High-resolution photoemission study of γ- and α-cerium

D. M. Wieliczka, C. G. Olson, and D. W. Lynch
Ames Laboratory—U. S. Department of Energy and Department of Physics, Iowa State University, Ames, Iowa 50011
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High-resolution photoemission studies on the α and γ phases of cerium show changes in the binding energies of the two $4f$-related features. The location of the two $4f$-related features in the γ phase are at -0.2 and -2.0 eV, while in the α phase these features are located at the Fermi level and -2.1 eV. These results are a direct test of the theories proposed to explain the presence of the two features.

Cerium exhibits an isostructural phase transiton, γ-α, in which its face-centered-cubic lattice collapses by approximately 15%.[1] Understanding the behavior of the $4f$ electrons in this phase transition of cerium has been considered pivotal in explaining the role of $4f$ electrons in the physical properties of Ce and Ce compounds. Recent ultraviolet photoemission (UPS) studies of Ce in the γ and α phases[2] and a Ce-Th alloy[3] have shown two $4f$-related features in the valence-band spectra, one at 2 eV and the other near the Fermi level.

Several theories have been proposed recently for explaining the UPS results. They all involve a many-body interaction as the cause of the two-peak spectra, but they differ in what the key interaction is. Liu and Ho[4] use the screened Coulomb interaction between the $4f$ hole and the s-p-d valence-band electrons. Their model is applicable to both α- and γ-Ce, as well as to other materials, but it deals primarily with only the UPS spectrum. The models of Gunnarsson and Schönhammer,[5,6] of Allen and Martin,[7] and of Lavagna *et al.*[8,9] use the one-body f-d hybridization as the key interaction. It has been used to give an account of many physical properties of cerium, including the phase change itself, but the UPS spectrum has been calculated only for the α phase.[5,6] These models are basically the same in initial assumptions. Schlüter and Varma[10] studied the ground state of Ce, proposing an excitonic model that can give two $4f$-related peaks in both α- and γ-Ce. All of these models, except that of Liu and Ho, require one of the $4f$ UPS peaks to be located at the Fermi energy, although the model of Liu and Ho allows this placement. Only the model of Liu and Ho can be used to date to describe the UPS spectrum of γ-Ce. (A survey of the spectroscopy of $4f$ electrons in Ce and Ce compounds has recently been presented by Hüfner and Steiner.[11])

This paper reports additional information on the $4f$-related features in the UPS valence-band spectra of α- and γ-Ce. With improved resolution the spectra show a slight shift in the positions of the peaks in the two phases. Previous results, with lower resolution, showed the two peaks to be coincident. These shifts must be addressed by each of the proposed models.

The samples were prepared by evaporation *in situ* of high-purity, Ames Laboratory cerium. The γ phase was prepared by evaporation onto a room-temperature substrate, and the α phase was evaporated onto a substrate held at 15 K by a closed-cycle refrigerator. Previous tests[2] showed that negligible amounts of β-Ce should be present, especially since we did not cycle any samples through the β-phase region. The samples were prepared at a pressure of 10^{-10} Torr and the measurements performed at a pressure of less than 10^{-10} Torr. The energy analysis was performed by a commercial double-pass cylindrical-mirror analyzer with a theoretical resolution of 80 meV at a pass energy of 5 eV. The light source was the Tantalus storage ring located at the Synchrotron Radiation Center in Stoughton, Wisconsin. The light was monochromatized by using a Grasshopper monochromator with a resolution of 60 meV. The overall calculated resolution was 100 meV.

The energy distribution curves (EDC's) for α-cerium are shown in Fig. 1. The total experimental resolution, as determined by the width of the Fermi level, is 120 meV. The EDC's cover a photon-energy range from 40 to 60 eV and have been normalized to the intensity at an energy of -1.0 eV. As the photon energy is increased several changes occur. The most noticeable change is the growth of the two features located at -2.1 and -0.1 eV. These effects are caused by the decrease in $5d$ and increase in $4f$ photoionization cross sections as the photon energy increases.

The results for γ-cerium are shown in Fig. 2. Again the EDC's cover a photon-energy range from 40 to 60 eV and have been normalized to the intensity at a binding energy of -1.0 eV. The figure shows that the EDC's for γ-cerium are very similar to those for α-cerium. The Fermi level shows an increased width to 150 meV due to thermal broadening. The two $4f$-related features are now located at binding energies of -2.0 and -0.2 eV and there is a noticeable shoulder between the feature at -0.2 eV and the Fermi level.

We have shown previously that these are two $4f$-related features in the valence-band EDC's of α- and γ-Ce.[2] It is clear from Fig. 3 that there is a shift in the binding energy of the two $4f$-related features between the two phases. The two features shift in opposite directions, so that a simple temperature dependence cannot account for all of the observations. For the range of photon energies used, the electron escape depth is quite small, near its minimum value, and our spectra thus sample the surface and the bulk. A recent study[12] of Yb has shown that films eva-

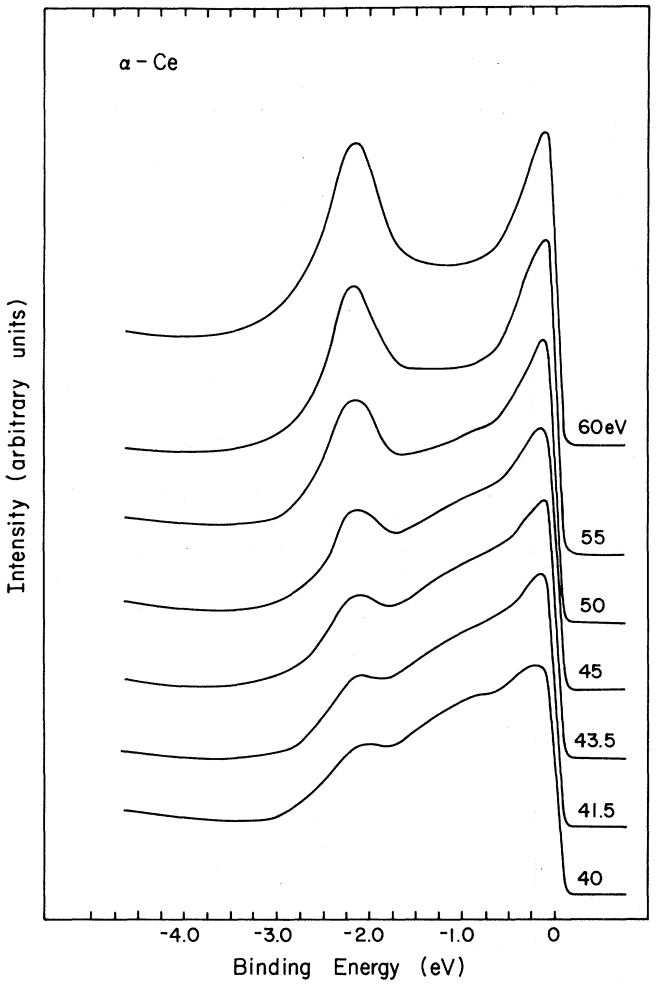

FIG. 1. Photoemission EDC's for α-Ce in the photon-energy range of 40—60 eV. The photon energy is given to the right of each curve. The curves have been normalized to the intensity at an energy of -1.0 eV.

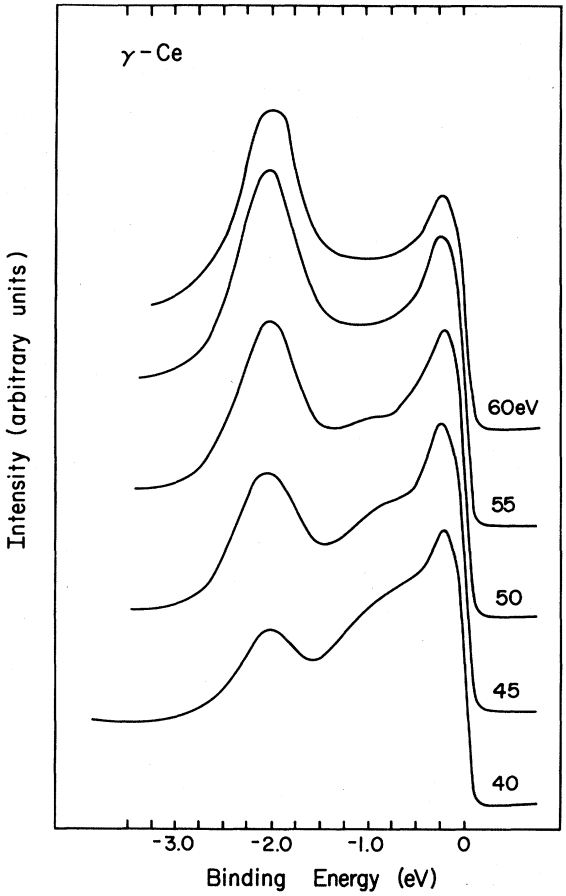

FIG. 2. Same as for Fig. 1 except for γ-Ce.

porated onto substrates at different temperatures, as were ours, gave $4f$ spectra that had different surface shifts. This was ascribed to a different coordination for surface atoms in films deposited at different temperatures. (The two $4f$ features in the Yb EDC's have a different origin than those in Ce. They both have identical surface shifts in Yb.) Such an effect cannot be conclusively ruled out in Ce, but we point out that the surface shift in the $4f$ binding energy is only 0.3 eV (Ref. 13) or less[14] for Ce, rather than the 0.9 eV in Yb.[12] Surface coordination changes in Yb produce differential shifts in binding energy of about one-third of the surface shift. In Ce a comparable shift would be 0.1 eV or less, presumably in the same direction for both peaks. We do see shifts of this size, but one is in the opposite direction. Because the surface binding energy shifts are so small, and the spectra are less amenable to decomposition into components than those of Yb, it will be difficult to carry out studies like those done on Yb.

The key question to be answered is where the peaks are actually located. The deeper peak is at -2.0 eV in γ-Ce and -2.1 eV in α-Ce. The shallower peak is very close to -0.2 eV in γ-Ce, and there is a second valence-band structure between it and the Fermi energy. In α-Ce the corresponding peak has shifted closer to the Fermi level, but it lies on a rapidly varying background composed of the "density of states" of the valence electrons and the Fermi function cutoff. This, when convolved with the in-

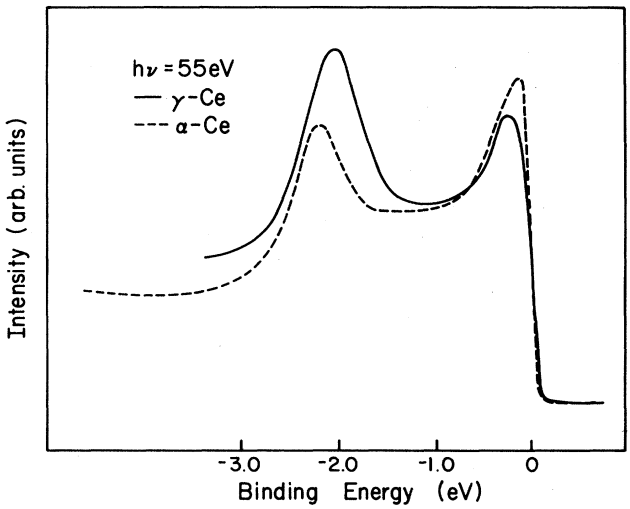

FIG. 3. EDC's for γ- and α-cerium at a photon energy of 55 eV. The two EDC's have been normalized to -1.0 eV.

strument function, can cause the peak to appear shifted in the spectrum. Since we do not know the intrinsic shape for the peak, nor that of the underlying density of states, we cannot fit the spectra to any model with conviction. The use of a Lorentzian peak[15] to mimic crudely the $4f$ peak, cutoff by a Fermi function, then convolved with our instrument function (assumed Gaussian) showed that a peak at the Fermi level easily could be shifted to -0.1 eV in the observed spectrum. This peak could also be located at a binding energy of 0.05 eV and be consistent with the observed -0.1-eV peak.

The present results put restrictions on the proposed theories for the UPS of Ce. The peak at -2.0 (-2.1) eV in γ (α) Ce is, in all cases a "direct"-like peak, and the shift of 0.1 eV can result from the lattice contraction upon entering the α phase. The peak at (or within 0.5 eV of) the Fermi level in α-Ce is consistent with all models. Its occurrence at -0.2 eV in γ-Ce is consistent with the Liu-Ho model. Its location in the model of Varma and Schlüter appears to be at the Fermi level, not in agreement with our measured result. The "Kondo" models[5–9] have not yet addressed the position in γ-Ce.

The quantitative aspects of all models to date rely heavily on fits to the two experimental features. The abilities of the theories to explain the detailed differences with the phase transition await more exact calculations. Our results have established that any model which pins one feature to the Fermi level in *both* phases of Ce is inappropriate. It is at the Fermi level in α-Ce, but 0.2 eV below in γ-Ce.

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[1]For a review, see D. C. Koskenmaki and K. A. Gschneidner, Jr., in *Handbook of the Physics and Chemistry of the Rare Earths,* edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), Vol. 1, Chap. 4.

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[15]Gerken (Ref. 14) fit the -2-eV peak in α-Ce with a Lorentzian of FWHM of 0.45 eV. A fit to the Doniach-Sunjić line shape was attempted, resulting in an asymmetry parameter of 0, i.e., a Lorentzian.