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Original contributions

Resonant photoemission at the *2p* thresholds of Fe, Co, and Ni metal

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Abstract. Resonant photoemission studies have been performed at the $2p$ soft-x-ray absorption thresholds of Fe, Co, and Ni metal. At resonance, the photoelectron intensity exhibits a strong enhancement in the region of the two-hole satellites, which is shown, however, to be mostly due to an incoherent superposition of a photoemission signal with a more intense signal from an $L_3M_{4,5}M_{4,5}$ Coster-Kronig decay of the core-ionized state. The resonant enhancement of the valence-band photoemission satellite in Ni metal amounts to a factor of $\simeq 12$. In contrast, no photoemission satellites are observed for Fe and Co metal.

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1. Introduction

The appearance of electron-correlation satellites in the high-energy excitation spectra of $3d$ transition elements, rare earths, and actinides has attracted considerable scientific interest in the past two decades. Among these, the 6-eV valence-band PE satellite of Ni metal and the possible existence of similar structures in the valence-band PE spectra of Co and Fe have been widely discussed in the literature [1–11]. Experimentally, the Ni satellite has been identified as a two-hole bound state by means of resonant photoemission (PE) [1–4]. Here, close to the $2p$ and $3p$ x-ray absorption thresholds, the interference of the direct PE channel with the Auger-decay channels of the $2p \rightarrow 3d$ or $3p \rightarrow 3d$ core-excited states leads to strong variations in the PE cross section and, in particular, to a resonant enhancement of the PE cross section for that particular final state, which is also populated by an Auger decay of the dipole-excited $3d$ state. For the case of Fe and Co metal, the existence of an analogous valence-band satellite originating from a two-hole bound state is not clear [7–11]. The present theories [12–17] do not guarantee the existence of a two-hole bound state in transition metals (TM) with more than one $3d$ hole per atom. The possibility to enhance even weak satellite structures with resonant PE might be used to test experimentally the existence of these correlation effects. However, for the proper application of this method it is important to decide whether the observed enhancement of the PE signal reflects really an interference phenomenon or simply consists on an incoherent superposition of PE and Auger processes. In case of Ni metal it has been shown that at resonance the photoelectron spectra are in fact dominated by strong incoherent Auger emission, and the real resonant PE effect is much weaker than anticipated from the raw data [18].

In this work, we report on a comparative PE study of polycrystalline Ni, Fe, and Co metal at the Ni, Fe, and Co $2p$ soft-x-ray absorption thresholds, respectively. At resonance, large electron emission intensities are observed for all three systems in the satellite energy region 5 to 7 eV below the Fermi level. It is shown that this effect is mostly due to a superposition of an intense Coster-Kronig Auger signal with a weaker PE signal. For the PE signal, we observe a weak enhancement of the 6-eV valence-band PE satellite in case of Ni metal, but no resonant enhancement in the satellite regions for Fe and Co metal, showing that there is no evidence for the existence of valence-band PE satellites due to a two-hole bound state in Fe and Co.

2. Experimental details

The measurements were carried out using the SX700/II high-performance soft-x-ray monochromator operated by the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). The spectra were recorded with a VG-CLAM hemispherical electron-energy analyzer. The energy resolution was set to $\simeq 0.4$ eV (FWHM) for valence-band PE spectra at low photon energies, and to $\simeq 1.0$ eV for Fe and $\simeq 1.7$ eV for Co and Ni spectra at high photon energies. X-ray absorption near-edge structure (XANES) spectra were taken at the L_{III} thresholds in the 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 during the measurements was better than $3 \cdot 10^{-10}$ mbar.

3. Results and discussion

Figures 1 to 3 show valence-band PE spectra of Ni, Fe, and Co metal, respectively, taken at various photon energies close to the L_{III} soft-x-ray absorption threshold. For a proper determination of the photon energies, the corresponding XANES spectra are shown in the insets. The solid lines through the data points as well as the subspectra are the results of a least-squares fit analysis discussed further below. The general behavior of the spectra upon changes of the photon energy across the absorption edge are very similar in all three cases. At the absorption maximum, on resonance, a huge enhancement of the electron intensity is observed, particularly in the energy regions of possible satellite emissions 5–7 eV below E_F. For photon energies above the absorption maximum, a strong Coster-Kronig Auger peak moves away from the Ni-3d valence-band PE signal, the intensity of which is much larger than the valence-band signal. This behavior is in sharp contrast to resonant $4d \rightarrow 4f$ and $3d \rightarrow 4f$ PE in rare-earth materials, where directly above threshold the intensity of a corresponding (Super-)Coster-Kronig Auger signal is negligible [19].

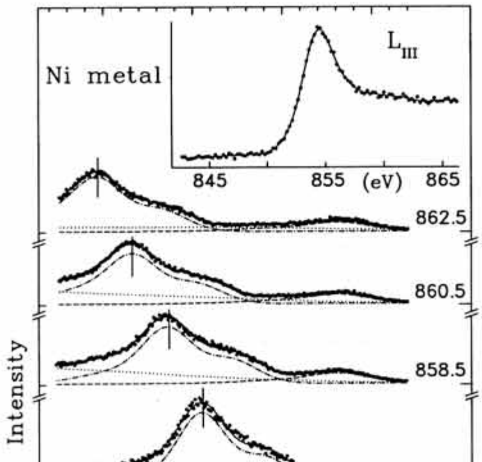

Fig. 1. Photoelectron spectra of Ni metal taken at various photon energies. The solid lines through the data points represent the results of least-squares fits (see text), with the dashed subspectra giving the PE signals and the dash-dotted subspectra the Coster-Kronig Auger contributions. The dotted curves represent the integral background. The inset shows the L_{III} XANES spectrum

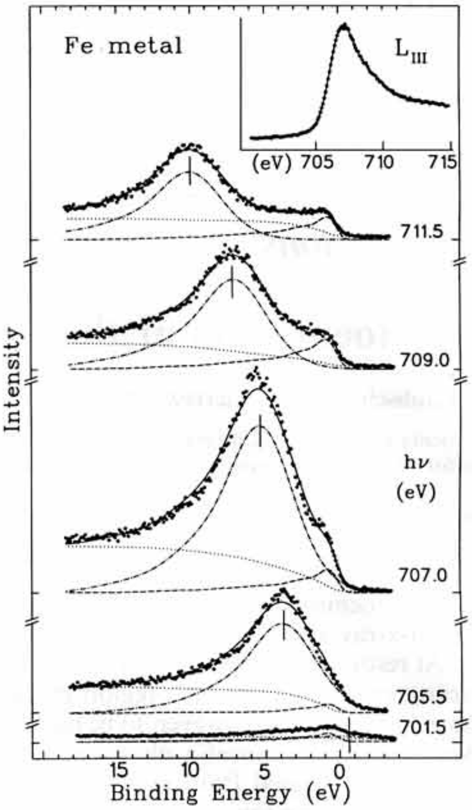

Fig. 2. Photoelectron spectra of Fe metal, taken at various photon energies. The solid lines through the data points represent the results of least-squares fits (see text), with the dashed subspectra representing the PE signal and the dash-dotted subspectra the Coster-Kronig Auger contributions. The inset shows the L_{III} XANES spectrum

In order to estimate the contribution of the Auger lines to the photoelectron spectrum at resonance, it was assumed that the data represent a simple incoherent superposition of a PE spectrum with an Auger emission spectrum. The underlying shape of the PE and Auger emissions were deduced from corresponding photoelectron spectra taken far from resonance (Figs. 4 and 5). To this end, the shapes of the PE and Auger spectra were modelled by a best fit to a set of Gaussian or Lorentzian lines, the specific positions, widths, and intensities of which have no particular physical significance. In case of Ni, the Auger signal was described by three Gaussians and the valence-band PE spectrum by three Lorentzians, one to account for the 6-eV satellite and two others to reproduce the main-peak region. The spectra taken in the L_{III} resonance region were then analyzed with a superposition of a Coster-Kronig Auger signal with a PE spectrum. Thereby, the three Gaussians of the Auger spectrum were assumed to maintain their widths, positions, and relative intensities; only the relative intensity of the line at lowest kinetic energy was

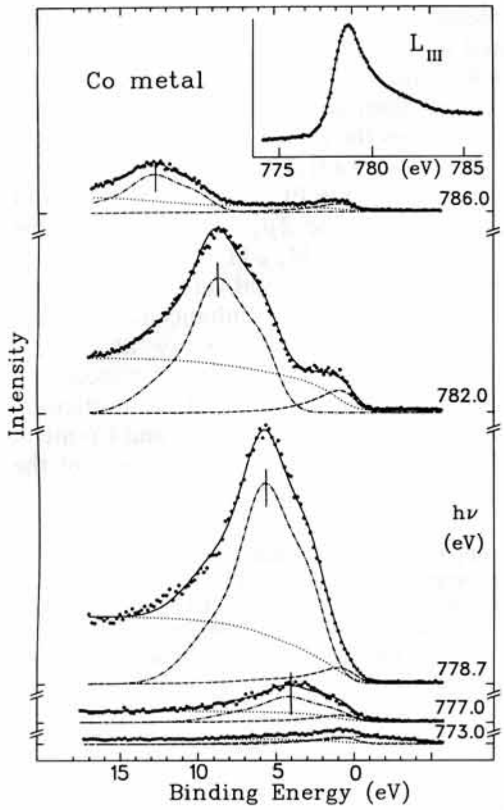

Fig. 3. Photoelectron spectra of Co metal, taken at various photon energies. The solid lines through the data points represent the results of least-squares fits (see text), with the dashed subspectra representing the PE signal and the dash-dotted subspectra the Coster-Kronig Auger contributions. The inset shows the L_{III} XANES spectrum

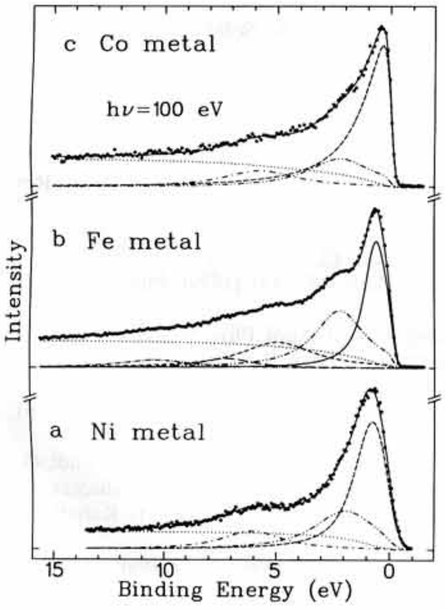

Fig. 4. Valence-band PE spectra taken at $h\nu=100$ eV: **a** for Ni metal, **b** for Fe metal, and **c** for Co metal. The solid lines through the data points represent the results of a modelling by a set of Lorentzians indicated by the subspectra

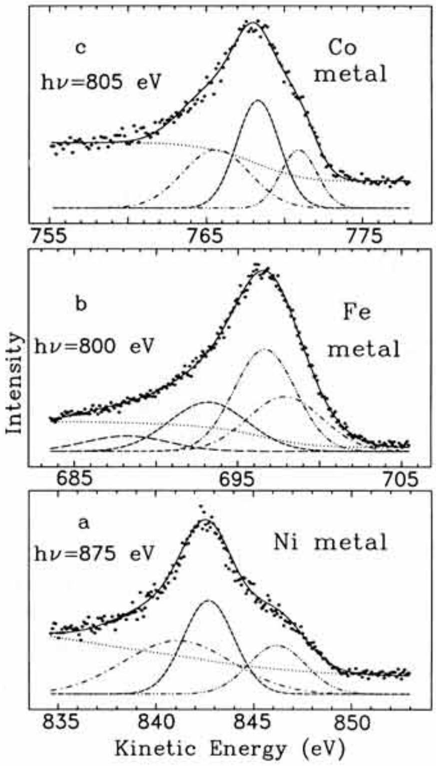

Fig. 5. **a** $L_3 M_{4,5} M_{4,5}$ Coster-Kronig Auger spectra of Ni metal taken at $h\nu=875$ eV; **b** of Fe metal taken at $h\nu=800$ eV, and **c** of Co metal taken at $h\nu=805$ eV. The solid lines through the data points represent the results of a modelling by a set of Gaussians indicated by the subspectra

allowed to vary freely, leading to an increase in intensity with photon energy. This confirms the observations in [20] for Cu and Zn. An analogous procedure was applied to the PE subspectrum, where now the intensity of the satellite with respect to the main peak was allowed to vary freely.

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 the Auger spectra. As a result, the spectra can be perfectly described by the superposition of a PE signal with a stronger, resonantly enhanced Coster-Kronig spectrum that is not coupled to the PE channel. For the PE component, the intesity ratio of satellite to valence-band emission is found to be 0.2 ± 0.02 at $h\nu=100$ eV, increasing to 2.5 ± 0.3 at $h\nu=854.5$ eV. This corresponds to a resonance of the PE satellite by a factor of $\simeq 12 \pm 3$ [18]. This value is much smaller than the one reported previously for the isoelectronic compound CuO, where an additional Auger contribution was not considered [4]. This discrepancy was subject to a controversial debate [21] which, however, did not lead to changes in our interpretation, i.e. the dominance of a huge Auger contribution to the resonant PE spectrum.

The discrepancy between the large intensity of the Auger signal and the relatively weak $3d$ PE signal can be explained by the fact that the core-excitation cross section of a Ni-$2p$ core level and, therefore, the Auger recombination rate are about 15 times larger than the

PE cross section of the $3d$ band [22]. At resonance, the $2p$ cross section is further enhanced due to transitions into the unoccupied $3d$ states just above E_F [23], readily explaining the resonant enhancement of the Auger intensities for the corresponding photon energies.

In case of Fe, four Gaussians have been used to describe the Auger curve and five Lorentzians the PE valence-band spectrum (Figs. 4b and 5b, respectively). In the PE valence-band spectrum, a weak signal was observed at 5.4 eV binding energy, which might be ascribed to a correlation satellite. This structure had also been observed previously [8–11], and its intensity has been found to vary critically with the degree of surface contamination. Thus, this feature might be ascribed to O-$2p$ or S-$3p$ emissions. In any case, we used a Lorentzian line at 5.4 eV in order to reproduce this structure in the valence-band PE spectrum. For the description of the resonance data, as in the case of Ni metal, the various Gaussians in the Auger subspectrum maintained their widths, positions, and intensities relative to each other. The same procedure was applied to the valence band; only the intensity of the Lorentzian line positioned at 5.4 eV was varied freely in order to take into acount the possibility of a resonant enhancement of this spectral feature.

Figure 2 shows the results of this procedure. As in the case of Ni metal, the spectra were found to be dominated by an incoherent Auger emission. In contrast to Ni, however, the weak PE component does not show any enhancement of the 5.4-eV feature. From this result we exclude, in contrast to [8], a many-body character of this structure and assign the 5.4-eV peak to a surface contamination.

For Co metal we followed the same procedure as described for Ni and Fe metal. We used three Lorentzians for describing the PE valence-band spectrum, two of them in order to simulate the main peak and the third one at 5.7 eV to account for a possible satellite (Fig. 4c). The Auger spectrum was fitted by three Gaussians (Fig. 5c). The intensity of the Lorentzian line in the PE component taken in order to describe a possible Co satellite was again varied as a free parameter. The fit results are presented in Fig. 3. As in case of Fe metal, a strong Auger emission and no PE satellite enhancement is observed on resonance. This behavior agrees clearly with a previous result [11] on resonant PE at the M_{III} threshold of Co metal, where the conclusion was reached that the two-hole bound state is absent in this material; our finding, however, is again in sharp contrast to the conclusion in [8], where on the basis of resonant PE studies the existence of such a satellite was claimed.

On resonance, the intensity of the Auger emission signal is stronger for Fe and Co than for Ni; all three metals, however, show a similar behavior of the Auger intensity when the photon energy is varied. These results clearly demonstrate that in case of Fe and Co there is no evidence for the existence of a valence-band PE satellite caused by a two-hole bound state. This conclusion agrees with previous findings in PE studies at the M_{III} threshold [8–11], showing that the valence-band satellite is absent in clean Fe and Co, and that the Auger decay dominates the resonant behavior. While several theories have contributed to a fair understanding of the satellite in Ni metal, where the electron correlation effects are significantly stronger than in Fe and Co metal, no theoretical model guarantees the existence of such a two-hole bound state in the earlier $3d$ transition metals.

In summary, the resonante PE spectra of Fe, Co, and Ni metal in the region of the $2p_{3/2}$ thresholds can be described by an intense $L_3 M_{4,5} M_{4,5}$ Coster-Kronig Auger emission signal superimposed on the weaker valence-band PE signal. The large enhancement of the $L_3 M_{4,5} M_{4,5}$ Auger signal at the x-ray absorption threshold is attributed to a large density of unoccupied $3d$ states directly above the Fermi level. In particular, no two-hole bound state is observed for Fe and Co metal in contrast to Ni metal, were a weak resonance of the 6-eV two-hole bound state satellite was confirmed.

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