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Spectator states in 3d → 4f resonant photoemission of Eu and Gd metal

M F López and A Gutiérrez

Departamento de Corrosión y Protección, Centro Nacional de Investigaciones Metalúrgicas (CSIC), Avenida Gregorio del Amo 8, Madrid 28040, Spain

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Abstract. We report on a resonant photoemission study of Gd and Eu metal at the M_V x-ray absorption threshold. The 4f photoemission signal exhibits a strong enhancement at resonance which is due to a true resonant photoemission process. For a photon energy corresponding to a satellite structure in the absorption spectra, a ^{5}X final state assigned to a spin-flip phenomenon in the excitation process is observed. Resonant photoemission spectra of the 4d states of Gd and Eu metal at the M_V thresholds are also presented. No enhancement of the 4d emission is found. However, the appearance of a large emission at ≈8 eV higher binding energy is observed. It is proposed that this feature originates from a more probable Auger transition, which reduces the probability of a resonant photoemission of the 4d states.

1. Introduction

The phenomenon of resonant photoemission (PE) is understood as an interference between direct PE and a discrete de-excitation of the core excited state, occurring at energies close to a core excitation threshold [1–8]. Resonant PE is well established for rare-earth (RE) materials, particularly in the case of the 4d → 4f threshold [9–11], but also at the 3d → 4f threshold [12–15]. Apart from variations of the intensities of the different multiplet lines upon tuning the photon energy across an absorption threshold, very weak states, which are absent in non-resonant PE spectra, can be observed at resonance. This is the case for ^{5}X final states in Gd, which were first observed at the 4d → 4f resonance by Gerken *et al* [16], and were explained in terms of a spin-flip process in the Auger decay, in which the excited 4f electron acts as a spectator. Subsequent studies at the 3d threshold [12] revealed that the appearance of ^{5}X states is related to a particular absorption channel given by a satellite in the x-ray absorption (XAS) spectrum, which is not described by calculations based on the dipole approximation. Therefore, at least at the 3d threshold, the spin flip appears to occur in the excitation process.

In the present article, we report on a comparative resonant PE study of polycrystalline Eu and Gd metal at the 3d absorption threshold. Qualitatively, the same effects as are observed for Gd are observed for the 4f states of divalent Eu metal. In Eu metal, the energy separation between the ^{7}F and ^{5}X states is about 10% smaller than that in Gd metal, as expected from its lower atomic number. The resonant PE of the 4d states is suppressed due to resonant Auger emission, where the excited 4f electron acts as a spectator and the 4d electrons are involved in the recombination of the 3d hole.

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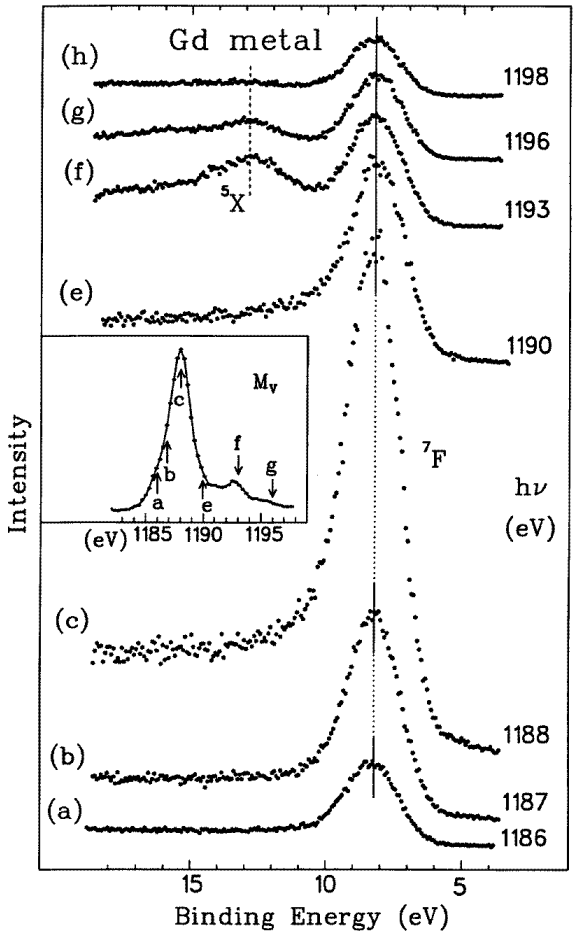

Figure 1. Resonant $4f^6$ final-state PE spectra of Gd metal taken at various photon energies in the region of the M_V absorption threshold. The inset shows the M_V XANES spectrum, with the arrows indicating the photon energies at which the PE spectra were taken. Note the resonance of the ^{5}X satellite at a photon energy corresponding to satellite (f) in the M_V absorption spectra.

2. Experimental details

The measurements were performed with the double-crystal monochromator (KMC) at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY), using beryl crystals. The PE spectra were recorded with a hemispherical electron-energy analyser (VG-CLAM), with the total-system energy resolution set to ≈1.5 eV. X-ray absorption near-edge structure (XANES) spectra were taken at the M_V threshold in the total-electron-yield mode. The samples studied were in polycrystalline form: in the case of Gd, the sample was a bulk piece of metal that was repeatedly scraped with a diamond file in order to remove surface contaminants; Eu was studied in the form of a metal film (100 Å thick) deposited onto a copper substrate. Fresh surfaces were prepared every 20 minutes. The base pressure in the UHV chamber during the measurements was better than 2×10^{-10} mbar.

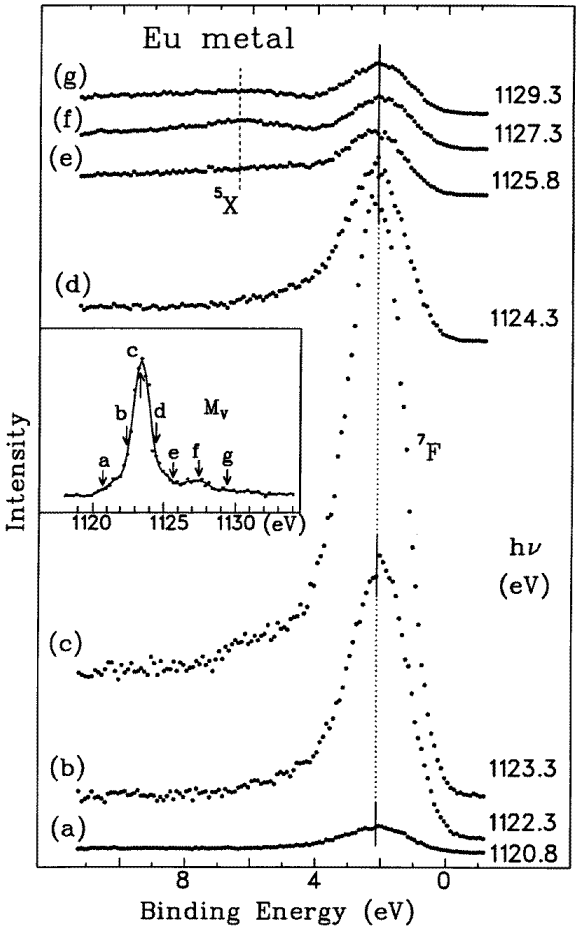

Figure 2. Resonant $4f^6$ final-state PE spectra of Eu metal taken at various photon energies in the region of the M_V absorption threshold. The inset shows the M_V XANES spectrum, with the arrows indicating the photon energies at which the PE spectra were taken. Note the resonance of the ^{5}X satellite at a photon energy corresponding to satellite (f) in the M_V absorption spectra.

3. Results and discussion

Figure 1 shows 4f PE spectra of Gd metal taken at various photon energies in the region of the M_V absorption threshold. For an appropriate reference for the photon energies, the total-electron-yield XANES spectrum is shown in the inset; the vertical arrows refer to the labelling of the PE spectra. At the absorption maximum (spectrum (c)), a strong enhancement of the electron intensity is observed in the region of the ^7F_J final-state multiplet. This is the well-known 3d → 4f resonant PE process [12], where the $3d^94f^8$ core excited intermediate state decays via a Coster–Kronig Auger process to the PE final state. Note the satellite at ≈5 eV higher binding energy in the (f) and (g) spectra, which resonates at the photon energy corresponding to satellite (f) in the absorption spectrum (see the inset). At this point we should note that there are no noticeable Auger structures in the resonant PE spectra of Gd metal, which would apparently move to higher 'binding energies' with increasing photon energies. This is in contrast to observations at the L_{III} and

M_{III} absorption thresholds of 3d transition metal materials, where Auger emissions were observed for photon energies slightly above the absorption maxima [17, 19].

Figure 2 displays the analogous 4f PE spectra of Eu metal taken at various photon energies in the region of the M_V absorption threshold. The labelling of the PE spectra refers again to the photon energies defined by the vertical arrows in the XANES spectrum given in the inset. At the photon energy of the absorption satellite in the XANES spectrum (PE spectrum (f)), again a satellite at ≈4.5 eV higher binding energy with respect to the main ^7F_J multiplet is observed. The resonance behaviour of this satellite is quite similar to the case for Gd metal, as both behaviours originate from ^5X PE final states.

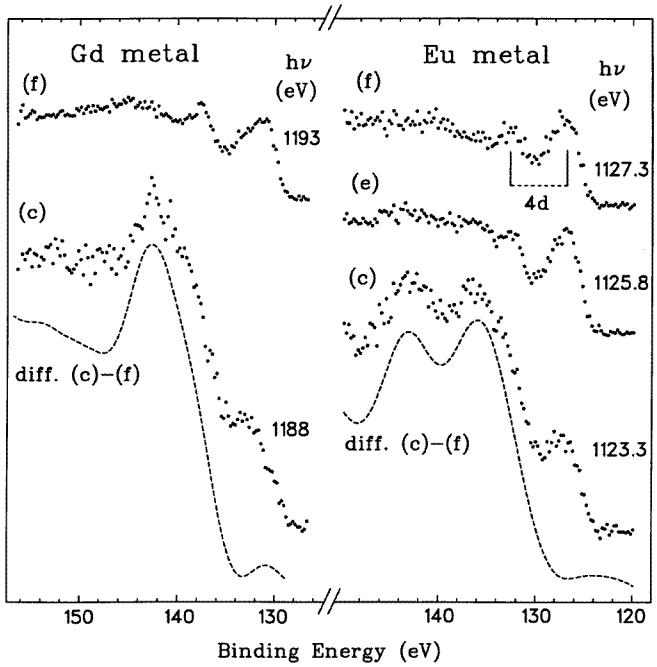

Figure 3. Photoelectron spectra of the 4d states of Gd (left-hand panel) and Eu metal (right-hand panel) taken at photon energies in the region of the Gd and Eu M_V absorption thresholds, respectively. The labelling of the spectra refers to the insets in figures 1 and 2. The dashed curves represent difference spectra.

Figure 3 shows the 4d PE spectra of Gd (left-hand panel) and Eu metal (right-hand panel) taken at photon energies in the region of the M_V absorption thresholds. The spectra are normalized to the photon flux in both cases. The results show that 4d PE intensities remain unchanged when the photon energy is varied across the resonance. However, at the resonance maximum, the appearance of a large peak at about 8 eV higher binding energy is observed. This huge emission disappears at larger photon energies. In particular, this signal is not observed for the photon energy corresponding to the XANES satellite. The general behaviour is similar for Gd and Eu, but for Eu a double-peaked feature instead of a single line is observed at about the same energy relative to the 4d emission. This difference in the spectral shape is not an indication of different natures of these resonant structures.

An explanation for the appearance of the additional spectral structures may be given in terms of different spin configurations, in analogy to the appearance of the ^5X states in the 4f spectra. To see how this can be produced, it is instructive to consider the processes leading

to a resonant enhancement of a 4d emission. Since in the ground state, $4f^7$, the 4f shell is half-filled, after the 3d → 4f excitation, only the excited electron has the correct spin orientation for recombination with the 3d hole. A true resonant photoemission process would be given by the interference between the 4d Auger electron emitted after recombination of the 4f electron with the 3d hole, and the 4d photoelectron originated by direct PE. However, an additional de-excitation channel, consisting in the decay of a 4d electron and the emission of a 4f electron, competes with the Auger process which can lead to resonant photoemission (4f decay and 4d emission). For the $4f^8 3d^9 \rightarrow 4f^7 3d^{10}$ recombination there is only one possibility, but for the $4d^{10}3d^9 \rightarrow 4d^9 3d^{10}$ recombination there are five possible channels, corresponding to the five 4d electrons with the correct spin orientation. Therefore, assuming the same recombination probabilities for a 4f and a 4d electron, as might be taken to be indicated by the similar radial distribution functions, the probability of getting a 4f final-state configuration that is not ^{8}S is $(5/6) \times (7/8) = 0.73$, where the second factor gives the probability of ejecting any f electron except the spectator. On the other hand, the probability of getting a 4f final-state configuration that is ^{8}S, i.e., with all 4f final electrons with the same spin orientation, is the probability of the occurrence of the $4f^8 3d^9 \rightarrow 4f^7 3d^{10}$ recombination plus the probability of the excitation of the 4f electron with the minority-spin orientation after the $4d^{10}3d^9 \rightarrow 4d^9 3d^{10}$ recombination—that is, $(1/6)+(5/6\times 1/8) = 0.27$. From this simple probability calculation, we can deduce that the most favourable final-state configuration of the 4f states after the 3d → 4f excitation is the one that leaves the 4f excited state as a spectator. The existence of this stronger channel could also have the effect of reducing the possibility of Fano resonance of the 4d states, in nice agreement with the experiment.

4. Conclusions

In summary, the resonant 4f PE spectra of Gd and Eu metal in the region of the M_V thresholds behave like resonant PE processes. For photon energies corresponding to the absorption satellite, a ^{5}X emission is observed. In contrast with the case for transition metals [17, 18], no Auger emission is observed at photon energies close to the absorption threshold. This may be due to the highly localized character of the 4f states. In the transition metal systems, the less-localized character of the 3d states leads to a loss of coherence between the two possible channels, and just a superposition of the two is obtained. For the rare-earth case, the process is a resonant photoemission phenomenon, due to the coherence between the two channels. The same conclusion has been reached previously for the case of CeGd metal using an angle dependence experiment [19]. In the case of the 4d PE spectra of Gd and Eu metal in the region of the M_V resonance, no enhancement of the 4d signal was observed. However, for a photon energy corresponding to the maximum of the M_V threshold, additional spectral features appear at ≈8 eV with respect to the 4d-emission binding energy, with a higher intensity than the 4d signal. These features may be ascribed to a strong Auger emission that could reduce the probability of a Fano resonance process.

Acknowledgments

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