

## Core-hole screening in lanthanide metals

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The multicomponent structure of the  $3d$  x-ray photoemission spectra of the light rare-earth metals is elucidated in terms of recent x-ray absorption and appearance-potential spectroscopy results for these materials. Both multiplet splitting due to  $3d$ - $4f$  exchange and satellite structure due to two competing screening mechanisms are identified. The main component of the  $3d$  line arises when the core hole is screened by  $5d$  conduction electrons; the satellite from a  $4f^n \rightarrow 4f^{n+1}$  process. The satellites in the metals occur at lower binding energies because the empty  $4f$  level falls below the Fermi energy. This interpretation is supported by an "equivalent cores" argument.

Recent appearance-potential spectroscopy experiments on the  $M_{IV}$ - and  $M_V$ -level excitation spectra of metallic barium<sup>1</sup> and lanthanum<sup>2</sup> have shown that the position of empty  $4f$  states is very sensitive to the electron configuration of the final core state. In the ground state, the empty  $4f$  level in Ba is believed to lie about 10 eV above the Fermi level.<sup>3</sup> Liefeld *et al.*<sup>4</sup> have obtained continuum isochromat spectra for La which show a peak about 2-eV wide located 5.5 eV above threshold which they interpret as the empty  $4f$  level. If the incident electron energy is increased to the  $M_\alpha$  threshold, excitation of  $3d$  electrons into  $4f$  states becomes possible. Since the  $4f$  states are localized in the core region, they are extremely sensitive to the attractive Coulomb potential of the  $3d$  hole. In the case of Ba, the  $3d^9 4f^1$  state still lies 3.8 eV above  $E_F$ ,<sup>2</sup> however, in La, the  $3d$  hole pulls the empty  $4f$  level down 1.8 eV below the Fermi energy. As has been pointed out by Wendin<sup>3</sup> and Kanski,<sup>2</sup> the  $3d$  hole has the same effect as a unit increase of the nuclear Coulomb potential, lowering the energy of the empty  $4f$  level. By photoemission of a  $3d$  electron we are therefore in principle able to create an empty  $4f$  level below occupied conduction-band states near the Fermi energy. In the following we consider the consequences of this core-ionization induced  $4f$  level shift on the x-ray photoemission (XPS) spectra of rare-earth metals.

For convenience we initially restrict our discussion to the  $3d$  spectrum of lanthanum. The general conclusions should be applicable as well to the light-rare-earth metals Ce, Pr, and Nd, but additional complications are expected in those cases because of multiplet splitting due to  $3d$ - $4f$  exchange.<sup>5-7</sup> However, unlike the  $4d$  spectra in which the  $4d$ - $4f$  multiplet coupling considerably exceeds the spin-orbit coupling, leading to extremely complicated structures,<sup>8</sup>  $3d$ - $4f$  exchange produces a multiplet splitting which is at most

comparable to the lifetime width of the  $3d$  levels.<sup>7</sup> Multiplet effects will be considered in greater detail below.

The effect of the core hole on the x-ray photoelectron spectra of *insulating* La compounds has been well known for some time.<sup>9-11</sup> We begin by summarizing previous work on these materials and then apply the same principles to the metal. The reference energy in the insulators is the edge of the ligand-derived valence band. In  $\text{LaF}_3$  the empty  $4f$  level is pulled down to an energy about 4.5 eV above the valence band by a  $3d$  core hole. A charge-transfer process from the valence band to the empty  $4f$  level is then possible, leading to a configuration  $3d^9 4f^1$  plus a delocalized hole in the  $F$   $2p$ -derived valence band. This ligand-to-metal charge-transfer process requires energy which is taken from the kinetic energy of the outgoing photoelectron, resulting in a high-binding-energy satellite, a common feature of insulating  $\text{La}^{3+}$  compounds.

As far as the outer electron orbitals are concerned,  $3d$  ionization has an effect very similar to that of adding another proton to the nucleus. Consequently the valence-band configuration of a core-ionized lanthanum compound should closely resemble the ground state of the corresponding  $\text{Ce}^{3+}$  compound, i.e., the separation between the  $3d$  line and its satellite in  $\text{La}^{3+}$  compounds should be very similar to the valence-band- $4f$  separation in the isostructural  $\text{Ce}^{3+}$  compound. This "equivalent cores" argument has been used to identify the origin of the high-energy satellites in insulating  $\text{La}^{3+}$  compounds.<sup>9,12,13</sup> In this context it is important to realize that the La satellite- $3d$  separation is equal not to the ionization potential of the Ce  $4f$  state, but to the energy separation between the states at the top of the valence band and the  $4f$  state. Two properties of the satellite structure in ionic rare earth compounds should be kept in mind, because the same mechanisms lead to quite

different consequences in the metals<sup>14</sup>: (i) The energy separation between satellite and  $3d$  decreases with increasing  $Z$  because of the increase in binding energy of the  $4f$  level. This leads to a decrease of the valence-band-edge- $4f$  separation,<sup>9,12</sup> which in the  $\text{LnF}_3$  ranges from 5 eV (La) to  $\sim 0$  eV (Eu). (ii) The intensity of the satellite is in some cases comparable to that of the  $3d$  line,<sup>10</sup> and of the order of 20% even in an unfavorable case like that of the fluoride.<sup>9</sup>

In the metals the empty  $f$  state is pulled below the Fermi energy, i.e., below filled conduction-band states.<sup>2</sup> If the  $4f$  level is now filled by an electron from conduction-band states, energy is gained in the process. In the light-rare-earth metals, we should consequently expect a low-energy satellite in the  $3d$  XPS lines. In Ba the  $4f$  level remains about +3.8 eV above  $E_F$  even in the presence of the  $3d$  hole so that no low-energy satellite should appear in XPS.

In order to check the validity of these concepts, we have examined the  $3d$  levels and the valence-band region of Ba and the light rare earths from La to Nd by XPS. The samples were prepared by *in situ* evaporation of the metals. Pressure during evaporation was always below  $1 \times 10^{-9}$  Torr. To minimize the effects of oxidation, data were taken only for about 20 min. Then a new film was evaporated. Data accumulation was always stopped when the oxygen  $1s$  signal became noticeable. The experiments were performed with monochromatized Al  $K\alpha$  radiation in a HP 5950A spectrometer, modified for UHV operation.

Spectra of the  $3d_{5/2}$  lines of Ba, La, Ce, Pr, and Nd are shown in Fig. 1. The data have not been corrected for background. The figure also contains theoretical curves fitted to the main peak of the data. In the cases of Ba, La, and Ce these are single lines with shapes given by the theory of Doniach and Šunjić.<sup>15</sup> For Pr and Nd the complete multiplet spectra calculated by Spector *et al.*<sup>7</sup> were used. In the case of Ce some multiplet structure is also expected. This is discussed below. In all cases, the theoretical line shapes were convoluted with the experimental resolution function which is represented by a skewed Gaussian of 0.6-eV FWHM. The asymmetry parameter in the Doniach-Šunjić theory was adjusted so as to give a fit to the high-energy tail of the lines. Also shown in Fig. 1 are the differences between the experimental data points and calculated curves. It is evident that all but the Ba spectrum show a low-energy satellite in agreement with expectations.

The intensity of the satellites in the metals in Fig. 1 is very small compared with the  $3d_{5/2}$  line and in no case exceeds 6%. This is in sharp con-

trast to the intensity of the high-energy satellites in insulating La compounds.<sup>9</sup> It is undoubtedly due to the fact that in metals screening of the core hole by the conduction electrons provides an effective competing process. The main line, which corresponds to the screened core hole, is by far the dominant final state according to the results in Fig. 1.

For a more detailed comparison, the satellites alone are shown in Fig. 2 with the energy zero taken at the position of the  $3d_{5/2}$  line. Three facts stand out: (i) as already mentioned, there is no

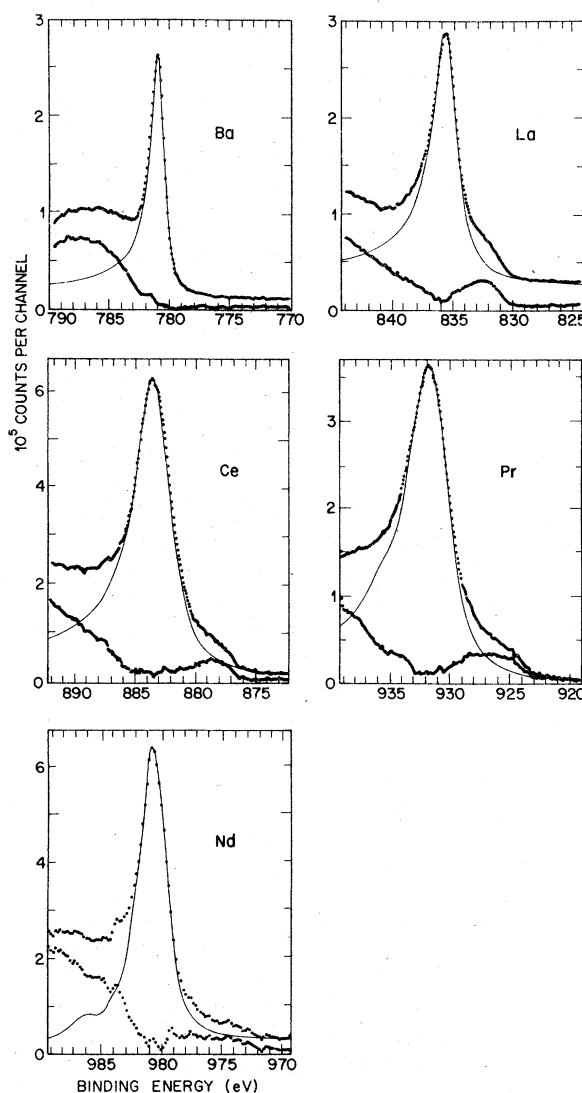


FIG. 1. X-ray photoemission spectra of the  $3d_{5/2}$  level in Ba, La, Ce, Pr, and Nd. Solid lines are fits to the experimental data assuming single Doniach-Šunjić lines in Ba, La, Ce, and multiplet-split lines in Pr and Nd. The difference between measured and calculated curves, indicative of low-energy satellites, are also plotted.

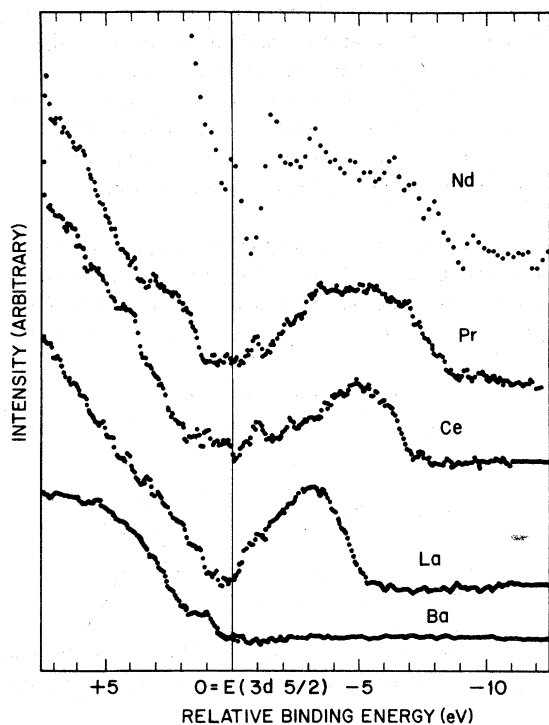


FIG. 2. Differences between measured and calculated curves of Fig. 1 with the  $3d_{5/2}$  position as the energy zero, showing shape and position of low-energy satellites.

indication of a low-energy satellite in Ba; (ii) the shape of the satellites is asymmetric and does not resemble that of the screened core hole state. This is no surprise because the shape of the satellite is determined not only by the lifetime and multiplet splitting of the  $3d$  core-hole state, but also by the shape of the density of occupied states in the  $5d$  conduction band. Unfortunately the shape of the satellite is not very well determined because it depends on the details of the main line which is subtracted, and thus on the lifetime width and multiplet splitting used to fit this line. (iii) The satellite- $3d$  separation in the metals increases with increasing  $Z$ . This is a natural consequence of the fact that in the metals the  $4f$  level drops further below the Fermi energy as  $Z$  increases (see Fig. 3).

The energy of the satellites in the insulating compounds could be quite accurately estimated simply on the basis that, as far as the outer electrons are concerned, ionization of the  $3d$  shell has an effect which is well approximated by adding a proton to the nucleus. In the metals there is a second independent check based on the observation that the XPS final-state corresponding to the filled  $4f$  state, i.e., the one corresponding to the satellite, is formally identical to the state produced by x-ray absorption at the  $M_V$  edge. Consequently,

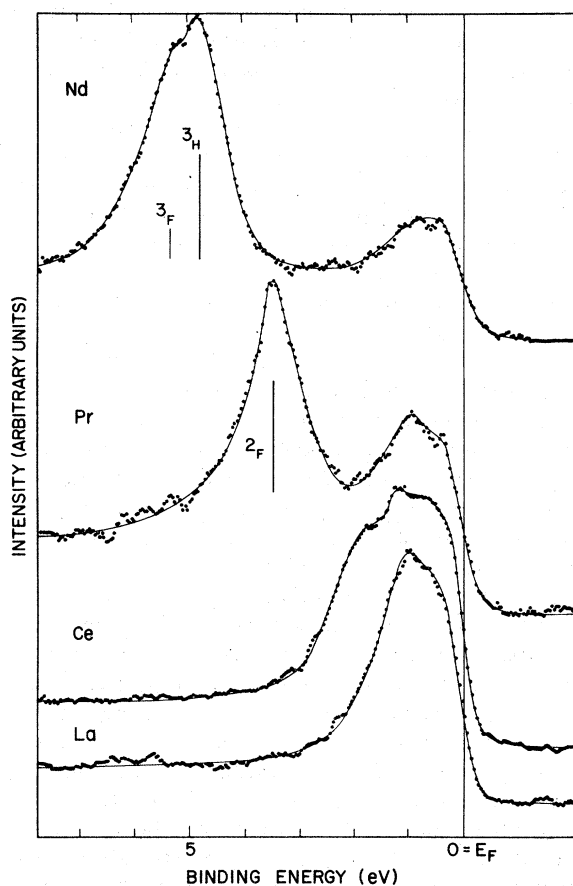


FIG. 3. X-ray photoelectron spectra of the valence bands of the light rare earths. Comparison of the portion of the conduction band immediately below  $E_F$  strongly suggests that the  $4f$  level in Ce is at  $-1.8$  eV.

we would expect a close correspondence between the binding energy of the low-energy satellites in the rare-earth metals and that of the  $M_V$  absorption edges. In Table I we present the  $3d_{5/2}$  binding energies and the satellite energies as determined from our experiments together with the  $M_V$  absorption edges determined by Fischer

TABLE I. Comparison of rare-earth  $3d_{5/2}$  excitation energies.

	$E_{3d_{5/2}}^a$	$E_{ABS M_V}^b$	$E_{SAT}^c$	$E_{APS}^d$
Ba	780.1(1)	...	...	...
La	835.6(1)	833.5(4)	832.4(4)	833.8
Ce	883.7(1)	881.5(4)	878.8(4)	880.1
Pr	931.9(1)	928.7(4)	927.0(4)	926.9
Nd	980.6(1)	976.0(4)	975.3(8)	975.4

<sup>a</sup>XPS  $3d$  binding energy.

<sup>b</sup>X-ray absorption edge energy, from Ref. 16.

<sup>c</sup>XPS satellite energy.

<sup>d</sup>APS resonance, from Ref. 17.

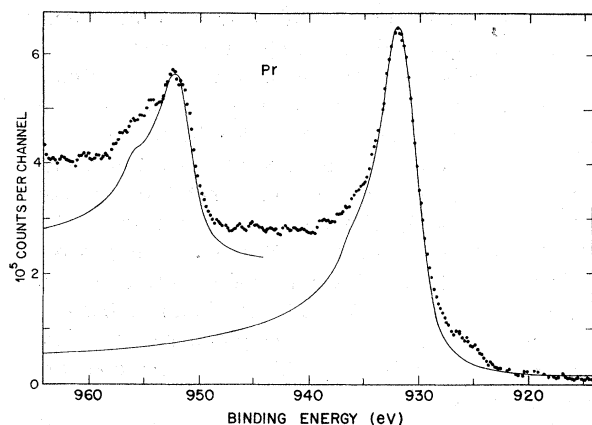


FIG. 4. X-ray photoelectron spectrum of the  $3d$  doublet in Pr metal. The solid line has been calculated using the theoretical multiplet energies of Spector *et al.* (Ref. 7) showing good agreement between theory and experiment. No background subtraction has been performed.

and Baun.<sup>16</sup> Both satellite energy and  $M_V$  absorption edge are clearly shifted to smaller values, however, in every case but Nd the displacement of the satellite from the  $3d_{5/2}$  line exceeds that of the absorption edge. Since the data of Ref. 16 were taken on oxidized samples one may not wish to attach too much significance to this discrepancy. Fortunately another estimate of the  $3d^9 4f^{n+1}$  final-state energy has been obtained from appearance-potential spectra (APS) of rare earths in dilute solution in a NiCr alloy.<sup>17</sup> The values obtained from Fig. 4 of Ref. 17 (see Table I) are generally in better agreement with the XPS satellite energy, but the discrepancy in the case of La is not reduced. A possible explanation may be found in the observation that the dipole selection rule restricts the states populated in the x-ray absorption process to a subset of those accessible in the XPS satellite process. Since the XPS satellites are broad and of poorly determined shape one can only remark that the  $M_V$  edge energy falls within the satellite envelope, though not at its peak.

The equivalent cores argument provides an alternate though less direct determination of the satellite energy. Postulating an equivalence between core-ionized La and Ce in an ionic salt may be a reasonable approximation, but the extension to metals introduces additional uncertainties, especially if data for Ce metal instead of dilute Ce in La are used. In the case of metals the  $3d$ -satellite separation in the  $Z$  element should be approximated by the binding energy of the  $4f$  level measured relative to the Fermi level in the  $Z+1$  element. We have therefore measured the valence bands of the light rare earths in question with the

results given in Fig. 3. The  $4f$  level is readily identified in the Nd and Pr spectra and does not appear at all in the spectrum of La. We identify the  $4f$  level in Ce with the shoulder about 1.8 eV below  $E_F$  at the bottom of the conduction band. In Table II we have summarized the  $4f$  binding energies obtained from Fig. 3. They are in fair agreement with the values obtained by Baer and Busch.<sup>18</sup> Also shown are the satellite separations and the displacement of the  $M_V$  absorption edge from the  $3d_{5/2}$  level in the  $Z-1$  elements. Considering the uncertainties inherent in the equivalent cores argument, the close agreement between the values given in columns 1 and 3 is quite astonishing.<sup>19</sup> Both values, however, show only poor agreement with the satellite energies. Herbst *et al.*<sup>20,21</sup> have calculated the energy  $\Delta_-$  required to promote a  $4f$  electron into the conduction band at  $E_F$ . This is also the energy gained by a rare-earth ion upon condensation of a conduction electron into the empty  $4f$  level and should thus correspond to the satellite energies. Values of  $\Delta_-$  which assume complete screening are shown in column 4 of Table II. "Complete screening" in this connection means that the final state after photoemission is represented by an electrically neutral atomic sites. Comparison of columns 1 and 4 in Table II shows that measured and calculated  $4f$  binding energies agree quite well and also agree with the displacement of the  $M_V$  absorption edges. The satellite energies are, however, larger in both La and Ce metal.

We would also now like to comment briefly on the question of the position of the  $4f$  level in  $\gamma$ -Ce. In their original work Baer and Busch<sup>18</sup> attribute the band at 1.8 eV to the  $4f$  level. In a later investigation<sup>22</sup> the peak around 0.9 eV was identified with the  $4f$  level. Recently Steiner *et al.*<sup>23</sup> produced a sharp peak close to  $E_F$  in a difference spectrum of Ce and La metal by shifting the La spectrum by 0.9 eV towards higher binding energy. The shift was motivated by the assertion that the work function of La exceeds that of Ce by that amount. The systematics of the structure in the

TABLE II. Comparison of various estimates of the location of the empty  $4f$  level, in eV measured from  $E_F$ .

	$E_{4f}$ <sup>a</sup>	$\Delta E$ <sup>b</sup>	$\Delta M_V$ <sup>c</sup>	$\Delta_-$ <sup>d</sup>
Ce	1.8(1)	3.2(2)	2.2(5)	1.9
Pr	3.5(1)	4.9(2)	3.2(5)	3.8
Nd	5.0(1)	5.3(3)	4.6(5)	5.1

<sup>a</sup>XPS  $4f$  binding energy.

<sup>b</sup>XPS  $3d$  satellite shift in next-lower- $Z$  element.

<sup>c</sup>Difference between  $M_V$  edge and XPS binding energy.

<sup>d</sup> $4f$  excitation energy calculated in Refs. 20 and 21.

TABLE III. Lifetime widths in eV of light-rare-earths  $M_V$  levels.

	$\Gamma$ (expt)	$\Gamma$ (theor) <sup>a</sup>
Ba	0.82(5)	0.71 <sup>b</sup>
La	1.87(5)	0.73
Ce	2.19(8)	0.82 <sup>b</sup>
Pr	2.27(5)	0.92 <sup>b</sup>
Nd	1.44(8)	1.00

<sup>a</sup>From Ref. 25.

<sup>b</sup>Obtained by interpolation.

valence bands in La, Ce, and Pr shown in Fig. 3 strongly suggest the identification of the shoulder at 1.8 eV with the  $4f$  state in Ce. The equivalent cores interpretation of the La  $M_V$  absorption edge and the XPS spectra also points towards a  $4f$  energy of about 2 eV in Ce. This has the additional merit of being in agreement with recent theoretical evaluations.<sup>21</sup>

We finally want to consider the widths of the screened core-hole final-state lines in Fig. 1. The total width increases monotonically from Ba to Pr, but is smaller in Nd. Although the contributions due to phonon excitation are not exactly known, the calculations of Flynn<sup>24</sup> provide an upper limit for the phonon widths of the order of 150 MeV, i.e., entirely negligible in the present context. Although multiplet splitting makes an appreciable contribution in Pr and Nd, the width of the  $3d_{5/2}$  line is mainly due to lifetime (see below). The spectrum of Ce is the only one which shows some marginally resolved structure. Calculations for the configuration  $3d^9 4f^1$  which corresponds to the Ce  $3d$  XPS final state are available only for the photoabsorption process in La.<sup>6</sup> In this case the dipole selection rules permit only one transition corresponding to the  $M_V$  line. Although other states may be accessible in the Ce XPS experiment, we have nevertheless made a single-line fit to the Ce  $3d_{5/2}$  spectrum in Fig. 1. In Table III we have collected our experimental lifetime widths and compared them to theoretical values obtained by McGuire<sup>25</sup> for isolated atoms. The agreement between theory and experiment is reasonably good only for Ba. In all other cases the experimental width exceeds the theoretical one by a substantial margin. The basic reason is that the state created by  $3d$  photoemission has an empty  $4f$  level below the Fermi energy which is also shortlived. As a result the final state corresponding to the main XPS line has two decay paths, Auger deexcitation of the  $3d$  hole and filling of the  $4f$  state. Only the former is included in the calculations of McGuire. The latter can be esti-

mated from the width of the  $4f$  state in the valence-band spectrum of the  $Z+1$  element. For Pr we find a  $4f$  state FWHM of about 1.1 eV, sufficient to account for the extra width of the main  $3d$  line of Ce. In the cases of Ce and Nd the lifetime widths are not as well defined by the valence-band spectra but are clearly of comparable magnitude and seem capable of accounting for the width of the La and Pr  $3d$  spectra. The decrease in width of the  $3d$  spectra at Nd is probably related to the narrowing of the  $4f$  linewidth with increasing  $Z$  as the  $4f$ -valence-band overlap decreases. It thus appears that the  $3d$  linewidths are understood, at least qualitatively.

The  $3d$  multiplet splitting in Pr and Nd was calculated in the work of Spector *et al.*<sup>7</sup> They also compared the resulting energy levels with XPS experiments on Nd and Pr  $3d$  levels, but were able to obtain a correspondence with the shape of their experimental curves only by expanding the theoretical energy scale by a factor of 1.5. In Fig. 4 we present a superposition of our Pr  $3d_{3/2, 5/2}$  data with a theoretical curve obtained using the line positions and intensities from Ref. 7 and a lifetime width adjusted to reproduce our measured curves. (The calculated spectrum was also convoluted with our experimental resolution function.) It is evident that the agreement between theory and experiment is satisfactory without use of an energy expansion factor. (No background correction was applied to our data.) It seems likely that the difficulties encountered in Ref. 7 were due to partial oxidation of their samples. The authors claim that during their experiment the O 1s to rare-earth  $3d_{5/2}$  intensity ratio never exceeded 0.2. However, in view of the fact that the oxygen 1s cross section is small compared to the rare-earth  $3d$  cross section this limit actually corresponds to a large amount of surface oxide.

To summarize, we have shown that the dominant final state in x-ray photoemission from the  $3d$  levels of the light rare earths is produced by screening the core hole within the  $5d$  conduction band. This leaves the  $4f^{n+1}$  level empty even though it is pulled below the Fermi energy by the unscreened  $3d$  hole. The decay of this empty  $4f$  level contributes to the width of the  $3d$  core hole state. A state of lower energy, obtains with much smaller probability when the  $4f^{n+1}$  level is filled by an electron from conduction-band states close to  $E_F$ . This state appears as a lower-binding-energy satellite in the  $3d$  spectrum. Evidence for this interpretation is obtained both from an equivalent cores argument and from the displacement of the  $M_V$  x-ray absorption edge. Measured  $4f$  binding energies are in excellent agreement with the theory of Herbst *et al.*

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