

# Surface Effects in Angle-Resolved Photoemission of CeRu<sub>2</sub>Si<sub>2</sub>

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## INTRODUCTION

Strong surface effects in core-level and valence photoemission of rare-earth compounds have been appreciated since the mid-1970's [1]. In particular, for Ce compounds, there is a sizable body of literature with discussion of surface effects in terms of increased  $4f$  binding energy and reduced  $f$ -hybridization resulting from smaller near-neighbor coordination of the rare-earth atoms at the surface [2, 3]. The high reactivity of these rare-earth surfaces to adsorption of gases, especially oxygen, and correspondingly shortened lifetime of the sample surfaces even at ultra-high vacuum pressures ( $<1 \times 10^{-10}$  torr) is well established.

Angle-integrated Ce valence spectra exhibit three main features: (i) a broad  $f^d \rightarrow f^0$  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. The reduced hybridization and increased binding energy at the surface universally result in an enhancement of the 2 eV peak and a reduction of the  $E_F$  peak relative to the spin-orbit sideband. It has been demonstrated that 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 [4], and that this surface and bulk decomposition is essential for an understanding of the spectra in relation to bulk thermodynamic properties [3]. Recent advances in energy resolution of valence photoemission at high photon energies ( $\sim 1$  keV) [5] where bulk sensitivity is enhanced, show promise for refinement of quantitative modeling of angle-integrated  $f$ -spectral weight.

In the course of angle-resolved photoemission (ARPES) studies of CeRu<sub>2</sub>Si<sub>2</sub> with  $h\nu > 100$  eV, we have accumulated various observations bearing on surface effects aided by the  $k$ -dependence of the valence band spectra. The photon energy range used, higher than typical ARPES studies (20-40 eV), is important for the resonant enhancement of  $4f$  spectral weight at the Ce  $4d$  absorption threshold (122 eV). Also, the kinetic energies of these valence electrons are close to the minimum of the inelastic mean free path "universal curve" and hence surface sensitivity is expected to be enhanced in these studies. Here we present some data that suggests, despite these surface caveats, that bulk states are being revealed.

## EXPERIMENT

Single crystal CeRu<sub>2</sub>Si<sub>2</sub> samples were cleaved in ultra-high vacuum ( $<6 \times 10^{-11}$  torr) at  $<130$  K exposing the [001] surface. ARPES measurements were performed at ALS Beamline 7.0.1.2 in the photon energy range of 80-200 eV with a total instrumental resolution of  $\approx 80$  meV and full angular acceptance of  $\approx 0.7^\circ$ . Important for these studies was the use of a finely focused  $100 \mu\text{m}$  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.

## RESULTS

Fig. 1 shows intensity images of on-resonance valence band spectra along Z-X-Z, *i.e.* the [110] azimuth direction, for two different “good” and “bad” cleaved surfaces of CeRu<sub>2</sub>Si<sub>2</sub>. The “good” data in panel (a) exhibit strongly dispersing *d*-band states and large *f*-weight intensity variation near  $E_F$ . The “bad” data in panel (b), in contrast, show streaks of *k*-independent spectral weight at 0.3, 0.8 and 1.6 eV binding energy, and a relatively smaller amplitude of dispersing *d*-bands and near- $E_F$  *f*-states. The 0.3 eV peak corresponds to the Kondo sideband energy while the precise origin of the other two peaks is currently unknown. Also, since the reverse grayscale of each image has been separately adjusted to optimally enhance the intensity contrast, the  $k_{||}$ -averaged spectrum of each data set has additionally been plotted in Fig. 1 for a more direct comparison of the different amplitude variations of the two cleaves.

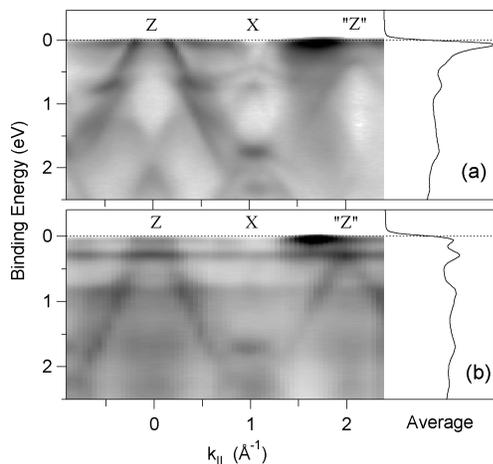
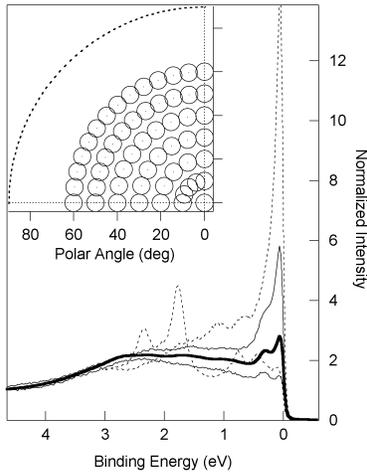


Figure 1. Comparison of on-resonance (122 eV) valence spectra for CeRu<sub>2</sub>Si<sub>2</sub> for two different cleave surfaces. Angle-averaged spectra for each data set are also shown.

We cannot make a unified picture yet from this one observation, but there are two main considerations of: (i) different possible cleavage planes of CeRu<sub>2</sub>Si<sub>2</sub>(001) which contains an alternating atomic layering of -Ce-Si-Ru-Si-Ce-, and (ii) the different number of steps and edges contributing *k*-independent surface spectral weight. While the surface structure of the cleaved CeRu<sub>2</sub>Si<sub>2</sub> system has not been experimentally determined yet, all cleaved surfaces exhibit sharp 1×1 LEED patterns indicating a lack of multi-zone reconstruction. Macroscopically rough regions on the cleaved surface will contain a significant enhancement of the surface area in general, especially of the edge-type of Ce atoms which lack long range order and which have smaller near-neighbor coordination leading to the spectral changes consistent with what is observed in Fig. 1(b).

Another important objective, which also involves the surface contribution, is to make connection back to angle-integrated resonant photoemission, a rather difficult task for single-crystal surfaces. While the averaging of ARPES spectra in Fig. 1 represents an initial step in this effort, Fig. 2 illustrates an attempt a fuller angular averaging in which the angular acceptance mode of the spectrometer input lens was increased from 0.7° to ≈4° (“transmission” mode) and valence spectra at 53 angles in a 90° azimuthal quadrant out to 60° from normal emission (Fig. 2, inset) were acquired and averaged (bold spectrum). The extreme 4*f* enhancement at  $E_F$  and strong *d*-bands peaks at ~2 eV in the ARPES spectra (dashed lines) are clearly suppressed by the “transmission” mode (solid lines)

It is very interesting to note that the ratio of the Kondo sideband to the main Kondo peak in the averaged spectrum in Fig. 2 is similar to that reported in a bulk-sensitive angle-integrated resonant photoemission study of CeRu<sub>2</sub>Si<sub>2</sub> at the Ce 3*d* edge performed with 0.1 eV resolution [5]. Fig. 3 illustrates this point with a comparison of angle-integrated valence spectra at the 3*d*-edge with the 4*d*-edge angle-averaged spectrum from Fig. 2. The resolution of the 3*d*-edge spectrum was 0.2 eV the relative surface sensitivity is illustrated by the dashed spectrum resulting from oxygen dosing of the surface. Also interesting to compare to the bulk-sensitive 3*d*-edge spectrum are the 4*d*-edge normal emission ARPES spectra from Fig. 1(a,b) where *d*-band weight is



(left) Figure 2. Angle-integration of on-resonance (122 eV) spectra for  $\text{CeRu}_2\text{Si}_2$ . The bold spectra is the average from a cleaved single crystal (bold spectra). Inset shows the data set angle sampling and approximate angular acceptance ( $4^\circ$ ) of individual spectra. The bold spectrum is the angle-average of the data in the inset while solid line spectra represent extremum behavior of this data set. Dashed lines represent extremum spectra of the data in Fig. 1 with higher angular resolution ( $0.7^\circ$ ).

(below) Figure 3. Comparison of on-resonance angle-resolved spectra at the center of the normal emission Z-point from the two different cleaves of  $\text{CeRu}_2\text{Si}_2$  in Fig. 1(a,b) to the angle-integrated spectra repeated from Fig. 2. Also shown is the Ce 4f difference spectrum at the Ce 3d edge for a clean surface (solid) and after slight oxygen dosing (dashed).

minimized for  $\approx 1.5$  eV below  $E_F$  at the center of the Z-point hole pocket. Again, the near- $E_F$  4f weight for the “good” surface (1a) is rather similar to the 3d-edge spectrum, whereas the “poorer” surface (1b) is similar to the spectrum reported in Ref. 4 as being typical of  $\text{CeRu}_2\text{Si}_2$  at the Ce 4d-edge.

## CONCLUSION

Thus, it may be that, for  $\text{CeRu}_2\text{Si}_2$  at least, spectra mostly characteristic of the bulk *can* be obtained at lower photon energy if the surface is sufficiently free of steps, edges, etc., or if the analysis area is very small. Additional experiments, including correlation of Si 2p surface core-level shifts to surface topography and valence spectra, are required to further understand the effects of various surface structures.

## REFERENCES

1. B. Johansson, Phys. Rev. B **19**, 6615 (1979), and references therein.
2. C. Laubschat, *et al.*, Phys. Rev. Lett. **65**, 1639 (1990).
3. L. Z. Liu, *et al.*, Phys. Rev. B **45**, 8934 (1992).
4. L. Duo, Surf. Sci. Rep. **32**, 233 (1998).
5. A. Sekiyama, *et al.*, Nature **403**, 396 (2000).

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