Valence-Band Photoemission in La and Pr: Connections with the Ce Problem

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Abstract
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Keywords
Ames Laboratory, cerium, Fermi level

Disciplines
Atomic, Molecular and Optical Physics | Physics

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Valence-Band Photoemission in La and Pr: Connections with the Ce Problem

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(Received 17 January 1984)

Energy distribution curves from La and Pr were taken from 32 to 80 eV photon energies. Above 50 eV the valence-band photoemission in La is very weak, implying that previous studies of Ce have underemphasized the 4f contributions. Pr exhibits two peaks attributable to 4f electrons, similar to the structures in Ce.

PACS numbers: 79.60.Cn

The valence-band photoemission of Ce, and its compounds and alloys, exhibits two peaks attributable to 4f emission. To determine whether Ce is unique, it is useful to study the neighboring elements, La and Pr. We have done so, using the same techniques applied previously to Ce, obtaining two new results that place the photoelectron spectra of Ce in better perspective.

The 4f and valence electrons (derived from the 5d, 6s, and 6p electrons) overlap in the photoemission spectrum of Ce. The problem has been to separate the two contributions, on the assumption that the two types of states do not hybridize enough to make such a separation meaningless. The two 4f-related features were isolated in cerium by subtraction techniques in which energy distribution curves (EDC’s) at two photon energies were normalized at a binding energy for which there was no apparent 4f character in the EDC, and then a difference curve was produced. A more accurate technique would be to take the difference between Ce (4f) and La (4f) EDC’s, although the crystal structures are different. We find in La that the 5d, 6s, and 6p photoelectron cross sections fall to negligibly small values at photon energies where the 4f cross section in Ce is still large. This means that the subtraction methods used previously to emphasize the 4f contribution to the Ce spectrum actually overcorrected for the non-4f-electron contribution.

The Pr spectra show two features attributable to 4f-electron emission, one at 3.6 eV, in agreement with x-ray photoemission spectroscopy results, and a new feature at about 0.75-eV binding energy, analogous to the peak in Ce which is near the Fermi level.

The experiments were carried out with the apparatus described previously. Samples of La and Pr were obtained from the Ames Laboratory and outgassed extensively in a vacuum of 1x10^-10 Torr. Films were evaporated onto substrates at approximately 0°C to slow the diffusion of contaminants to the surface. The photoelectron spectra were measured for a series of photon energies, with synchrotron radiation from the storage ring Tantalus at the Synchrotron Radiation Center of the University of Wisconsin, Madison. The light was monochromatized by a grasshopper grazing-incidence monochromator and the photoelectrons were analyzed by a commercial double-pass cylindrical-mirror analyzer. The total resolution for the spectra displayed is about 0.25 eV. The oxygen 2p emission was monitored and is barely visible in the spectra we present.

Figure 1 shows the EDC’s for La obtained over a range of photon energies. The EDC’s have been corrected for changes in incident photon flux at the various photon energies. As the energy increases, the valence-electron photoexcitation cross sections fall to very small values. The significant point is that while the magnitudes of the EDC’s change with energy, the shapes do not change. This is not the case for the La-Th data presented in Ref. 5, in which a peak at ~ 1 eV grew as the photon energy increased. The lack of shape changes in the EDC’s means that band-structure effects play little role at these high photon energies. The inset of Fig. 1 shows the logarithm of the integrated area of each EDC. Notice that the intensity at 60 eV is two orders of magnitude smaller than the intensity at 32 eV. The cross sections at higher photon energies are determined primarily by the part of the radial wave function within the atom. Hybridization effects should not be large there, and so we expect the large falloff in the valence electron photoelectron cross section for double hcp La to be applicable to fcc Ce as well. The addition of the 4f electron in Ce should not cause a problem since the 5d6s occupancy remains essentially unchanged, even if Ce has a 4f count of only 0.8 electron.

The La spectra indicate that at a photon energy of 60–80 eV, very little of the photoemission in Ce (and in many Ce compounds and alloys) come directly from the valence electrons. The sub-
FIG. 1. Energy distribution curves for photoelectrons from La excited with photons between 32 and 60 eV, marked on the right of each curve. The ordinates are in arbitrary units, but they are the same for all EDC's. A correction for the incident flux has been applied. The inset shows the integrated areas of the EDC's as a function of photon energy.

traction techniques we, and others, have used thereby overcorrected for the valence-electron contribution to the EDC's and the true 4f related intensity consists not only of the two peaks reported, but also of a region between them, and a tail extending to the deeper binding-energy side of the deeper peak. In short, it resembles the full EDC measured with 60–80-eV photons, after correction for scattered electrons. This is in accord with two of the models proposed for the photoemission spectrum of Ce.6,7

Figure 2 shows the EDC's of the valence-band region of Pr. The large peak at 3.6-eV binding energy is from the 4f electrons, and is well known from x-ray photoemission spectroscopy.8 It grows in prominence as the photon energy increases because the 4f photoexcitation cross section decreases less rapidly than the valence-electron cross sections.

An additional structure is observed to grow in parallel at lower binding energy. This is better seen in Fig. 3, where only the 0–2-eV region of binding energy is shown. (The curves in this figure have been arbitrarily normalized so that the low-energy feature can be seen for all photon energies.) The broad valence-band structure in the 0.3–0.8-eV region diminishes in relative strength as the photon energy increases, and is replaced by a peak at about 0.75 eV. This peak is very broad. Its width is difficult to estimate, but is on the order of 0.5–1 eV. Because the 5d, 6s, and 6p cross sections become so small relative to the 4f cross section in the region of 80-eV photon energy, most of the spectra shown for this energy in both figures arise from 4f excitations. Thus Pr has two peaks arising from the 4f electrons, as does Ce, but the difference is that in Pr, the shallower peak ("fully screened peak") is weaker and broader than the deeper peak. It is not tied to the Fermi energy, but from Fig. 3, there is some 4f character to the photoemission intensity at the Fermi level. The peak at 0.75 eV has been seen
FIG. 3. Same as Fig. 2, but with an expanded scale.

in a Pr$_{0.9}$Th$_{0.1}$ alloy, but it was believed to arise from valence electrons at the time.

There are two models for the two-peak contribution of the 4$f$ electrons to the photoelectron spectrum in Ce. One emphasizes the 4$f$-5$d$ hybridization, while the other emphasizes the 4$f$-5$d$ Coulomb interaction, with the hybridization, treated as small, added later. The latter picture easily allows a two-peak structure for the 4$f$ contribution to the EDC in Pr. It is less obvious that the former picture does so as well. With reasonable parameters, the one-electron picture of a discrete level hybridizing with a partly filled band can yield a two-peak structure resembling that in Pr. If the subsequent many-body effects do not alter the spectral function too much, the model of Ref. 7 could also account for the double peak. A third model for the Ce EDC involves a Ce 4$f$ radial wave function which is not the usual one. If it can be applied to Pr, it appears to yield a second peak, if present, at or near the Fermi level, in disagreement with our results.

In summary, we have shown that the 5$d$, 6$s$, and 6$p$ photoionization cross sections in La are extremely small for photon energies above 40 eV, presumably remaining small until the 4$d$ threshold near 100 eV. This means that previous studies of the 4$f$ photoemission in light rare earths have underestimated the contributions of the 4$f$ electrons to the spectra. Moreover, the 4$f$ electrons are seen to contribute to the EDC's in the region between the two observed peaks in Pr, as well as in Ce. The fact that such 4$f$ spectra are seen in both elements raises questions about the necessity of having the 4$f$ level near the Fermi level in order to yield such a complex 4$f$ spectrum.

We wish to acknowledge the receipt of samples of pure La and Pr from B. J. Beaudry and O. D. McMasters of the Ames Laboratory, and help from the staff of the Synchrotron Radiation Center, operated under National Science Foundation Contract No. DMR8020164. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the U.S. Office of Basic Energy Sciences.

10W. Allen, private communication.
12C. M. Varma, private communication.