PHYSICAL REVIEW B VOLUME 56, NUMBER 3 15 JULY 1997-I

Angle-resolved resonant photoemission at the M_{III} absorption threshold of Co and Fe metal

A. Gutiérrez and M. F. López
Departamento de Corrosión y Protección, Centro Nacional de Investigaciones Metalúrgicas, CSIC,
Avenida Gregorio del Amo 8, E-28040 Madrid, Spain

(Received 5 February 1997)

We report on an angle-resolved resonant photoemission study of Co and Fe metal at the M_{III} absorption threshold. The intensity of the various spectral components was measured as a function of the electron emission angle relative to the **E** vector of the incident light. On M_{III} resonance, the main valence-band photoemission (PE) intensity of Co and Fe metal, located between E_F and 3 eV, follows a $\cos^2\theta$ behavior, as is expected for a photoemission process. However, the intensity of the enhanced feature located at ≈ 5 eV is found to be almost independent of the emission angle, as expected for an incoherent Auger process. This clearly shows that the enhancement of the 5 eV PE signal is mainly caused by an incoherent Auger decay and not by a resonant PE process. [S0163-1829(97)03128-7]

The resonant photoemission (PE) phenomenon is understood as an interference between two different channels leading to the same final state. The two channels considered are the direct PE and the dipole transition of a core electron to a discrete unoccupied state, ocurring at energies close to a particular absorption threshold. The result is a strong variation of the PE cross section.[1–3] Since the probability for resonant PE critically depends on the strength of configuration interaction and, therefore, on the localization of the core-excited state, the question arises whether the signal observed in resonant PE reflects exclusively this excitation process or is in part due to a secondary process of the excited state. Only in the first case can the spectral features be interpreted as resonant PE, whereas in the second case an incoherent superposition of PE and Auger signals occurs.[4–6] The distinction between resonant PE and noncoherent Auger decay process is of great interest for a proper interpretation of the observed spectral structures. In the past two decades, one of the most studied resonant PE processes has been the enhancement of the 6 eV valence-band PE satellite of Ni metal, produced when the photon energy is varied across the M_{III} absorption threshold. This phenomenon was identified as a resonant PE process.[7–9] For other transition metals, such as Co and Fe, a resonant photoemission process at the M_{III} absorption threshold has also been reported.[10] In a previous work, however, it was shown that the photoelectron spectra of Ni, Fe, and Co metal 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 with a relatively weak PE signal.[11] This finding dramatically deviates from the established picture of resonant PE, especially in the case of Ni metal, and was explained as a loss of coherence between the two channels originated by the itinerant character of the intermediate state, $2p^53d^{n+1}$. Therefore, it became necessary to test whether an analogous mechanism was responsible for the established *resonant PE* of the 6 eV valence-band satellite at the M_{III} threshold in the photoelectron spectrum of Ni metal. This question can be addressed by measuring the intensity of the various spectral components of the valence band as a function of the electron emission angle relative to the **E** vector of the incident light. In the case of a PE process the intensity should show a $\cos^2$ behavior, while an Auger signal ought to be isotropic in the case of a polycrystalline sample. On the basis of these arguments, a distinction between PE and Auger contributions should be possible by means of angle-dependent electron-spectroscopy measurements. This kind of experiment was performed in the case of Ni metal, and demonstrated that the resonant enhancement of the 6 eV satellite is almost completely due to an incoherent superposition of an Auger and a PE signal.[12,13] This has been recently corroborated in a resonant photoemission study with both angular and energy depencence, where it is concluded that the interference effects at the 6-eV satellite are very small, resulting in a Fano asymmetry parameter $q \gtrsim 9$.[14]

In this work, we report on a resonant PE study of polycrystalline Fe and Co metal at the M_{III} absorption threshold. The intensity of the various spectral components was measured as a function of the electron emission angle relative to the **E** vector of the incident light. Whereas the intensity of the valence-band PE signal varies roughly according to a $\cos^2$ law, the intensity of the enhanced feature at ≈ 5 eV is found to be almost independent of the emission angle, as expected for an incoherent Auger process. This result agrees with the previous work on Ni metal.

The measurements were performed at the TGM-5 beamline of the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) using a VSW-ARIES angle-resolved electron spectrometer with an electron-acceptance cone of $\pm 2°$. The photoelectrons were collected at different angles with respect to the **E** vector. The total energy resolution was better than 0.4 eV. Polycrystalline samples were used to avoid angular dispersion effects. The surfaces of the samples were cleaned by scraping with a diamond file. During the experiments, the pressure in the experimental chamber was better than 2×10^{-10} mbar.

Figure 1 shows the valence-band PE spectra of polycrystalline Co metal, taken at $h\nu=68$ eV (off resonance) for three different values of θ, where θ is the angle between the electron emission direction and the **E** vector of the incident light. The spectra can be separated into three regions: the valence-band emission at binding energies (BE's) between E_F and 3 eV, the emission at ≈ 5 eV, and the $M_3M_{4,5}M_{4,5}$ Super-Coster-Kronig (SCK) Auger emission at ≈ 12 eV. The spectra have been normalized to equal intensities of the Auger signal. This is justified on the basis of an isotropic Auger emission for a polycrystalline sample. All spectra were ana-

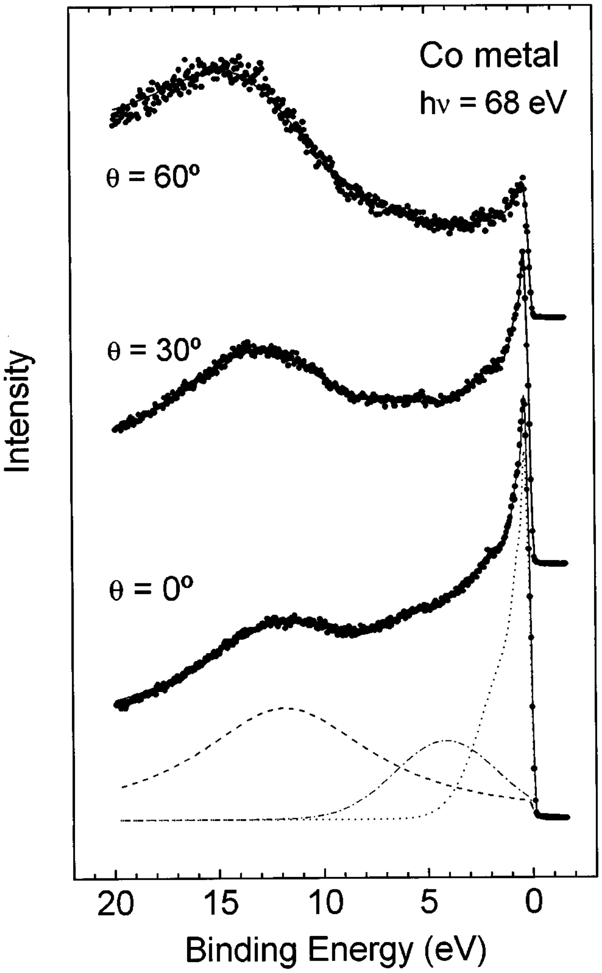

FIG. 1. Photoelectron spectra of Co metal taken at a photon energy of 68 eV (off resonance) for three different angles, θ, where θ is the angle between the electron emission direction and the **E** vector of the incident light. The solid lines through the data points represent the result of least-squares fits (see text). The dotted line represents the PE signal, the dashed line the Auger emission, and the dash-dotted line the emission at ≈5 eV.

lyzed by means of a least-squares fit procedure, using a Gaussian and a Lorentzian to model the Auger signal (dashed subspectrum), three Gaussians for the valence-band signal (dotted subspectrum), and one Gaussian for the 5-eV emission (dash-dotted subspectrum). The solid lines through the data points represent the result of least-squares fit analyses. The position and width of these lines was kept constant for all spectra. Table I summarizes the relative intensity values obtained for the main valence-band emission after normalization for the different angles studied. The theoretical value, corresponding to $\cos^2\theta$ is also shown. From these data we can conclude that the intensity of the nonresonant valence band varies roughly as $\cos^2\theta$, as expected for a PE process.

Figure 2 shows the valence-band PE spectra of polycrystalline Co metal, taken at $h\nu=60$ eV (on M_{III} resonance) for three different values of θ. In order to normalize the on-resonance spectra, the same angular dependence of the valence-band emission with θ as in the nonresonant case was assumed. Therefore, the spectra were analyzed following an analogous least-squares fit analysis as in the nonresonant case, normalizing the intensity of the valence-band emission to the values given in Table I for Co. The solid lines through the data points represent the results of the fit analysis. The valence-band emission was modeled with three Gaussians with the same energy positions and widths as in the off-resonance case. For the 5-eV emission one Lorentzian and one Gaussian were used. The dotted subspectrum describes the valence-band PE signal and the dashed curve the feature located at ≈5 eV. By appliyng the normalization procedure with the values of Table I, the intensity of the 5 eV feature remains almost independent of θ with only a small decrease that reaches a 5% at $\theta=60°$. At this point one has to consider that, on resonance, the Auger component and the 5-eV

TABLE I. Relative intensities of the valence band PE of Fe and Co metal for different values of θ with respect to the intensity for $\theta=0$. The corresponding $\cos^2\theta$ values are also shown for comparison.

θ	Co $I(\theta)/I(\theta=0°)$	Fe $I(\theta)/I(\theta=0°)$	$\cos^2\theta$
0°	1	1	1
30°	0.67	0.78	0.75
60°	0.25	0.27	0.22

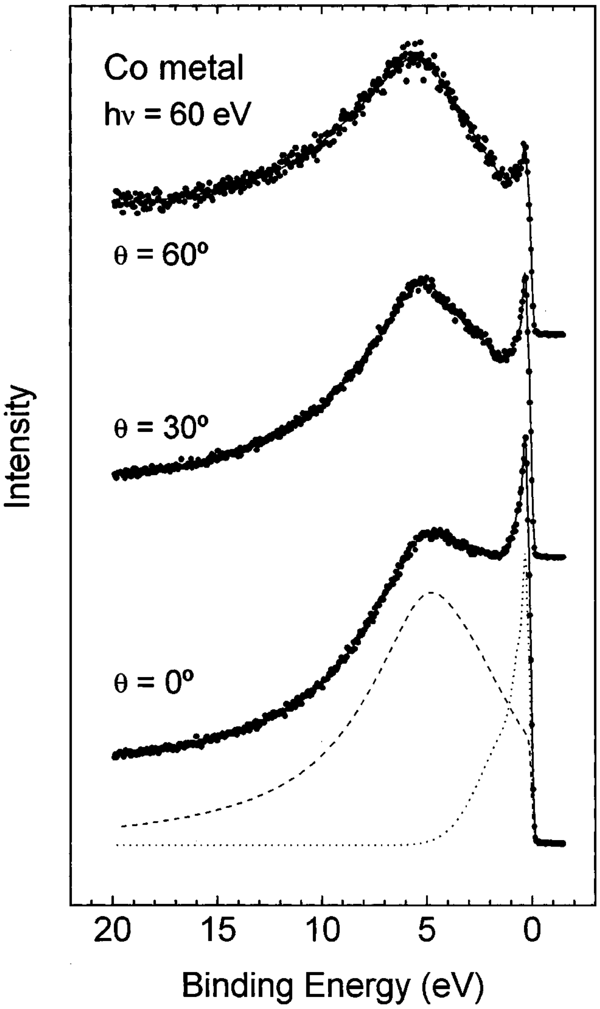

FIG. 2. Photoelectron spectra of Co metal taken at a photon energy of 60 eV (on resonance) for three different angles, θ, where θ is the angle between the electron emission direction and the **E** vector of the incident light. The solid lines through the data points represent the result of least-squares fits (see text). The dotted line represents the PE signal and the dashed line the emission at 5 eV.

component are at the same energy position. Assuming the same intensity ratio between the main valence-band emission and the 5-eV emission as in the off-resonance case, the intensity decrease should have reached a 10% at $\theta = 60°$. This deviation with the measured value indicates that, though the 5-eV peak on-resonance behaves mainly like an Auger signal with almost isotropic behavior, a small resonant effect is also present. In any case, the Auger process is predominantly responsible for the observed enhancement of the 5-eV photoelectron peak at the ''on-resonance'' photon energy.

Figure 3 shows the valence-band PE spectra of polycrystalline Fe metal, taken at $h\nu = 54$ eV (on resonance) for three different values of θ. The spectra show two main features: the main valence-band emission, at binding energies between E_F and 2.5 eV, and the emission located at 5 eV. To normalize these on-resonance spectra the same procedure as in the Co metal case was followed. Valence-band PE spectra of Fe metal off resonance ($h\nu = 60$ eV) for three vaues of θ were measured, analyzed by least-squares fit analysis, and normalized to obtain the same Auger intensity for all angles. The resulting intensities of the main valence-band emission after normalization are listed in Table I. The same angular dependence of the valence-band emission as in the nonresonant case was assumed for the on-resonance spectra, which were analyzed following an analogous least-squares fit analysis as the nonresonant case. The solid lines through the data points represent the results of the fit analysis. The valence-band emission was modeled with three Gaussians with the same positions and widths as in the off-resonance case. For the 5 eV emission one Lorentzian and one Gaussian were used. The dotted subspectrum describes the valence-band PE signal and the dashed curve the feature located at ≈ 5 eV. After the normalization procedure, the 5 eV emission intensity remains almost constant with only a 5% decrease for $\theta = 60°$. This indicates that, on $M_{\rm III}$ resonance, Fe behaves similarly to Co, with the Auger decay being the main responsible for the observed enhancement of the 5-eV photoelectron peak.

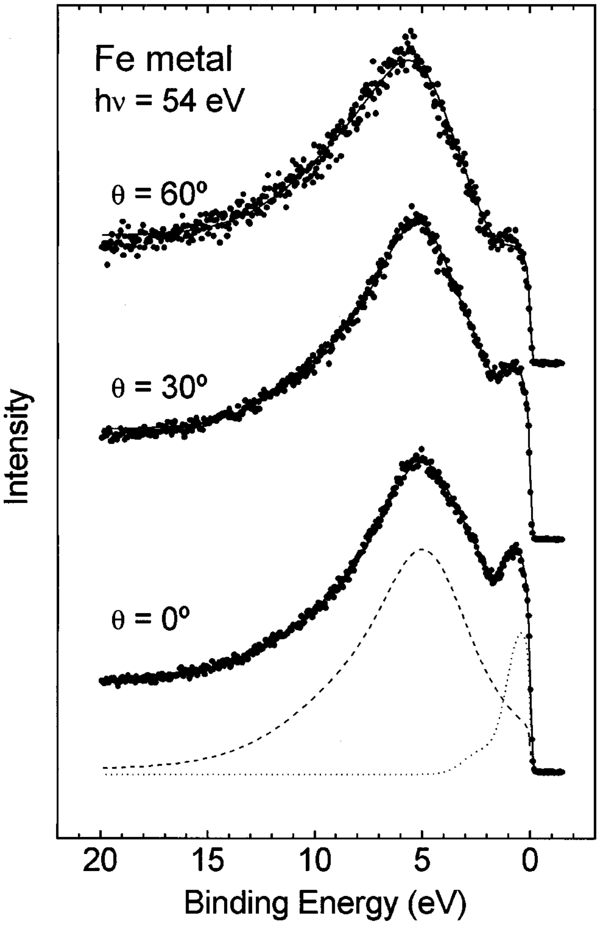

FIG. 3. Photoelectron spectra of Fe metal taken at a photon energy of 54 eV (on resonance) for three different angles, θ, where θ is the angle between the electron emission direction and the **E** vector of the incident light. The solid lines through the data points represent the result of least-squares fits (see text). The dotted line represents the PE signal and the dashed line the emission at 5 eV.

In conclusion, we have shown that the resonant enhancement of the 5-eV feature in the on-resonance spectra of the valence-band signal on Fe and Co metal is mainly due to an Auger emission. This result agrees with a previous angle-resolved resonant PE work performed on Ni metal,[12,13] and with a resonant PE study on the $L_{\rm III}$ threshold on Fe and Co metal.[11] The reason for this phenomenon is the lack of coherence between the two channels necessary for the ocurrence of the resonant PE process. This loss of coherence is probably originated by the relatively weak localization of the $3d$ states in the transition metals. The situation is different in resonant PE from rare-earth materials, where the resonantly enhanced signal reflects a true PE process.[15,16] The main difference between both cases is the degree of localization of the discrete excited state. While the excited $4f$ state in the case of rare earths is highly localized, the more bandlike character of the transition metal $3d$ states favors a decay of the core-excited state by a secondary SCK process.

This work was supported by the EU Human Capital and Mobility program under Contract No. CHGE-CT93-0027. We acknowledge Dr. T. Kachel and the BESSY staff for their help during the measurements. Fruitful discussions with G. Kaindl and E. Weschke are also acknowledged.

---

[1] U. Fano, Phys. Rev. **124**, 1866 (1961).

[2] L. C. Davis and L. A. Feldkamp, Phys. Rev. B **23**, 6239 (1981).

[3] T. Jo, *et al.*, J. Phys. Soc. Jpn. **52**, 2581 (1983).

[4] M. F. López *et al.*, Surf. Sci. **307**, 907 (1994).

[5] M. F. López *et al.*, Europhys. Lett. **20**, 357 (1992).

[6] K.-H. Walker, *et al.*, Phys. Rev. B **35**, 1616 (1987).

[7] C. Guillot *et al.*, Phys. Rev. Lett. **39**, 1632 (1977).

[8] O. Björneholm *et al.*, Phys. Rev. B **41**, 10 408 (1990).

[9] J. Barth, *et al.*, Phys. Lett. **74A**, 360 (1979).

[10] D. Chandesris *et al.*, Phys. Rev. B **27**, 2630 (1983).

[11] M. F. López *et al.*, Z. Phys. B **95**, 9 (1994).

[12] M. F. López, *et al.*, Z. Phys. B **94**, 1 (1994).

[13] M. F. López, *et al.*, J. Electron Spectrosc. **71**, 73 (1995).

[14] M. Weinelt *et al.*, Phys. Rev. Lett. **78**, 967 (1997).

[15] W. D. Schneider *et al.*, Phys. Rev. B **28**, 2017 (1983).

[16] C. Laubschat, *et al.*, Phys. Scr. **41**, 124 (1990).