Z. Phys. B 94, 1–2 (1994)

ZEITSCHRIFT FÜR PHYSIK B

Resonant photoemission in highly localized versus weakly localized solids

M.F. López, C. Laubschat, A. Gutiérrez, G. Kaindl

Institut für Atom- und Festkörperphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany

Received: 28 September 1993

Abstract. We report on comparative study of angle-resolved photoelectron spectra of Ni metal and CeGd at the M_{III} and $N_{\mathrm{IV,V}}$ soft-x-ray absorption threshold, respectively. On M_{III} resonance, the valence-band photoemission (PE) intensity of Ni follows a $\cos^2$-behavior, while the intensity of the 6-eV satellite is independent of the angle of emission relative to the **E**-vector of the incoming beam. On the other hand, the $4f$ Ce PE signal behaves $\propto \cos^2$ on $N_{\mathrm{IV,V}}$ resonance. This clearly shows that the resonant enhancement of the 6-eV PE satellite of Ni is mainly caused by an incoherent Auger decay and cannot be described as a resonant PE process.

PACS: 79.60.Cn; 78.70.Dm

The nature of the resonant enhancement of the 6-eV satellite structure in the valence-band photoemission (PE) spectra of Ni metal has been investigated intensely since the original work by Guillot et al. [1–4]. As is well known, the intensity of the 6-eV satellite is enhanced when the photon energy is varied across the M_{III} absorption threshold at $\simeq 67$ eV, a phenomenon that has been assigned to a strong Fano-type resonance [4–7]. Such a resonance is understood as an interference between two different channels leading to the same final state, i.e. a resonant PE process. The two channels considered are the direct photoionization of $3d$ valence-band states and an $M_{2,3}M_{4,5}M_{4,5}$ Super-Coster-Kronig (SCK) Auger decay of the core-excited $3p^5 3d^{10}$ intermediate state. Necessary for the occurrence of a Fano-type resonance is a coherence between the two channels. In a recent paper [8] it was shown that the photoelectron spectra of Ni metal and of CuO at the L_{III} thresholds have to be described by an incoherent superposition of an intense $L_3M_{4,5}M_{4,5}$ Coster-Kronig Auger signal with a relatively weak PE signal. This finding deviates dramatically from the established picture of resonant PE phenomena, and was explained on the basis of a loss of coherence between the two channels caused by the itinerant character of the $2p^5 3d^{10}$ intermediate state. It has to be tested whether an analogous mechanism causes the well-known resonant enhancement of the 6-eV valence-band satellite in the photoelectron spectrum of Ni metal at the M_{III} threshold [18].

In this Paper, we present the results of a comparative study of resonant electron-emission processes at the M_{III} threshold of Ni metal (Ni $3p \rightarrow 3d$ resonance) with those occurring at the Ce $N_{\mathrm{IV,V}}$ threshold of the alloy CeGd (Ce $4\mathrm{d} \rightarrow 4f$ resonance). The intensities of the various spectral components were measured as a function of the electron-emission angle relative to the **E**-vector of the incident light. In case of a PE process, the intensity should show a $\cos^2$-behavior, while an Auger signal ought to be isotropic in case of a polycrystalline sample. On the basis of these angle-dependent electron-spectroscopy measurements, a distinction between PE and Auger contributions is achieved. It turns out that only in case of highly localized rare-earth systems, the observed resonance phenomena originate from a true resonant PE process, while in case of Ni metal, the resonant enhancement of the 6-eV satellite is predominantly caused by an incoherent superposition of the valence-band PE spectrum with an intense Auger emission signal.

The measurements were performed at the TGM-1 beamline of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using a VSW-ARIES angle-resolved electron spectrometer with an electron-acceptance cone of ±2°. The photoelectrons were collected at different angles with respect to the **E**-vector. The experimental geometry including a definition of the emission angle Θ is schematically given in Fig. 1. Polycrystalline samples were intentionally used to avoid angular dispersion effects. The surfaces of the samples were cleaned by scraping with a diamond file. Oxygen contamination was monitored via O-$2p$ PE at $h\nu = 52$ eV and found to be negligible. During the experiments, the pressure in the experimental chamber was better than $2 \cdot 10^{-10}$ torr.

Figure 2 shows valence-band PE spectra of Ni metal, taken at (a) $h\nu = 75$ eV (non-resonant) and (b) $h\nu = 67$ eV

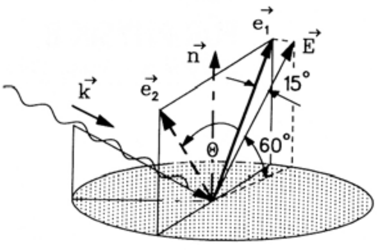

Fig. 1. Experimental geometry: **E** and **k** represent the direction of the electric field vector and the photon momentum, respectively, **n** the surface normal, and $\mathbf{e}_{1,2}$ the directions of electron emission. This geometry was chosen to assure the same surface sensitivity for $\Theta_1 = 0°$ and $\Theta_2 = 60°$

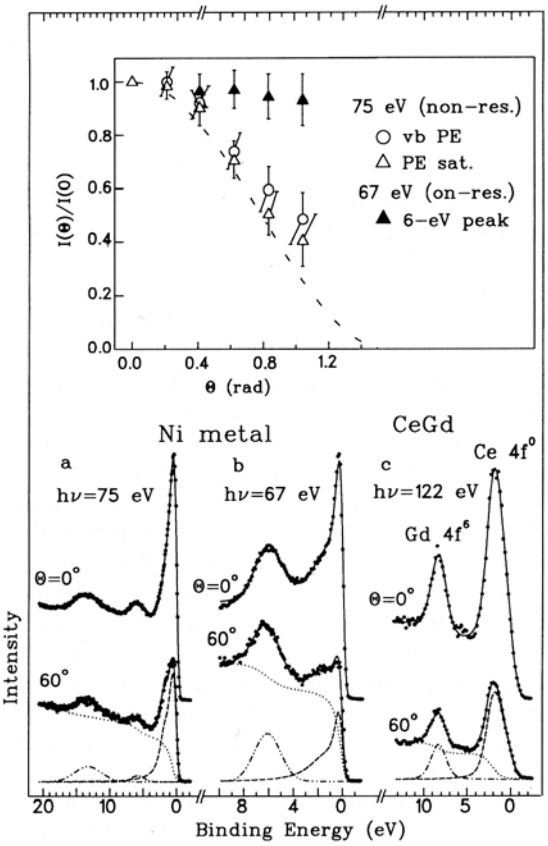

Fig. 2a–c. Photoelectron spectra of Ni metal taken at **a** $h\nu = 75$ eV (non-resonant) and **b** $h\nu = 67$ eV (on-resonance), and of CeGd at $h\nu = 122$ eV (Ce $4d \rightarrow 4f$ resonance) for two different angles Θ. The inset shows the angular dependences of the intensities of the valence-band signal (open circles) and the 6-eV satellite (open triangles) in the non-resonance spectra, and of the 6-eV feature in the on-resonance spectra (filled triangles)

(on-resonance), and of CeGd taken at (c) $h\nu = 122$ eV (Ce $4d \rightarrow 4f$ resonance) for two different angles Θ. The Ni non-resonant spectra were normalized to equal intensities of the Auger signals (dash-double-dotted curve). This is justified on the basis of an isotropic Auger emission for a polycrystalline sample. The resulting intensity angular variations of the non-resonant valence-band (dashed curve) and satellite (dash-dotted) emission are given for several values of Θ in the inset of Fig. 2 by open symbols. The dashed curve in the inset represents a $\cos^2\Theta$ behavior. Both intensities vary roughly as $\cos^2\Theta$ as expected for a PE process. The Ni on-resonance spectra in Fig. 2b were normalized to valence-band intensities equal to those in the non-resonant spectra. This leads to an approximately isotropic behavior of the on-resonance 6-eV feature of Ni metal as given in the inset by the filled triangles, contrasting the $\cos^2\Theta$-behavior of the 6-eV PE satellite in the non-resonance spectra (open triangles). Thus, the 6-eV peak on-resonance behaves like an Auger signal and cannot be described as resonant PE.

To insure that the Auger-like angular character of the satellite emission is not a general property of resonant PE, Fig. 2c shows PE spectra of the polycrystalline alloy CeGd, taken in Ce $4d \rightarrow 4f$-resonance at $h\nu = 122$ eV; the spectra were taken at the same angles Θ as those of Ni metal and the same normalization procedure was applied. At a BE of 2 eV, the resonantly enhanced emission from the Ce $4f$ states is observed, while the weaker emission at $\simeq$8-eV BE represents non-resonant PE from Gd $4f$ states, which can be used for internal calibration. When increasing the angle Θ from 0° to 60°, the intensity of both resonant Ce-$4f$ and non-resonant Gd-$4f$ emissions decrease proportional to $\cos^2\Theta$ in exactly the same way. The internal calibration given by the ratio of intensities of the Ce-$4f$ and Gd-$4f$ PE signals, which does not change from $\Theta = 0°$ to $\Theta = 60°$, proves in addition that the resonantly enhanced Ce-$4f$ PE signal has the same angular dependence as that of the non-resonant Gd-$4f$ PE signal, i.e. the angular dependence of a PE process.

In conclusion, we have shown that the resonant enhancement of the 6-eV satellite in the PE spectrum of Ni metal in the $3p \rightarrow 3d$-resonance is almost completely due to an incoherent superposition of the valence-band PE signal with an $M_3M_{4,5}M_{4,5}$ Auger emission. It should be mentioned that a similar conclusion has been reached more than ten years ago [9], but neglected since then in the literature. This clear difference to the true resonant PE behavior in rare-earth systems is probably caused by the weaker localization of the $3d$ states in Ni metal, where a strong hybridization of the core-excited intermediate state with conduction-band states leads to delocalization and thereby to a loss of coherence. We hope that these results will stimulate further theoretical work on resonant photoemission.

This work was supported by the Bundesminister für Forschung und Technologie, project 05-5KEAXI-3/TP01, and the Deutsche Forschungsgemeinschaft, project Ka564/2-2. Two of the authors (M.F.L. and A.G.) thank the Spanish Ministerio de Educación y Ciencia for financial support.

References

1. Hüfner, S., Wertheim, G.K.: Phys. Lett. **51**A, 299 (1975)
2. Penn, D.R.: Phys. Rev. Lett. **42**, 921 (1979)
3. Liebsch, A.: Phys. Rev. Lett. **43**, 1431 (1979)
4. Guillot, C., Ballu, Y., Paigné, J., Lecante, J., Jain, K.P., Thiry, P., Pinchaux, R., Pétroff, Y., Falicov, L.M.: Phys. Rev. Lett. **39**, 1632 (1977)
5. Fano, U.: Phys. Rev. **124**, 1866 (1961)
6. Iwan, M., Himpsel, F.J., Eastman, D.E.: Phys. Rev. Lett. **43**, 1829 (1979)
7. Barth, J., Kalkoffen, G., Kunz, C.: Phys. Lett. **74**A, 360 (1979)
8. López, M.F., Höhr, A., Laubschat, C., Domke, M., Kaindl, G.: Europhys. Lett. **20**, 357 (1992)
9. Traum, M.M., Smith, N.V., Farrell, H.H., Woodruff, D.P., Normann, D.: Phys. Rev. B**20**, 4008 (1979)