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Comparative photoemission study of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce and Pt(111)(2×2)La

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Careful examination of the low-energy electron diffraction image from Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce shows the designation to be only approximate and suggests a close structural similarity to Pt(111)(2×2)La. This is backed up by angle-resolved photoemission spectroscopy, which reveals the valence-band structure of the two alloys to be remarkably similar. The use of the La alloy to identify the non-f features in the photoemission spectra of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce is thus put on a firm footing. The Kondo peak in He II angle-resolved ultraviolet photoemission spectroscopy data of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce is observed at the first and second $\overline{\Gamma}$ points, suggesting the presence of surface umklapp scattering. [S0163-1829(98)10039-5]

I. INTRODUCTION

Despite the advances made in the field of heavy fermion materials through the application of photoemission,[1,2] the surface sensitivity of this technique can be seen as a shortcoming when measuring scraped polycrystalline compounds.[3] By using well-ordered single-crystal samples one can hope to further understanding of these heavy fermion systems past the single impurity model (SIM), based on the Anderson Hamiltonian. This model, although successful, can only be viewed as a first approximation to a full description of the problem. Recent progress in the preparation of Ce-containing samples which display long-range surface order has been made through evaporation of Ce onto single-crystal substrates.[4–18] In our laboratory, we have applied high-resolution ultraviolet photoemission spectroscopy (UPS) to examine the low-energy excitations in a well-ordered thin-film Ce-containing alloy: Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce.[19] In an attempt to identify the $4f$ contribution to the spectra, a second alloy was prepared in which the Ce was replaced by La.[19] Despite the different low-energy electron diffraction (LEED) pattern displayed by the La-containing alloy, Pt(111)(2×2)La, a detailed comparison between the two systems holds. This will be demonstrated in the current paper. We present a close examination of the LEED images from the two systems and a comparison of the d-band valence-band structure as revealed by He I angle-resolved UPS.

II. SURFACE PREPARATION AND DIFFRACTION RESULTS

The Pt(111) substrate was cleaned by standard sputtering-annealing cycles (Ar$^+$ 1 kV, 800 °C), to give a chemically clean and well-ordered surface, as indicated by Auger electron spectroscopy and LEED measurements, respectively. Evaporation of Ce was carried out in a pressure better than 2×10^{-10} Torr, using a quartz microbalance to ensure a rate of typically 1 Å/min. We have mainly studied samples prepared by depositing 4 ML of Ce on the clean substrate, as this use of a relatively thick Ce coverage prevents problems of mixed phases observed at lower Ce concentrations.[4,5] After evaporation of Ce the sample was annealed at 600 °C for 10 min. Such a treatment produces the LEED pattern shown in Fig. 1(a). By comparing this LEED pattern to that of the clean substrate, shown superimposed in the figure, a quasi-($\sqrt{3}\times\sqrt{3}$)$R30°$ symmetry is identified. The contraction of the LEED pattern observed for the surface alloy over that of the clean substrate [Fig. 1(a)] means that a more precise identification for the surface is ($1.1\sqrt{3}\times1.1\sqrt{3}$)$R30°$, one which does not appear in the phase diagram for the Ce/Pt(111) system proposed by Tang *et al.*[4] Such a LEED pattern was observed by Tang *et al.*[4] and Baddeley *et al.*,[5] but only ever in conjunction with a quasi-(2×2) image. We observed this mixed pattern after evaporation of a lesser quantity of Ce (~2 ML).

The same procedure was followed for preparation of the La/Pt(111) sample (annealing at 700 °C), resulting in a (2

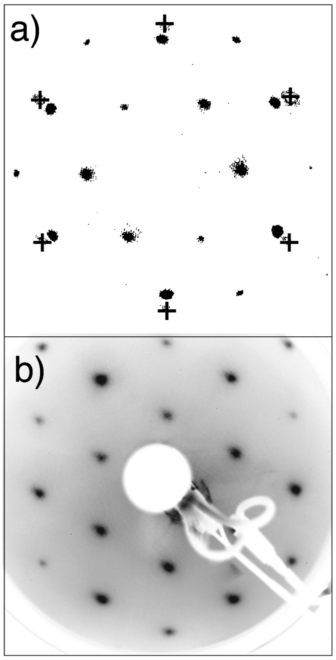

FIG. 1. (a) LEED pattern of Pt(111)($\sqrt{3}\times\sqrt{3}$)$R30°$Ce at $E_p=104$ eV. Superimposed is the equivalent LEED pattern for Pt(111) (crosses). (b) LEED pattern of Pt(111)(2×2)La at $E_p=104$ eV. The azimuthal orientation of the underlying substrate in both images is the same.

$\times 2)$ LEED pattern for ~4 ML coverage, Fig. 1(b). This seems to be a precise designation. During initial evaporations of La, a superimposed $(2\times 2)R30°$ LEED pattern was also observed. This symmetry was not seen after the first few treatments. Such surface alloy systems have a complicated evolution[5] and it is possible that residual quantities of the evaporant produce a seed favoring formation of the nonrotated (2×2) phase.

The $(1.1\sqrt{3}\times 1.1\sqrt{3})R30°$ designation for the Ce/Pt alloy gives a surface lattice vector of $1.9a$, where a is the substrate lattice vector. This is 5% less than the surface lattice vector for Pt(111)(2×2)La. Without the dilation observed for Ce/Pt, the mismatch between the two systems would be nearer 15%. This provides a first indication that despite the difference in the LEED patterns of our two samples, the two thin-film alloy crystal structures are very similar. This speculation is supported by the observation that the lattice constants of CePt$_n$ and LaPt$_n$, $n=2$, 3, and 5 are identical to within 0.5% for corresponding n.[20,21] The valence-band photoemission spectra presented below show indeed that the electronic structures of these two surfaces are closely related.

The Ce/Pt(111) system was found to be very stable. Although the intensity of the $4f$ structure seen in photoemission spectra (see next section) vanishes after 10–20 min of exposure to the UV radiation of our He lamp, a simple annealing of the sample at 600 °C for 10 min was found to rejuvenate the surface. The insensitivity of the surface to any residual contamination, despite the known high reactivity of cerium, is probably due to the alloy's structure. The passive nature of this sample is in line with other studies of Ce/Pt alloy formation on Pt(111) (Refs. 4 and 5) and suggests the presence of a pure Pt layer at the surface. Although there is a disagreement in these previous studies concerning the stoichiometry of the thin-film alloy, both structural models proposed, CePt$_{2+x}$ (Ref. 4) and CePt$_5$,[5] allow the presence of a surface terminated uniquely by Pt. The model based on CePt$_5$ is one that covers five different surface structures observed.[5] Whatever the true microscopic details might be, it seems likely that the underlying structure of our surface bears close resemblance to those of the earlier studies.

III. PHOTOEMISSION RESULTS

Photoemission measurements were performed using a hemispherical electron analyzer and a high intensity He UV source. The base pressure in the system was in the low 10^{-11}-Torr range, rising to 1×10^{-10} Torr during operation of the He lamp. All spectra reported here were recorded at 10 K. The off-normal angle-resolved spectra for Pt(111)$(\sqrt{3}\times\sqrt{3})R30°$Ce presented have all been measured along the $\overline{\Gamma K}$ direction of Pt(111). As discussed in the previous section, the LEED data suggest that the structures of the two alloys studied are very similar, the main difference being a rotation of 30° when compared with the underlying substrate. Photoemission data from Pt(111)(2×2)La were thus recorded with the Pt sample rotated azimuthally by 30°.

Angle-resolved He I (21.2 eV) photoemission spectra from the two surfaces under consideration are displayed in Fig. 2. The two data sets correspond to equivalent symmetry directions and show transitions between bands, those of the initial state being formed by hybridization of the Pt $5d$ electrons with the Ce valence electrons ($5d$, $6s$ levels). Although a detailed interpretation of the angle-resolved spectra would require more information than the surface symmetry available to us, it is seen that each major structure observed in a He I angle-resolved ultraviolet photoemission spectrum of Pt(111)(2×2)La is reproduced in the equivalent Pt(111)$(\sqrt{3}\times\sqrt{3})R30°$Ce spectrum. However, away from normal emission there is a shift of the spectral features towards the Fermi level for the Ce-containing alloy. This is unambiguously seen for those features lying between −1.5 eV and E_F, and is particularly evident in the spectra recorded at $\theta=9°$ and 12° (Fig. 2). The origin of this difference lies in the Ce $4f$ occupation. This orbital provides inefficient screening, and so, in the atomic situation, the occupied Ce $5d$ levels are expected to lie deeper in energy than those of La. In the solid state the situation is more complicated and the energies of the transitions observed with angle- resolved photoemission are modified. A more quantitative discussion of the spectra of Fig. 2 would require calculation and precise knowledge about the structural details of the two alloys, but the important feature is the remarkable similarity of the two data sets, showing that the band structures of these two surfaces are extremely close to one another. This supports the conjecture made on the basis of the LEED data that the two surface alloys are closely related, and adds strength to the use of such a comparison as a method to determine which features in the spectra derive from the $4f$ electrons.[19]

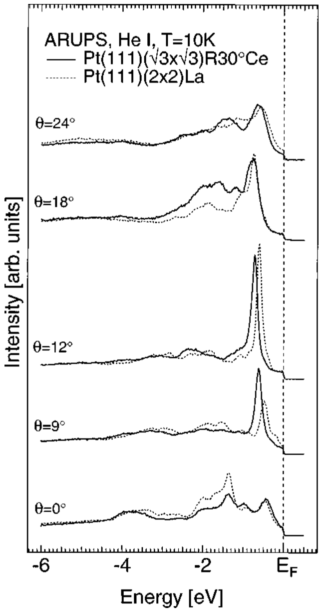

FIG. 2. Angle-resolved He I photoemission spectra of Pt(111)$(\sqrt{3}\times\sqrt{3})R30°$Ce and Pt(111)$(2\times 2)$La. For details regarding the directions of measurement, see text.

The Ce $4f$-photoionization cross section for He I photons is negligibly small and so to obtain the contribution of the $4f$ electrons we have to consider spectra measured with He II radiation. Under these conditions, angle-integrated photoemission reveals the presence of a sharp peak cut at the Fermi level uniquely in the Ce-containing alloy.[19] This peak is due to the Ce $4f$ electrons and is identified with the tail of the Kondo resonance, which is usually seen in photoemission spectra from polycrystalline Ce compounds.[1]

The SIM, which is usually used to describe the photoemission spectra of Ce compounds,[2] treats the Ce atoms as isolated impurities. Possible interaction, direct or indirect, between Ce atoms is thus ignored. With the intention of looking for possible momentum dependence in the Kondo peak, we have performed He II angle-resolved UPS of the Pt(111)$(\sqrt{3}\times\sqrt{3})R30°$Ce surface alloy in the near-E_F region. The details of these measurements, the angular and temperature dependencies of the Kondo peak are discussed in more detail elsewhere.[19] In brief summary, we have not been able to measure any dispersion of the peak maximum. The peak is situated 4 meV below E_F and we believe its position to be determined purely by our instrumental resolution (5 meV). Away from normal emission its intensity rapidly decreases.[19] At $\theta = 26°$, however, there is an indication of the reappearance of the Kondo peak (Fig. 3). This angle lies close to the second $\bar{\Gamma}$ point of the surface Brillouin zone. This observation is similar to an independent one made on a single crystalline Ce/Pt system at higher photon energy (120 eV),[6] suggesting that an effect of surface umklapp scattering is being observed.

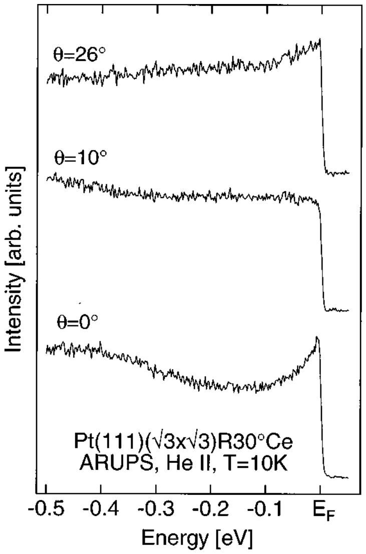

FIG. 3. Angle-resolved He II photoemission spectra of Pt(111)$(\sqrt{3}\times\sqrt{3})R30°$Ce in the near E_F. The azimuthal orientation is as in Fig. 2.

IV. SUMMARY

The two surface alloys Pt(111)$(\sqrt{3}\times\sqrt{3})R30°$Ce and Pt(111)$(2\times2)$La have been examined using LEED and photoemission. The LEED data suggest that the two systems are closely related structurally. This is supported by angle-resolved photoemission data that demonstrate remarkable similarity in the electronic structure of the two surfaces. The Ce $4f$ contribution to the photoemission spectra is thus easily isolated by comparing He II data from the two systems.

ACKNOWLEDGMENT

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