Electronic structure of a Kondo lattice system $CeCuAs_2$

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Abstract. We study the electronic properties of a Ce-based Kondo material, $CeCuAs_2$ employing high-resolution hard *x*-ray photoemission spectroscopy. The measurements were done with different photon energies to probe the surface-bulk differences of the electronic structure. Experimental results show significant difference in the hybridization physics for the surface and bulk electronic structures indicating different Ce valency at the surface compared to the bulk. Surface termination appears to play an important role in the correlation physics of this system. In addition, the experimental spectra show loss features due to plasmon excitations. These results bring out complexity of this novel Kondo lattice system that does not show magnetic order down to the lowest temperature studied and have significantly different surface-bulk properties.

1. Introduction

The rare-earth-based systems are one of the most intriguing topics in condensed matter physics due to their unusual properties arising from strong electron correlation [1]. These materials show several exotic phenomena like Kondo behavior [1-3], unconventional superconductivity [4], the fluctuating valency [5-6], *etc*. arising from the hybridization between the localized 4*f* electronic states and the valence states. Among the rare earth series, Ce has some unique properties, as the radial distribution of the $4f$ electron is relatively more extended for Ce leading to a relatively larger itineracy of the $4f$ electrons, proximity of the occupied $4f$ band to the Fermi level and the presence of one 4*f* electron [7]. Ce has predominantly magnetic trivalent ($4f^1 5d6s^2$) and non-magnetic tetravalent ($4f^0 5d^2 6s^2$) electronic configurations. The mixing of these two configurations in the ground state is associated to the fluctuating valency in Ce compounds. Many Ce-based Kondo lattice systems possesses uncompensated Ce moments leading to magnetically ordered ground states. $CeCuAs_2$ is a unique system which does not show magnetic order down to the lowest temperature studied and hence is a good platform to study the Kondo physics [8].

In this paper, we have report the electronic structure of $CeCuAs_2$ studied by hard *x*-ray photoemission spectroscopy. $CeCuAs_2$ forms in $ZrCuSi_2$ type layered tetragonal structure. The unit cell forms by stacking of the As(2)-CeAs(1)-Cu-As(1)Ce-As(2) layer. Here, As(1) and As(2) are the two non-equivalent As atoms with different Wycoff positions. This crystal has a space group *P4/nmm* (129), with the lattice constants, a = 4.045 Å and c = 10.111 Å. The bulk properties studies of this material show several interesting phenomena. For example, electrical transport exhibits logarithmic increment of resistivity, ρ with the decrease in temperature, T [8]. Below 5 K, the temperature dependence of the resistivity changes to $\rho \propto T^{-0.6}$ [8]. This is different from the behaviour of other members of $RCuAs_2$ (here R = rare earth element) family [9]. In magnetic measurements, no long-range magnetic order has been observed from room

temperature (RT) down to 45 mK. The effective magnetic moment in the paramagnetic phase is found to be 2.33 μ_B/Ce and 2.50 μ_B/Ce at low and high temperature regimes, respectively for the magnetitic field applied perpendicular to *c* axis. Such reduced effective magnetic moment from the moment of the trivalent Ce atom (2.54 μ_B/Ce) indicates compensation of the moment due to Kondo coupling. The other possibility could be an over valency greater than (+3) in this material, fluctuating valency case, etc. The hard *x*-ray photoemission spectroscopy study reported earlier suggests a pseudogap at the Fermi level [10]. We prepared high quality single crystals of this material and found interesting features that may be corroborated to the exoticity of this material.

2. Experimental details:

We have prepared high-quality single crystals of $CeCuAS_2$ using flux method. To check the elemental composition, we have performed energy dispersive analysis of *x*-rays and found close to 1:1:2 ratio of the elements. By this observation we can rule out the presence of an easily formable Cu_2As phase in this material. Good crystallinity of the sample is confirmed by the bright spots in the Laue diffraction pattern shown in the Fig. 1.

The hard *x*-ray photoemission spectroscopy (HAXPES) was carried out using 2500, 6000 and 8000 eV photon energies at 45 K and 120 K. The experiments were performed at the P22 beamline of Petra III, Desy, Germany. The energy resolution was about 150 meV at 6000 eV photon energy. The sample was cleaved in the ultrahigh vacuum chamber before the measurements.

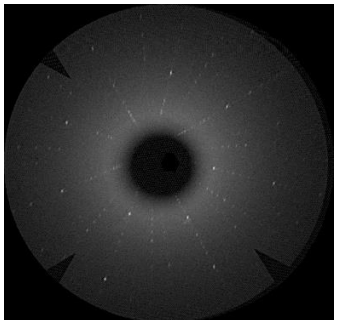

Fig. 1. Laue diffraction pattern of $CeCuA_2$

3. Results and discussions

In Fig.2, we have shown the Cu 2p core level spectra of $CeCuAs_2$ measured at 45 K using 6 keV photon energy. The experimental data is shown by the black open circles. We have fitted the curve to identify each peak separately, the overall simulated envelop is shown by the red line superimposed over the experimental data. There are two strong, intense, peak structures in the spectrum representing the spin-orbit split features, Cu $2p_{1/2}$and Cu $2p_{3/2}$. Binding energies of these features are 952.8 eV and 933 eV; the spin-orbit coupling is about 19.8 eV. These lineshape of the features is asymmetric with the tail in the higher binding energy side. This type of tail appears due to the excitation of the valence electron across the Fermi level along with the core level excitations and hence, this is an indication of the metallic ground state of the material [11]. In addition, we observe a broad hump lying about 15.8 eV higher binding energy relative to the main peaks. Similar features have been observed for other core level excitations. Thus, these features can be attributed to the loss feature due to excitation of the collective modes; here the energy of the loss feature suggests plasmon excitations. The single peak structure of Cu 2p core level peaks suggests (+1) valency of Cu in this material. This result is consistent with the earlier reported HAXPES study [10].

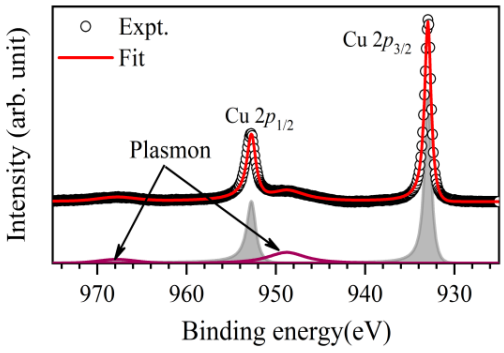

Fig. 2. Cu 2p core level spectrum (open circle) and the fit curve (line). Peaks in the lower panel are the constituent peaks.

In Fig.3, we show the Ce 3d core level spectra of $CeCuAs_2$ measured at 45 K using 6 keV and 2.5 keV photon energies. The experimental data are shown by the black open circles. There are many distinct features in each of these spectra. The intensity of the peaks depends on the excitation photon energies. Since the photoemission escape depth strongly depends on the kinetic energy of the photoelectrons, these results suggest significant surface-bulk differences in the electronic structure. To examine these spectra in more details, we have simulated the experimental spectra with a set of asymmetric Voigt functions. The fit results are shown by the red line superimposed over the experimental data in the figure.

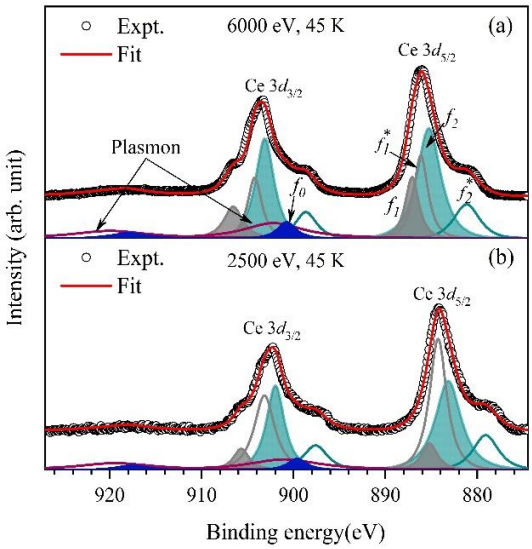

Fig. 3. Ce 3d core level spectra at (a) 6 keV and (b) 2.5 keV photon energy and 45 K temperature. The symbols are the experimental data and the line are simulated data. The shaded peaks are the bulk feature and the same color-outlined peaks are the surface feature.

The Ce 3d spectra exhibit three-peak structures corresponding to different final states of photo-excitations. These final states are often termed as poorly screened f_1 feature (final state electronic configuration $3d^9 4f^1$) and well-screened f_2 feature where a valence electron hopped to the $4f$ level of the photoemission site to screen the core hole, the final state electronic configuration will be $3d^9 4f^{\ 2}$). In addition, these materials show f_0 feature having the final state electronic configuration $3d^9 4f^0$, which corresponds to a tetravalent like Ce site and often show growth at low temperatures. This feature is considered as a signature of Kondo effect [12]. In Kondo lattice system, an increment of the f_0 feature intensity is observed with the lowering of the sample temperature due to the formation of the Kondo singlet [13]. In this material, the position of these f_0, f_1 and f_2 features associate to Ce-3$d_{5/2}$ features are respectively 899.6 eV, 885.2 eV and 883.2 eV. In Fig.3, the f_0, f_1 and f_2 features are shown by blue, grey and green shaded region respectively. Their spin orbit split peaks appear at about 18.8 eV higher binding energy side of each above-mentioned features respectively.

In the experimental data, we find a second set of the f_1 and f_2 peaks. The features for 3$d_{5/2}$ excitations appear at 884.3 eV and 879.1 eV. In Fig.3, they are shown by the grey and green line and marked as f_1^* and f_2^* respectively. The intensity of these peaks becomes stronger at 2.5 keV data compared to 6 keV data. Since the technique is more bulk sensitive at 6 keV compared to 2.5 keV case, these features are attributed to the surface electronic structure. Evidently the unstarred ones are the bulk peaks and appear at higher binding energies relative to the surface peaks. This suggests that the effective Madelung potential at the bulk Ce sites is higher than that at the surface Ce sites. Moreover, we observe that the intensity of the bulk f_2 feature is larger than bulk f_1 peak which indicates larger hybridization in the bulk electronic structure that leads to more efficient screening of the core holes. The surface features show the opposite scenario reflecting the more local behavior of the surface Ce [6]. Ce 3d spectra also show plasmon features as found in Cu 2p spectrum.

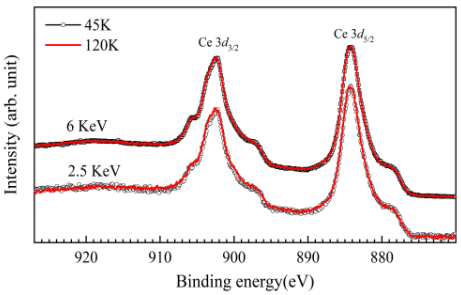

Fig. 4. Temperature evolution of Ce 3d spectra. Top and the bottom panels are the spectra in 6 keV and 2.5 keV photon energy at 45 K (black Line + symbol) and 120 K (red line) temperature.

In Fig.4., we show the temperature variation of Ce 3d spectra. We do not observe any change in any of the 2.5 keV and 6 keV data. This is unusual for a Kondo lattice system hosting f_0 feature. Considering the fact that Ce moments are not fully compensated in the magnetization results, this observation suggests that the experimental temperature is much higher than the temperature regime required to observe changes in f_0 feature. Further studies are required to understand this scenario.

4. Conclusion

In summery we have studied the electronic properties of $CeCuAs_2$ with high-resolution hard x-ray photoemission spectroscopy. Core level spectra show signature of plasmon loss features and Cu is found to be monovalent in this material. We find the signature of strong Ce 4f-valence state hybridization and significant differences in the surface and bulk electronic structure. Though the bulk measurements show Kondo behavior, we have not observed temperature dependence of the Kondo feature down to 45 K studied, which is the lowest temperature achievable in the experimental setup. We hope these results will help to initiate further studies in this direction.

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