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LETTER TO THE EDITOR

The origin of the EXAFS-like structure in secondary electron spectra above $M_{2,3}VV$ Auger lines of 3d metals

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Abstract. It is shown that the generally accepted so-called re-emission model for the formation of the extended fine Auger structure (EXFAS) in secondary electron spectra above $M_{2,3}VV$ Auger lines of 3d metals fails to account for this structure. The straight calculations reveal that the 3d indirect excitation (re-emission) process ($3p^63d^{10} \rightarrow 3p^53d^{10}\epsilon'd \rightarrow 3p^63d^9\epsilon f$) contributes about 10–15% to the total 3d-shell ionization cross-section in the case of Cu. The mechanism for EXFAS formation is proved to be the same as that for EELFS. Namely, the EXFAS structure is due to the direct electron emission from both 3p and 3d closely spaced shallow levels and is mainly determined by the oscillations of the f-partial density of the final states. The adequacy of the mechanism proposed is confirmed by the reasonable agreement of the theoretical Cu $M_{2,3}$ EELFS and EXFAS spectra with the experimental ones.

In early investigations, the extended fine Auger structure (EXFAS) in secondary electron spectra observed on the high-energy side of the $M_{2,3}VV$ Auger line for the 3d metals was assigned to a diffraction effect [1]. More recently the good agreement between EXFAS, the extended x-ray absorption fine structure (EXAFS), and the electron energy loss fine structure (EELFS) enabled the authors [3, 4] to propose the EXAFS-like origin of EXFAS. Although the problem of the relative contributions of the EXAFS-like and diffraction effects still remains [5, 6], it has been convincingly shown through the use of angle-integrated spectrometers that the EXAFS-like mechanism may dominate EXFAS [6].

In the EXFAS experiment, an incoming electron of energy around several keV is inelastically scattered by an atom, causing the excitation of a core electron to continuum. The measured oscillations in the secondary electron spectra for the transition metals are generally considered [3, 4, 6, 7] to be caused by the Auger-like process (figure 1) leading to the electron emission from the conduction sd band. The latter occurs due to the recombination of the electron–3p-hole pair created by the incoming electron impact. The oscillations of the partial densities of the intermediate (k) and final (n) states are considered to give rise to EXFAS. The first attempt to describe EXFAS within this scheme has been made in [7]. However, the calculations carried out in [7] have included adjustable parameters and, therefore, are not considered to lead to a reliable conclusion.

In this paper we show that the mechanism for the EXFAS formation above the $M_{2,3}$ edge for the 3d transition metal edge is the same as that for EXAFS and EELFS [8]. The adequacy of the model proposed is confirmed by the reasonable agreement of the theoretical Cu $M_{2,3}$ EXFAS and EELFS spectra with the experimental ones.

There are, in fact, two steps in our studies. First, we have evaluated the contribution of the Auger-like indirect 3d-ionization process (diagrams (b) and (c) in figure 2) into the

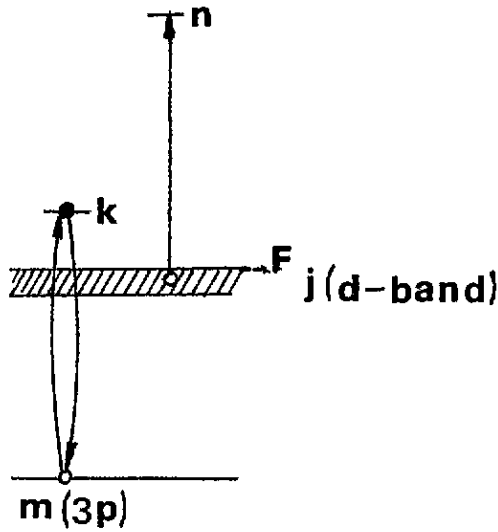


Figure 1. A schematic representation of the re-emission mechanism proposed for EXFAS [3, 4, 6, 7].

total 3d-emission probability. The calculations of the amplitude, M_1 , of this process have been carried out using the Green's function method as described earlier [9]. The total probability amplitude for 3d electron emission is equal to the sum of the amplitudes of the direct process, determined by diagram 2(a) (M_2) and the indirect one (M_1):

$$I \equiv |M_1 + M_2|^2 = |M_1|^2 + 2 \operatorname{Re} M_1^* M_2 + |M_2|^2 \equiv I_1 + I_2 + I_3. \quad (1)$$

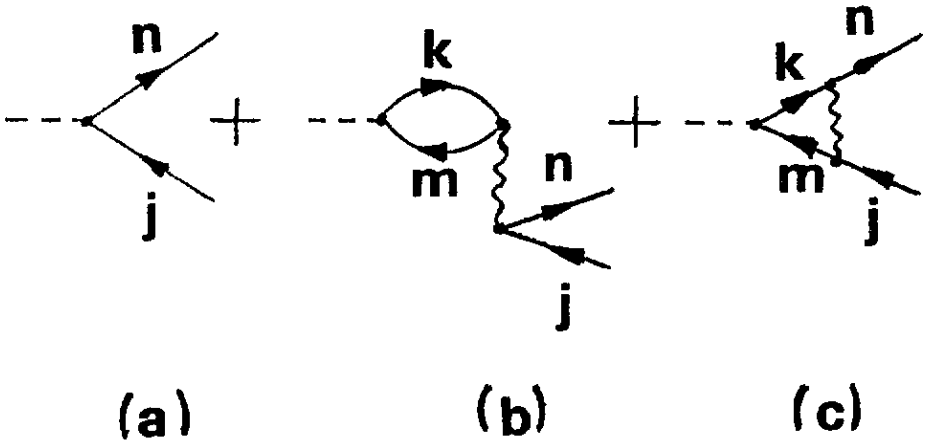


Figure 2. The emission amplitude from the j level in the first order of the perturbation theory. The lines with the arrows to the right and to the left denote the electrons and holes respectively; the dashed line denotes the photon (or primary electron) while the wavy line presents the Coulomb interaction.

The calculations have been performed for the $M_{4,5}$ excitation process in a copper crystal. For simplicity, we have considered only the photoexcitation process. The results of our

numerical studies are presented in figure 3 where the intensities I , I_1 and $I_1 + I_2$ are displayed versus the kinetic energy of the ejected electron. One can see that the contribution of the indirect process is mainly determined by the interference term I_2 , which provides, nevertheless, no more than 10–15% of this process. Hence, the 3d-shell emission intensity is mainly due to the one-electron direct $3d \rightarrow \epsilon f$ excitation process, whereas the indirect many-electron processes can be ignored.

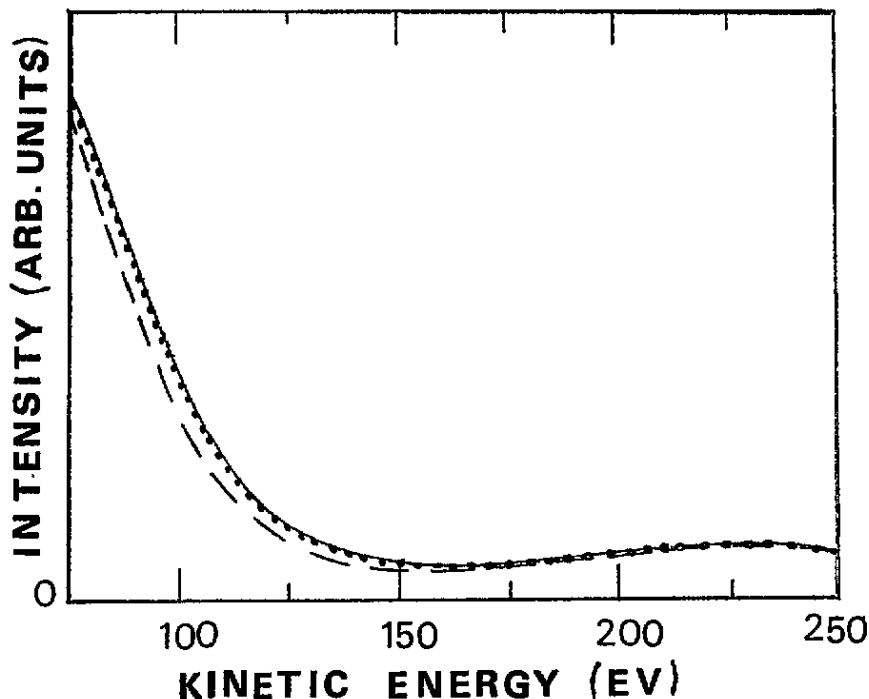


Figure 3. The atomic contributions into the Cu $M_{4,5}$ -photoemission intensity versus the electron kinetic energy: I_1 is the intensity due to only the direct $3d \rightarrow \epsilon f$ excitations (dashed curve), $I_1 + I_2$ is the intensity including the interference term in formula (1) (dotted curve) and I is the total intensity (full curve).

The second step of our studies concerns the contributions of the direct 3p- and 3d-ionization processes into EXPAS and EELFS. In our recent paper [8] we have shown that to achieve good agreement between the theoretical and experimental $M_{2,3}$ BELFS (or EXAFS) one should add together both 3p ($\sigma_{3p}(E)$)- and 3d ($\sigma_{3d}(E)$)-shell EXAFS-like contributions to the total cross-section

$$\begin{aligned} \sigma(E) &= \sigma_{3p}(E) + \sigma_{3d}(E) = S_{3p}(E)(1 + \chi_{3p}(k_{3p})) + S_{3d}(E)(1 + \chi(k_{3d})) \\ &\equiv S(E)[1 + \chi(E)] \end{aligned} \quad (2)$$

where $k_{nl} = (E - I_{nl} - \epsilon_{mt})^{1/2}$ is the wavevector of the electron ejected from the nl shell; E is the incoming electron energy loss (or photon energy); I_{nl} is the ionization energy of the nl shell determined relative to the vacuum level; ϵ_{mt} is the averaged interstitial potential relative to the vacuum level; $S_{nl}(E)$ and $S(E) \equiv S_{3p}(E) + S_{3d}(E)$ are the nl -shell and the

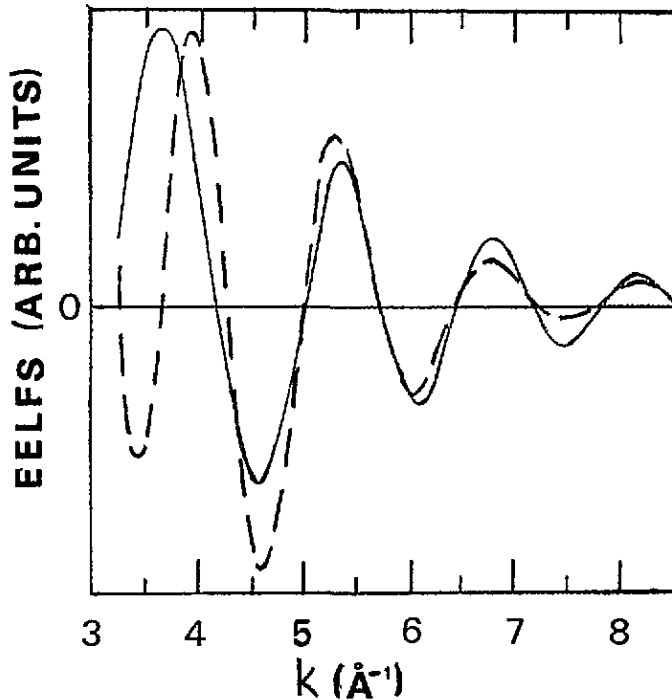


Figure 4. Comparison between the theoretical and experimental unnormalized Cu $M_{2,3}$ EELFS spectra versus $k = (E - E_0)^{1/2}$ ($E_0 = 74$ eV) weighted by a factor k : the spectrum calculated within a nearest-neighbour approach $S(k)\chi(k)k$ (full curve) and the Fourier filtered nearest-neighbour contribution to the EELFS signal detected in the second derivative mode [10] (dashed curve).

total atomic ionization cross-sections respectively; the normalized fine structure $\chi_{nl}(k)$ is defined as usual [2].

To calculate EXFAS one should also add together the similar contributions, but unlike EELFS or EXAFS, these contributions should be determined for the same kinetic energy (E_{kin}) of the electrons ejected from 3p and 3d levels. Therefore, in the case of EXFAS, one needs to use in (2) E_{kin} instead of E and to consider $k_{3p} = k_{3d} = (E_{\text{kin}} - \epsilon_{\text{ml}})^{1/2}$.

It is worth noting that the application of EXAFS-like formulae for the valence 3d-shell ionization process is justified by the atomic-like character of the 3d wavefunctions in 3d atoms in solids and small widths of the 3d bands in comparison with the lengths of the EXAFS oscillations.

As far as the normalized fine structure, $\chi(E)$, in equation (2) depends on the atomic partial cross-sections $S_{nl}(E)$, one needs to determine those in the case of the electron excitation process. We have calculated these cross-sections in the Born approximation, taking into account only dipole-resolved transitions into $(l + 1)$ states, employing the equations similar to those used in [8, 11].

The calculations of the $M_{2,3}$ EXFAS and EELFS spectra for polycrystalline Cu have been carried out within a nearest-neighbour approach for the fully angle-integrated scheme for the incoming electron energy equal to 2 keV. The method developed earlier [12] for calculating the atomic scattering amplitudes and phase shifts has been applied. A Debye-Waller factor $\sigma^2 = 0.0043$ [au]² has been used. In order to compare experimental and theoretical spectra

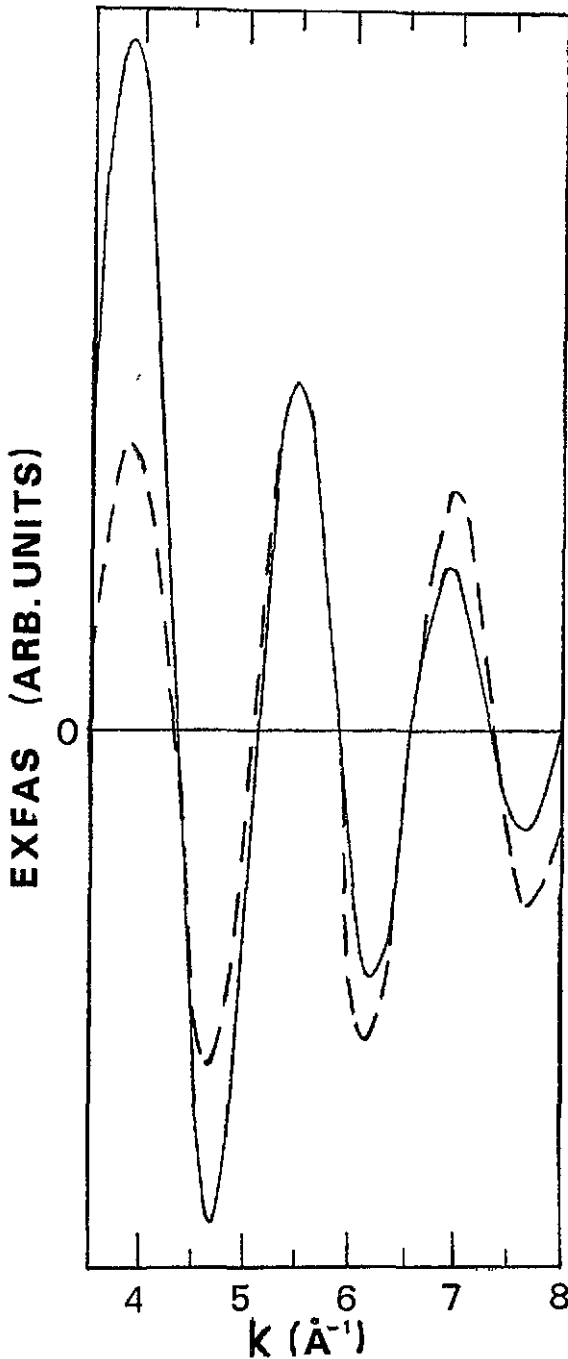


Figure 5. Comparison between theoretical and experimental unnormalized Cu $M_{2,3}$ EXFAS spectra versus $k = (E - E_0)^{1/2}$ ($E_0 = 60$ eV) weighted by a factor k : the spectrum calculated within a nearest-neighbour approach $S(k)\chi(k)k$ (full curve) and the Fourier filtered nearest-neighbour contribution to the EXFAS signal from [6] (dashed curve).

on the absolute energy scale, the data obtained by the x-ray photoelectron spectroscopy [13] have been used for the nl -shell ionization energies: $I_{3p} = 79$ eV, $I_{3d} = 7$ eV.

Our results for the unnormalized fine structures $S(k)\chi(k)k$ in comparison with the experimental Fourier filtered signals (weighted by k) [6, 10] are presented in figure 4 for EELFS and in figure 5 for EXFAS. The common k -scale is defined as $k = (E - E_0)^{1/2}$. E_0 is chosen at the $M_{2,3}$ VV Auger line for EXFAS (60 eV in kinetic energy scale) and at the inflection point for EELFS (74 eV in energy loss scale). One can see that, like the case of Ni $M_{2,3}$ EXAFS [8], the reasonable agreement between the theoretical and experimental spectra proves the adequacy of the mechanism and calculational method proposed. The noticeable disagreement between relative intensities of the experimental and theoretical spectra can be caused by the approximations made or by the errors in the background subtraction from the experimental EELFS and EXFAS spectra. The latter may also cause the mismatch around 3.5 \AA^{-1} .

The results obtained reveal that, contrary to the widespread opinion, the mechanism of the $M_{2,3}$ EXFAS and EELFS formations in the 3d metals is common. Both fine structures are mainly due to the direct $3d \rightarrow \epsilon f$ transitions. The indirect processes contribute only around 10–15% in the case of Cu $M_{2,3}$ EXFAS. As regards the atoms with the unoccupied 3d shell, in which strong resonance $3p \rightarrow 3d$ transitions in intermediate states are present giving rise to giant resonances in photoabsorption and resonant photoemission, additional investigation has to be performed.

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