

Doublet structure of x-ray spectra and final-state interaction of the valence-fluctuation compounds

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The x-ray absorption and emission spectra are calculated in an exactly solvable model which takes into account the interaction of the s and f electrons with the localized p hole. An explanation is offered for the structural features in the spectra of the valence-fluctuation compounds observed upon changing the external conditions.

1. Experimental studies of x-ray absorption (XAS) and photoelectron emission (XPS), which make use of synchrotron radiation, have revealed the presence of two well-resolved peaks, separated in energy by $\Delta \sim 7-12$ eV, in the L_{III} , M_{IV} , and M_V x-ray spectra of the valence-fluctuation compounds when the electron is transferred from the deep $2p$ and $3d$ shells, respectively, to the Fermi level and to the states above the vacuum level.^{1,2} These data can be used to distinguish between the contributions of the two electronic configurations, $4f^n$ and $4f^{n-1}s$, which are in the ground state at resonance, and to determine the valence or the occupation number (n_f) of the f level from the relative intensity of the peaks. A change of the external conditions results in a redistribution of the intensities of the peaks which reflect the change in n_f .^{2,3}

In the present letter we give a qualitative description of these structural features of the x-ray spectra near the electron absorption and emission edge in a simple model of valence-fluctuation compounds which takes into account the quantum fluctuations of the ground-state electron and the Mahan-Noziers-De Dominicis final-state interaction.^{4,5}

2. Let us examine the resonant model of the electronic structure of valence-fluctuation compounds, in which the f level lies below the Fermi level ($E_0 \leq E_F$) and is hybridized (V_i) with the conduction band (ϵ_k) with a constant state density ρ :

$$H = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + E_0 f^{\dagger} f + \sum_{\mathbf{k}} (V_i a_{\mathbf{k}}^{\dagger} f + \text{H.a.}) - E_p b^{\dagger} b + \{-g \sum_{\mathbf{k}'\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}'} - G f^{\dagger} f + \Delta V \sum_{\mathbf{k}} (a_{\mathbf{k}}^{\dagger} f + \text{H.a.})\} b b^{\dagger}. \quad (1)$$

Here E_p is the binding energy of the electron in the $2p$ shell, reckoned from the conduction band bottom. The last term is the Coulomb interaction of the system of s and f electrons with a hole formed in the final state.

In the absence of a hole in the ground state ($b^{\dagger} b = 1$), the trial wave function can be written as a quantum superposition of the $4f^n$ state and a state obtained from it as a result of the transition of a single f electron to the conduction band ($4f^{n-1}s$):

$$\Psi_{GS} = (\alpha_0 + \sum_{\mathbf{k} > k_F} \beta_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} f) f^{\dagger} b^{\dagger} |g\rangle, \quad |g\rangle = \prod_{\mathbf{k} < k_F} a_{\mathbf{k}}^{\dagger} |0\rangle, \quad (2)$$

where α_0 and $\beta_{\mathbf{k}}$ satisfy the conditions $\alpha_0^2 + \sum_{\mathbf{k} > k_F} \beta^2 = 1$ and $\alpha_0^2 = n_f$. From the variational equation we find the ground-state energy E_{GS} and $\beta_{\mathbf{k}} = V_i/z - \epsilon_{\mathbf{k}}$,

$$E_{GS} = z + \tilde{\epsilon} - E_p, \quad z = E_0 + V^2 \rho \ln((z - E_F)/B), \\ \tilde{\epsilon} = \sum_{\mathbf{k} < k_F} \epsilon_{\mathbf{k}}, \quad \Gamma = \pi V_i^2 \rho. \quad (3)$$

The XAS and XPS spectra can be described by using the golden rule:

$$F_{\alpha}(E) = \sum_f |\langle f | M_{\alpha} | \Psi_{GS} \rangle|^2 \delta(E - E_f + E_{GS}), \quad (4)$$

where $M_1 = \omega \sum_{\mathbf{k} > k_F} a_{\mathbf{k}}^{\dagger} b$ for the XAS spectrum. For the XPS spectrum $M_2 = vb$ and, in addition, we should assume that $E = \Omega - A - E_{\text{kin}}$ in (4), where Ω is the γ -ray energy, A is the work function, and E_{kin} is the energy of the emitted electron.

The response function (4) can be reduced to the form

$$F(E) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt F(t) \exp(i(E_{GS} + E)t), \\ F(t) = \langle \Psi_{GS} | M^{\dagger} \exp(-iH_f t) M | \Psi_{GS} \rangle \quad (5)$$

where H_f is the Hamiltonian of system (1) in the final state with the excited hole in the $2p$ shell ($bb^{\dagger} = 1$).

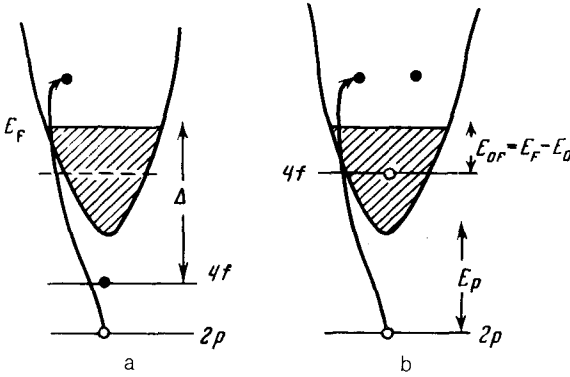


FIG. 1. X-ray absorption in the (a) $4f^n$ state and (b) $4f^{n-1}s$ state. The arrow indicates the transition of an electron from the p level to the conduction band at the Fermi level.

The contribution to the singularities near the $4f^n$ and $4f^{n-1}s$ absorption edges accounts for the processes with a final-state excitation of one and two electrons, respectively, near the Fermi level (Fig. 1). As a result of the interaction with the hole, the binding energy of the f level in the $4f^n$ state (see Fig. 1a) is greatly reduced (by an amount G), and, to the extent that $V_f^2/\Delta \ll 1$ is small ($\Delta = E_F - E_0 + G$, $V_f = V_i + \Delta V$), we can ignore the electron transfer and the interference of the $4f^n$ and $4f^{n-1}s$ states and, correspondingly, we can represent the absorption spectrum as a contribution of two purely electronic configurations, $4f^n$ and $4f^{n-1}s$, with the appropriate weights α_0^2 and $1 - \alpha_0^2$. As a result, expression (5) can be reduced to

$$F(t) = \alpha_0^2 \langle g | f M^+ \exp(-iH_f^0 t) S(t) M f^+ | g \rangle + \sum_{\mathbf{k}\mathbf{k}'} \frac{\bar{V}_i^2}{(z - \epsilon_{\mathbf{k}})^2} \langle g | a_{\mathbf{k}} M^+ \exp(-iH_f^0 t) S(t) M a_{\mathbf{k}}^+ | g \rangle \quad (6)$$

Here $S(t) = \exp(-iH_f t) \exp(iH_f t)$ is the scattering matrix, and $H_f^0 = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} + (E_0 - G) f^+ f$.

Using the theorem of coupled diagrams,⁴ we can reduce the correlation functions in (6) to the form

$$\sum_{\mathbf{k}\mathbf{k}'} \exp(-i\epsilon_{\mathbf{k}'} t) \langle g | a_{\mathbf{k}} S(t) a_{\mathbf{k}'}^+ | g \rangle = \sum_{\mathbf{k}\mathbf{k}'} L_{\mathbf{k}\mathbf{k}'}(t) \exp C, \quad (7)$$

$$\sum_{\mathbf{k}\mathbf{k}'\mathbf{k}_1\mathbf{k}_i} \exp(-i(\epsilon_{\mathbf{k}'} + \epsilon_{\mathbf{k}_1}) t) \langle g | a_{\mathbf{k}} a_{\mathbf{k}_1} S(t) a_{\mathbf{k}_1}^+ a_{\mathbf{k}'}^+ | g \rangle = \left(\sum_{\mathbf{k}\mathbf{k}'} L_{\mathbf{k}\mathbf{k}'}(t) \right)^2 \exp C, \quad (8)$$

where $C(t)$ is the sum of all single vacuum loops, and $L_{\mathbf{k}\mathbf{k}'}(t)$ is the single-electron Green's function of the final-state s electron. In the asymptotic limit $Bt \gg 1$ (B is the band width) we find the following expressions after carrying out the summation in all

orders of $\tilde{g}\rho$:

$$C(t) = -\delta^2/\pi^2 \ln(iBt), \quad (9)$$

$$B^{-1} \sum_{\mathbf{k}\mathbf{k}'} L_{\mathbf{k}\mathbf{k}'}(t) = \rho \exp \left[-iE_F t - \left(1 - \frac{2\delta}{\pi}\right) \ln(iBt) \right], \quad (10)$$

where the scattering phase δ is related to the constant $\tilde{g} = g - (V_f^2/\Delta)$ by $\tan \delta = \tilde{g}\rho\pi$. As a result, we obtain the following expression for the XAS spectrum:

$$F_{XAS}(E) = \frac{n_f \rho \omega^2}{\Gamma(1 - \Phi_1)} \left(\frac{B}{E - E_1} \right)^{\Phi_1} \theta(E - E_1) + \frac{(1 - n_f) \omega^2}{(E_F - E_0) \Gamma(1 - \Phi_2)} \left(\frac{B}{E - E_2} \right)^{\Phi_2} \theta(E - E_2), \quad (11)$$

where $\Gamma(\Phi)$ are the gamma functions, $\theta(E)$ is the Heaviside function, $E_1 = E_0 - G + \tilde{\epsilon} - E_{GS} + E_F$, $E_2 = \tilde{\epsilon} - E_{GS} + 2E_F$, and the exponents Φ_1 and Φ_2 are related to δ by

$$\Phi_1 = \frac{2\delta}{\pi} - \frac{\delta^2}{\pi^2}, \quad \Phi_2 = -1 + \frac{4\delta}{\pi} - \frac{\delta^2}{\pi^2}. \quad (12)$$

For the XPS spectrum the F_{XPS} contributions to the intensity near the $4f^n$ and $4f^{n-1}s$ edges account, respectively, for a process without an electron excitation and a process with only a single electron excitation near E_F . This spectrum can be obtained from (11) through the substitution $\omega \rightarrow \nu$, $E \rightarrow \Omega - A - E - E_{kin}$, $E_1 \rightarrow E'_1 = E_1 - E_F$, $E_2 \rightarrow E'_2 = E_2 - E_F$, where the exponents $\Phi'_{1,2}$ are, respectively,

$$\Phi'_1 = 1 - \frac{\delta^2}{\pi^2}, \quad \Phi'_2 = \frac{2\delta}{\pi} - \frac{\delta^2}{\pi^2} \quad (13)$$

3. In contrast with the simple metals, XPS and XAS spectra of valence-fluctuation compounds contain not one but two features near the edges of pure electronic configurations $4f^n$ and $4f^{n-1}s$. The first (low-energy) feature corresponds to the $4f^n$ state (Fig. 1a); in this feature the $2p$ hole is screened by the f electron. The second feature, which corresponds to the $4f^{n-1}s$ state, is higher in energy by the amount Δ . In reality, the constant G is on the order of the intratomic Coulomb interaction (5–10 eV). This circumstance accounts for the fact that $4f^n$ and $4f^{n-1}s$ configurations, which have approximately the same ground-state energy [$E_{OF} \simeq 1-2$ eV (Ref. 6)], are separated in energy by the amount $\Delta \sim 7-12$ eV in the XAS and XPS spectra. A slightly higher value of n_f obtained from the data on XAS can be explained by the additional contribution to the intensity of the first $4f^n$ peak of the process which stems from the fact that a dipole transition, $M = \tilde{\omega}f^+b$, of an electron can occur from the p shell directly to the empty f level in the $4f^{n-1}s$ state. The intensities of the peaks in (11) have appropriate weights which depend on n_f and $1 - n_f$ and which can change with changing n_f due to external conditions. This circumstance can account for the fact that the phase transition from the divalent to the trivalent state (n_f varies between

1 and 0) under pressure⁷ (SmSe), upon changing the composition of one compound ($Tm_{1-x}Y_xSe$) and the temperature of another ($EuPd_2Si_2$), leads to a decrease of the first peak and an increase of the second.^{2,3} We estimate $n_f \simeq \Gamma/E_{OF}$ and find $\Gamma \sim 0.01-0.05$ eV and the scale time for the valence fluctuation $\tau_{fl} = \hbar/\Gamma \simeq 10^{-13}-10^{-12}$ s. The finite lifetime of the hole gives rise to the damping γ of the level $E_p \rightarrow E_p - i\gamma$ and to the smearing out of the power-law singularity.⁸ Since the quantity $\gamma \sim 3-5$ eV (Ref. 1) and the corresponding lifetime $\tau \sim 10^{-15}-10^{-14}$ s of the excited state are small ($\tau \ll \tau_{fl}$), the x-ray spectra can give an instantaneous picture of the electron ground-state distribution.

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