

“ γ - α ” Phase Transition of Monolayer Ce on W(110)

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As Ce is adsorbed on a W(110) substrate at 300 K an epitaxial layer develops at a coverage of 0.5 monolayer. LEED patterns indicate a hexagonal pattern consistent with Ce(111). As Ce is added, the lattice parameter shrinks continuously from 9% larger than that for γ -Ce to 3% smaller than that for α -Ce. 4*f* photoelectron spectra reveal two peaks similar to those of γ -Ce, changing relative intensity with increasing coverage to resemble those of α -Ce.

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Elemental cerium exhibits an interesting phase transition at high pressures [1,2]. The fcc γ phase transforms into the fcc α phase. By suitable application of pressure and temperature, one can go continuously from the normal γ phase at room temperature and pressure to the α phase, i.e., there is a critical point, the only one for an elemental solid. One can produce this phase change at atmospheric pressure simply by cooling, but there is an intermediate hexagonal β phase [2]. The γ - α transition is an interesting one, for both phases have the same structure, but at atmospheric pressure, the α phase has a 17% smaller volume. Several models have been proposed to account for the phase change [3–8]. Photoemission studies, when interpreted, show a slight difference in the number of 4*f* electrons in the ground state for the two phases, not the loss of the 4*f* electron upon entering the α phase [8–13].

The γ - α transition has been studied by photoemission on thick films of Ce [14] and on bulk Ce_{0.9}Th_{0.1} (which does not have a β phase) [15]. The photoelectron energy distribution curves (EDCs) of both phases exhibit a pair of peaks which originate from states with 4*f* character, even though there is only about one 4*f* electron per atom [14–16]. Following the Gunnarsson-Schönhammer (GS) model, the peak near the Fermi level is from the “well-screened” final state, with the 4*f* hole “filled” by a valence electron, and the other is from the “poorly screened” final state, with valence electrons (5*d*) partially screening the hole. There is also 4*f* character in the unstructured region between these peaks. Photoemission studies of Ce clusters on Si [17] and on Ce matrix isolated in Xe [18] have shown that the double-peak structure does not appear until the clusters are large enough to be metallic, i.e., to show a Fermi edge.

In the following, we report the appearance of both α - and γ -like phases in an overlayer of Ce on the (110) surface of W. The photoelectron spectra show changes in the relative intensities of the two peaks with Ce coverage. At a coverage of about a Ce monolayer, the Ce 4*f* photoelectron spectrum is γ -like, changing continuously to α -like as the coverage increases slightly to make a more compact monolayer. LEED patterns show a hexagonal pattern, expected for an fcc (111) or hcp (0001) layer,

the lattice parameter of which decreases continuously as the Ce coverage increases.

The photoemission studies were carried out on the Ames-Montana State beam line on Aladdin at the Synchrotron Radiation Center [19]. The overall (electron and photon) resolution was 0.36 eV. The W(110) substrate was cleaned by repeated anneals at 2300°C. The pressure in the chamber did not exceed 1×10^{-10} Torr during evaporation of previously outgassed Ce from a W basket and 5×10^{-11} Torr afterwards. LEED patterns were taken between photoelectron spectral scans. The thickness of the Ce was monitored with a quartz oscillator calibrated against the formation of a monolayer as observed by LEED. In addition, separate LEED studies were carried out. The surface cleanliness was verified by the sharpness and stability of the LEED patterns and by the W surface 4*f* core-level shift, which is very sensitive to contamination.

Figure 1 shows angle-resolved photoelectron EDCs in the valence-band region taken at normal emission with a photon energy of 122 eV (Ce 4*d* → 4*f* resonance [16]) for several coverages of Ce on W(110). At this energy the contributions of the Ce 4*f* electrons dominate the EDCs, W 5*d* contributions being negligible. The inset shows the spectra for γ - and α -Ce taken from Ref. [14]. The changes in relative intensity of the two peaks in Fig. 1 with increasing coverage are similar to those for the γ -to- α transition, except that they are larger. We discuss this later. EDCs taken away from normal emission show similar changes, so band dispersion is not important here. Partial yield spectra in the region of the 4*d* → 4*f* transitions of Ce were taken intermittently, but they showed no observable change. Such spectra can monitor significant changes in ground-state 4*f* occupancy. Only a slight change in this spectrum occurs upon producing the phase transition by cooling bulk Ce [14], reflecting the small change in 4*f* occupancy.

Figure 2 shows LEED patterns for several coverages in the range of those in Fig. 1. For $\Theta < 0.5$ monolayer (ML) [in units of the W(110) surface density, 1 ML = 14.17×10^{14} atoms/cm²] the LEED pattern [Fig. 2(a)] consists of rows of new spots along the dashed lines arising from chains of Ce atoms along the $[\bar{1}10]$ direc-

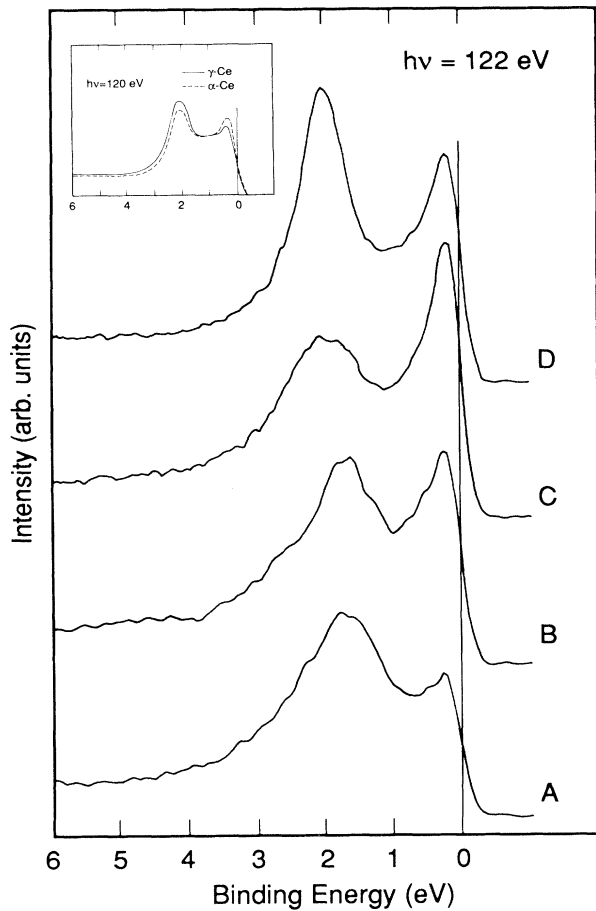


FIG. 1. Photoelectron energy distribution curves in the valence band and $4f$ region of Ce overlayers on W(110) taken with a photon energy of 122 eV. The LEED patterns for each are as follows: *A*, (2×1) , just before changing to hexagonal; *B*, hexagonal with the spacing about that of γ -Ce (111); *C*, hexagonal with the spacing about that of α -Ce (111); *D*, no LEED pattern from Ce, about 7.5-Å coverage. The spectra are normalized to the intensity at 1 eV. Inset: Corresponding spectra taken at 120 eV with comparable resolution on bulk γ - and α -Ce, taken from Ref. [14].

tion. Their spacings decrease with coverage, going through several commensurate ($n \times 1$) and incommensurate patterns. The last pattern in this stage is the (2×1) at $\Theta = 0.5$ ML. See Figs. 2(a) and 2(c). At this stage the Ce $4f$ EDC is dominated by a broad peak near 2 eV, with a weaker peak near the Fermi energy similar to that of small clusters just going metallic [16,17]. This is spectrum *A* in Fig. 1. After a (2×1) pattern is reached at 0.5 ML the LEED pattern changes abruptly to a hexagonal pattern, as from, e.g., an fcc (111) or hcp (0001) plane [Fig. 2(b)]. The LEED pattern shows that the interatomic spacing in the plane is about 9% greater than that in the (111) plane of bulk γ -Ce, and this coverage, about 0.5 ML in units of the substrate atomic density, is about 0.83 ML in units of the atomic density of the (111) plane

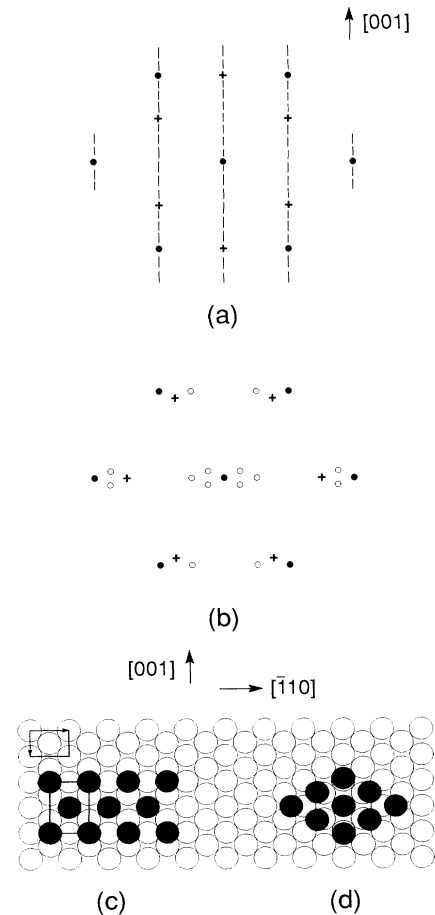


FIG. 2. (a) LEED pattern for a coverage of just under 0.5 ML of Ce on W(110). The solid dots are the W(110) reflections. The crosses are from the Ce overlayer at the (2×1) stage. The dashed lines indicate where spots appear at lower coverage. (b) LEED pattern for the hexagonal phase. The solid dots are the W(110) reflections. The crosses are primary reflections from the Ce overlayer. They move radially outward as the coverage increases. The open circles are secondary reflections. (c) Schematic picture of Ce (black balls) in the (2×1) structure on W(110) (white balls). (d) Schematic picture of Ce in the hexagonal phase on W(110). The lattice spacing for Ce is that of α -Ce. For clarity the Ce atom diameter was drawn smaller than the actual value.

of bulk γ -Ce. The number of atoms in the commensurate (2×1) structure should yield a lattice spacing in the hexagonal structure that is 10.7% larger than that of bulk γ -Ce (111), close to that observed. As more Ce is added, this hexagonal pattern expands gradually, corresponding to a steady reduction in interatomic spacing in the plane of the surface. EDC *B* in Fig. 1 is for a coverage at which the interatomic spacing is about that for bulk γ -Ce. Upon further deposition the $4f$ EDC becomes more like that of α -Ce. For spectrum *C* in Fig. 1 the interatomic spacing is about the same as for bulk α -Ce. Fur-

ther deposition of Ce leads to a further shrinkage of the surface lattice parameter. In later LEED experiments the limiting contracted lattice parameter was $(9.1 \pm 0.6)\%$ smaller than that of bulk γ -Ce (111). Thus about 44% more Ce atoms had been added since the appearance of the hexagonal LEED pattern. At this point, the LEED spots have become broad. Further deposition causes the loss of the hexagonal LEED pattern, and only a few faint W(110) spots can be seen. The spectrum for highest coverage (7.5 \AA), D in Fig. 1, is for this stage. Epitaxy has been lost.

Figures 2(c) and 2(d) show how the Ce may be arranged on the surface in the (2×1) structure and the hexagonal structure. In these figures, the lattice parameters and diameters of the W atoms are to scale. The Ce atom diameters are drawn too small so the Ce spacing and registry with the substrate can be seen better. The relative orientations of the two layers are correct, and the registry of the incommensurate overlayer is unimportant. In view of the lack of registry in the hexagonal phase the interaction between the overlayer and the substrate appears to be weak for $\Theta > 0.5 \text{ ML}$. Spectra of the W 4f core levels were also recorded. They will be reported elsewhere [20]. Briefly, there is a significant shift of the surface components when the Ce is in an $(n \times 1)$ or incommensurate "rectangular" phase, but the surface component returns nearly to its position on the clean surface when the Ce is in the hexagonal structure. This indicates, as does the poorer registry, that there is far less Ce-W interaction in the hexagonal phase than in the phase at lower coverage. Ce-W hybridization appears to be weak for both structures, however, for there is no obvious change in the spectra of Fig. 1 when the structure change occurs.

The LEED data show that Ce forms a close-packed epitaxial layer on W(110), the lattice parameter of which shrinks continuously as Ce is added. There is no evidence of domains of different lattice parameter up to the limit of contraction, when the spots broaden. Since these layers are about a monolayer thick in Ce units, one cannot expect them to be identical to a (111) plane of bulk material. The fact that the changes in the relative heights of the peaks in the photoelectron spectra are greater than for the bulk would have been puzzling, but recent studies have shown that the "error" lies in the interpretation of the peaks in the bulk. Laubschat *et al.* [21] and Weschke *et al.* [22] have shown that α -Ce surfaces have a layer of γ -Ce on them, reducing the full extent of the change in relative peak heights upon transformation.

Homma, Yang, and Schuller [23] reported the epitaxial growth of 50- \AA -thick films of "(111) Ce" on V(110), and determined an in-plane lattice parameter contraction of 8% and an out-of-plane expansion of 2% with respect to bulk γ -Ce. Thus the crystal structure was trigonal, not cubic. The density was about that of α -Ce. The relationship between the substrate and overlayer planes was

found to be unusual with the Ce $[0\bar{1}1]$ direction parallel to the substrate $[\bar{1}10]$ direction. No electronic structure information was available. In our monolayer films, we have no second layer, so the out-of-plane lattice parameter is meaningless, but we do find about the same in-plane contraction at the full monolayer coverage. Our Ce $[0\bar{1}1]$ direction is parallel to the substrate $[001]$ direction, so the relative orientation is the more common Nishiyama-Wassermann [24] type. The EDC for greatest coverage in Fig. 1 probably is not that for the phase discovered by Homma, Yang, and Schuller, but some of our later multiple-layer LEED patterns may have resulted from this phase. We note that Homma, Yang, and Schuller used epitaxial V films on sapphire as substrates, not a V crystal. It may be that the steps and defects on the W crystal we used impede the easy epitaxial growth of more than a monolayer in this lattice-mismatched system.

Finally, we summarize. The LEED results indicate a surface lattice spacing larger than that of γ -Ce, which decreases to that of γ -Ce, then α -Ce, becoming even smaller for increasing coverage. The EDCs in Fig. 1 resemble those of γ -Ce at low coverage, then become more α -like as coverage increases, consistent with the LEED results. Beyond monolayer coverage, the EDC is more like that of γ -Ce. The film then was not epitaxial, however, so it is not clear that the EDC was the same as that that would have been obtained for the epitaxial second layer or for the phase of Homma, Yang, and Schuller. The relative peak heights of the 4f EDC are governed by several parameters which change with lattice parameter and structure: density of states, Fermi-level placement with respect to the band, and 4f-conduction-band hybridization [8-11]. (It appears that hybridization with W states is weak.) Qualitatively higher resolution at 122 eV is possible [22] and desirable [25] when fitting to the Gunnarsson-Schönhammer model.

The large change in lattice parameter as the coverage increases, from 9% larger than that of γ -Ce to 3% smaller than that of α -Ce, affords a new and relatively clean opportunity to study models for the photoelectron, and other, spectra for a system with a 4f electron interacting with valence electrons and the photohole, or added electron, in the case of inverse photoemission.

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