

Spectral Evidence for Pseudogap Formation in Kondo Insulators CeRhAs and CeRhSb

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High-resolution photoemission spectroscopy has been performed on CeRhAs and CeRhSb to study the temperature-induced evolution of the "Kondo-insulator" gap. We have observed that a pseudogap opens at E_F at low temperatures while it is gradually filled with increasing temperature. The size of the pseudogap is well scaled with the Kondo temperature (T_K) of each compound while the temperature evolution is dominated by another characteristic temperature T_{coh} ($< T_K$). The results are qualitatively consistent with the theoretical prediction from the Anderson lattice model. [S0031-9007(99)08535-X]

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Cerium (Ce) and ytterbium (Yb)-based compounds have been intensively studied because of their various unusual properties such as the dense Kondo effect [1]. It has been proposed that $4f$ electrons in this class of materials behave as a single magnetic impurity at high temperature, while they condense into a local singlet state coupled with conduction electrons below a certain characteristic temperature named Kondo temperature (T_K) [2]. The single-impurity Anderson model (SIAM) has been successfully employed to interpret the angle-integrated photoemission spectra [3], while some recent angle-resolved photoemission results [4] have questioned its validity by showing a momentum dependence of a narrow peak near E_F as well as its temperature dependence weaker than predicted. According to the Anderson lattice model (ALM) including the periodicity of f electrons in the lattice [5], the f electrons begin to form the Fermi-liquid states due to the long-range coherence among local singlets below another characteristic temperature T_{coh} ($< T_K$). The hybridization between the conduction band and the heavy quasiparticle f band produces complicated hybridized bands near E_F [6], resulting in various unusual ground states such as heavy fermion, intermediate valence state, and exotic superconductivity [1].

Recently, a new type of insulating ground state has been discovered in some Ce- and Yb-based compounds named Kondo insulator [7]. A number of temperature-dependent physical properties suggest an opening of a small (pseudo)gap in the renormalized bands while the materials exhibit a metallic nature at high temperatures. It has been elucidated that the physics of Kondo insulators follows from a simple lattice model with one occupied f state interacting with a single half-filled conduction band [8]. One can expect that the small (pseudo)gap suggested by experiments is a simple energy gap of a conventional band insulator with even-numbered electrons in the unit cell. However, a Kondo insulator is totally different from a conventional band insulator in that the (pseudo)gap disappears above a characteristic temperature (T_{coh}) [7,9–11]. It has also been observed that the (pseudo)gap is very sensitive to the magnetic field [12], to pressure [13], and to a small amount of impurities [14]. These experimental

facts as well as many other anomalous magnetic properties strongly suggest that the (pseudo)gap originates in the many-body effect. One then expects temperature dependence of the (pseudo)gap correlated with the temperature dependence of the magnetic interaction. This suggests the importance of investigating the gap evolution as a function of temperature and c - f hybridization strength to address the mechanism of the Kondo-insulating state.

In this Letter, we report high-resolution photoemission spectroscopy (HR-PES) of CeRhAs and CeRhSb, which are isostructural and regarded as Kondo insulators with different T_K 's [15,16]. We have performed a systematic temperature-dependent measurement and clearly observed a pseudogap at E_F at low temperature as well as its evolution as a function of temperature. We found that the size of the pseudogap is well scaled with T_K while its temperature evolution is dominated by another characteristic temperature T_{coh} ($< T_K$). Comparing the present HR-PES results with reported magnetic/electrical properties [15,16] and the tunneling spectroscopy result [17] of these compounds, as well as previous optical/HR-PES results on other Kondo insulators [18–20], we discuss the physical nature of the pseudogap of Kondo insulators.

Polycrystalline CeRhSb and CeRhAs samples were prepared by argon arc melting with starting materials Ce (99.9% pure), Rh, Sb, and As (99.999% pure) in the respective composition ratio. X-ray diffraction, electrical resistivity, magnetic susceptibility, and specific heat measurements have been performed for characterization, and the results show a good agreement with the published data [15,16]. HR-PES measurements were carried out using a Scienta SES-200 with a GAMMADATA discharge lamp and a toroidal grating. The spectra presented here were recorded with an energy resolution of 8 meV. Samples were scraped *in situ* by a diamond file under a vacuum of 5×10^{-11} Torr. The Fermi level of the sample was referred to a gold film evaporated onto the sample substrate, and the accuracy was estimated to be less than 1 meV.

Figure 1 shows the PES spectra in the vicinity of E_F for CeRhAs and CeRhSb measured at 13.5 K using the He I α line (21.218 eV), compared with that of gold. The inset shows the comparison with the He II α (40.814 eV)

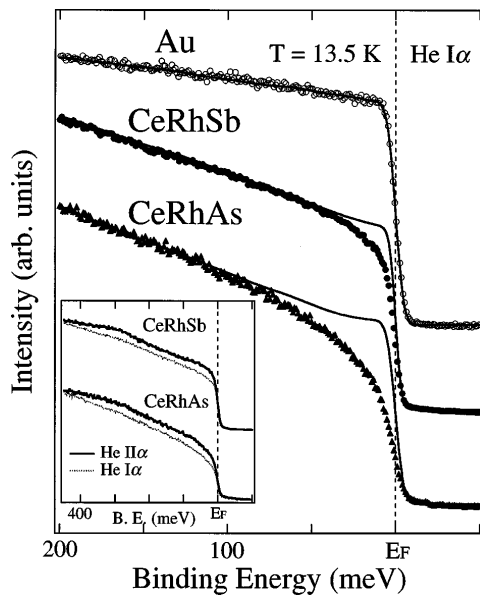


FIG. 1. High-resolution photoemission spectra near E_F of gold (open circles), CeRhSb (filled circles), and CeRhAs (triangles) measured with the He $I\alpha$ line at 13.5 K. Solid lines on each spectrum are calculated gapless spectra obtained from the DOS at high temperature (see text for details). The inset shows a comparison of PES spectra measured with the He $I\alpha$ and He $II\alpha$ lines in a wider energy range.

spectra in a wider energy range. According to the band structure calculation [21], the electronic structure near E_F is dominated by the Rh $4d$ states with a relatively small contribution from the Ce $4f$ states. Furthermore, the photoionization cross section of Ce $4f$ electrons is considerably smaller than that of Rh $4d$ electrons in both the He I and II energy ranges [22]. These facts suggest that both the He I and II spectra represent mainly the Rh- $4d$ derived density of states (DOS). Nevertheless, we certainly observe a small difference between the two spectra in the spectral intensity around E_F and 280 meV, which may correspond to the well-known Ce $4f^1$ final state [2,3] and indicate the Ce $4f$ states in this energy range. When we compare the He I spectra of CeRhSb and CeRhAs with that of gold, we find that the spectral intensity near E_F is substantially depleted in the Ce compounds. In order to see this difference more clearly, we have superimposed a “gapless” spectrum (solid line) on each spectrum. The gapless spectrum is obtained from the PES spectrum of each material at 300 K where the Kondo-insulator gap is expected to be completely closed (and is actually so in the experiment as shown later). We, at first, calculated the gapless DOS at 300 K by dividing the PES spectrum with the Fermi-Dirac (FD) function at 300 K convoluted with a Gaussian of 8 meV width representing the instrumental resolution [23,24]. The final gapless spectrum is obtained by multiplying the gapless DOS after smoothing with the FD function at 13.5 K and consequent convoluting with the instrumental resolution. A small hump-like structure near E_F in the gapless spectrum may be due to a broad flat minimum around

E_F in the gapless DOS at high temperatures (shown later in Fig. 3). In the case of gold the gapless spectrum matches quite well with the experimental spectrum at 13.5 K, while a clear deviation is seen near E_F in both CeRhSb and CeRhAs, and the deviation looks larger in CeRhAs. Close comparison shows that the deviation starts around 30–35 meV and 90–100 meV for CeRhSb and CeRhAs, respectively. A similar depletion of PES intensity near E_F has also been reported for $Ce_3Bi_4Pt_3$ [20]. Here we comment on an effect of the surface preparation method since there is an ongoing discussion on the PES spectral feature obtained by two different methods (scraping and cleaving) [3,4]. In $Ce_3Bi_4Pt_3$, these two preparation methods have been compared and found to give essentially the same result regarding the depletion near E_F . In contrast, the PES spectrum of a typical heavy fermion compound $CeSi_2$ measured for the scraped surface does not show such a depletion [20]. All these facts suggest that the depletion near E_F observed in CeRhSb and CeRhAs is intrinsic.

The next crucial issue is whether this depletion (pseudogap) disappears at high temperatures unlike a conventional band structure gap. Figure 2 shows the temperature dependence of PES spectra near E_F of CeRhSb

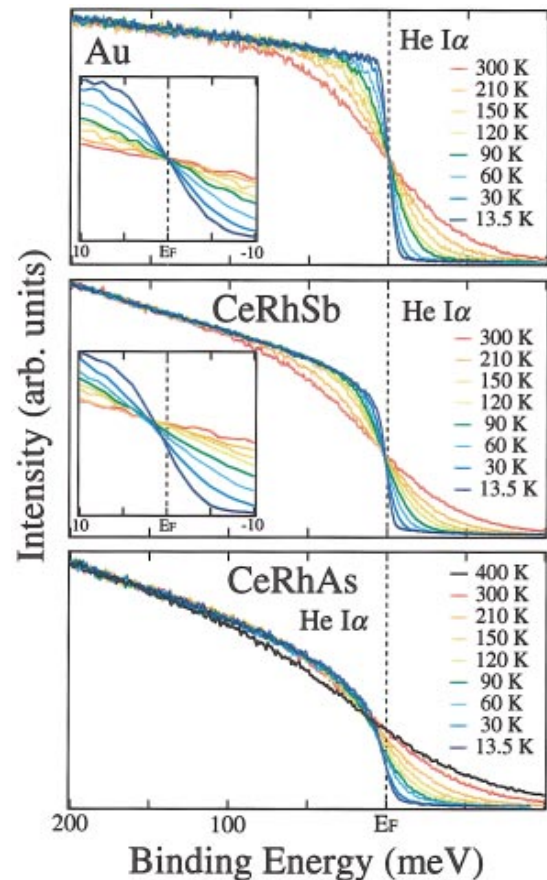


FIG. 2(color). Temperature dependence of a high-resolution photoemission spectrum near E_F of gold, CeRhSb, and CeRhAs. The insets show the spectra near E_F in an expanded energy scale.

and CeRhAs compared with gold. Intensity of spectra is normalized at 150–200 meV where the spectra show no temperature dependence, and the FD function has negligible influence. The insets show the expansion near E_F . The temperature-induced change is considerably asymmetric with respect to E_F in both CeRhSb and CeRhAs in contrast to the symmetric behavior of gold. It is reasonable that every gold spectrum intersects the same point at E_F independent of temperature, because the FD function always takes the same value (0.5) at E_F irrespective of temperature. In return, the observed asymmetric behavior in CeRhSb and CeRhAs strongly suggests that there takes place a temperature-induced (pseudo)gap opening/closure unlike a conventional band structure gap. It is clear, in particular, for CeRhAs that a pseudogap observed at low temperature is gradually filled on increasing temperature, as evident from the higher spectral intensity at E_F at higher temperatures.

In order to obtain the change of DOS, we have divided the PES spectra by the FD function convoluted with instrumental resolution [23,24]. The results are shown in Fig. 3. A flat DOS across E_F obtained for gold demonstrates the validity of this data-analyzing method as well as the precise determination of the E_F position in the experiment. In contrast, the DOS of CeRhAs clearly exhibits a pseudogap at E_F at low temperatures. The gap is not a full gap but a pseudogap with a finite DOS at E_F . The temperature dependence of DOS in CeRhAs is quite unusual. The DOS at low temperatures is strongly depleted up to a characteristic energy ($\Delta_{\text{PES}} = 90\text{--}100$ meV), which coincides with the energy position where a deviation from the gapless spectrum begins (see Fig. 1). With increasing temperature the pseudogap gradually disappears by filling with additional intensity within the pseudogap, but no clear transfer of weight of DOS is seen in the present energy range ($E_F - 150$ meV). We also find that there is no discernible change of the pseudogap size with temperature. The DOS at 300 K is almost the same as that at 400 K, indicating that the pseudogap collapses at 300 K in CeRhAs. At the lowest temperature (13.5 K), on the other hand, we find an additional “narrow” dip at E_F within the “wide” pseudogap. The width is about 10 meV, being comparable to the observed transport gap of about 12 meV [16].

The temperature dependence of DOS for CeRhSb shows a similar behavior to that of CeRhAs except that the energy scale dominating the pseudogap formation is much smaller in CeRhSb. We find in the inset to Fig. 3 that the pseudogap collapses at 120 K and Δ_{PES} is 30–35 meV in CeRhSb. According to an electron tunneling spectroscopy (ETS) of CeRhSb [17], the semiconductor–insulator–normal metal junction spectrum shows a sharp peak around 10–15 meV together with a broad hump around 35–40 meV at low temperature. While we can correlate the Δ_{PES} to the broad hump in the ETS experiment, we have not observed a sharp peak around

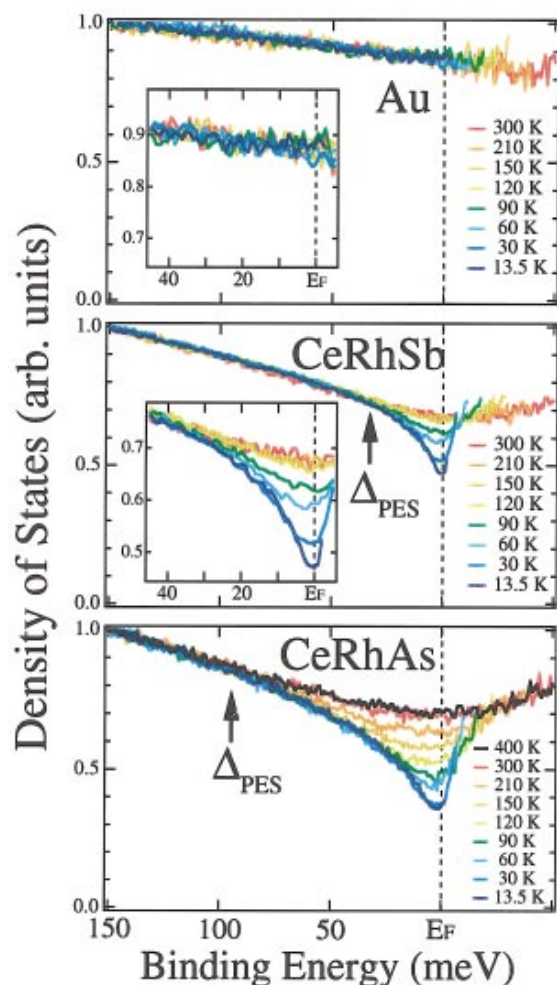


FIG. 3(color). Temperature dependence of spectral density of states near E_F of gold, CeRhSb, and CeRhAs. The insets show the expansion near E_F .

10–15 meV in the PES experiment. As is clear in Figs. 2 and 3, a significant amount of DOS disappears in the energy region from E_F to Δ_{PES} at low temperatures while there is little temperature-induced changes beyond Δ_{PES} . This is in sharp contrast to the ETS result which shows a temperature-induced spectral-weight transfer between the in- and out-of-gap regions. The present PES results on CeRhAs and CeRhSb are consistent with the optical measurement on $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ [18], which reported that the depleted spectral weight in the gap does not pile up out of the gap. A similar simple depletion of photoemission spectral weight at low temperature has been observed in YbB_{12} [19] and $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ [20]. These facts suggest that the depleted spectral weight is distributed over a wider energy range [18].

We now address the physical nature of the pseudogap size (Δ_c). Assuming the Fermi level is located at the middle of the gap [25], the gap size ($\Delta_c = 2\Delta_{\text{PES}}$) is estimated to be 60–70 meV and 180–200 meV for CeRhSb and CeRhAs, respectively. It is worthwhile to compare the Δ_c with the Kondo temperature (T_K) which is defined as the binding energy of the local Kondo singlet.

We have estimated the T_K for both compounds from the susceptibility measurement and obtained $T_K = 360$ and 1200 K for CeRhSb [15] and CeRhAs [16], respectively. In the estimation we assume that $T_K \sim 3T_{\max}$ according to the SIAM model with the full degeneracy of the $j = \frac{5}{2}$ manifold [2], where T_{\max} is the temperature at which the susceptibility has a broad maximum. As a result, we obtain the ratio $\Delta_c/k_B T_K$ being 1.9–2.3 and 1.7–2.0 for CeRhSb and CeRhAs, respectively. These values are in good agreement with that of Ce₃Bi₄Pt₃ determined by the optical measurement ($\Delta_c/k_B T_K \sim 1.7$) [18] and also by PES ($\Delta_c/k_B T_K \sim 1.9$ – 2.4) [20]. This strongly suggests that the Kondo energy ($k_B T_K$) is an essential physical parameter to describe the pseudogap. Since the Kondo energy is independent of temperature, the temperature invariability of Δ_{PES} observed in the present PES experiment supports this picture.

Finally we discuss the temperature dependence of the pseudogap in comparison with theoretical predictions. We find in Fig. 3 that the pseudogap formation in CeRhAs starts at 210–300 K [(0.18–0.25) T_K] and saturates at 30 K (0.025 T_K). In CeRhSb, the pseudogap formation starts at 90–120 K [(0.25–0.33) T_K], and the saturating temperature is considered to be below 13.5 K (<0.038 T_K). These values are in qualitative agreement with those from the optical measurement on Ce₃Bi₄Pt₃ ($\sim 0.42T_K$ and $0.10T_K$) [18]. This suggests another characteristic temperature different from T_K for the pseudogap formation. Both the one-dimensional ALM with the quantum Monte Carlo method [10] and the infinite-dimensional ALM within dynamical mean-field theory [11] have predicted the existence of two different characteristic temperatures (T_K and T_{coh}) in Kondo insulators. According to the calculations [10,11], the gap starts to open at $T_{\text{coh}} = (0.4$ – $0.6)T_K$ and saturates at $0.2T_{\text{coh}}$. These values are consistent with the result of the optical measurement on Ce₃Bi₄Pt₃ [18], while they are slightly larger than those from the present PES result. This quantitative discrepancy may originate in the strongly anisotropic c - f hybridization gap in CeRhSb and CeRhAs [15] in contrast with the isotropic gap in Ce₃Bi₄Pt₃ [7], suggesting the importance to include the realistic electronic structure in the ALM calculation.

In conclusion, we have observed a Kondo-insulator pseudogap in CeRhAs and CeRhSb and its temperature evolution using high-resolution photoemission spectroscopy. We found that the size of the pseudogap is independent of temperature, being well scaled with the Kondo temperature (T_K) while the temperature evolution is dominated by another characteristic temperature T_{coh} ($< T_K$). Experimental results are qualitatively consistent with the theoretical prediction based on the Anderson lattice model. The observed quantitative discrepancy suggests a strong anisotropy of the c - f hybridization gap in these compounds.

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