h\nu)\alpha_{1/2}(h\nu)]$, because the allowed decay processes are L_3VV for a $2p_{3/2}$ hole, and either the direct L_2VV or the cascade (1) for a $2p_{1/2}$ hole. This is accurate apart from a 6% systematic error that originates from the spurious contributions to $I_{3/2}$ discussed in conjunction with the full Auger spectra.

Below the L_2 threshold only the $2p_{3/2}$ holes can be created, and $\alpha_{1/2}(h\nu) = 0$. Hence, the shapes of TEY and PEY are identical and proportional to $\alpha_{3/2}(h\nu)$ in this region.

The two measured spectra have been normalized to each other by using a linear multiple regression in the region from 850 to 868 eV photon energy. The regression procedure takes into account an incoherent background, whose shape and intensity are evaluated below the L_3 threshold and linearly extrapolated above it.

Above the L_2 threshold, the $\beta(h\nu)\alpha_{1/2}(h\nu)$ contribution to the PEY has been evaluated by subtracting the linear extrapolation of $\alpha_{3/2}(h\nu)$ (LE, dotted line in Fig. 2) measured in the range 862–868 eV. Then, for each photon energy sampled above 870 eV, a $\beta(h\nu)$ value is obtained by the ratio (PEY-LE)/(TEY-LE) and the results are displayed in Fig. 3.

Circles indicate the ratio as derived by row data, the continuous line represents the same profile after a ten-point average repeated three times, performed to filter out the high frequency component of the noise. The residual noise level does not allow to assess a clear photon energy dependence over the investigated range. By assuming β to be constant, an average value of $(73\pm^{2}_{8})\%$ (dashed line in Fig. 3) is deduced from the data. The asymmetric error bar is a consequence of the systematic error that is introduced in the assumption of PEY to be proportional to the L_3VV signal, neglecting the spurious contributions from the valence band and the L_2VV emission (see discussion of Fig. 1). This branching ratio coincides, within uncertainties, with the value $(78\pm 12)\%$ measured by APECS at high photon energy.[15] Nevertheless, it has to be noted that the smoothed curve clearly indicates an increasing trend of β with the photon energy.

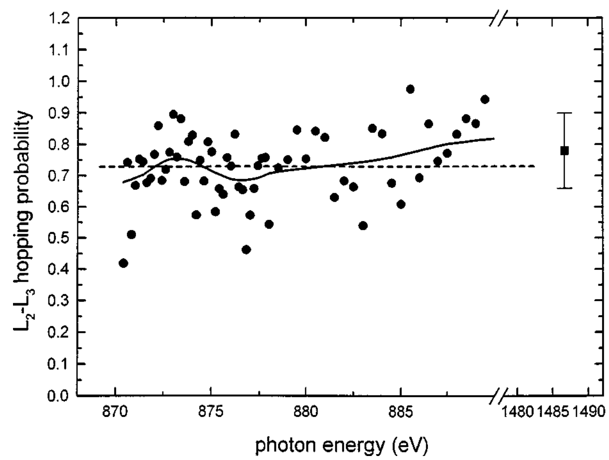

FIG. 3. Branching ratio $\beta(h\nu)$ (close circles) as derived from the ratio between partial and total electron yield intensities (Fig. 2). The continuous line is the same quantity after smoothing. The dashed line is the mean value of the all experimental points. The high-energy point represents the β value derived by APECS measurements (Ref. 15).

These findings, obtained in the near-edge region, represent a complement to the APECS results and give a further piece of information: the CK probability becomes independent upon photon energy already a few eV above threshold and asymptotically converges to the value measured in the high-energy regime. As a consequence, the double-step model usually adopted in the high-energy regime for the photoexcitation-Auger mechanism, in the case of Ni appears to be valid in the threshold limit as well.

Differential low-energy emission spectra

The second goal of our experiment was to measure directly the energy spectrum of the e_{CK} electron ejected from the $3d$ band as a consequence of the change in spin orbit coupling of the $2p$ core hole. Its kinetic energy E_{CK} is given by the separation energy between the $2p^5{}_{1/2}3d^n$ and $2p^5{}_{3/2}3d^{n-1}$ corrected for the work function Φ of the analyzer (5.2 eV). The main contribution to the separation energy comes from two distinct aspects that we assume uncorrelated.

(i) The variation of the spin orbit coupling of the $2p$ core hole from antiparallel to parallel alignment (17.3 eV in Ni).

(ii) The variation of the number of $3d$ electrons, whose contribution can be written as the binding energy of the single particle $3d$ electron (Δ) minus the Coulomb repulsion in the presence of the core hole (Q).

Hence we have

$$E_{\mathrm{CK}}(\mathrm{eV}) = 17.3 - (\Delta - Q) - \Phi. \tag{2}$$

Δ and Q have been calculated in Ni using Anderson impurity model, fitting polarization-dependent absorption[24] or $2p3p$ absorption and photoemission.[25] Jo and Sawatzky[24] obtained $\Delta = -1$ eV and $Q = 5$–6 eV, giving an expected E_{CK} that ranges from 5.1 to 6.1 eV. In the work of van der Laan and Thole,[25] based on a wider set of experimental data, values of $\Delta = -0.75$ eV and $Q = 5.5$ eV are reported, leading to $E_{\mathrm{CK}}(\mathrm{eV}) = 6.85$ eV.

Electrons of such a low kinetic energy are difficult to be discriminated against the high intensity of the secondary electron spectrum, 1/100 being the typical signal to background ratio.[26] To highlight this relatively weak signal we took advantage once more of the tunability of the photon energy, collecting electron distribution curve (EDC) spectra in the 4–20 eV kinetic energy range for four different photon energies which are below or above the L_2 edge. We assume that the shape of the secondary electron spectrum does not change when the photon energy changes between the extreme of the explored interval, whereas the CK and photoemission contribution to the EDC spectrum is present only with above threshold photon energies. On these grounds, the ratio of photoemission spectra measured above and below threshold are expected to bear the imprint of photoemission and CK processes alone.

The overall (photons and electrons) resolution of the experiment was about 0.8 eV.[21] At 854 and 861 eV no photoemission peak is expected to appear in the analyzed range. For $h\nu = 867$ and 872 eV we expect $2p_{3/2}$ photoemission to contribute at 7.8 and 12.8 eV, respectively. Figure 4(c) shows the ratio between EDC spectra taken at 867 and 861 eV, and the $2p_{3/2}$ photoemission peak is clearly visible at the expected kinetic energy. Also in Fig. 4(b) (ratio between 872 and 861 eV spectra) and Fig. 4(a) (872 vs 854 eV) the $2p_{3/2}$ peak is located at the correct kinetic energy, but in addition a second structure centered at 6.7 eV is clearly detectable and it can be assigned to CK transitions on the basis of the energy position expected according to Eq. (2). The agreement with calculated values[23,24] is good in view of the many assumptions and approximations that have been made in both calculations and data analysis. It is beyond the scope of our work and the quality of our present data to discriminate between different models, but it is clear from these results that the direct measure of the L_2L_3V CK spectrum is an interesting way to experimentally evaluate the $(\Delta - Q)$ energy term, an important parameter for model calculations of the electronic properties of highly correlated systems.

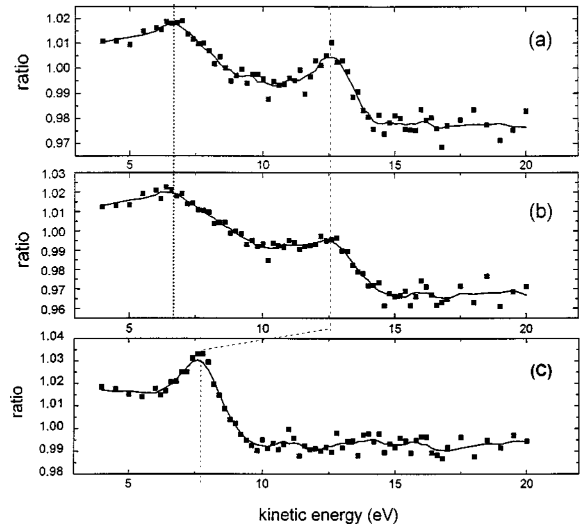

FIG. 4. Ratios between photoemission spectra measured for different photon energies through the Ni $2p$ edges. The continuous line is a three-point average. The profile in (a) is the ratio between EDC spectra measured at $h\nu = 872$ eV and $h\nu = 854$ eV, the profile in (b) between $h\nu = 872$ eV and $h\nu = 861$ eV, the profile in (c) between $h\nu = 867$ eV and $h\nu = 861$ eV. In (a) and (b) the high kinetic energy structure is the $2p_{3/2}$ photoemission peak, the low-energy structure is the L_2L_3V Coster-Kronig peak. In (c) only the $2p_{3/2}$ photoemission peak is visible.

CONCLUSIONS

To conclude our investigation addressed two experimental points relevant to the electron spectroscopy of correlated systems. We have given a quantitative estimate of the probability that a $2p_{1/2}$ core hole in Ni will decay through a L_2L_3V Coster-Kronig process. We find a value of $(73\pm^{2}_{8})\%$ that agrees with previous results obtained by Auger-photolectron coincidence spectroscopy in the high-energy regime. The use of monochromatic synchrotron radiation of tunable energy allowed us to obtain this result in the near threshold energy region which is complementary to the one investigated by APECS.

We have at the same time measured directly the Auger electron emitted in the CK decay following the absorption process at the L_2 edge of Ni. The experiment demonstrates the feasibility of a direct detection of the CK spectrum in the solid state. Knowledge of the exact transition energy is useful information that can be exploited to refine models of the electronic properties of correlated systems. The observation that the CK branching ratio reaches its asymptotic value already for energies just above the L_2 threshold supports the validity of the sudden approximation also in the near edge region, a result far from being obvious for highly correlated systems.

ACKNOWLEDGMENTS

We are grateful to Professor P. Weightman of the University of Liverpool (UK) for interesting discussion and for his critical reading of the manuscript. This work was partially supported by the European Project ERBCHBICT940998 and by MURST ''Propetti di Ricerca di rilevante interesse nazionale.''

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