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ON THE NATURE OF NONSTRUCTURAL LOW-R PEAK IN FOURIER TRANSFORMS OF SOME EXAFS-SPECTRA

A.G. KOCHUR, A.M. NADOLINSKY and V.F. DEMEKHIN

*Rostov Railway Engineers Institute, Chair of Physics,
344017 Rostov-on-Don, U.S.S.R.*

ABSTRACT

K-absorption spectra of krypton and zirconium are calculated considering additional monopole excitations of 3d-shell. It is shown that the disturbance of smoothness of the atomic photoionization cross section due to multi-electron excitations including 3d-shells lead to the appearance of low frequency EXAFS-oscillations that do not correspond to the structure of atomic encirclement of the absorber. Such an effect can make data analyses difficult for the spectra with weak structural signal.

It is known that magnitudes of the fourier transforms (FT) of some EXAFS-spectra have low-R peaks which cannot be attributed to any interatomic distances^[1]. This means that the normalised spectra

$$\chi = \frac{\mu - \mu_0}{\mu_0} \quad (1)$$

contain low-frequency oscillations. Here μ_0 is the absorption coefficient of an isolated atom which is normally supposed to be a smooth discenting curve and is being obtained approximating experimental spectrum with a comparatively smooth analytical function.

Studying the spectrum of gaseous krypton it was supposed^[2] that the low frequency oscillations of χ may be incorporated in μ_0 and be caused by multielectron excitations. Peaks in FT of ZrK-spectra of amorphous Zr-Ni alloys were obtained at $R \sim 1 \text{ \AA}$ ^[3]. It was supposed that each minimum of corresponding low-frequency oscillations of χ is caused by the additional excitation of the specific nl-level.

This paper's aim is to study theoretically how the effects of multiple ionization influence the shape of absorption spectra far beyond the edge and how this may affect the EXAFS data analyses via FT method.

K-absorption spectra of Kr and Zr were calculated considering additional monopole excitations $3d \rightarrow \{n, \xi\}d$.

Atomic photoionization cross section may be expressed through a matrix element of dipole transition operator :

$$M = \langle f | D | i \rangle \quad (2)$$

$|i\rangle$ and $|f\rangle$ being the wavefunctions of initial and final states. One-electron wavefunctions of $|i\rangle$ were obtained by solving the Hartree-Fock (HF) equations for the configurations $K_0 = 1s^2 2s^2 2p^6 - 3s^2 3p^6 3d^{10} 4s^2 4p^6$ in Kr, and $K_0 = [Kr] 4d^2 5s^2$ in Zr. Calculating $|f\rangle$, the monopole core electrons' rearrangement was taken into consideration: radial nl -orbitals were obtained from HF equations for the configuration $K_1 = 1s^{-1} \xi p$ (the populations N_{nl} will be hereafter noted relatively to K_0). Substitution of $|i\rangle$ and $|f\rangle$ in (2) by their one-determinant functions leads^[4] to the following expression for the K-ionization matrix element:

$$M_1(\xi) = N \left(\langle \xi p_+ | r | 1s \rangle - \sum_{n=2,3,4} \frac{\langle \xi p_+ | np \rangle \langle np_+ | r | 1s \rangle}{\langle np_+ | np \rangle} \right), \quad (3)$$

where $N = \frac{1}{\langle 1s_+ | 1s \rangle} \prod_{nl} \langle nl_+ | nl \rangle^{N_{nl}}$, N_{nl} are the population numbers of K_0 , "+" sign denoting the nl -functions of K_1 .

The final state for $K_{4,5}$ -ionization is described by the configuration $K_2 = 1s^{-1} 3d^{-1} \xi' p \{n, \xi''\} d$, $\xi' p$ -orbitals being the same as in previous calculation while $\{n, \xi''\} d$ -orbitals were obtained in a potential formed by the core $1s^{-1} 3d^{-1}$ constructed of the orbitals of configuration K_1 . $K_{4,5}$ -ionization matrix element may be obtained by substituting $|i\rangle$ and $|f\rangle$ in (2) by the functions of K_0 and K_2 :

$$M_2(\xi) = \langle \{n, \xi''\} d | 3d \rangle M_1(\xi') \quad (4)$$

where $\xi = 0$ at the K-ionization threshold.

If E_K is the K-ionization threshold energy and E_{KM}^n , E_{KM} are the energies of KM-excitations and KM-ionization then when excitation takes place

$$\xi = \Delta E_{KM}^n + \xi' \quad (5a)$$

and during ionization

$$\varepsilon = \Delta E_{KM} + \varepsilon'' + \varepsilon' \quad (5b)$$

where $\Delta E_{KM}^n = E_{KM}^n - E_K$; $\Delta E_{KM} = E_{KM} - E_K$

Let $\sigma_1(\varepsilon) \sim N_{1s} M_1^2(\varepsilon)$ be the K-ionization cross section at the energy ε beyond the edge. Then using (4,5) and omitting a weak dependence of cross section on photon energy one has the following expression for the multiple excitation cross section:

$$\begin{aligned} \sigma_2(\varepsilon) = N_{3d} \left[\sum_{\substack{n \geq 4 \\ \varepsilon - \Delta E_{KM}^n \geq 4}} N_{nd}^h \langle nd | 3d \rangle^2 \sigma_1(\varepsilon - \Delta E_{KM}^n) \right. \\ \left. + \int_0^{\varepsilon} \langle \varepsilon'' d | 3d \rangle^2 \sigma_1(\varepsilon - \Delta E_{KM} - \varepsilon'') d\varepsilon'' \right] \quad (6) \end{aligned}$$

Here N_{nd}^h is the number of vacancies in nd-shell. ΔE_{KM}^n and ΔE_{KM} were calculated as differences of full energies of corresponding atomic hole states, they are $\Delta E_{KM}^4 = 117.4$ eV, $\Delta E_{KM} = 126.1$ eV for Kr and $\Delta E_{KM}^4 = 207.6$ eV, $\Delta E_{KM}^5 = 225.9$ eV, $\Delta E_{KM} = 231.3$ eV for Zr. Only two terms in the sum of (6) were considered because the overlap integrals $\langle nd | 3d \rangle$ decrease sharply while increasing n (see table 1).

n \ Atom	Kr	Zr
4	-0.0318	0.0319
5	0.0040	0.0112
6	—	0.0037

Table 1.

Overlap integrals $\langle nd | 3d \rangle$.

Calculated spectra are shown

in fig. 1. For the comparison with the experiment the spectra were convoluted with a gaussian curve. At the $KM_{4,5}$ threshold there is a slight rise of spectrum due to the opening of channels for the additional discrete $3d \rightarrow nd$ excitations. At the region beyond the $KM_{4,5}$ threshold

the descent of spectrum becomes noticeably less steep which is caused by the donation of double transitions $1s3d \rightarrow \varepsilon_p' \varepsilon'' d$, $3d$ -electrons going into the states of continuous spectrum.

Calculated spectra were treated via the standard FT method using a polynomial approximation for μ_0 . Approximation of the spectra having the features described above with a polynomial (or any other smooth curve) on a wide energy scale leads to multiple intersection of the true μ_0 function with the approximating curve. This leads to the appearance of low frequency oscillations in $\chi(1)$ which give rise to nonstructural low-R peaks in FT's of the spectra. Fig. 2 shows the magnitudes of FT for calculated and experimental Kr and Zr spectra having the peaks at $R \sim 1$ Å.

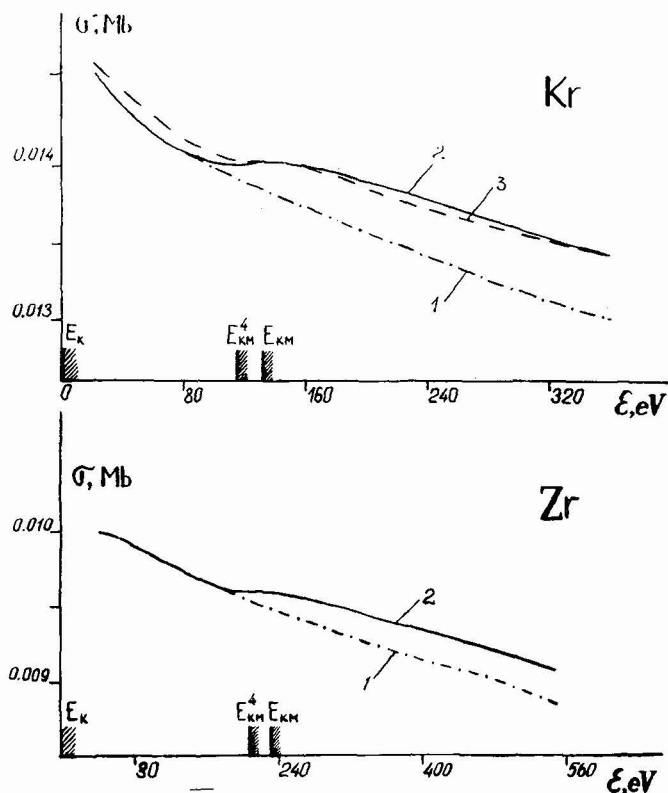


Figure 1.
Atomic K-absorption spectra.

- 1 - calculated not considering $KM_{4,5}$ -ionization;
 2 - calculated considering $KM_{4,5}$ -ionization;
 3 - experiment [2].

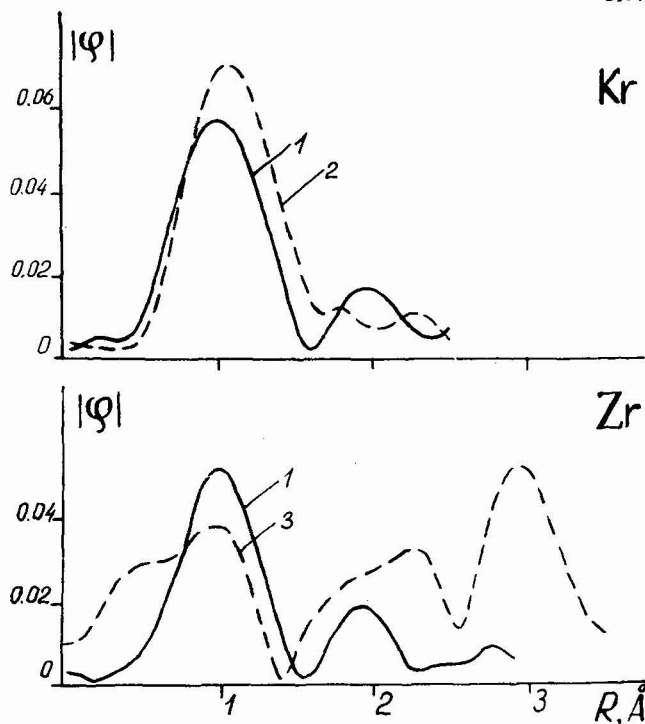


Figure 2.
Magnitudes of FT
 1 - calculated spectra
 2 - experimental spectrum of gaseous Kr [2],
 3 - experimental spectrum of amorphous alloy $Ni_{0.241}Zr_{0.759}$ [3].

One should expect that nonstructural maxima of the same origin may appear in FT's of another atoms' absorption spectra. The leading role must be played by the additional monopole excitations $nl-\{n, \ell\}l$ having the thresholds $100 + 300$ eV beyond the edge of single ionization. In this case the smoothness of atomic cross section is affected in the region crucial for EXAFS data analyses. The main donation will be from the additional ionizations of nl -shells with the highest l for they have maximum probability^[5]. Therefore the effect discussed will be most noticeable in spectra of heavy atoms where $100 + 300$ eV deep are the levels of d - and f -symmetry, though the influence of $2p$ -additional ionizations must be investigated for lighter elements.

The amplitude of structural oscillations of χ due to the influence of atomic encirclement may be several times greater than that caused by double ionizations, thus low- R nonstructural FT peak being negligible compared to the structural ones. Nevertheless those amplitudes may become of the same order of magnitude in spectra with weak EXAFS-signal, the meddling FT peak being quite high compared to structural ones. Such a situation may take place in spectra of amorphous compounds^[3]. The effects discussed may be noticeable also in spectra of the compounds where a heavy absorber is surrounded by light ligands having weak backscattering amplitudes. Finally, structural oscillations may be small at high temperatures of substance under study. In this case, as it is known, the structural FT peaks become shorter and widen while multiple ionization peaks must remain unchanged.

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