

New Low-Temperature Phase of Yb Metal and its Relation to α -Ce

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A new fcc phase of Yb metal has been prepared by epitaxial growth below 190 K, which is stable at least up to 400 K. As determined by x-ray diffraction *in situ*, the spacing between close-packed layers is reduced by $\approx 0.6\%$ compared to the well-known fcc phase β -Yb, corresponding to a lower $4f$ binding energy observed by photoemission. Growth at room temperature, in contrast, results in β -like Yb films. The existence of two fcc phases of Yb metal is discussed in analogy to the isostructural γ - α phase transition of Ce metal.

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In recent years, investigations of lanthanides have regained interest due to the availability of high-quality, monocrystalline samples that can be obtained by epitaxial growth on refractory-metal substrates [1–3]. Studies of such films that are well suited for surface-sensitive techniques such as electron spectroscopies have led to an improved understanding of the $4f$ and valence-band structure of the lanthanide elements [3–7]. Among the lanthanides, Yb and Ce are of fundamental interest, because a strong interaction between $4f$ and valence states leads to mixed-valent and Kondo phenomena in a number of compounds [8,9]. This analogy between Yb and Ce systems has been explained on the basis of the electron-hole symmetry of the quasiautomatic $4f$ shell [9–12]. While the correspondence has been established for a number of compounds, no evidence for such a symmetry has been reported up to now for the pure metals. Ce undergoes the well-known isostructural γ - α phase transition below a temperature of ≈ 150 K, accompanied by a volume collapse of $\approx 17\%$ [13], and driven by an increase of the $4f$ - $5d$ interaction strength [9,14,15]. Yb metal, on the other hand, has a closed $4f$ shell with a stable $4f^{14}$ configuration and corresponds to La rather than Ce metal [9]. Nevertheless, experimental evidence for a finite $4f$ moment has been found in the paramagnetic behavior of β -phase Yb [16], indicating a small $4f^{13}$ admixture to the ground state.

For Yb metal, a phase transition has been observed below room temperature from the face-centered cubic (fcc) β phase to a hexagonal close-packed (hcp) α phase [16,17]. This transition is accompanied by a volume increase and a loss of the magnetic moment [16,18] and hence cannot be driven by an increase of the interaction between $4f$ and valence states. From a Yb phase corresponding to α -Ce, one would rather expect an increased $4f$ moment and a reduced volume due to a larger $4f^{13}$ contribution to the ground state.

In this Letter, we report on a new phase of Yb metal, prepared by epitaxial growth at low temperatures in the form of typically 100- Å -thick films. X-ray diffraction (XRD) and photoemission (PE) experiments showed that the new phase is stable over a wide temperature range between at least 35 and 400 K. It is characterized by a reduced lattice parameter with respect to β -Yb and a changed $4f$ -electronic structure. We argue that the new phase possibly corresponds to the α phase of Ce metal, establishing the electron-hole symmetry also for the metals.

The XRD and PE experiments were performed in two different experimental setups. In both experiments, Yb-metal films were grown in the same way under ultrahigh vacuum (UHV) conditions with base pressures of $\leq 1 \times 10^{-10}$ mbar, rising to at most 5×10^{-10} mbar during evaporation. The 99.99% pure Yb was evaporated from a radiatively heated Ta crucible onto a W(110) substrate, cooled with the help of a closed-cycle He refrigerator and a continuous-flow cryostat in XRD and PE, respectively. All films were briefly annealed to 400 K in order to improve their crystallinity. Film thicknesses were measured with a quartz balance and also determined from specular x-ray reflectivity [19]. For XRD *in situ*, a small UHV chamber equipped with Be windows was directly attached to the diffractometer, allowing investigations of film growth and structure [19]. The experiments were performed with Cu- K_α radiation from a rotating-anode x-ray source using a graphite (002) monochromator crystal. Because of the low intensities obtained from the thin films of the present study, no analyzer crystal was used, resulting in a resolution of $\approx 0.24^\circ$.

The PE experiments were performed with a Scienta SES-200 electron-energy analyzer and a Gammadata vacuum ultraviolet source with a total-system energy resolution of ≈ 25 meV (FWHM). Surface-sensitive PE at

$h\nu = 40.8$ eV was used to check the cleanness of the films, with no contaminations having been detected.

Under these conditions, two different Yb films could be grown reproducibly by deposition at high and low temperatures, respectively. In both cases, damped growth oscillations were observed in x-ray reflectivity up to the final thickness of ≈ 100 Å, indicating a rather good layer-by-layer growth [19]. The Yb films grow in close-packed layers as confirmed by sharp hexagonal low-energy electron diffraction (LEED) patterns observed in both cases, with the nearest-neighbor distances being the same for the two films within the experimental error ($\pm 2\%$). In energy-dependent LEED studies (I/V LEED), the intensity variations of the LEED spots as a function of electron energy were found to be almost identical for the two films, reflecting identical crystal structures. Since growth at 300 K leads to β -Yb films as shown further below, an fcc structure is thus established also for the low-temperature grown film.

Both Yb films reveal high bulk crystallinity, as monitored via the specular x-ray reflectivity, with oscillations of the reflected intensity observed both at small scattering angles and in the vicinity of the (111) Bragg peak. From the oscillations at small angles, caused by an interference of x-rays scattered from the film surface and the film/substrate interface, the film thickness can be readily determined [20]. Laue oscillations around the Bragg peaks are due to a finite number of scattering planes [21], providing information about the coherence of the film perpendicular to the planes. For both Yb films, the thickness was found to agree with the number of scattering planes, showing that crystalline coherence extends across the whole film.

Figure 1 (inset) displays (111) Bragg peaks, corresponding to the layer spacing between close-packed planes of the fcc lattice, for films grown at a substrate temperature of (a) 300 K and (b) 35 K. The different peak positions reveal a smaller layer spacing of the film grown at low temperatures by $\approx 0.6\%$. Changes of this order of magnitude could not be resolved by LEED but are easily observable by XRD. A temperature-induced shift can be ruled out, since both curves were recorded at 300 K. The Bragg peak position of film (a) corresponds to a layer spacing of $d_{111} = (3.167 \pm 0.002)$ Å, which is exactly the room-temperature value of β -Yb [16], while for film (b) $d_{111} = (3.147 \pm 0.002)$ Å. The existence of two distinct phases of Yb metal is further established by the temperature dependences of d_{111} , investigated between 35 and 400 K (see Fig. 1). In both cases, linear dependences are observed, with no indication of a transition between the two phases in the temperature range of the present study. The data clearly demonstrate that the phase prepared at low temperature is not the α phase observed earlier [16–18], but instead represents a new phase with a *contracted* spacing of close-packed layers. The coefficients of linear expansion derived from the data of Fig. 1 are $\alpha_l(300\text{ K}) = (3.9 \pm 0.2) \times 10^{-5} \text{ K}^{-1}$ and $\alpha_h(300\text{ K}) = (3.0 \pm 0.3) \times 10^{-5} \text{ K}^{-1}$ for films grown at low temperature and room temperature,

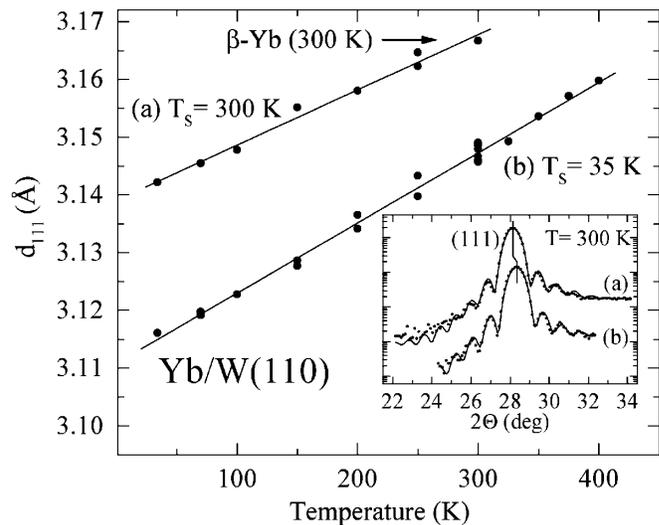


FIG. 1. Temperature dependence of spacings between close-packed layers, d_{111} , for ≈ 33 -ML-thick Yb-metal films on W(110), grown at substrate temperatures, T_s , of (a) 300 K and (b) 35 K. The inset shows related (111) Bragg peaks recorded at 300 K.

respectively. The latter is exactly the value reported for bulk fcc Yb [22], which further supports our view that the 300-K-grown film represents the well-known β phase of Yb metal.

The lattice contraction is also reflected in the electronic structure, as inferred from the $4f$ -PE spectra. For Yb metal with a $4f^{14}$ ground-state configuration, $4f^{13}$ PE final-state doublets are observed, split into $4f_{7/2}$ and $4f_{5/2}$ lines. Figure 2 displays the $4f_{7/2}$ emission, consisting of two components due to contributions from bulk and surface atoms. Bulk and surface contributions are separated by the so-called surface core-level shift of $\delta_s \approx 450$ meV [3]. Here, these components are extremely well resolved due to the narrow intrinsic linewidths and the high crystalline order, with negligible inhomogeneous broadening [23].

Spectra (a) and (b) were recorded from films grown at substrate temperatures of 76 and 300 K, respectively, and are characteristic of the two phases. They reveal different $4f$ binding energies (BE's) in the bulk and at the surface as indicated by the vertical lines. Both spectra were recorded at 76 K, ruling out temperature-induced BE shifts [24]. This was possible since the x-ray data (Fig. 1) ensure that the room-temperature-grown film does not convert into the low-temperature phase upon cooling. The BE of the bulk component has shifted from $E_B = 1.236$ eV for the film grown at room temperature to $E_B = 1.192$ eV for the film grown at low temperature, resulting in a shift of $\Delta E_B^b = -44$ meV, with error bars of the order of 5 meV. It could be argued that the increase of the surface BE of $\Delta E_B^s = 16$ meV is induced by a less perfect surface order of the low-temperature-grown film [23] rather than related to the formation of the new phase. A disorder-induced shift, however, is generally accompanied by a substantial inhomogeneous broadening of the PE line [23], which

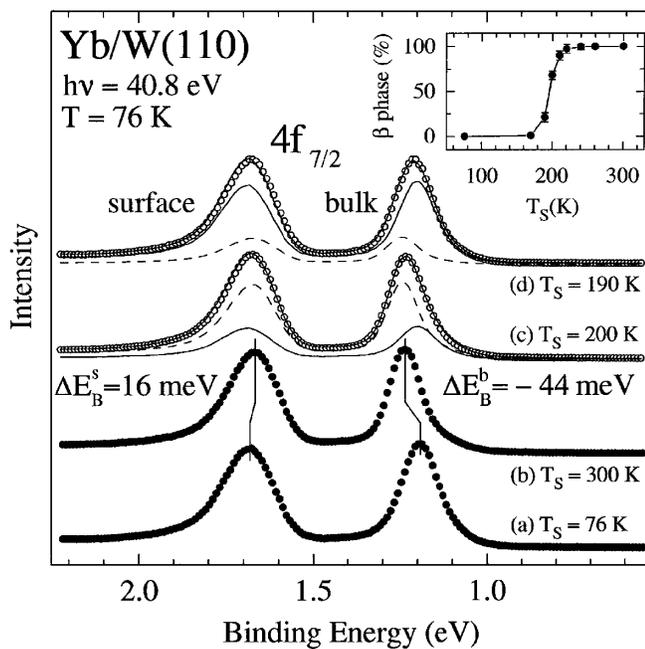


FIG. 2. $4f_{7/2}$ -PE spectra recorded from epitaxial Yb films on W(110), grown at various substrate temperatures (a)-(d). The inset displays the percentage of β phase in the Yb films as a function of substrate temperature, obtained from an analysis of the $4f$ -PE lines; for details see text.

is not observed here. It is therefore plausible to also interpret the higher BE of the surface component as characteristic of the low-temperature phase.

The properties of the low-temperature phase were further investigated by PE, with two interesting results.

(i) The formation of the low-temperature phase is not induced by the substrate but is an intrinsic property of elemental Yb. This was found by depositing Yb at 76 K directly onto a β -Yb film grown at room temperature. Subsequent annealing to 400 K resulted in a very well-ordered film characterized by a sharp LEED pattern with a quality close to that of the room-temperature film. The PE spectrum of such a film was found to be identical to that of a low-temperature film grown directly on W(110), confirming the formation of the low-temperature phase independent of the substrate.

(ii) The temperature range of the formation of the low-temperature phase was explored by depositing Yb metal at various substrate temperatures. In all cases, PE spectra were recorded after annealing to 400 K and subsequent cooling to 76 K. As examples, spectra recorded from films grown at 200 and 190 K are displayed in Figs. 2(c) and 2(d). These spectra can be readily described by a weighted sum of spectra (a) and (b), with the contributions given by the solid and dashed subspectra, respectively. Obviously, films deposited at these intermediate temperatures consist of a mixture of the two phases. The PE spectra could be analyzed in this way without any assumption about line shapes, giving the admixture of β -Yb to the various films. The result is displayed in the inset of Fig. 2 and reveals that the transition from growth temperatures favoring

β -like films to conditions favoring the low-temperature phase takes place in a small temperature interval between 210 and 190 K. This behavior rules out a disorder-induced change of the electronic structure as also indicated by the narrow width of the PE lines observed in the low-temperature phase. The sharp transition at this comparably high temperature also rules out a hydrogen-induced stabilization of the low-temperature phase. This was further confirmed by hydrogen-adsorption experiments on Yb films of different morphology and at different temperatures, with the result that the sticking of hydrogen is negligible for the duration of film growth and data recording under the present conditions.

The smaller $4f$ BE of the low-temperature phase is in accordance with the reduced lattice parameter, both indicating a stronger bonding as compared to the β phase. The relation between cohesive energies and $4f$ BE's in metallic Yb systems is obtained from a thermochemical model [4,25,26], which readily explains the surface core-level shift to higher BE as due to the reduced cohesive energy at the surface. Accordingly, the shift of the bulk $4f$ component of 44 meV to lower BE indicates an increase of cohesive energy in the low-temperature phase, possibly induced by an increased interaction of $4f$ and valence electrons as in case of the α phase of Ce metal.

Considering the electron-hole symmetry between Ce and Yb [9–11], it is therefore tempting to speculate on an analogy between the two Yb phases reported here and the isostructural γ - α phase transition of Ce metal. For both Ce and Yb, contracted fcc phases are observed at low temperatures with a stronger bonding and a changed $4f$ -electronic structure. Although the volume decrease is not as spectacular as in the case of Ce, an increased interaction of $4f$ and valence states might similarly characterize the low-temperature phase of Yb. Even for β -Yb, evidence for a nonintegral $4f$ occupation was obtained from the paramagnetic behavior, indicating a fraction of 0.8% of trivalent ions. This has been explained in terms of a possible resonance broadening of the $4f$ states by conduction electrons [16]. Similarly, the PE spectrum of Yb has been described in the framework of a single-impurity (SI) model with a finite hybridization [9]. The $4f$ PE from Yb metal, however, is not sensitive enough to detect small admixtures of the $4f^{13}$ configuration to the ground state. The BE of the $4f^{13}$ final state (see Fig. 2) alone cannot provide information about the hybridization between $4f$ and valence states. Within a simple SI model [27], an estimate of the hybridization parameter, Δ , can be obtained from the $4f$ PE binding energy, E_B and the number of $4f$ holes in the ground state, n_f . In the limit of a large energy separation between $4f^{14}$ and $4f^{13}$ states compared to Δ and for large on-site Coulomb repulsion, the hybridization parameter is given by $\Delta = [n_f(1 - n_f)]^{1/2} E_B$. With $n_f = 0.008$ and $E_B = 1.28$, one obtains $\Delta = 0.11$ eV for β -Yb. In this parameter range, the small decrease

of E_B by 44 meV in the low-temperature phase leads to essentially the same value of Δ , if n_f is not changed, indicating that not E_B but rather n_f is a sensitive measure of the hybridization between $4f$ and valence states in the present case. In order to obtain Δ in the low-temperature phase of Yb metal, it is therefore essential to determine the $4f$ occupation with a more sensitive probe than PE, such as, e.g., by magnetic measurements. The hybridization values for Yb are much smaller than those for Ce metal. Applying the same model to the $4f$ PE spectra of γ - and α -Ce, one obtains $\Delta = 0.4$ eV [28] and $\Delta = 0.9$ eV [7], respectively. This larger effect in Ce is not surprising, if one considers the $4f$ -shell contraction across the lanthanide series, which is expected to lead to a reduced interaction between $4f$ and valence states in the case of Yb.

In summary, the existence of a new phase of Yb metal has been established by a combination of *in situ* x-ray diffraction and photoemission studies of films grown on W(110). The new phase can be prepared by epitaxial growth at low temperatures and has a fcc crystal structure such as β -Yb metal, with the d_{111} layer spacing reduced by $\approx 0.6\%$. Such a phase has not been observed in high-pressure studies of Yb metal [29,30] and also does not represent the hcp α phase, which is characterized by an expanded lattice. The new phase is stable at least between 35 and 400 K, and its electronic structure is characterized by a reduction of the $4f$ BE by (44 ± 5) meV as compared to β -Yb. In view of the electron-hole symmetry of the quasiatomic $4f$ shell, it is suggested that the new phase possibly represents the counterpart of the low-temperature α phase of Ce metal. On the basis of the presently available data, however, it is not yet clear, whether this phase is characterized by an increased $4f$ hybridization with valence states or by a change in the $4f$ -level position alone, i.e., a mere change of $5d$ - $6s$ hybridization. Solving this problem will require the determination of the $4f$ occupation, which is an interesting subject for further experimental and theoretical investigations.

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