ELECTRONIC STATES OF THE KONDO SEMICONDUCTOR CeRhAs AND RELATED COMPOUNDS: A HIGH-RESOLUTION RESONANT PHOTOEMISSION STUDY*

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Ce $4f$ states of the Kondo semiconductor CeRhAs, semimetal CeRhSb, and metal CePtSn single crystals were observed directly by high-resolution resonant photoemission spectroscopy. A large gap and a pseudogap at E_{F} were found in CeRhAs and CeRhSb, respectively.

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1. Introduction

CeRhAs and CeRhSb, with the orthorhombic ε-TiNiSi-type structure, are Kondo semiconductor and Kondo semimetal, respectively [1–3]. They have attracted much interest for a small energy gap or pseudogap formation in the ground state without magnetic ordering [1, 4]. In this paper, we report high-resolution, low-temperature resonant photoemission spectra of CeRhAs and CeRhSb single crystals. We discuss unusual Ce $4f$ electronic states in these compounds comparing them with that of the iso-structural Kondo metal CePtSn single crystal [5, 6].

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2. Experiment

CeRhAs and CeRhSb single crystals were grown by the Bridgman method, [2,3] and CePtSn single crystals were grown by the Czochralski method [5]. The Kondo temperatures for CeRhAs, CeRhSb, and CePtSn were estimated to be $T_K \sim 1500\,K$ ($\sim$130 meV), $\sim$360 K ($\sim$30 meV), and $\sim 10\,K$ ($< 1\,meV$) [5], respectively. The former two temperatures were inferred by assuming the relation $T_K \sim 3\,T_m$ [7]. The present measurements were carried out on a high-resolution linear undulator beamline (BL-1) connected to the compact electron-storage ring (HiSOR) located at Hiroshima Synchrotron Radiation Center (HSRC), Hiroshima University [8]. The beamline is equipped with a high-resolution, hemispherical electron analyzer (SCIENTA ESCA200). The total instrumental energy resolution was set at 18–20 meV at $h\nu = 126\,eV$. The samples were mounted on a He-flow type cryostat and cooled down to 10–12 K. To obtain clean surfaces, we fractured the single crystalline samples *in situ* in ultrahigh vacuum (3×10^{-10} Torr) at 10–12 K. The binding energy was calibrated using the Fermi edge of Au with the accuracy of ± 2 meV. Surface cleanliness was checked by using the spectral feature around 6 eV, which is sensitive to oxygen contamination. We performed angle-integrated photoemission spectroscopy by collecting photoelectrons emitted normally with an acceptance angle of $\pm 6^\circ$ and $\pm 1.3^\circ$ along and perpendicular to the analyzer slit, respectively. The spectral features were highly reproducible. At photon energy of $h\nu = 126\,eV$, which is close to the Ce $4d$–$4f$ photoemission resonance peak at 122 eV, the Ce $4f$ contribution is enhanced significantly, and dominates the spectra. The off-resonance spectra of these compounds taken at $h\nu = 115\,eV$ (not shown) have almost flat spectral shapes above $E_B \sim 2\,eV$, and have much weak intensity compared with those taken at $h\nu = 126\,eV$.

3. Results and discussion

Fig. 1(a) shows the Ce $4f^1$ derived spectra. The intensities are normalized to the peak at $\sim 300\,meV$. The Ce $4f^1$ spectra of CeRhSb and CePtSn are split by the spin-orbit interaction into two peaks at $\sim 300\,meV$ and $\sim E_F$. Based on the single-impurity Anderson model (SIAM), the spectral features at $\sim E_F$ are due either to a Ce $4f^1_{5/2}$ contribution, or to the tail of the Kondo resonance (KR), while those at $\sim 300\,meV$ are due to the Ce $4f^1_{7/2}$ derived states. It is noteworthy, on the other hand, that the peak structure near E_F is fully absent in the spectrum of CeRhAs.

In order to estimate the spectral density-of-states (SDOS), we divided the photoemission spectra (normalized at $\sim 300\,meV$) by a Fermi-Dirac distribution function (FDD), convoluted with a Gaussian which represents the instrumental resolution [9], as shown in Fig. 1(b). The resulting spectra are assumed to give the SDOS broadened with the instrumental resolution.

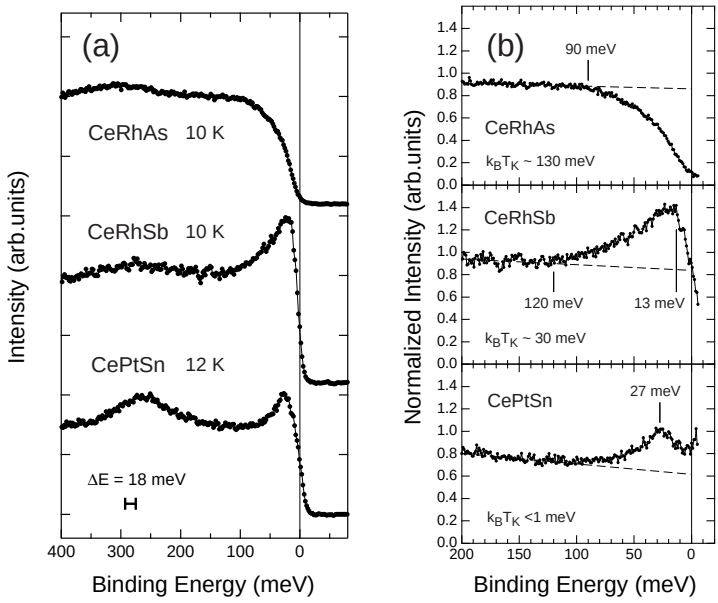

Fig. 1. (a) High-resolution photoemission spectra of CeRhAs, CeRhSb, and CePtSn near E_F. The spectral intensities are normalized to the peak at ~ 300 meV. (b) Photoemission spectra of CeRhAs, CeRhSb, and CePtSn divided by broadened FDD. These spectra are assumed to reflect the SDOS broadened with the instrumental resolution. Dashed lines are guides to the eyes.

One notices again that CeRhAs exhibits quite different spectral features as compared with those of CeRhSb and CePtSn. There is no KR at E_F. The spectral intensity decreases monotonically above ~ 90 meV, forming a large gap structure. It is remarkable that the energy gap of CeRhAs is very close to a fullgap rather than a pseudogap.

As shown in Fig. 1(b), the spectral intensity of CeRhSb shows enhancement above ~ 120 meV, which is similar to that of Kondo metals with high T_K [10]. However, above ~ 13 meV the spectral intensity decreases steeply, which is an important feature different from that of CePtSn and other Kondo metals [9,10]. The rapid decrease in the spectral intensity strongly supports the existence of a narrow pseudogap. It should be noted that the size of the pseudogap ~ 13 meV coincides well with the Δ_{p-p} values of 10–13.5 meV obtained by tunneling spectroscopy [11].

The spectral intensity of CePtSn exhibits no remarkable enhancement near E_F, except for a peak structure at $\sim$27 meV. The peak structure is in good agreement with crystal field excitations observed in inelastic neutron scattering [6]. Weak KR is consistent with either the low $k_B T_K < 1$ meV, or a weak c–f hybridization [10]. The spectral features of CePtSn can be well interpreted within the framework of the SIAM.

Based on the periodic Anderson model (PAM), Ikeda and Miyake [12] and Moreno and Coleman [13] showed the semimetallic spectral density for CeNiSn or CeRhSb. The observed spectrum for CeRhSb can be qualitatively understood in terms of these models. However, the observed spectral feature of CeRhAs is significantly different from the spectral density given by the PAM. The absence of a peak structure near E_F is highly suggestive of much stronger c–f hybridization. More realistic energy band dispersions should be taken into account. It is desirable to compare the spectral features with the density-of-states given by band-structure calculations.

In summary, the Ce $4f$ derived electronic states of the iso-structural single crystalline CeRhAs, CeRhSb and CePtSn have been investigated, by utilizing high-resolution, low-temperature resonant photoemission spectroscopy. The spectral intensity of the Kondo semiconductor CeRhAs monotonically decreased above ~ 90 meV. The spectral feature considerably differs from what the PAM predicted so far. The observed SDOS of the semimetal CeRhSb enhanced above ~ 120 meV but decreased above ~ 13 meV, which can be well described based on the PAM. The spectral features of the metal CePtSn are well explained by the SIAM with low T_K.

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