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X-RAY ABSORPTION SPECTRA THEORY IN VARIABLE
VALENCY COMPOUNDS

ЦНИИатоминформ

ЕРЕВАН-1986

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Կազմված է ռենտգենային L^{III} , M^{IV} , M^V ապեկտրերի որակական տեսությունը, որը բացատրում է ապեկտրի կրկնակի կառուցվածքը / XANES / կլանման եզրում: Առաջարկված է էլեկտրոնային կառուցվածքի մոդելը լավ է նկարագրում կլանման երկու ռեզոնանսային գագաթների հարաբերական ինտենսիվության փոփոխությունը՝ կախված վալենտականությունից՝ ծնշման և ջերմաստիճանի դեպքում:

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А.Н.КОЧАРЯН

ТЕОРИЯ РЕНТГЕНОВСКИХ СПЕКТРОВ ПОГЛОЩЕНИЯ
В СОЕДИНЕНИЯХ С ПЕРЕМЕННОЙ ВАЛЕНТНОСТЬЮ

Построена качественная теория рентгеновских L^III , M^{IV} , M^V спектров поглощения в редкоземельных соединениях с переменной валентностью, объясняющая дублетную структуру спектра вблизи края поглощения (XANES). Предложенная модель электронной структуры хорошо описывает характер изменения относительной интенсивности двух резонансных пиков поглощения при изменении валентности в зависимости от давления и температуры.

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X-RAY ABSORPTION SPECTRA THEORY IN VARIABLE
VALENCY COMPOUNDS

A qualitative theory of X-ray L_{III} , M_{IV} , M_V absorption spectra in anomalous rare-earth compounds with variable valency is constructed, which explains a doublet X-ray absorption near edge structure (XANES). The model of electron structure suggested also describes well the character of variation in relative intensity of two resonance absorption peaks at valency change with pressure and temperature.

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The experiments on high-energy spectroscopy of deep 2p, 3d levels from compounds with variable valency on the basis of heavy rare-earth elements Sm, Eu, Tm, Yb revealed a doublet structure near the X-ray absorption edge (XAS) as well as in photoemission spectra in the X-ray region (XPS) [1]. It turned out that, e.g. the absorption spectrum near the L_{III} ($2p_{3/2}$) edge consists not of one [2] as in case of usual metals, but of two well-resolved maxima spaced by $E \sim 7 \pm 10$ eV. The recent experiments in vacuum ultraviolet revealed by means of synchrotron radiation (SR) two resonance peaks in $M_{IV}(3d_{3/2})$ and $M_V(3d_{5/2})$ absorption spectra from these compounds [3].

Under variation of 4f level occupation number, n_f at phase transition, there takes place a redistribution of maxima intensities, although the positions of the maxima themselves corresponding to absorption edges in pure ionic configurations $4f^n$ and $4f^{n-1}s$ are practically unchanged.

Below we shall give a simple physical interpretation of observed peculiarities of XAS and XPS spectra, which takes account of interaction in the final state of a core hole on 2p shell with sd conduction electrons and with localized f electron on the basis of a simplest spinless model of electron structure of compounds with variable valency, with partially occupied f level E_0 .

near Fermi energy ($E_0 \approx \epsilon_F$), initially hybridized with the broad conduction band (B is the band width).

It will be shown that XAS and XPS spectra contain information about the properties of the ground state at the external conditions variation and about effects of screening and interactions in the final state.

An initial model of electron structure in the absence of interaction with radiation can be taken in the form of the Anderson resonance model:

$$H_i = \sum_K \epsilon_K a_K^\dagger a_K + E_0 f^\dagger f + E_P b^\dagger b + \sum_K V_i (a_K^\dagger f + H. c.) \quad (1)$$

Here the first term is the kinetic energy of sd electrons with constant density of states $\rho \sim B^{-1}$ in conduction band, while the second and third ones are coupling energies of localized $4f$ and $2p$ electrons, respectively. The last term V_i is initial hybridization of s and f electrons.

Under coincidence of f level with Fermi energy or under hybridization of s and f states, when electron configurations with different number of f electrons are close in energy, the assumed wave function of ground state with occupied $2p$ shell turns out to be a quantum superposition of a state with occupied f shell ($4f^n$) and a state obtained from the former one by transferring f electron to the conduction s -band ($4f^{n-1}s$):

$$\Psi_{GS} = (\alpha_0 + \sum_{K > K_F} \beta_K a_K^\dagger f) f^\dagger b^\dagger \prod_{K < K_F} a_K^\dagger |0\rangle \quad (2)$$

where α_0 and β_K satisfy the normalization condition $\alpha_0^2 + \sum_{K > K_F} \beta_K^2 = 1$: the mean occupancy number $n_f = \alpha_0^2$. From the variational equation we find out the coefficient $\beta_K = V_K / (E_{GS} - \epsilon_K)$, where E_{GS} is the ground state energy with hamiltonian (1).

The interaction with radiation results in dipole transitions of electron from $2p$ core level to conduction band:

$$W = \omega \sum_{\kappa} (a_{\kappa}^{\dagger} \beta + \text{H.c.}) \quad (3)$$

Due to hole formation, there takes place in final state the Coulomb interaction of 2p hole with s conduction electrons (g), localized f electron (G) as well as additional hybridization of s and f electrons:

$$H_{\text{int}} = \left\{ -g \sum_{\kappa, \kappa'} a_{\kappa}^{\dagger} a_{\kappa'} - G n_f + \Delta V \sum_{\kappa} (a_{\kappa}^{\dagger} f + \text{H.c.}) \right\} \beta \beta^{\dagger} \quad (4)$$

As a result the system Hamiltonian in final state will take the form:

$$\begin{aligned} H_f &= H_f^{\circ} + \sum_{\kappa} \tilde{V}_f (a_{\kappa}^{\dagger} f + \text{H.c.}) - g \sum_{\kappa, \kappa'} a_{\kappa}^{\dagger} a_{\kappa'} \\ H_f^{\circ} &= \sum_{\kappa} \epsilon_{\kappa} a_{\kappa}^{\dagger} a_{\kappa} + \tilde{E}_o f^{\dagger} f \end{aligned} \quad (5)$$

where $\tilde{E}_o = E_o - G$ and $\tilde{V}_f = V_i + \Delta V$.

The absorption process can be described by means of the correlation function [4] (Kubo formula):

$$F(t) = -i \langle \Psi_{GS} | T W(t) W(0) | \Psi_{GS} \rangle \quad (6)$$

where operator $W(t)$ is calculated in the Heisenberg representation with H_f .

The contribution to singularities near $4f^n$ and $4f^{n-1}_S$ absorption thresholds is made by processes with excited in final state one and two s-electrons, respectively. Accordingly, for photoemission spectra of electrons from deep levels the contributions near $4f^n$ and $4f^{n-1}_S$ thresholds will be made by processes without excitation of s-electron and with excitation of only one s-electron.

After transformations, Eq.(6) is reduced to:

$$F(t) = -in_f \theta(t) \omega^2 \exp(-i(E_p - G)t) \sum_{\kappa, \kappa'} e^{-i\epsilon_{\kappa'} t} \langle g | f a_{\kappa'} S(t) a_{\kappa}^\dagger f^\dagger | g \rangle - \\ - i(1-n_f) \theta(t) \omega^2 \exp(-iE_p t) \sum_{\kappa', \kappa_1, \kappa_2} e^{-i(\epsilon_{\kappa'} + \epsilon_{\kappa_1})t} \langle g | a_{\kappa'} a_{\kappa_1} S(t) a_{\kappa_2}^\dagger a_{\kappa_2}^\dagger | g \rangle \quad (7)$$

Here $S(t) = \exp(iH_f t) \exp(-iH_f t)$ is scattering matrix in final state and $|g\rangle = b^\dagger \prod_{\kappa < \kappa_F} a_{\kappa}^\dagger |0\rangle$.

The correlation function $F(t)$ we consider in most divergent term approximation at $t \rightarrow \infty$ [4] and finally obtain after Fourier transformation the spectrum $F(E)$ near the absorption edge:

$$F(E) = \frac{2\pi\rho\omega^2 n_f}{\Gamma(1-\varphi_1)} \left(\frac{B}{E-E_1}\right)^{\varphi_1} \theta(E-E_1) + \frac{2\pi\rho\omega^2(1-n_f)}{\Gamma(1-\varphi_2)} \left(\frac{B}{E-E_2}\right)^{\varphi_2} \theta(E-E_2) \quad (8)$$

Here $\Gamma(\varphi)$ is the gamma function, $E_1 = E_p - G + E_0$, $E_2 = E_p + E_F$, φ_1 and φ_2 are connected with scattering phase δ by the relations:

$$\varphi_1 = \frac{2\delta}{\pi} - \left(\frac{\delta}{\pi}\right)^2 \quad \varphi_2 = -1 + \frac{4\delta}{\pi} - \left(\frac{\delta}{\pi}\right)^2 \quad (9)$$

where $t g \delta = \tilde{g} \rho$ and $\tilde{g} = g - V_f^2 / (\epsilon_F - \tilde{E}_0)$.

At deriving (8) we neglected in final state the transitions of f-electron from the level to the band as well as backward transitions of s-electron to unoccupied f level. Thus we neglected the so-called "shake-up" and "shake-down" processes which give small corrections of $V_f^2 / G \ll 1$ order. However these contributions, as will be published elsewhere, turn out rather essential at investigation of the processes of resonance photoemission of f-electrons from the light rare-earth compounds like Ce, CeO, CeN, etc.

The absorption spectrum contains at $(2-\sqrt{3})\pi < \delta < \pi$ power-law singularities near absorption edges in configurations $4f^n$ and $4f^{n-1}s$. The

first maximum in position of E_1 refers to $4f^n$ configuration, in which p-hole is well screened by localized f-electron. The second one spaced farther by energy $\Omega = E_f - E_0 + G$ corresponds to $4f^{n-1}s$ configuration with unscreened p-hole. As is seen from (8), intensities of both peaks enter with corresponding weights dependent on n_f and $1 - n_f$. The additional unscreened core-hole potential for 4f electron (G) turns out to be nearly $5 + 10$ eV, which is by an order of magnitude higher than for s-electrons (g) since f electrons are localized nearer to the nucleus [1]. This circumstance may account for the fact that the two configurations $4f^n$ and $4f^{n-1}s$ which are close in energy in the ground state (0.1 - 1 eV) turn out appreciably spaced in the absorption spectra: $G \sim 5 + 10$ eV (see Fig.1). Attenuation of the hole results in p level broadening $\gamma \sim 3$ eV [1]. The attenuation can be taken into account by transition from $E_p \rightarrow E_p - i\gamma$; finally from (7) we obtain:

$$F(E) = 2B\rho\omega^2 n_f \int_0^\infty \frac{dt \exp(-it(E_1 - E - i\gamma))}{(itB)^{1-\varphi_1}} + 2B\rho\omega^2 (1-n_f) \int_0^\infty \frac{dt \exp(-it(E_2 - E - i\gamma))}{(itB)^{1-\varphi_2}} \quad (10)$$

Then, after integration we have:

$$F(E) = \frac{2\pi\rho\omega^2 n_f \Gamma(\varphi_1)}{[(E - E_1)^2 + \gamma^2]^{\varphi_1/2}} \cos\left[\frac{\pi}{2}(1 - \varphi_1) + \beta_1(E)\right] + \quad (11)$$

$$+ \frac{2\pi\rho\omega^2 (1 - n_f) \Gamma(\varphi_2)}{[(E - E_2)^2 + \gamma^2]^{\varphi_2/2}} \cos\left[\frac{\pi}{2}(1 - \varphi_2) + \beta_2(E)\right]$$

where

$$\beta_{1,2}(E) = -\varphi_{1,2} \arctg\left(\frac{E - E_{1,2}}{\gamma}\right)$$

In the limit $\gamma \rightarrow 0$ we arrive at (8). As seen from Fig.1, this leads to partial smearing of the picture and occurrence of two resonance maxima. Here the relative shift of maxima is:

$$\Delta \Omega = \gamma \left(\operatorname{ctg} \frac{\pi}{1-\varphi_1} - \operatorname{ctg} \frac{\pi}{1-\varphi_2} \right) \quad (12)$$

The dependence of n_f on external parameters is to be found from the corresponding consistency equations [5]. This dependence allows to analyze also the character of changes in absorption spectra at variation in temperature, pressure and composition of compounds. The phase transition from divalent to trivalent state (n_f varies from 1 to 0) at variation in composition of $Tm_x Y_{1-x} Se$ results in intensity decrease for the first maximum and increase for the second one [3]. Experiments under pressure in SmSe at transition from divalent to trivalent state revealed also a direct correlation between the decrease of $n_f(\rho)$ and redistribution of intensity maxima (see Fig.2), in the pressure range up to 60 kbarn [6]. The direct dependence of the absorption spectrum variation on n_f follows also from the analysis of its temperature variation in $EuPd_2 Si_2$ [7].

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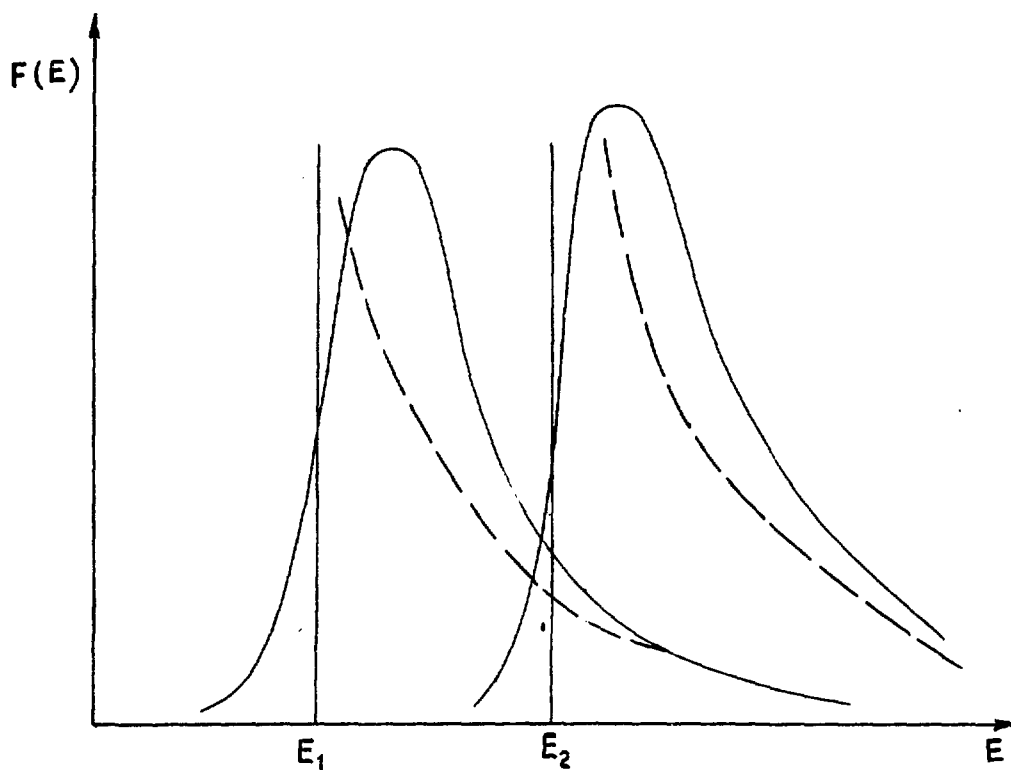


Fig.1. The doublet structure of absorption spectrum in the variable valency state with $\chi = 0$ (solid curve refers to the case $\chi \neq 0$).

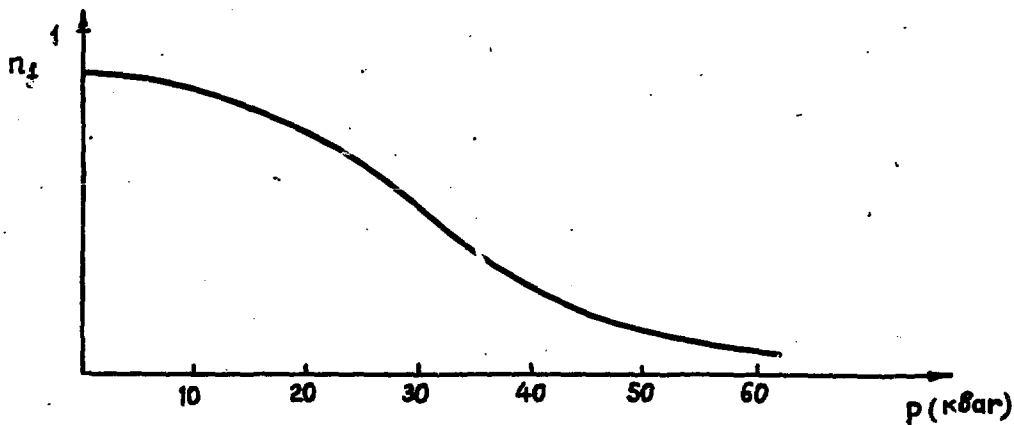
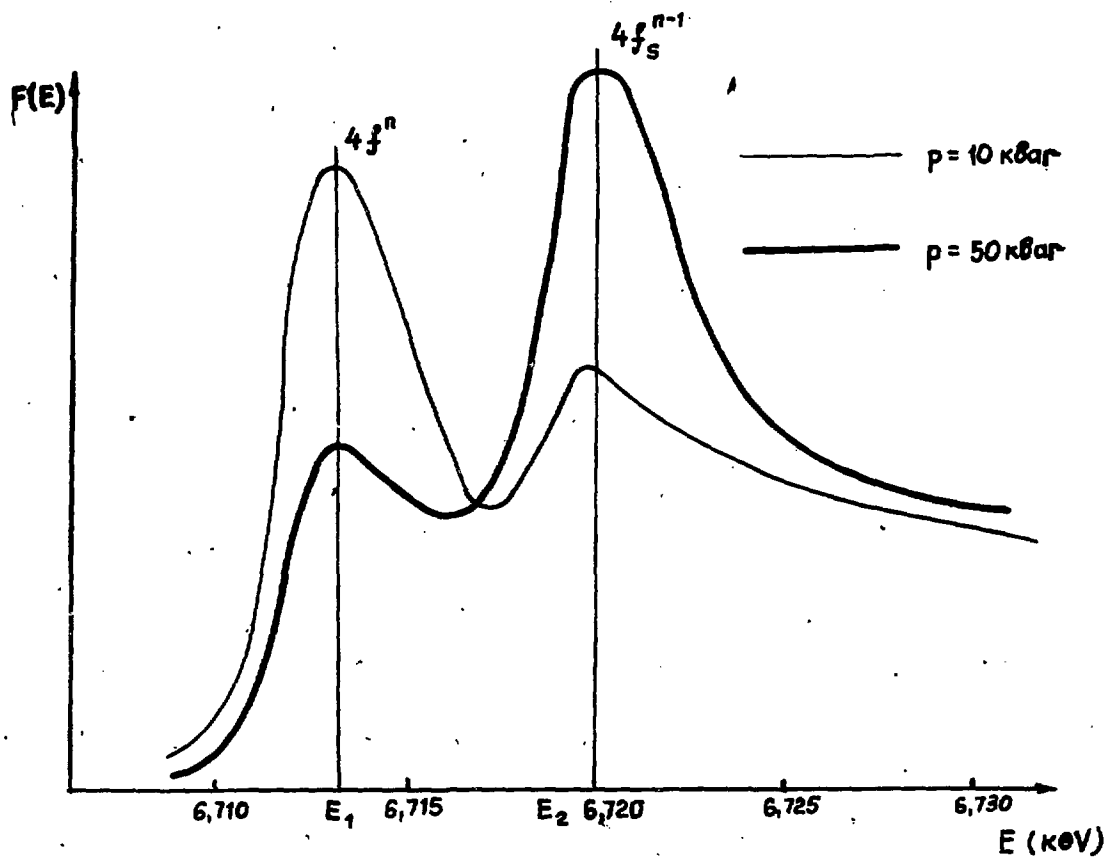


Fig.2. The variation of the absorption spectrum coefficient and n_s under pressure in SnSe .

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