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Invalidity of 4*f* count determination and possibilities for determination of 4*f* hybridization in intermetallics of the light rare earths by core-level spectroscopy

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We follow up a previous suggestion that x-ray photoelectron spectroscopy line shapes can be used to estimate the degree of screening orbital delocalization. Using compounds $R\mathrm{Pd}_3$ ($R=\mathrm{La}$, Ce, Pr, Nd, and Sm) we show that there can be appreciable but decreasing mixing of the 4*f* states with the extended conduction-band states in the series of $R\mathrm{Pd}_3$ compounds in going from La to Nd. This mixing is, however, not detectable by photoemission in SmPd_3. We discuss this mixing in both initial and final states. We conclude that the major initial-state mixing involves f^0-f^1 configurations in CePd_3. The major mixing in the final states always involves the f^n and f^{n+1} configurations, where the f^{n+1} configuration has a negligible effect for Sm and heavier elements. The implication of this is that core-level spectroscopies can give reliable information on the *f* count in compounds of samarium and the heavier rare-earth metals.

INTRODUCTION

In certain rare-earth compounds of Ce, Sm, Eu, Tm, and Yb, indisputable evidence has been found for nonintegral occupation numbers of the 4*f* levels (i.e., nonintegral *f* counts).[1-4] As the 4*f* levels are spatially well localized the picture of configuration fluctuations with characteristic fluctuation times in the region $10^{-10}-10^{-13}$ sec has evolved.[1-5] Ce and some of its compounds are special cases among these materials as it has become accepted in the last five years that the individual 4*f* orbitals of Ce have sufficient spatial extension to interact or "hybridize" strongly with other valence orbitals (6*s*, 5*d*, or 4*f*) of the same, or neighboring atoms.

A central problem in the physics and chemistry of Ce compounds is understanding whether the anomalous properties are determined by changes in the *f*-level hybridization and band character, or by changes in the *f* count, or both. As an example of this dilemma we cite the example of the α-γ Ce phase transition. The α-γ transition was once thought to involve (partial) promotion of ~ 0.6 4*f* electrons to the 5*d*-6*s* conduction band,[6-9] with concomitant decrease in the atomic volume. However, more recent experimental evidence from Compton scattering[10] and positron annihilation[11] support the view[12] that the phase transition is a Mott transition from a phase with localized 4*f* electrons (γ-Ce) to one with (partially) delocalized *f* electrons (α-Ce). In this latter model the number of *f* electrons remains nearly unchanged.[13]

It is generally believed that in all the rare earths except Ce the 4*f* levels are too strongly localized to give a significant contribution to a chemical bond, although isolated observations, such as phase transitions of Pr in metallic systems under pressure consistent with a Mott-type transition,[14] may conflict with this viewpoint. It is the purpose of this paper to provide evidence by photoelectron spectroscopy of a weak coupling of the 4*f* states with delocalized electrons, even in Nd. We will argue that core-level spectroscopies of La, Ce, Pr, and Nd and their compounds give primarily information on the coupling of the *f* electrons to the other electrons, and not on the *f* count. However, the implication of our work is that in Sm and the heavier rare earths these spectroscopies will yield direct information on the *f* count.

In principle, hybridization of the 4*f* levels in light rare earths could be inferred from measurements of the 4*f* level widths in photoemission from the valence bands. In practice the widths of the *f* "bands" are small so that some resolution problems occur. In addition major difficulties might well be related to lifetime broadening[15] and surface effects (see, e.g., Refs. 15-17). A further problem is the small cross section of the 4*f* levels in light rare earths and in Ce. It is not even possible to be sure of the position of the occupied 4*f* level[18-22] or indeed if the 4*f* level is located in just one position. These difficulties with direct studies of the position of the occupied 4f level in the valence bands give additional impulse to studies utilizing the core-level line shapes to diagnose hybridization of the 4f levels as suggested in a previous paper.[23] The use of core-level line shapes in this way is based on the concept that when a rare-earth atom has n 4f electrons in the ground state, the lowest-energy core-ionized state is one with $(n+1)$ 4f electrons and with the core hole screened by an extra 4f electron in an excitonlike level centered on the core-ionized atom. In the nomenclature of Ref. 23, the states with and without occupation of this screening level ϕ_i are termed "well screened" and "poorly screened." The probability that the screening level will be occupied depends critically on the coupling to the other occupied levels. This coupling is described in terms of a hopping integral, or degree of hybridization with the delocalized electrons of the system (see, e.g., Refs. 24–26). If this degree of hybridization is small then the probability of transferring an electron to ϕ_i is small and most of the x-ray photoelectron spectroscopy (XPS) intensity will be found in the poorly screened peaks at higher binding energy.

XPS of rare-earth core levels for studies of screening effects is restricted to the 3d and 4d levels because lifetime broadening of the other levels masks fine structure related to screening effects. In addition the exchange interaction between 4d holes and the unfilled 4f levels gives rise to complicated multiplet structures which cannot be easily separated from screening effects. We thus restrict the present report to the 3d core levels. In the elements La, Ce, Pr, and Nd the well screened $4f^{n+1}$ peaks always contribute less than 5–10% to the total 3d XPS peaks[27–29] so that it is difficult to observe trends in their weight as a function of atomic number. We have thus studied the series of $R\mathrm{Pd}_3$ intermetallic compounds because the intensity was known to be more evenly distributed between the well-screened and poorly screened peaks in CePd_3.[23,29]

EXPERIMENTAL

The compounds were prepared by melting preweighed portions of the pure elements in a cold crucible under clean argon. Metallography and x-ray diffraction were used to check that the samples are primarily single phase. LaPd_3, PrPd_3, and NdPd_3 contained approximately 1% of a second phase; in CePd_3 and SmPd_3 no second phase was detectable.[30]

The samples were scraped clean at $1-2\times10^{-10}$ Torr and measured in a vacuum of $2-4\times10^{-11}$ Torr. Monochromated Al $K\alpha$ radiation was used to excite the spectrum and total resolution was 600 meV. Wider XPS scans were used to check the absence of contamination. Oxygen gave the most problems, although in all spectra shown here less than $\frac{1}{4}$ monolayer was present. LaPd_3 was most reactive to oxygen (for instance it blackened in air, which the other samples did not).

RESULTS AND INTERPRETATION

The XPS spectra of these alloys in the region of the 3d peaks is shown in Fig. 1 and some peak energies are listed in Table I. The 3d levels have a spin-orbit splitting ranging between 17.0 eV for La and 26.7 eV for Sm. The shoulders on the low-binding energy side of the $3d_{3/2}$ and $3d_{5/2}$ peaks are attributed to the well-screened $3d^9 \ldots 4f^{n+1}$ final-state configurations while the more intense peaks are attributed to the poorly screened $3d^9 \ldots 4f^n$ configurations. The main 3d peaks are quite broad [$3d_{5/2}$ full width at half maximum (FWHM) ~3 eV] which is due to a combination

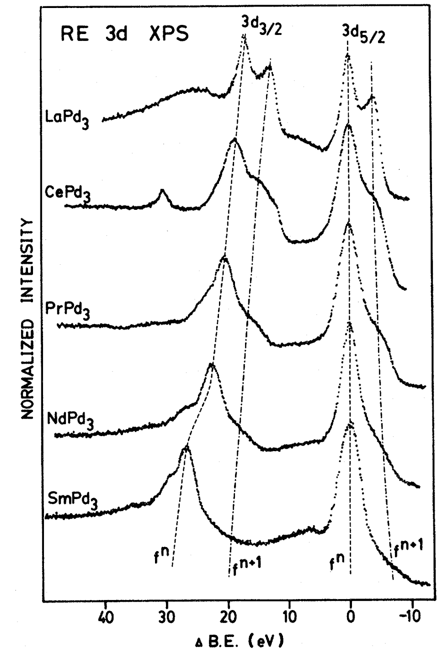

FIG. 1. XPS spectra in the region of the rare-earth 3d levels for $R\mathrm{Pd}_3$ alloys (R = La, Ce, Pr, Nd, and Sm). The spectra have been normalized to the height of the $3d^{5/2}$ peaks. Peak binding energies are given in Table I.

TABLE I. Rare-earth $3d$ XPS peak binding energies. (All energies in eV with respect to E_F; numbers in parenthesis give error limit for the last digit.)

Compound	$3d_{3/2}$				$3d_{5/2}$			
	f^{n-1}	f^n	f^{n+1} (well screened)	ΔE (f^n-f^{n+1})	f^{n-1}	f^n	f^{n+1} (well screened)	ΔE (f^n-f^{n+1})
$LaPd_3$		854.0(2)	849.8(4)	4.2(4)		837.0(2)	832.9(4)	4.1(4)
$CePd_3$	914.7(5)	903.1(4)	898.7(6)	4.4(4)	895(2)	884.7(4)	880.2(6)	4.5(4)
$PrPd_3$		953.0(2)	947.3(4)	5.7(4)		932.8(2)	926.8(4)	6.0(4)
$NdPd_3$		1004.0(2)	998.2(4)	5.8(4)		981.5(2)	976.3(4)	5.2(4)
$SmPd_3$		1109.1(2)				1082.4(2)		

of lifetime effects[31] and exchange interaction between the $3d$ hole and the partially filled $4f$ shell in Ce-Sm. This interaction may lead to some of the high BE shoulders observed, particularly for Nd and Pr,[32] but not in La which has no f electrons in the initial state. (The "well-screened" contribution to the La spectra has, of course, f^1 in the final state, but it seems to produce no significant splitting of the $3d$ peaks.) Ce also shows $4f^{n-1}$ ($4f^0$) peaks related to the partial emptying of the $4f$ level but we remind the reader that its intensity is much smaller than expected on the basis of the f-level occupancy and cannot be simply related to the ground-state f count.[16,23,29] The separations of the peaks are in agreement with theoretical estimates,[33] insofar as these exist.

The $3d_{5/2}$ peaks are shown with an expanded scale in Fig. 2 where the contributions of well-screened $4f^{n+1}$ peaks clearly decrease from about 40% in La to about 10% in Nd and are too weak to be unambiguously identified in $SmPd_3$. A quantitative estimate of the $4f^{n+1}$ contribution from our data is not desirable because the multiplet splitting due to $3d^9$-$4f^{n+1}$ interaction must produce a tail under the stronger $3d^9 4f^n$ peaks. The form of this tail is not well known and its separation from the main peak would be unreliable.

Oxidized samples also exhibit spectra with the peaks split into a well-screened and poorly screened doublet.[23,34] The low binding-energy (BE) peaks of oxidized samples lie between the well and poorly screened peaks of the RPd_3 samples and the high BE oxide peaks were situated to the high BE side of the poorly screened RPd_3 peaks. The observation of a clear separation of the well-screened and poorly screened peaks in $LaPd_3$ or $CePd_3$ is an additional indication of sample cleanliness.

DISCUSSION

The wave functions of lanthanide atoms in a solid can be represented as N-dimensional determinants of the single-particle wave functions whereby it is the $4f$ electrons which interest us here. Until quite recently the $4f$ electrons were regarded as core electrons with only integral occupation numbers being allowed. This was the starting point for the idea of interconfigurational fluctuations. For Ce it is now accepted that some form of f band is possible[1-4,12,13] and it has been argued that the f-orbital occupation (f count) varies be-

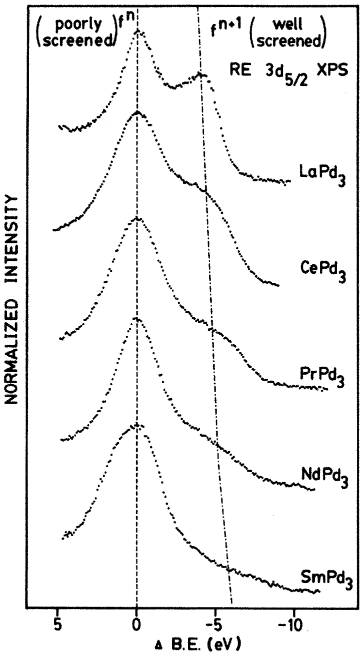

FIG. 2. $3d^{5/2}$ XPS peaks for RPd_3 alloys.

tween 0 and 1 depending on the chemical environment of the Ce atom. The ground state of the atoms in a solid can be represented as a combination of f^0, f^1, and f^2 wave functions (i.e., there is some configuration interaction between these states). In a general formalism which is applicable to all the light rare earths we could write the many-body functions as

$$\begin{aligned}\Psi_1&=a\psi(f^{n-1})+b\psi(f^n)+c\psi(f^{n+1}),\\ \Psi_2&=a'\psi(f^{n-1})+b'\psi(f^n)+c'\psi(f^{n+1}),\\ \Psi_3&=a''\psi(f^{n-1})+b''\psi(f^n)+c''\psi(f^{n+1}),\end{aligned} \tag{1}$$

where Ψ_1 is the ground state and is normally nearest ψf^n. Ψ_2 is regarded as an excited state (without a core hole) which has mostly ψf^{n-1} character, and Ψ_3 has nearly f^{n+1} character. n is 0 for La, 1 for Ce, 2 for Pr, etc. It is understood that changes in the numbers of $6s+5d$ valence electrons are included in the $\psi(f^n)$.

The final states after core ionization can be written

$$\begin{aligned}\Psi_1^*&=d\psi(f^{n-1})+e\psi(f^n)+f\psi(f^{n+1}),\\ \Psi_2^*&=d'\psi(f^{n-1})+e'\psi(f^n)+f'\psi(f^{n+1}),\\ \Psi_3^*&=d''\psi(f^{n-1})+d''\psi(f^n)+f''\psi(f^{n+1}),\end{aligned} \tag{2}$$

where it is understood that a core hole is present in all these states. The photoemission process involves transitions from Ψ_1 to Ψ_1^*, Ψ_2^*, or Ψ_3^*. If there is no mixing of the f^x states in either initial or final states (e.g., if $a,c=0$, $b=1$ and $d,f=0$, $e=1$) then a single peak will be observed. If we find more than one peak we know that transitions to alternative Ψ are involved. The more mixing there is the higher the contributions of the "satellite" XPS peaks will be, although the peak ratios are determined by all the coefficients a, b, c, d, e, and f. Therefore, we normally cannot say that peak ratios are *directly proportional* to any subgroup of coefficients.

One factor influencing the degree of mixing of the ψf^x in either the initial or final states is the radial extension of the 4f levels and the overlap of the 4f with other orbitals. We can say from the general trend of the ratio of the $4f^{n+1}$:$4f^n$ peaks that the degree of mixing decreases in the order La > Ce > Pr > Nd > Sm. This is surely related to the decrease in radial extension of the 4f levels across the lanthanide series. The most important aspect of our observations is that the mixing cannot be totally neglected in Pr and Nd, at least for photoelectron spectroscopy *and by inference for all spectroscopies in which the number of core-holes changes* (e.g., x-ray adsorption and emission).

A second factor influencing mixing of the ψf^x is the energy difference between the pure ψf^x or $\psi^* f^x$ configurations. A small energy difference is the first prerequisite for mixing. The relative energies of Ψ_1, Ψ_2, and Ψ_3 in the initial state, without a core hole, are known from photoemission[35,36] and Bremsstrahlung Isochromat studies.[35] In Table II the energies of the lowest f^x multiplets with respect to the ground state are listed (for La, Pr, Nd, and Sm the values for the elements are used). Likewise the relative energies of Ψ_1^*, Ψ_2^*, and Ψ_3^* can be derived from measurements of the satellite energies in XPS and are also given in Table II. The situation in initial and final states of La and Ce is illustrated in Fig. 3, where the states have been given widths, to illustrate the mixing of the different ψf^x and hybridization with the *s-d* valence band. Typical full widths at half max-

TABLE II. Energies of the lowest $4f^{n-1}$ and $4f^{n+1}$ levels relative to the $4f^n$ level in the initial and final state of XPS 3d excitations (in eV), + indicates a higher or more excited state. The average of $3d^{3/2}$ and $3d^{5/2}$ is used where possible.

Compound	Initial state		Final state	
	f^{n-1}	$f^{(n+1)}$[a]	f^{n-1}	f^{n+1}
LaPd$_3$		5.3		−4.1
CePd$_3$	~0.0[a]	3.5	11.6	−4.5
PrPd$_3$	3.4[b]	2.1		−5.9
NdPd$_3$	4.8[b]	1.7		−5.5
SmPd$_3$	5.1[b]	0.5		

[a] Values for R (Ref. 35) are given. In CePd$_3$ f^{n+1} apparently lies 1 eV higher than in Ce (Ref. 22).

[b] From Refs. 35 and 36 for the pure rare earths. Position not identified in RPd$_3$.

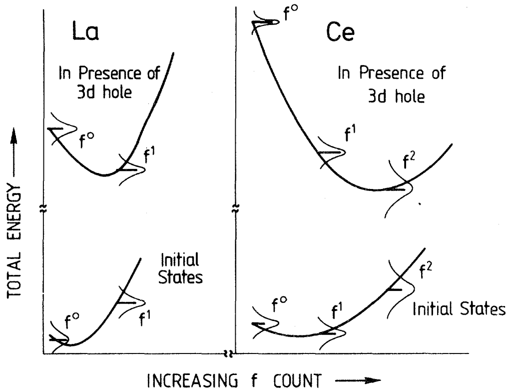

FIG. 3. Illustration of the relative energies of the $4f^0$, $4f^1$, and $4f^2$ states for La and Ce, with (final states) and without (initial states) a $3d$ core hole.

imum of the states are 0.5 — 1.5 eV (Ref. 35) so that it is not unrealistic to expect f^{n+1} eigenfunctions 5 eV above the ground state to contribute a few percent to that ground state and this is sufficient to lead to satellite peaks in XPS.[24–26]

Using this formalism it is clear that in $CePd_3$ $\psi_1(f^0)$ and $\psi_2(f^1)$ are strongly mixed, which is equivalent to saying that the f count is nonintegral in $CePd_3$ (see also Refs. 37 and 38). In $LaPd_3$, $CePd_3$, $PrPd_3$, and $NdPd_3$ the energy separation of the dominant f^n and f^{n+1} multiplets in the XPS spectra is comparable in the initial and the final states so that their mixing in the initial and the final states must be considered on an equal footing, i.e., they probably have similar amounts of mixing. It is because of these configurational interactions that core-level spectroscopies do not yield a direct measure of the initial-state f count in the light rare earths (see also Refs. 16, 23, and 29).

The f^{n-1} final-state configuration has only been directly observed for Ce compounds and is 10 eV above the next highest configuration (see also Refs. 16, 29, and 33) so that it can be regarded as a "pure" $3d^9 f^{n-1}$ final state (i.e., $d'=1$, $e'=f'=0$ in the expression for Ψ_2^*). Thus, in the case of Ce compounds we can say that observation of a core-level f^0 peak indicates a contribution of ψf^0 to the ground initial state. Note, however, that even when ψf^0 is mixed into the ground state, ψf^2 may also contribute and the f count is not *necessarily* less than one. In general, estimation of the ground-state f count from core-level spectra of Ce compounds seems hopeless because the relative peak intensities depend on the coefficients a, b, c, d, e, f, d', e', f', d'', e'', and f'' in Eqs. (1) and (2), not just a, b, and c.

CONCLUSIONS

In this paper we have shown with the example of XPS that screening processes can lead to large satellites in core-level spectroscopies of Pr and Nd compounds as well as Ce and La. The intensity in the screened peaks is observed because of mixing of the different $4f^x$ configurations. On the basis of their small energy separations, we note that mixing of the $4f^n$ and $4f^{n+1}$ configurations in the final state must be taken into account in any theoretical treatment of photoelectron or absorption spectroscopies of compounds of the elements La-Nd. However, as we do not observe significant satellites in $SmPd_3$, we tentatively conclude that the f^x levels are not normally mixed in the final states (in the presence of a core hole) because of the small radial extension of the Sm $4f$ level. In principle, similar mixing is involved in the pure rare earths, but it has a smaller magnitude. Two important consequences arise from these observations. Firstly we can now see a trend in the mixing of the f^x configurations in the light rare earths. Spectroscopic studies of heavy rare earths apparently reproduce the ratios of f^x configuration weightings in the initial-state wave functions deduced from techniques probing the ground state more directly[39,40] (e.g., lattice constants, magnetic properties)—mixing of the f^x configurations is negligible in heavier rare earths.

There are several techniques which probe the ground state more directly than photoelectron spectroscopy, such as measurements of lattice constants or magnetic properties.[39,40] The second consequence of our observations is that we can now rationalize why the ratios of f^x configuration weightings obtained from XPS core levels agree with these more direct measurements for heavier rare earths.[39,40] This must occur because the mixing of the f^x configurations is negligible in the final states for the heavier rare earths. One must, of course, still expect complications in surface-sensitive techniques (e.g., XPS) due to the different properties of the surface layer.[16,39,41] But the spectra of the RPd_3 compounds show the strongest effects of f^n-$f^{(n+1)}$ mixing and if the mixing is not observed in these alloys beyond Sm, then it probably will not be important in other RE materials beyond Sm.

The second point is that the XPS studies have given evidence that the f orbitals of Pr and Nd in the Pd_3 alloys are not completely "inert," and do mix with other states. To be sure, we did choose a series of compounds where the effect was strongest to investigate the effect. But there is at present no method to deduce mixing coefficients for the f^x configurations to give a quantitative estimate of the degree of hybridization and this clearly needs theoretical investigation. In the absence of results from such theoretical studies we do not know if core-level spectroscopies are particularly sensitive to mixing of the different f^x states, or if this mixing plays a dominant role in the general properties of these materials. We also suggest that where XPS shows the mixing of f^x configurations to be strongest (e.g., in the $R\mathrm{Pd}_3$ alloys of Nd and Pr) measurements of the classical properties of the materials under high pressure should show anomalies similar to those in Ce compounds.

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