

Observation of a Relationship between Core-Level Line Shapes in Photoelectron Spectroscopy and the Localization of Screening Orbitals

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It is observed that the line shapes of core levels in photoelectron spectroscopy of Ti, Th, and Ce and some of their intermetallic compounds and lanthanide oxides are directly related to the degree of localization of screening orbitals.

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In the last few years it has become recognized that a detailed understanding of the mechanism of core-hole screening is crucial in core-level spectroscopies, and in particular in x-ray photoelectron spectroscopy (XPS). These screening processes are often well described by excitonlike models in which the screening electron is considered to occupy an orbital centered on the core-

ionized atom.¹⁻⁴ In such cases the line shapes of core-level peaks in XPS depend critically on the coupling of the screening levels to the other, delocalized, occupied levels of the initial state (see, e.g., Refs. 5-7). The model derived from the Schönhammer-Gunnarsson (SG) treatment of this problem is shown schematically in Fig. 1, left side. The role of an empty screening level, φ_i ,

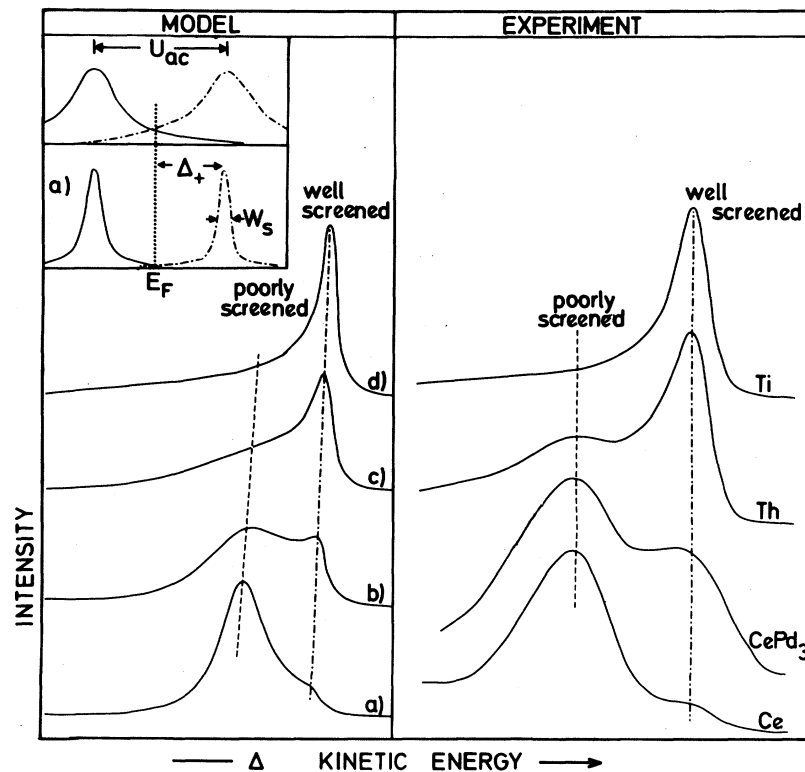


FIG. 1. Left: Illustration of the Schönhammer-Gunnarsson model of screening and its implications for the core-level line shapes. The values of W_s/Δ_+ were $a = 0.94$, $b = 0.75$, $c = 0.56$, $d = 0.38$, and U_{ac} was $1.5 \Delta_+$ (Ref. 6). Right: Ce $3d_{5/2}$, Th $4f_{7/2}$, and Ti $2p_{3/2}$ XPS peaks from Ce, CePd₃, Th, and Ti. The peak binding energies are ~ 883 , ~ 333 , and ~ 454 eV for the Ce, Th, and Ti levels, respectively.

is basically determined by its position, Δ_+ , relative to the Fermi energy E_F of the system and its coupling to the other occupied levels. This coupling, described in terms of a hopping integral or the degree of hybridization with the delocalized electrons of the system, can be expressed in terms of the width W_s of the screening level. In the final state after core ionization, the energy of φ_i is lowered by an energy U_{ac} with respect to E_F .⁸ The total energy of the final state will thus be lowered if an electron is transferred from E_F to the screening level. SG showed that, for isolated adsorbates on a metal substrate, when $W_s \ll \Delta_+$ the probability of transferring an electron to φ_i is small and when $W_s \gg \Delta_+$ the probability is large. This means that the amplitude of the so-called "well-screened" XPS peaks associated with occupied φ_i reflects directly the coupling of φ_i to the occupied states in the initial state.⁹ As illustrated in Fig. 1 the peak shape varies continuously as the ratio W_s/Δ_+ is varied.

The experimental support for this interesting approach has been scarce. The models have been used to explain structure in XPS peaks from La,⁵ Ni,¹⁰ and several adsorbates. (See, e.g., Refs. 11, 12.) However, *trends* in line shapes have only been found in adsorbate systems in which it is difficult to vary the degree of localization of φ_i without significantly changing other parameters.

In this Letter we present results indicating that the spectra of large classes of rare-earth and actinide compounds realize more closely the assumption of the model in Fig. 1. They are thus suitable candidates for providing more detailed understanding of recently discovered non-Lorentzian lifetime broadening of core levels and interference between XPS and Auger events.¹³ In addition we find the shapes of core-level lines to be very sensitive to the chemical environment of the core-ionized atom. Trends in peak shapes follow trends in the degree of localization of the screening level and this leads us to believe that such observations may eventually result in a quantitative scale of localization.

Two different ultrahigh-vacuum photoelectron spectrometers with base vacua at the sample of better than 10^{-8} Pa were used for this work. Measurements on metals and intermetallic compounds were made in Jülich, mostly using a novel large solid angle x-ray monochromator with 54 quartz single crystals mounted on a toroidal substrate.¹⁴ For these measurements the system only had a single detector so that the analyzer slits had to

be opened to give a total resolution of 550 meV. The clean metal and intermetallic surfaces were prepared by scraping polycrystalline material in UHV. The measurements on oxides were made with the Linköping University XPS instrument^{15,16} using unmonochromatized Mg $K\alpha$ radiation and 1 eV total resolution. The clean oxide films were prepared by evaporating metal films *in situ* and then exposing them to clean oxygen. That these films give spectra representative of the oxides is shown by their similarity to the lower-resolution spectra of Berthou and Berthou.¹⁷

The XPS spectra of the Ce $3d_{5/2}$, Th $4f_{7/2}$, and Ti $2p_{3/2}$ levels are shown in Fig. 1. Metallic Ce in the γ phase has Ce atoms with the configuration $[\text{Xe}]4f^1(5d6s)^3$. The $4f^2$ configurations in the absence of a core hole are known from bremsstrahlung isochromat spectroscopy (BIS) to be 3–7 eV above E_F .¹⁸ However, for core-ionized Ce the situation must be more like that in Pr where the $4f^2$ level lies 3.3 eV below E_F .^{16,19} This implies that the $4f$ orbitals are the most effective screening orbitals for a core hole on Ce.^{20,21} For the SG model we note that the $4f^2$ levels of Ce are poorly hybridized with the other delocalized levels of Ce and (neglecting term splitting) have a width W_s of 0.1–1.0 eV (Ref. 22) which is less than Δ_+ of 3–7 eV. Ce thus corresponds to the weakly coupled limit in the SG model and most of the XPS intensity is in the poorly screened peak.

For deep core holes in Th, the best screening level is the $5f^1$ level which is unoccupied and 3–5 eV above E_F (Ref. 23) but is known to be occupied in Pa.²⁴ As the $5f$ levels are more extended than the $4f$ they form a true band in Th (Ref. 23) and are more strongly hybridized with other delocalized conduction electrons than is the case for Ce. This is consistent with the observation that the Th $4f_{7/2}$ peak in Fig. 1 has more intensity in the screened peak. Finally, for Ti we know that although the $3d$ orbitals are sufficiently localized for the excitonic model to apply, the d^{n+1} levels are close to E_F . Core ionization must then be described by the strong-coupling limit of the model of Fig. 1, in agreement with the observation that all the XPS intensity is in the well-screened peak.

The trend of relative intensities of "well-screened" and "poorly screened" peaks shown in Fig. 1 so clearly follows the trends in our preconception of the degree of localization of the orbitals involved in screening that we were led to believe that one could even use XPS line shapes to set up a scale of degree of localization of such screening orbitals. To this end a series of inter-

metallic compounds of Ce and Th were studied, making use of the extensive similarities of the binary phase diagrams of Ce and Th. The XPS spectra of the same $3d_{5/2}$ and $4f_{7/2}$ core levels as in Fig. 1 for Ce and Th are presented in Fig. 2 for a series of compounds. The trends really are very similar for the two series. The effects are strong, which satisfies the first criterion for a method which could be used to build up a scale of localization effects for comparison with other data. In the elements and in the MAl_2 alloys, the relative intensity of the poorly screened Ce and Th peaks is stronger than in the other compounds, indicating maximum decoupling of the $4f$ and $5f$ electrons from the conduction electrons. In intermetallics with Pd and Ni the well-screened peaks reach their maximum intensity relative to the poorly screened peak. This we believe implies stronger coupling of the f system to the conduction electrons.

The rare-earth oxides, M_2O_3 , provide another series in which a trend in line shapes can be related to trends in screening level localization. The core-level spectra of La_2O_3 show double peaks with the lower-binding-energy peaks attributed to "well-screened," $4f^1$, final states.¹⁵ Figure 3 shows the $3d_{5/2}$ XPS spectra La_2O_3 , Ce_2O_3 , Pr_2O_3 , and Nd_2O_3 in which the relative intensity of the well-screened peak can be seen to decrease progressively in the heavier elements, although multiplets do smear somewhat the Pr and Nd spectra. In the light of the ideas described above we can now recognize this to be due to the $4f$ orbital contraction as one proceeds across the lanthanide series.

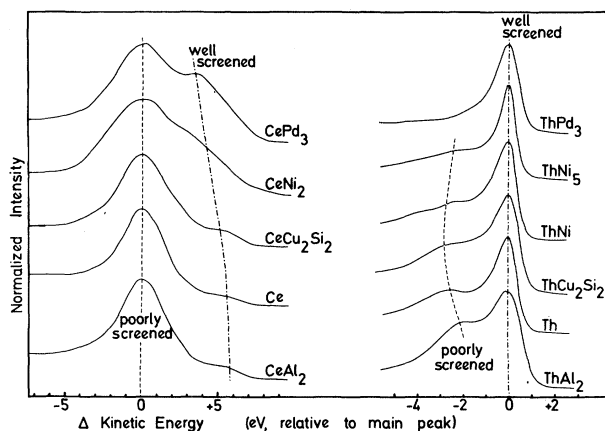


FIG. 2. Ce $3d_{5/2}$ and Th $4f_{7/2}$ peaks from series of intermetallic compounds. In each case the strongest peaks have been lined up.

The change in f count on core-level photoemission has important consequences for the interpretation of core-level XPS spectra from mixed-valence materials. It means we cannot derive the relative amplitudes of the $4f^{n-1}$, $4f^n$, and $4f^{n+1}$ states in the initial-state system from the relative intensity of the relevant XPS peaks. When we first noted that f -count changes distorted "average valence" estimates for Ce compounds we recognized that the criteria for deciding their significance did not exist.^{20, 21} Intuitively one could argue that as the $4f$ wave function is more extended in Ce the effects in heavier lanthanides should be much smaller and only poorly screened peaks should be observed. The results in Fig. 3 show that at least for the light rare earths this is not true as even in Nd_2O_3 (25–30)% of the intensity is in the well-screened peak where the f count has increased during photoionization.

In concluding we draw special attention to the present demonstration of how widespread changes in f count during photoemission really are in lanthanide and actinide materials. This provides exciting new possibilities for study of interferences between XPS and Auger processes.¹³ These systems have the added advantage that the change in occupation of the empty screening levels, φ_i , is very near unity which makes theoretical treatment simpler.

The distance Δ_+ of the screening orbital above E_F is one of the two most important parameters determining core-level line shapes in XPS and in solids this can be measured by BIS. The other most important parameter is the degree of localization of the screening level. We note that if

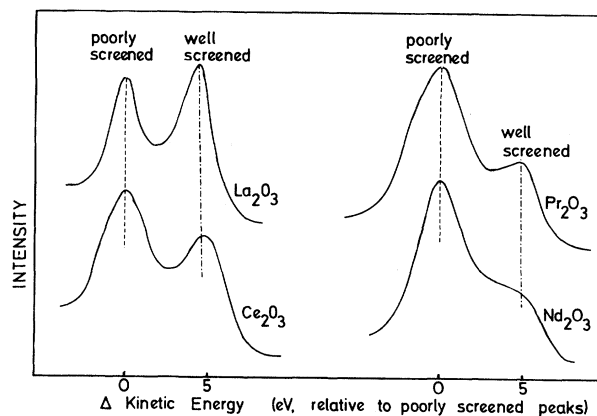


FIG. 3. Lanthanide $3d_{5/2}$ XPS peaks from La_2O_3 , Ce_2O_3 , Pr_2O_3 , and Nd_2O_3 with the "poorly screened" peaks lined up.

the localization which controls screening in core ionization can be described by a formalism in which the important parameters can be directly calculated, then studies of core-level line shapes will become a large potential source of information on the factors controlling, for instance, magnetic behavior.

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⁸Note that for systems in which ϕ_i is either an f or a d shell Δ_+ and U_{ac} are not independent of the effective Coulomb interaction between valence electrons, U_{eff} . In the notation of J. Herbst, N. D. Lowy, and R. E.

Watson [*Phys. Rev. B* **6**, 1913 (1972)] and J. Herbst, R. E. Watson, and I. Lindgren [*Phys. Rev.* **14**, 3265 (1976)], Δ_+ is the energy necessary to transfer an electron from E_F to the empty localized ϕ_i level, while Δ_- is the energy necessary to promote an f or d electron from the occupied level to E_F . Then $U_{\text{eff}} = \Delta_- + \Delta_+$. It is clear that large values of U_{eff} (strong localization) will be associated with either large Δ_+ or Δ_- values.

⁹Note that in the solids considered here the situation is slightly more complicated than for an isolated adsorbate species. In solids ϕ_i may even form a band whose width, in the case of f orbitals for instance, may be due to interatomic f - f interactions. The width required for the calculation of peak amplitudes is not the total width of the ϕ_i band, but is better described by the hopping integral between ϕ_i and the occupied states of the system.

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