Possibility of Minimal Surface Contributions to Low Photon Energy Angle-Resolved Photoemission of $CeRu_2Si_2$

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Abstract

Surface-related effects in angle-resolved valence spectra of $CeRu_2Si_2$ at the Ce $4d \rightarrow 5f$ resonance threshold for different cleaved surfaces are presented and compared to angle-integrated valence spectra and to bulk-sensitive Ce $3d$-edge valence spectra. Evidence that Ce $4d$-edge photoemission spectroscopy on ideal cleaved surfaces is dominated by bulk Ce $4f$ states is presented.

Key words:
$CeRu_2Si_2$, angle-resolved photoemission, surface effects

For Ce compounds a sizable surface effect literature has been developed largely in studies applying the Anderson impurity model to angle-integrated Ce $4f$ spectra of polycrystalline material. The spectra exhibit three main features: (*i*) a broad $f^1 \rightarrow f^0$ electron removal peak at $\approx$2 eV, (*ii*) a Kondo resonance spin-orbit sideband at $\approx$0.3 eV and (*iii*) a narrow peak impinging on E_F corresponding to the occupied tail of the Kondo resonance. Reduced hybridization and increased binding energy at the surface [1] universally result in a reduction of the spin-orbit peak relative to the 2 eV peak and a reduction of the E_F peak relative to the spin-orbit peak [2,3]. Quantitative separation of surface and bulk contributions to the f-spectral weight in angle-integrated valence band photoemission can be achieved by exploiting the variable electron escape depths at multiple photon energies [3,4], and this surface and bulk decomposition is essential for an understanding of the spectra in relation to

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bulk thermodynamic properties [3]. Recent advances in energy resolution of valence photoemission at high photon energies (≈1 keV) [5] where bulk sensitivity is enhanced, show promise for refinement of quantitative modeling of angle-integrated f-spectral weight.

We have been making detailed angle resolved photoemission spectroscopy (ARPES) studies of $CeRu_2Si_2$ with h$\nu \geq$100 eV [6]. It is important to assess surface effects in these studies, both because we compare the data to bulk band structure calculations and to bulk transport properties, and because, by angle summing of ARPES spectra, we want to make contact back to previous angle-integrated studies done on polycrystalline samples. The photon energy range used, higher than in typical ARPES studies (20-40 eV), is important for the resonant enhancement of $4f$ spectral weight at the Ce $4d$ absorption threshold (122 eV). The kinetic energies of these valence electrons are close to the minimum of the inelastic mean free path "universal curve" and thus large surface effects might be expected. Nonetheless we present here some data that suggests, surprisingly, that these effects can be minimal.

Single crystal $CeRu_2Si_2$ samples were cleaved in ultra-high vacuum ($\leq 6\times10^{-11}$ torr) at $\leq$130 K exposing the [001] surface. ARPES measurements were performed at ALS Beamline 7.0.1.2 with a total instrumental resolution of ≈80 meV (200 meV) at the Ce 4d (3d) edge and full angular acceptance of ≈0.7°. Important for these studies was the use of a finely focused 100 μm synchrotron beam spot and automated sample motions for probing of surface spatial homogeneity as well as for acquisition of Fermi-edge angular intensity maps and data sets for angle-summing of spectra.

Figures 1(a,b) show normal emission on-resonance (hν=122 eV) valence spectra for two different "bad" and "good" cleaved surfaces of $CeRu_2Si_2$. This energy and angle corresponds to the Z-point in k-space. Note the very large difference in the near E_F f-weight. Full valence band dispersions along Z-X-Z, i.e. the [110] azimuth direction, for these two surfaces have previously been published in Ref. [6]. The "good" surface data exhibit strongly dispersing d-band states (open dots in Fig. 1b) and large f-weight intensity variation near E_F. The "bad" data, in contrast, show streaks of k-independent spectral weight and a relatively smaller amplitude of near-E_F f-states and dispersing d-bands.

Fig. 1(c) shows the $4d$-edge angle-averaged spectrum of a"good" surface, obtained as shown in Fig. 2, by increasing the angular acceptance mode of the spectrometer input lens from ±0.35° to ±4° ("transmission" mode, ≈1/9 of a Brillouin zone), taking valence spectra at 53 angles in a 90° azimuthal quadrant out to 60° from normal emission (Fig. 2 inset), normalizing at 5 eV, and then averaging (Fig. 2 bold spectrum). The k-dependences of E_F f-weight and strong d-bands peaks at ≈2 eV are reduced in the progression from ARPES

spectra (Fig. 2, dashed lines) to "transmission" mode spectra (Fig. 2, solid lines) to the final averaged spectrum. Fig. 1(d) shows an angle-integrated bulk sensitive valence spectrum taken at the 3*d*-edge, consistent except for the 0.2 eV energy resolution with a published 3*d* edge spectrum [5] obtained with 0.1 eV resolution. It is very interesting to note that the ratio of the spin-orbit side-band peak to the main Kondo peak in the angle-averaged 4d-edge spectrum of a "good" surface is very similar to that of the bulk sensitive spectrum. It seems possible that the spectrum reported in [5] as being typical of $CeRu_2Si_2$ at the Ce 4*d*-edge corresponds to that of our "bad" surface.

We cannot yet make a fully unified picture from these observations. All cleaved $CeRu_2Si_2$ surfaces exhibit sharp 1×1 LEED patterns indicating a lack of multi-zone reconstruction. An alternating atomic layering of -Ce-Si-Ru-Si-Ce- allows cleavage planes of $CeRu_2Si_2(001)$ with buried or surface Ce atoms. The non-Ce atom termination may be essential to obtain the data of Fig. 1(a). Also, macroscopically rough steps, contained within the analysis area, will contain a significant enhancement of the surface area in general, especially of the edge- and corner- type of Ce atoms which lack long range order, in addition to having smaller near-neighbor coordination, and thus may be the origin of the spectral weight changes in observed in Fig. 1(b).

Thus it appears for $CeRu_2Si_2$ at least, that spectra mostly characteristic of the bulk can be obtained at lower photon energy if the surface is (fortuitously) not terminated by Ce atoms and is sufficiently free of macroscopic steps. But we also see that such homogeneity is not routinely obtained merely by cleaving a single crystal, as has sometimes been claimed, requiring in general that the analysis area be very small.

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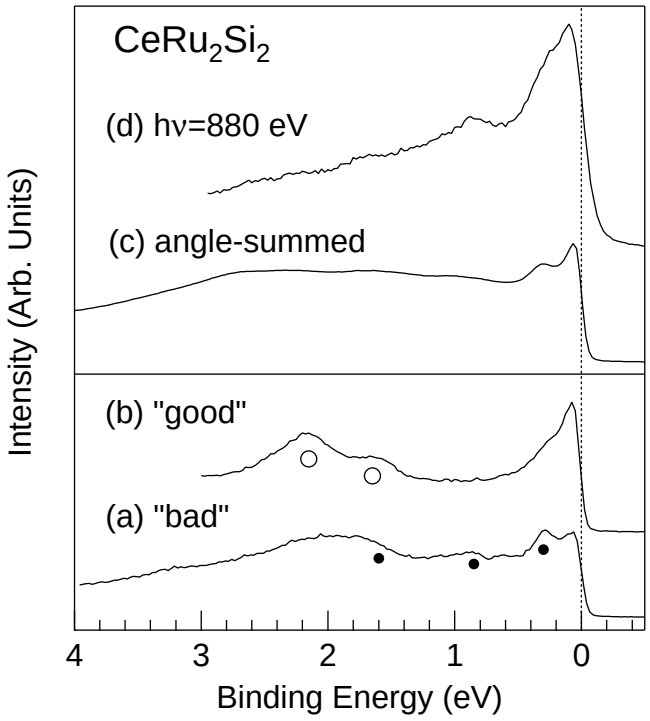

Fig. 1. Comparison of Ce $4d$ edge on-resonance (a,b) angle-resolved valence spectra at the center of the normal emission Z-point from two different cleave surfaces of $CeRu_2Si_2$ (see text) to (c) an angle-integrated spectrum (see Fig. 2) and to (d) a Ce $4f$ difference spectrum at the Ce $3d$ edge. Open dots label d-band states and solid dots label energies of k-independent spectral weight.

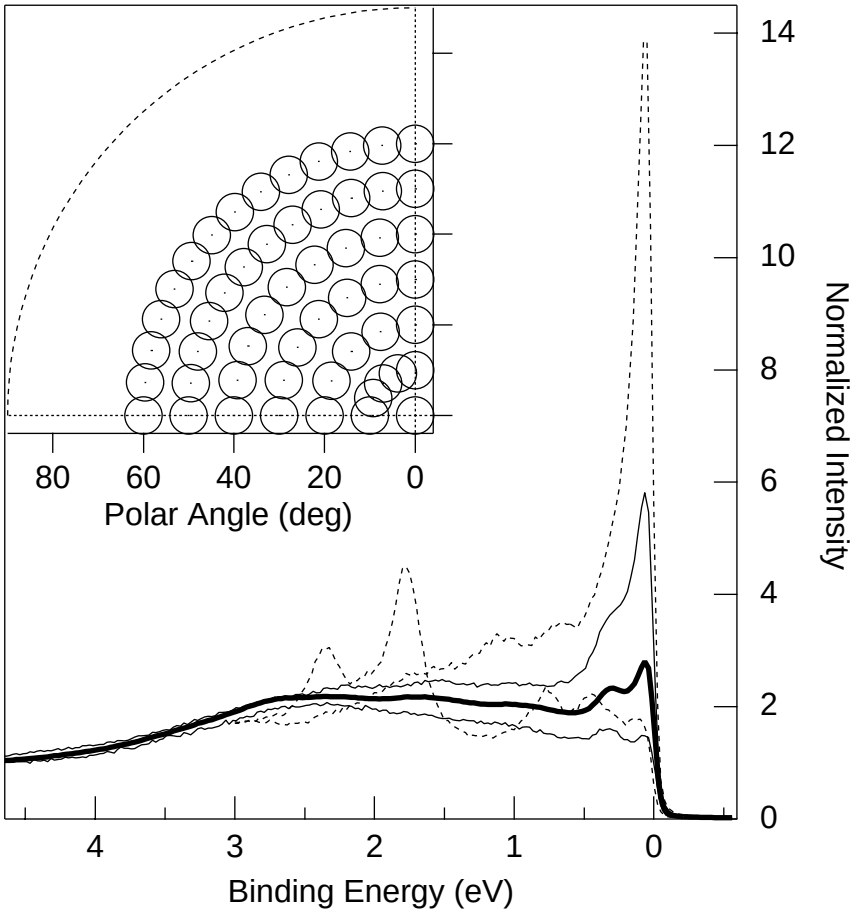

Fig. 2. Angle-integration of on-resonance (122 eV) spectra from the same $CeRu_2Si_2$ surface as in Fig. 1(b). The inset shows angle sampling and approximate angular acceptance ($\pm 4°$) of individual spectra in the full data set. The bold spectrum is the angle-average while the solid line spectra represent extremum behavior of this data set. Dashed lines represent extremum spectra of the data in Ref. [6] with higher angular resolution ($\pm 0.35°$).