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RESONANT 3*p* AND 3*s* CORE-LEVEL PHOTOEMISSION AT THE 2*p* THRESHOLDS OF Ni AND Co METAL

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We report on a resonant photoemission study of Ni and Co metal at the L_{III} soft-X-ray absorption threshold. The valence-band spectra as well as the 3*p* and 3*s* emission exhibit an enhancement at resonance. For Ni metal, a quantitative analysis shows that the increase of the 3*p* and 3*s* emission signal is mainly due to an incoherent superposition of the photoemission and the Auger channels. In case of Co metal, an analogous behavior is directly evident from the experimental data.

Keywords: A. metals, D. electronic states, E. photoelectron spectroscopies, E. synchrotron radiation.

PHOTOEMISSION (PE) spectra of both the valence-band and core-level regions of nickel metal exhibit satellite structures that have attracted much attention during the past decade [1–12]. These satellites are connected with the atomic-like properties of the metallic state and are located about 6 eV below the main emission lines (3*d*, 3*p*, 3*s*) [4]. Most of the work has dealt with the well-known 6-eV satellite in the valence-band (PE) spectrum of Ni metal. This satellite corresponds to a two-hole ($3d^8$) final state, and exhibits a strong enhancement at the 3*p* threshold around 67 eV which was assigned to a strong Fano resonance [1–3]. Such a resonance process is understood as an interference phenomenon between two different channels leading to the same final state. The two channels are the direct 3*d* PE and a discrete de-excitation of the core-excited $3p^5 3d^{10}$ state. Necessary for the occurrence of a Fano-type resonance is a coherence between these two channels.

In an earlier work [13] it was shown that the photoelectron spectra of CuO and Ni metal at the L_{III} thresholds can be described by an incoherent superposition of an intense $L_3M_{4,5}M_{4,5}$ Coster–Kronig Auger emission with a PE signal. This effect was explained as the consequence of a loss of coherence between the two channels caused by the itinerant character of the $2p^5 3d^{10}$ intermediate state. More recently, a PE study at the M_{III} and $N_{IV,V}$ thresholds of Ni metal and CeGd, respectively, showed that the resonant enhancement of the 6-eV PE satellite of Ni metal is mainly caused by an incoherent Auger decay and cannot be described as a resonant PE process [14].

The possibility to enhance even weak satellite structures with resonant PE has been used to test the existence of these correlation effects in an experimental way. However, it is important to investigate the question if the PE signal reflects resonant PE providing information on the satellite structures or reflects an incoherent superposition of PE and Auger processes.

In this work, we report on a comparative PE study of the 3*p* and 3*s* emission spectra of polycrystalline Ni and Co metal at the 2*p* soft-X-ray absorption thresholds. At resonance, a large emission in the 3*p* and 3*s* satellite region is observed. We show that the spectra of Ni metal can be described as the superposition of a Coster–Kronig Auger emission with a PE signal. In the case of Co metal a similar behavior is observed directly from the raw data.

The measurements were performed with the SX 700/II high-resolution soft-X-ray monochromator operated by the Freie Universität Berlin at the

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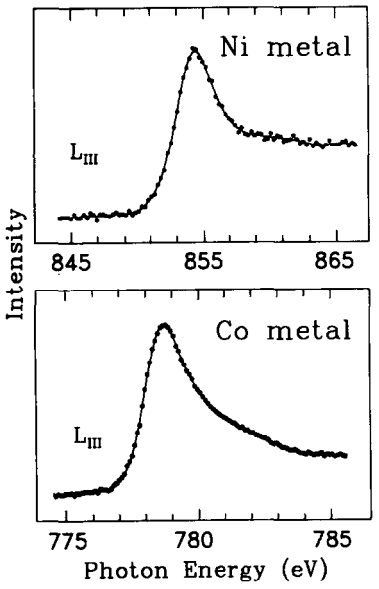

Fig. 1. L_{III} XANES spectra of Ni and Co metal.

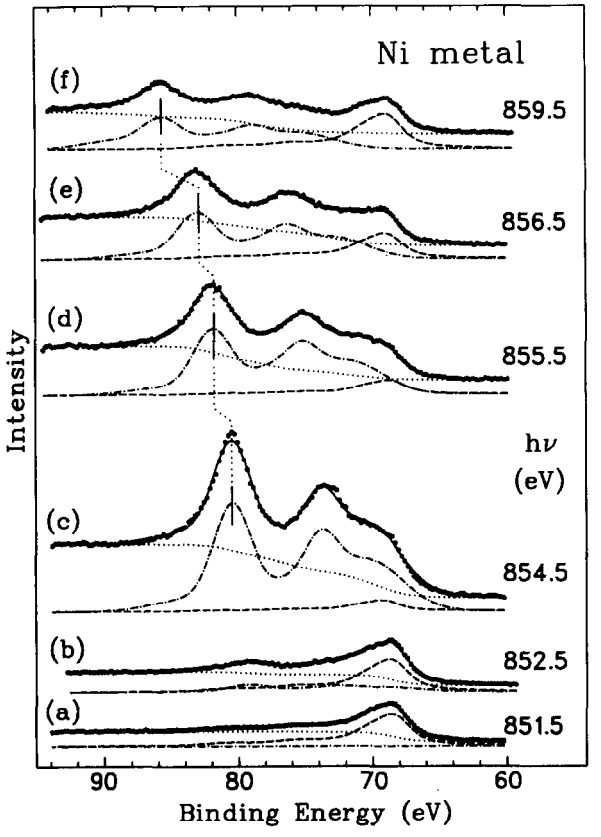

Fig. 2. 3p core-level photoemission spectra of Ni metal, taken at various photon energies. The solid lines through the data points represent the results of least-squares fits (see text), with the dashed subspectra representing the PE signal and the dash-dotted subspectra the Coster–Kronig Auger contributions. The integral background is given by the dotted curve.

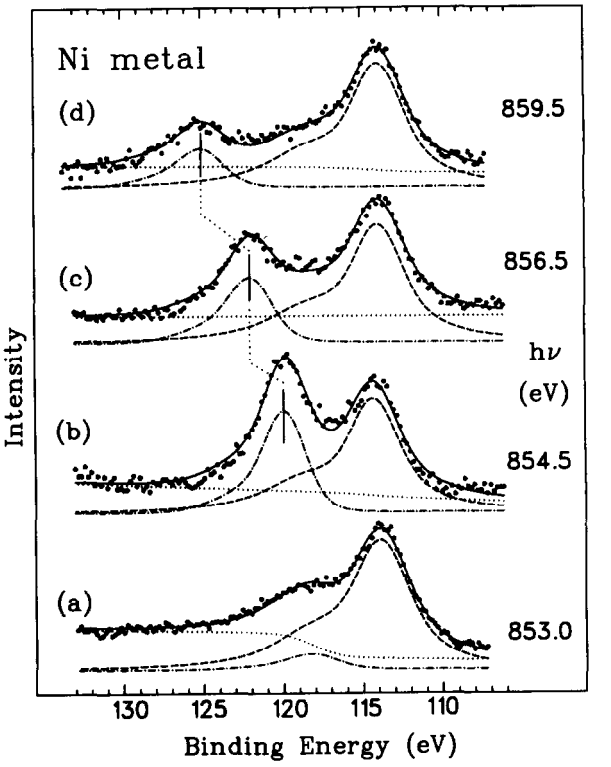

Fig. 3. 3s core-level photoemission spectra of Ni metal, taken at various photon energies. The solid lines through the data points represent the results of least-squares fits (see text), with the dashed subspectra representing the PE signal and the dash–dotted subspectra the Coster–Kronig Auger contributions. The integral background is given by the dotted curve.

Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). The spectra were recorded with a VG-CLAM hemispherical electron-energy analyzer. The energy resolution was set to $\simeq 0.7$ eV (FWHM) for Ni 3p and 3s PE signals taken at photon energies of 200 and 250 eV, respectively, and to $\simeq 1.7$ eV for Ni and Co spectra taken at higher photon energies. X-ray absorption near-edge spectra (XANES) were taken at the Ni and Co L_{III} thresholds in total-electron-yield mode. The samples studied were in form of polycrystalline materials and were repeatedly scraped *in situ* with a diamond file to remove surface contaminants. The base pressure in the UHV chamber was better than 3×10^{-10} mbar during the measurements.

Figure 1 shows the L_{III} X-ray absorption near-edge structures (XANES) spectra of NI and Co metal. The intense white lines at a photon energy of 854.5 eV in Ni metal and 778.7 eV in Co metal are due to a $2p^6 3d^n \rightarrow 2p^5 3d^{n+1}$ core excitation ($n = 9, 8$ in Ni and Co metal, respectively). These spectra were taken in order to precisely define the photon energies in resonant PE with respect to the L_{III} core-excitation resonance.

Figures 2 and 3 show 3p and 3s PE signals of Ni metal, respectively, taken at the indicated photon energies in the region close to the L_{III} soft-X-ray absorption threshold; they are normalized to constant stored electron beam in BESSY. In both cases, an enhancement of the electron emission in the region of the satellite (at $\simeq 6$ eV from the main emission line) is observed on resonance, i.e., for $h\nu = 854.5$ eV. For photon energies above the absorption maximum, a Coster–Kronig Auger peak moves away from the main 3p and 3s PE signals, respectively. This behavior is very similar to the one observed for CuO as well as valence-band PE from Fe, Co, and Ni metal at the L_{III} threshold [13, 15]. For this reason, the same analysis is applied. In case of 3p emission, an $L_3M_{2,3}M_{4,5}$ Coster–Kronig Auger spectrum was taken at $h\nu = 900$ eV and a 3p PE spectrum at $h\nu = 200$ eV, both off-resonance. These two spectra were analyzed by least-squares fit procedures in order to obtain analytical descriptions of their spectral shapes. Five Gaussians were used to describe the Auger spectrum and four Lorentzians to simulate the PE spectrum (see Fig. 4). In order to be able to estimate the contribution of the Auger lines to the 3p photoelectron spectra in the region close to resonance, it was assumed that the PE data in Fig. 1 represent simply an incoherent superposition of a PE with an Auger spectrum. The solid lines in Fig. 1 represent the results of this fit analysis, with the dashed subspectra representing the PE signal and the dash-dotted subspectra of the Auger contribution. The same analysis was performed with the 3s core-level PE spectrum. An $L_3M_1M_{4,5}$ Coster–Kronig Auger spectrum was taken at $h\nu = 870$ eV and a 3s PE spectrum at $h\nu = 250$ eV, both off-resonance. Two Gaussians were used to describe the Auger spectral shape and three Lorentzians for the Ni-3s PE spectrum (see Fig. 5). The 3s PE spectra in the region close to resonance were analyzed as a superposition of a Coster–Kronig Auger emission with the 3s-PE spectrum. The results of the least-squares fit are shown in Fig. 2 with the same nomenclature as in Fig. 1. In both cases, a description of the spectra within such a simple method is rather successful. The intensity of the Auger contribution is highest for $h\nu = 854.5$ eV due to the enhanced creation of a $2p_{3/2}$ core hole on resonance.

Figure 6 shows 3d, 3p, and 3s PE spectra of Co metal for photon energies close to the absorption

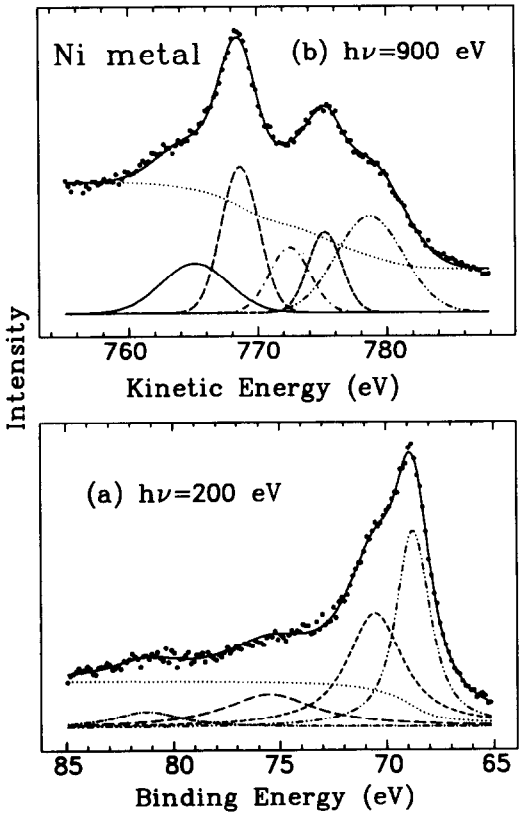

Fig. 4. (a) 3p core-level PE spectra of Ni metal taken at $h\nu = 200$ eV; (b) $L_3M_{2,3}M_{4,5}$ Coster–Kronig Auger spectrum excited with 900-eV photons.

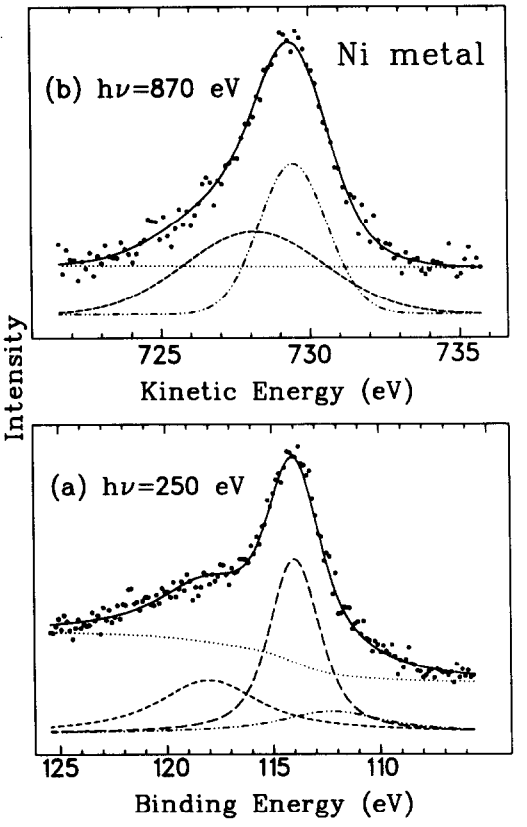

Fig. 5. (a) 3s core-level PE spectra of Ni metal taken at $h\nu = 250$ eV; (b) $L_3M_1M_{4,5}$ Coster–Kronig Auger spectrum excited with 870-eV photons.

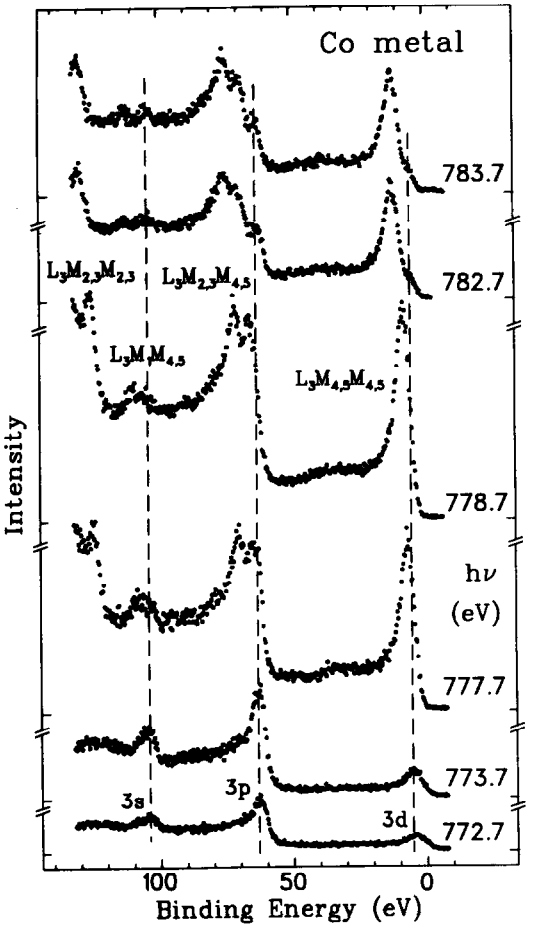

Fig. 6. 3*d*, 3*p*, and 3*s* PE spectra of Co metal taken at the indicated photon energies. The vertical dashed lines represent the position of the 3*d*, 3*p*, and 3*s* signals. The strong increases of these emissions on resonance ($h\nu = 778.7$ eV) are due to various Auger decays (see text).

threshold ($h\nu = 778.7$ eV). On resonance, a large enhancement in the region of the 3*d*, 3*p* and 3*s* region is observed. For higher photon energies the $L_3M_{4,5}M_{4,5}$, $L_3M_{2,3}M_{4,5}$, $L_3M_1M_{4,5}$, and $L_3M_{2,3}M_{2,3}$ Auger spectra move away to higher binding energies. This behavior is rather similar to the one observed and quantitatively analyzed for the 3*d* [13], 3*p*, and 3*s* emission of Ni metal. For the case of 3*d* PE from Co metal, an earlier work described the data as a superposition of Auger and valence-band [15]. Therefore, we can conclude that the large enhancement observed on resonance in the region of the 3*d*, 3*p*, and 3*s* emissions is mainly due to the different Auger decays.

In summary, the resonant 3*p* and 3*s* PE spectra of Ni metal in the region of the $2p_{3/2}$ threshold can be described as a superposition of an Auger signal ($L_3M_{2,3}M_{4,5}$ and $L_3M_1M_{4,5}$, respectively) with the direct 3*p* and 3*s* PE, respectively. The spectra for Co metal exhibit an analogous behavior. These findings agree with the results of earlier experimental studies on valence-band PE from CuO, Ni, Co, and Fe metal [13, 15], as well as with theoretical calculations [16] that affirm a strong increase on-resonance of 3*d*, 3*p*, and 3*s* PE for the case of Ni metal due to various Auger decays.

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