

Mixing-Decay Widths for 4f Ions in Solids*

L. L. Hirst

Institut für Theoretische Physik, Universität Frankfurt, Frankfurt am Main, West Germany
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The intrinsic lifetime width in x-ray photoemission spectroscopy, due to mixing decays, is shown to decrease rapidly as a function of the number of 4f electrons. In a system near configuration crossover, mixing decays may also strongly broaden (or render unobservable) ionic resonances at frequencies as low as the far infrared; this is illustrated by model calculations for Sm and Eu salts.

A 4f ion in a solid may be described by a generalized Anderson model, including a mixing interaction (defined below) which can transfer 4f electrons to conduction states or vice versa. A mixing strength $\Delta(\epsilon) = \pi |V_{\text{mix}}|^2 \rho(\epsilon)$, where $\rho(\epsilon)$ is the density of conduction-electron states per spin direction, characterizes the rate at which mixing transitions would spontaneously occur if intra-ionic energies did not interfere. If $\Delta(\epsilon)$ is small compared to the minimum energy needed to excite the ion out of its ground state into a different configuration, spontaneous mixing transitions are suppressed and the lowest ionic levels do *not* show a lifetime broadening $\sim \Delta$. But for ionic levels at higher energies, which may be excited spectroscopically, mixing decay is energetically allowed and a broadening $\sim \Delta$ is expected. The purpose of the present note is to supplement this qualitative insight¹⁻³ by quantitative results for certain simple cases which, in view of recent experimental developments,⁴⁻⁷ it may soon be possible to test.

In x-ray photoemission spectroscopy (XPS), one can detect electrons knocked out of the 4f shell by x-ray quanta.⁴ The excited ionic state, belonging to the configuration $4f^{n-1}$, reabsorbs a conduction electron by the mixing interaction to return to the ground configuration $4f^n$, giving the XPS line an intrinsic lifetime broadening $\sim \Delta$. Although instrumental broadening and dynamic screening effects^{8,9} are large, Wertheim and Hüfner have recently suggested a fitting procedure which may make extraction of this intrinsic lifetime width possible.⁵

I assume a mixing interaction of the form

$$\mathcal{H}_{\text{mix}} = \sum_{k m \sigma} V_{\text{mix}} (a_{m\sigma}^\dagger c_{k m \sigma} + c_{k m \sigma}^\dagger a_{m\sigma}), \quad (1)$$

where a^\dagger and c^\dagger denote creators for 4f and conduction electrons, respectively, the latter belonging to the $l=3$ partial wave. I denote the excited ionic state by $|n-1, \beta\rangle$. Its rate of decay, by

second-order perturbation theory, is

$$w_\beta = \sum_{\beta' m \sigma} 2\Delta(\epsilon) |\langle n, \beta' | a_{m\sigma}^\dagger | n-1, \beta \rangle|^2, \quad (2)$$

where $\epsilon = E_{n, \beta'} - E_{n-1, \beta}$ is the energy of the conduction electron absorbed in the mixing decay.

Let us first assume that all levels β of the configuration $4f^n$ are energetically accessible, and that Δ can be taken as constant over the relevant values of ϵ . Then Eq. (2) reduces by closure to the simple result

$$w_\beta = 2\Delta(N_0 + 1 - n), \quad (3)$$

where $N_0 = 14$ is the number of electrons in the full 4f shell. This implies a mixing-decay width which is proportional to the number of unoccupied 4f orbitals in the excited ionic state. In chemically similar materials the intrinsic XPS width would therefore be expected to decrease by more than an order of magnitude across the 4f series. This trend should be reinforced by a decrease in V_{mix} due to the lanthanide contraction. For Yb metal a lifetime width of 0.16 eV has been fitted,⁵ corresponding to $\Delta = 0.08$ eV; fits testing the dependence on atomic number are not yet available.

Situations can also arise in which the dependence of Δ on ϵ becomes important, or in which some states of the excited configuration $4f^{n-1}$ cannot reach all states of $4f^n$ via an energetically allowed mixing decay. Then mixing decays between specific intraconfigurational levels must be calculated, and different excited levels may have different widths; an example of such a calculation, although not for XPS, will be given below. Such effects become important as one approaches a configuration crossover.^{3,10} When the configuration crossover is reached, i.e., when the initial ionic state becomes configurationally unstable, we expect an extra width contribution $\sim \Delta$ corresponding to the initial-state lifetime.

If an ion has a configurationally stable ground

state, excited levels belonging to the same configuration may still be unstable against mixing decay. I consider this effect for the Sm monochalcogenides, which normally have $4f^6$ as the stable configuration, but with $4f^5$ only a fraction of an eV higher.^{6,7,10} Let $\epsilon(6, 5)$ be the energy difference between the lowest levels of the two configurations, and let ϵ_c be the energy of the bottom of the conduction band, which is empty at zero pressure and temperature; then $\epsilon_c - \epsilon(6, 5)$ is the energy necessary to transfer an electron from the ionic ground state to the conduction band. This energy decreases through the series SmTe, SmSe, SmS, and can be further decreased by pressure or by various chemical substitutions. I consider the widths of ionic resonances in the infrared range as the configuration crossover is approached in this way.

The levels of interest are the spin-orbit levels of the Hund term of each configuration, $4f^{6,7}F_J$ and $4f^5 H_{J'}$, abbreviated J and J' , where $J=0, 1, \dots, 6$ and $J'=\frac{5}{2}, \frac{7}{2}, \dots, \frac{15}{2}$. Let E_J and $E_{J'}$ denote the spin-orbit energy relative to the spin-orbit ground state. Consider a spectroscopic line corresponding to a transition from $J=0$ to an excited J level. The excited level can undergo a mixing decay to a level J' of $4f^5$, emitting a conduction electron of energy $\epsilon_{JJ'} = \epsilon(6, 5) + E_J - E_{J'}$, provided that this energy is larger than ϵ_c . To calculate the mixing-decay rate, the mixing interaction is projected first onto the Hund L - S terms of the two configurations and then onto the spin-orbit levels. This can be carried out straightforwardly and yields the result

$$w_J = \sum_{J'} 2\Delta(\epsilon_{JJ'}) (2J'+1)(2j+1) \times \begin{pmatrix} J' & j & J \\ S' & s & S \\ L' & l & L \end{pmatrix}^2 (n-1) \|\hat{a}\| n)^2, \quad (4)$$

where

$$(n-1) \|\hat{a}\| n)^2 = \left[\begin{pmatrix} L' & l & L \\ -L' & L'-L & L \end{pmatrix} \begin{pmatrix} S' & s & S \\ -S' & S'-S & S \end{pmatrix} \right]^{-2}.$$

Here the round and curly brackets are Wigner 3- j and 9- j symbols; S, L, S' , and L' are the ionic spin and orbital angular momenta of the two Hund terms; and $s=\frac{1}{2}$ and $l=3$ are the spin and orbital angular momenta of the conduction electron. Following Ref. 10, we assume a nearly-free-electron conduction band with bandwidth parameter W and density of states $\rho(\epsilon) = \frac{3}{4}(\epsilon/W^3)^{1/2}$ per

spin, where ϵ is the energy relative to ϵ_c . The mixing strength can then be written $\Delta(\epsilon) = (\epsilon/W)^{1/2} \Delta_1$, where $\Delta_1 = 3\pi |V_{\text{mix}}|^2 / 4W$ is the mixing strength corresponding to a band filling of one electron per cell, whose magnitude might be ~ 0.01 eV.

The linewidth behavior implied by Eq. (4) for Sm monochalcogenides near the configuration crossover is shown in Fig. 1. The excited J levels become unstable to mixing decays before the configuration crossover is reached. The highest level $J=6$ is the first to become unstable, and one might expect it to show the largest width. However, it is found that the mixing connects this level mainly to $J'=\frac{13}{2}$ and $\frac{15}{2}$; matrix elements to the lower J' levels are finite but small. Thus, for example, at $\epsilon(6, 5) - \epsilon_c = -0.05$ eV, which might correspond to SmS, the widths are

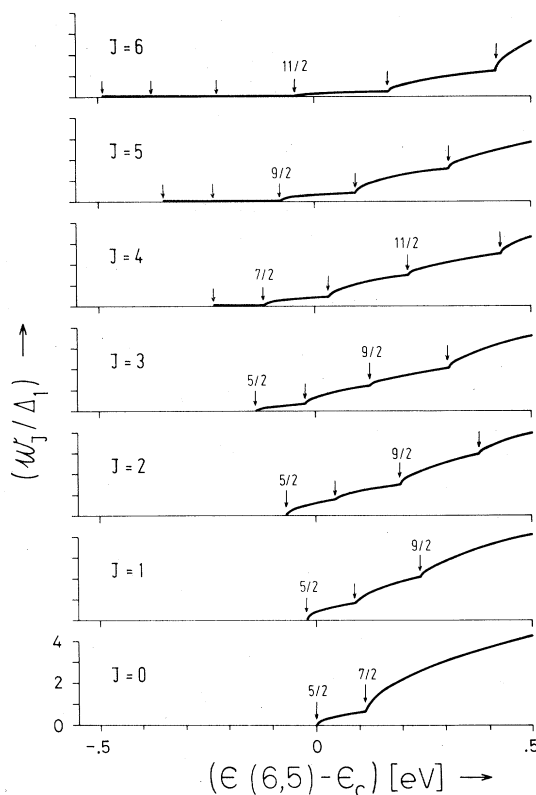


FIG. 1. Mixing-decay widths for spin-orbit levels, J , of Sm ions near crossover from $4f^6$ to $4f^5$, as a function of the energy of configurational stabilization. Arrows show where decays to new final-state levels J' become allowed. I used a spin-orbit splitting $\lambda \vec{L} \cdot \vec{S}$ with $\lambda = 0.0235$ and 0.0332 eV for $4f^6$ and $4f^5$, and a conduction-band parameter $W = 0.9$ eV.

0, 0.33, 0.30, 0.34, 0.22, and 0.02 times Δ_1 for $J=0, 1, \dots, 6$, so that $J=6$ is narrower than any other excited level except $J=1$. At higher $\epsilon(6, 5)$ values all levels become configurationally unstable, and their widths approach the common asymptote $w = \frac{44}{7} [\epsilon(6, 5)/W]^{1/2} \Delta_1$. (The $J=0$ width has come within 5% of this asymptote at the right-hand side of Fig. 1).

A somewhat different situation arises if we consider mixing decays of excited spin-orbit levels $4f^6 {}^7F_J$ to $4f^7 {}^8S$ via absorption of a valence electron in an insulator, as would apply to a Eu salt sufficiently close to the crossover from $4f^6$ to $4f^7$. In this case, there is no spin-orbit splitting in the S-state final ionic state. The energy of the absorbed electron is $\epsilon(7, 6) - E_J$, and must lie below ϵ_v , the top of the valence band, if mixing decay is to be possible. The mixing-decay widths are found to be simply

$$w_J = \frac{16}{7} [(\epsilon_v - \epsilon(7, 6) + E_J)/W]^{1/2} \Delta_1, \quad (5)$$

where I have assumed a valence band corresponding to inversion of the conduction-band form used above. Here the matrix elements for all mixing transitions have the same strength, and higher J levels are broader by virtue of their increased instability.

The $J=1$ level in Sm monochalcogenides has been observed spectroscopically^{6,7} but the experimental situation as to the higher spin-orbit levels is unclear; and Eu salts do not appear to have been studied sufficiently near to the configuration crossover to make the present calculation applicable. I shall therefore merely point to the desirability of further spectroscopic studies of such systems. Particularly interesting, although experimentally difficult, would be measurements

under hydrostatic pressure, allowing the configuration crossover to be approached continuously. The crossover may also be approached by means of chemical substitutions, but this technique has the disadvantage that it may introduce inhomogeneity broadening.

In the present brief discussion I have ignored excitonic effects, and effects of unresolved finer ionic splittings, which might be of practical importance in certain cases. A more extensive discussion, including the details leading to Eqs. (4) and (5), will be given elsewhere.

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