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Kondo scaling of the pseudogap in $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$

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Abstract

$CeOs_4Sb_{12}$ and $CeFe_4P_{12}$ are classified as Kondo semiconductors, which show coupled changes in electrical transport, thermodynamic and magnetic properties with a low-temperature semiconductor-like electrical resistivity. We have carried out core level and valence band photoemission spectroscopy on single crystal $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$ to study their electronic structure and the evolution of states at the Fermi level as a function of temperature (∼10–300 K). The Ce 3d core level spectra show the presence of f^0, f^1 and f^2 final states with very different relative intensities in the two compounds. Single-impurity Anderson model calculations provide f electron counts of $n_f = 0.97$ and 0.86 per Ce atom, suggestive of a low- and high-T_K (=single ion Kondo temperature) for $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$, respectively. The high-resolution temperature-dependent near-Fermi level spectra show pseudogaps of energy ∼50 meV and ∼110 meV in the valence band density of states (DOS) of $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$, respectively. The temperature dependence of the DOS at the Fermi level follows the change in effective magnetic moment estimated from magnetic susceptibility for both materials, confirming the Kondo nature of the pseudogap in $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$. A compilation of measured pseudogaps using photoemission and optical spectroscopy identifies the charge gaps Δ_C for Ce-based Kondo semiconductors and provides a direct relation with T_K given by $\Delta_C \sim 2k_BT_K$. In conjunction with the known behaviour of the spin gaps $\Delta_S \sim k_BT_K$, the results establish the coupled energy scaling of the spin and charge gaps in Kondo semiconductors.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The rare-earth filled skutterudites RT_4X_{12} (R = rare earth, T = transition metal, X = pnictogen) are a special class of materials [1] which manifest a variety of phenomena such as superconductivity in La filled skutterudites [2, 3], the quadrupolar Kondo effect and multi-phase superconductivity in Pr filled skutterudites [4–6], semiconducting behaviour in Ce filled skutterudites [7, 8] and heavy-fermion behaviour in Sm filled skutterudites [9]. Even the arsenide skutterudites, which were largely unexplored until recently, have revealed fascinating properties at low temperature: heavy-fermion behaviour evolving into antiferromagnetic order in $PrOs_4As_{12}$, a hybridization gap in $CeOs_4As_{12}$ as well as $CeRu_4As_{12}$ [10], while an early study showed superconductivity in $LaRu_4As_{12}$ and $PrRu_4As_{12}$ [11]. These properties are in addition to their high thermoelectric power and reduced thermal conductivity at room temperature, which are important for potential thermoelectric applications [1]. Filled skutterudite antimonides in particular are considered suitable for thermoelectric devices operated at elevated temperature due to their high ZT (Z is $\sigma S^2/\kappa$ where S = Seebeck coefficient, σ = electrical conductivity and κ = thermal conductivity) values at high temperatures. This property is believed to originate

from the characteristic crystal structure of the rare-earth filled skutterudites RT_4X_{12} consisting of a loosely held rare-earth atom R within the cubic cage made of eight TX_6 octahedra [1]. Interestingly, most of the Ce filled skutterudites show low-temperature semiconducting behaviour with different values of the gap size depending on transition metal and pnictogen atoms [7]. The semiconducting ground state in CeT_4X_{12} has been attributed to strong hybridization between a single localized f electron (Ce^{3+}: f^1) and an exactly half-filled conduction band [12]. Recent photoemission and inelastic neutron scattering reports on filled skutterudites show a charge gap and a spin gap, respectively, at low temperature, and support a Kondo semiconducting picture for Ce-based filled skutterudites [7–9]. Early reviews [12, 13] on the so-called Kondo semiconductors have discussed systematic property changes in magnetic susceptibility, electrical resistivity, carrier concentration and the optical response of typical materials belonging to this class, such as $CeBi_4Pt_3$, FeSi, SmB_6, etc. Riseborough has discussed and reviewed the Kondo pseudogap and its systematics based on theoretical studies, including the Anderson lattice model (ALM) [14].

In this study we investigate the electronic structures of $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$ and the temperature (T) dependence of their low energy electronic states. Both materials indicate low-temperature semiconducting behaviour in electrical resistivity. For $CeOs_4Sb_{12}$, the resistivity shows a very low activation energy of $\sim$1 meV over a limited temperature range of 25–50 K [15]. However, from careful measurements and a comparison with $LaOs_4Sb_{12}$ resistivity data, it was shown that the resistivity shows a faint maximum around 100–120 K. Also, the Hall coefficient shows a clear anomaly around 120 K and a shallow hump in the magnetic susceptibility is observed around 100 K [15, 16]. Subsequent resistivity results showed variable-range hopping-like behaviour at pressures $\geqslant$2 GPa and temperatures between 5 and 20 K [17]. A recent resistivity and magneto-resistance study of $Ce_{1-x}La_xOs_4Sb_{12}$ showed Kondo-hole behaviour and discussed the possibility of the pure compound $CeOs_4Sb_{12}$ also having a considerable number of Ce vacancies, which can create localized states in the pseudogap [18]. Optical spectroscopy shows a pseudogap with a broad inter-band transition setting the upper limit of the charge gap to be 60–70 meV and a weak shoulder feature at about 30 meV in $CeOs_4Sb_{12}$ [19]. A recent study using inelastic neutron scattering has also observed magnetic origin excitations at 27 and 48 meV, consistent with the optical spectroscopy results of $CeOs_4Sb_{12}$. Its specific heat showed a substantial electronic contribution ($\sim 120 - 220$ mJ K^{-2} mol^{-1}) in addition to a phase transition of unknown origin at very low temperature ($\sim$1 K) [15, 20], well below the temperature range of activated resistivity. In a recent study, we reported on the role of a symmetry-dependent hybridization in $CeOs_4Sb_{12}$ leading to the anomalous behaviour of a pseudogap just below the Fermi level (E_F) and a sharp feature just above E_F which explained the simultaneous observation of a heavy fermionic-like specific heat at low temperature [21].

For $CeFe_4P_{12}$, resistivity studies have reported activation energies of 1250 K [17] or 1500 K [22], suggesting that the corresponding anomalous feature, if any, in the magnetic susceptibility and Hall effect, should be far above room temperature. To date, the magnetic susceptibility and Hall coefficient above room temperature has not been reported. However, the Hall coefficient for $CeFe_4P_{12}$ is positive between 25 and 300 K and increases with decreasing temperature, thus suggesting that the dominant carriers are holes and its concentration decreases with decreasing temperature [17]. An optical gap of about 0.22–0.24 eV has been reported recently for single crystal $CeFe_4P_{12}$ [23]. Also, the magnetic susceptibility below room temperature shows a continuous decrease in the effective magnetic moment for $CeFe_4P_{12}$ [22]. Such coupled changes in the electrical resistivity, Hall coefficient and magnetic susceptibility are typical of Kondo semiconductors [12–14]. From systematic studies using inelastic neutron scattering for Kondo semiconductors and metals, a direct correlation of the spin gap Δ_S with T_K, given by $\Delta_S \sim k_B T_K$, has been reported recently [8b]. For this universal behaviour, T_K was estimated as $3T_{max}$, where T_{max} is the temperature corresponding to a broad maximum seen in the magnetic susceptibility of many Kondo semiconductors and metals. It is based on a single Ce impurity model with a six-fold degenerate $j = 5/2$ ground state hybridizing with a conduction band, and solved self-consistently for the Kondo resonance in the mixed valent regime [24]. However, a general relation for the charge gaps Δ_C with T_K, although expected from theoretical studies [25–28], has been experimentally elusive. One important reason is because the charge gaps as obtained by photoemission spectroscopy have not been consistent with optical gaps. While optics measures the full gap excitation from the occupied to the unoccupied states, one needs to be very careful with the gaps (or pseudogaps) measured using photoemission, as only the gap in the occupied part of the density of states is measured. Hence, one needs to confirm whether the gap is the full gap, or half the gap, or simply no gap, depending on the case that the Fermi level is pinned to the bottom of the conduction band, centre of the gap, or at the top of the valence band. In addition, in photoemission spectroscopy Kondo semiconductors have never shown a full gap but only a pseudogap. In order to address the issue of the charge gaps in Kondo semiconductors, we felt it important to study the electronic structure of $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$, which effectively correspond to a low- and high-T_K material, and to make a careful comparison with the charge gaps already reported for several Kondo semiconductors.

We study the electronic structures of $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$ using: (1) angle-integrated ultraviolet photoemission spectroscopy (UPS) for the whole valence band, (2) high-resolution temperature-dependent UPS around E_F, (3) Ce 3d core level x-ray photoemission spectroscopy (XPS) and (4) single-impurity Anderson model (SIAM) calculations. UPS provides the single particle DOS of a material and we discuss the overall valence band (VB) electronic structure of $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$ in relation to band structure calculations and recent soft x-ray photoemission results. Photon-dependent UPS is used to identify and describe the character of the electronic states. The Ce 3d core level XPS suggests the presence of mixed valency in both the

compounds which can be simulated using SIAM calculations. The results provide the conduction-electron–f-electron (c–f) hybridization and the f electron count (n_f) for both materials. High-resolution experiments reveal a temperature-dependent pseudogap formation with an energy scale of ∼50 meV and ∼110 meV in $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$, respectively. Our study confirms that these materials are Kondo semiconductors, whose DOS at E_F shows a systematic reduction which matches the quenching of the effective magnetic moment on reducing the tempeature. The present results, in conjunction with earlier studies, identify a direct relation of the charge gaps Δ_C with T_K for Ce-based Kondo semiconductors, given by $\Delta_C \sim 2k_BT_K$.

2. Experiment

Single crystals of $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$ were grown by the Sb-flux and Sn-flux method, respectively. Details of the preparation and characterization are reported elsewhere [17]. Electrical resistivity measurements indicated activation energies of ∼10 K and ∼1250 K for $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$, respectively, consistent with earlier reports [15–18, 22] and indicative of negligible defects or vacancies (⩽1%). The UPS measurements were carried out using a Gammadata He discharge lamp, a Scienta SES-2002 analyser and a toroidal-grating monochromator at ISSP, Japan. The base pressure of the spectrometer was 2×10^{-11} Torr. The temperature-dependent measurements were carried out using a combination of a flowing liquid ^{4}He cryostat and a heater mounted close to the sample holder. The energy resolution and the Fermi level were determined by fitting a convolution of the Gaussian function and the Fermi–Dirac (FD) function to the lowest temperature measurement of the Fermi edge of Au evaporated on the sample holder. At the lowest temperature reported here, the spectrometer energy resolution was obtained to be 7.8 meV full width at half maximum for the Gaussian function. The exact temperatures of the measurements were also determined by fitting the FD function (convoluted with the known fixed energy resolution) to the Fermi-edge data of Au measured at each temperature of the UPS measurements. Core level XPS was performed at undulator beamline BL17SU, SPring8, Japan using a Scienta SES-2002 analyser and an incident photon energy of 2100 eV, at 40 K sample temperature and ∼300 meV total energy resolution. All samples were fractured *in situ* for the UPS and XPS measurements.

3. Results and discussions

Figures 1(a) and (b) show the VB of $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$, respectively, measured with He Iα ($h\nu = 21.218$ eV) and He IIα ($h\nu = 40.814$ eV) photons. Early studies on Ce and Ce compounds showed that by changing photon energy from He Iα to He IIα, it was possible to extract the f electron partial DOS, since the relative f electron photoionization cross-section (PIC) was significantly larger than that of the other constituent s, p and d electron PICs [29–31]. However, the data in figure 1(a) show that the spectral intensities of $CeOs_4Sb_{12}$ do not change significantly by changing from a He Iα to a He IIα photon source. This suggests that the Ce 4f states do

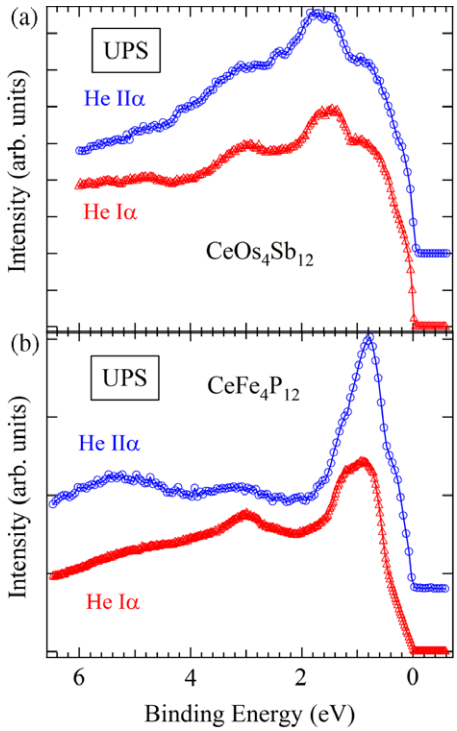

Figure 1. (a), (b) He Iα and He IIα excited valence band spectra of $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$.

not dominate the spectra and the spectra may be dominated by Os 5d and Sb 5p states at He Iα and He IIα photon energies in $CeOs_4Sb_{12}$ [32]. Indeed, the atomic PIC of Os 5d electrons at these photon energies is much larger than that of Ce 4f and Sb 5p electrons [33]. Further, while Ce 3d–4f resonant photoemission spectroscopy (RPES) of $CeOs_4Sb_{12}$ shows Ce $4f^1$ character states at E_F and within 0.5 eV, and a weak f^0 character feature at ∼3.0 eV, the He Iα and He IIα spectra are very similar to the off-resonance spectrum of $CeOs_4Sb_{12}$ [34] and $SmOs_4Sb_{12}$ [9] measured at soft x-ray photon energies. The similarity of the off-resonance soft x-ray data to He Iα and He IIα thus implies that the data represent intrinsic VB spectra which are dominated by the Os 5d partial DOS. The observed spectral shape also shows good correspondence with the Os 5d partial DOS obtained from band structure calculations [32]. On the other hand, the spectral intensities of $CeFe_4P_{12}$ clearly change with the change in photon energy. The peak feature at 0.8 eV is enhanced in the He IIα spectrum as compared to He Iα. This peak feature matches well with Ce 3d–4f RPES of $CeFe_4P_{12}$ confirming that the peak at 0.8 eV is dominated by Ce 4f partial DOS (PDOS) [34]. The Fe 3d derived feature is the shoulder positioned at about 1.3 eV binding energy and the Ce f^0 character feature occurs at ∼3.0 eV. The three-peak VB structure also matches well with the calculated DOS [32, 35] and the soft x-ray spectrum [36]. Thus the VB spectra provide the character of electronic states in terms of the Ce 4f, Os 5d/Fe 3d states, with weak intensity for phosphorus 3s–3p/Sb 5s–5p states spread over the entire VB for $CeOs_4Sb_{12}$/$CeFe_4P_{12}$, consistent with band structure calculations.

Core level XPS is an established tool for extracting information about important energy parameters that determine

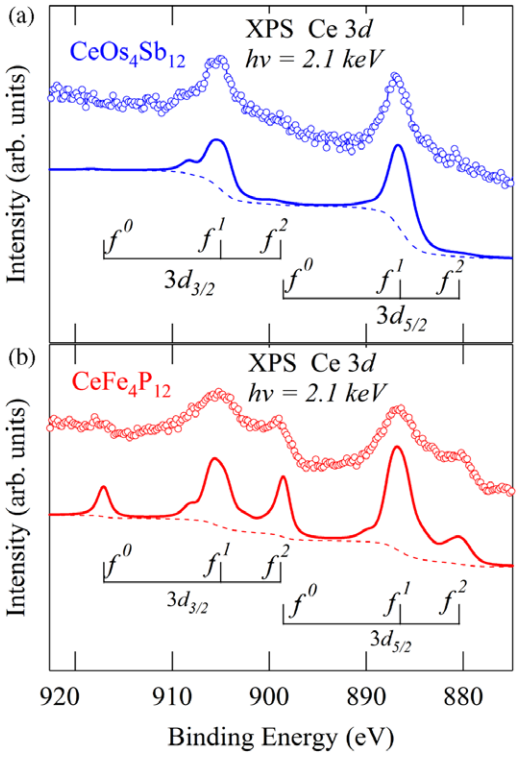

Figure 2. Experimental (symbols) and calculated (lines) Ce 3d spectra of (a) $CeOs_4Sb_{12}$ and (b) $CeFe_4P_{12}$. An integral background (dashed lines) was incorporated to facilitate comparison with the experiment.

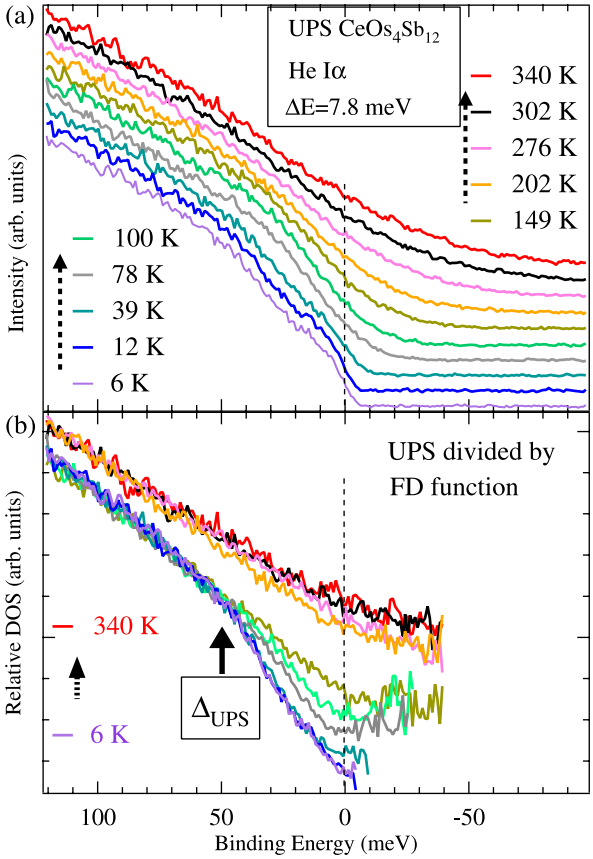

Figure 3. (a) The temperature-dependent high-resolution He Iα UPS on $CeOs_4Sb_{12}$. The legends show temperature values in ascending order for the lowest to uppermost curves, respectively. (b) Temperature-dependent DOS obtained by dividing UPS spectra by Fermi–Dirac function convoluted with resolution function. At E_F, the spectra are in ascending order from the lowest to the highest temperature values (same as in (a)). The curves for $T \geqslant 202$ K are offset by a common value on Y-axis for clarity.

the valence-electronic structure of Kondo materials [37]. In figure 2, we show the Ce 3d core level spectra of $CeFe_4P_{12}$ and $CeOs_4Sb_{12}$ measured using an incident photon energy of 2100 eV. In a recent study using several photon energies, we have shown that the Ce 3d core spectrum of $CeFe_4P_{12}$ does not show surface effects for a photon energy of 2100 eV or higher [34]. Hence we used a photon energy of 2100 eV to also measure $CeOs_4Sb_{12}$ and compare the Ce 3d spectra of both materials with a simulation of the spectra obtained from SIAM calculations with full multiplet effects as described in detail in [34]. The experimental spectra of both the compounds consist of two sets of features corresponding to $3d_{5/2}$ and $3d_{3/2}$ spin–orbit split levels. More importantly, one can see the existence of satellites corresponding to f^0 and f^2 final states around the main f^1 peak as clear features in $CeFe_4P_{12}$, but the satellites are weak or negligible in $CeOs_4Sb_{12}$. The f^0 and f^2 final states are indicative of mixed valency and show up in the core level spectra. In particular, the intensity of the f^2 peak in the spectra originates from screening of the f level by conduction electrons in the presence of a core–hole, and is a direct measure of the c–f hybridization strength. The relative intensities of these features thus suggest that $CeOs_4Sb_{12}$ is a weakly hybridized system as compared to $CeFe_4P_{12}$. It is well known that the SIAM calculations used to reproduce the experimental spectra quantify various energy parameters associated with the electronic structure of Kondo systems, such as the f electron count (n_f), c–f hybridization strength (V), on-site Coulomb repulsion (U_{ff}), core–hole potential (U_{fc}), charge-transfer energy (Δ) and bandwidth (W). The SIAM calculated spectra shown in figure 2 were obtained using common parameter values of $U_{ff} = 7$ eV, $U_{fc} = 11.8$ eV and $W = 2$ eV, while $\Delta = -1.0$ eV and $V = 0.18$ eV for $CeOs_4Sb_{12}$, and $\Delta = -0.9$ eV and $V = 0.44$ eV for $CeFe_4P_{12}$. Our analysis yields $n_f = 0.97$ for $CeOs_4Sb_{12}$ and $n_f = 0.86$ for $CeFe_4P_{12}$. This shows that $CeFe_4P_{12}$ is strongly hybridized compared to $CeOs_4Sb_{12}$. The relevant values reported for γ-Ce are $n_f = 0.94$, $V = 0.15$ eV, and for α-Ce are $n_f = 0.83$, $V = 0.23$ eV, as obtained from the SIAM calculations of the resonant x-ray emission spectra (XES) of Ce at 300 and 20 K [38]. Another recent XES study of Ce under pressure indicated a $T_K \sim 100$ K for γ-Ce and $T_K \sim 1700$ K for α-Ce [39], where T_K is estimated from the spectroscopy parameters in terms of the Gunnarsson–Schonhammer model [37]. The corresponding values for $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$ are $T_K \sim 100$ K and $T_K \sim 1400$ K, respectively. The present results are also consistent with the fact that $CeFe_4P_{12}$ has a significantly smaller lattice constant than what is expected from a trivalent lanthanide contraction [40].

We next discuss the temperature-dependent spectra near E_F for $CeOs_4Sb_{12}$. Figure 3(a) shows UPS near E_F measured

using He Iα photons ($h\nu = 21.218$ eV) at Ts from 6 to 340 K. All the spectra are normalized to the area under the curves extending up to 210 meV binding energy (BE), but are shown on a narrower energy range. As is clearly seen, the intensity at and below E_F shows a significant decrease with temperature in contrast to the Fermi edge of a typical metal. This indicates the opening of a pseudogap in the DOS with decreasing temperature. There is no other clear feature in the occupied DOS within 210 meV BE making up the compensation of the lost spectral weight at and near E_F, indicating that the weight may be distributed over a wider range. This observation is consistent with previous UPS studies of Kondo semiconductors [7, 30, 31, 41, 42]. To account for temperature effects near E_F, we divided the spectra shown in figure 3(a) by the FD function at the corresponding temperature convoluted with the known resolution (figure 3(b)) [7, 31, 41]. This procedure is known to be valid for angle-integrated spectra and provides the relative changes in the single particle DOS as a function of temperature. The result is a clear pseudogap of size $\Delta_{UPS} \sim 50$ meV in the occupied DOS, which opens systematically with decreasing temperature. Close observation reveals that the pseudogap opening starts around 150 K. The pseudogap behaviour has also been observed in more bulk sensitive ($h\nu \sim 7$ eV) laser PES [21], thus confirming that it does not arise due to surface effects. The high-resolution ($\sim$2 meV) laser PES study also showed a sharp feature lying just above E_F, indicating that UPS measures nearly the full gap in the case of $CeOs_4Sb_{12}$. The temperature-dependent pseudogap feature is consistent with the pseudogap reported in an optical spectroscopy study of $CeOs_4Sb_{12}$, which indicated a full gap of about 60–70 meV with a shoulder feature at about $\sim$30 meV [19]. The inelastic neutron scattering study identified magnetic excitations at energies of 27 and 48 meV in $CeOs_4Sb_{12}$ [8b]. A recent asymmetric periodic ALM-based study has nicely reproduced the pseudogap with a shoulder feature for $CeOs_4Sb_{12}$ [43].

Figures 4(a) and (b) present similar temperature-dependent UPS data and the extracted relative DOS for $CeFe_4P_{12}$ in the temperature range 14–296 K. As may be expected, the intensity at and around E_F is clearly decreasing with temperature in figure 4(b). The extracted DOS(E_F) of $CeFe_4P_{12}$ thus reveals a V-type depletion of spectral weight within $\sim$110 meV of E_F, and E_F would be centred at the middle of the gap. While an early optical spectroscopy study of the material reported a gap size of about 150 meV [45], a recent study has shown a gap of 0.22–0.24 eV [23]. Thus, UPS is measuring roughly half the gap seen in optical spectroscopy. In contrast to $CeOs_4Sb_{12}$ for which the pseudogap opening starts at 150 K, $CeFe_4P_{12}$ shows spectral weight suppression between 217 and 300 K. As discussed earlier, $CeFe_4P_{12}$ is a room-temperature semiconductor with an activation gap of $\sim$108 meV (1250 K) in electrical resistivity and hence the complete closing of the pseudogap may be expected to occur at temperatures above 300 K.

We note that a systematic depletion of the DOS over a PG scale has been reported in UPS studies of other Ce-based Kondo systems. The report on CeRhAs and CeRhSb had suggested that the pseudogap size scales with T_K [31].

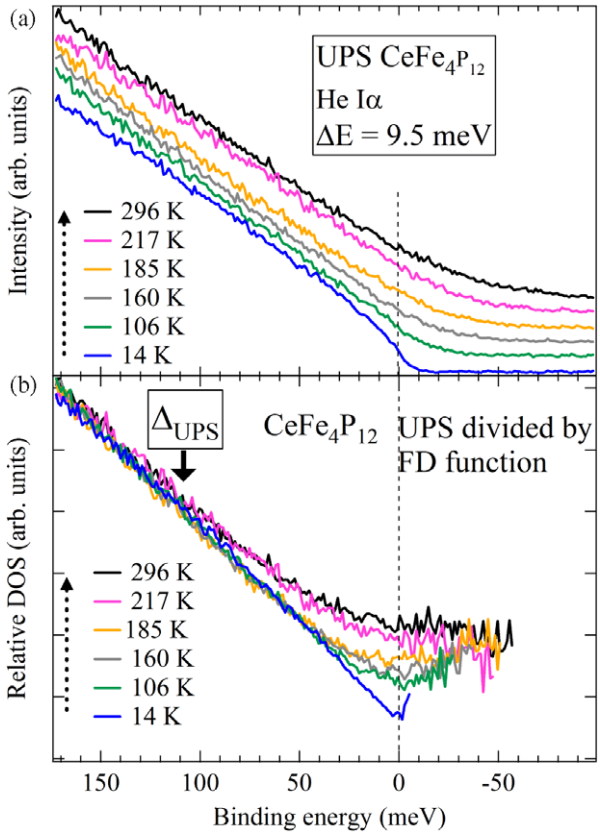

Figure 4. (a) The temperature-dependent high-resolution He Iα UPS on $CeFe_4P_{12}$. The legends show temperature values in ascending order for lowest to the upper most curves respectively.
(b) Temperature-dependent DOS obtained by dividing UPS spectra by the Fermi–Dirac function convoluted with a resolution function.

As was first shown by Bucher *et al* for $Ce_3Bi_4Pt_3$ using optical spectroscopy [46], charge gap formation in a Kondo semiconductor leads to a direct correlation between the temperature dependence of μ_{eff} and carrier concentration. This is because the gap originates in c–f Kondo hybridization, with the local spin interacting with the itinerant conduction electrons and forming a singlet state. Since DOS(E_F) reflects the carrier concentration, we felt it would be important to compare the temperature dependence of the DOS(E_F) with the temperature-dependent effective magnetic moment $\mu_{eff}(T)$ estimated from the magnetic susceptibility.

In figures 5(a) and (b), we plot the DOS(E_F) deduced from our experiments (figure 3(b) and 4(b)) and compare it with the effective magnetic moment, μ_{eff} obtained from the experimental magnetic susceptibility [15, 22], as a function of temperature. μ_{eff} as a function of temperature was extracted from the experimental magnetic susceptibility [15, 22] assuming that the deviation from Curie's law arises from the change in the effective magnetic moment of Ce ions, as is usually done for Kondo semiconductors [12, 15]. The behaviour of the two quantities matches fairly well for both materials. One can see that the DOS(E_F) is suppressed by $\sim$65% on reducing the temperature from 300 to 6 K for $CeOs_4Sb_{12}$ (figure 5(a)). In particular, it shows a clear decrease below T_0 (150 K). The effective moment curve re-plotted from

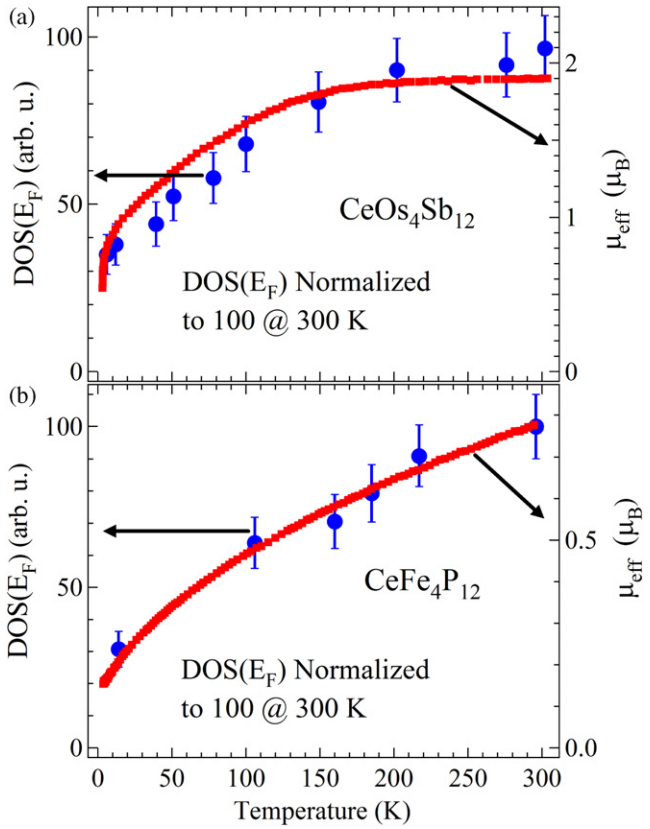

Figure 5. (a) The relative DOS(E_F) obtained from figure 3 and the μ_{eff} curve as reported in [15] for $CeOs_4Sb_{12}$. (b) The relative DOS(E_F) obtained from figure 4 and the μ_{eff} curve deduced from the χ curve reported in [22] for $CeFe_4P_{12}$.

figure 3 of [15] also shows a nearly linear decrease below T_0 (150 K). Moreover, the μ_{eff} is also suppressed by ∼60% compared to its value at 300 K if we ignore the sharp downturn at very low temperature (<6 K). In figure 5(b), the $\mu_{eff}(T)$ data of $CeFe_4P_{12}$ is obtained from the experimental data of [22]. Reference [22] shows susceptibility data for two different samples of $CeFe_4P_{12}$ in its figure 2. Though the temperature dependence of our DOS(E_F) data shows a good match to the $\mu_{eff}(T)$ obtained from both samples, we show the one with a better match in figure 5(b). The DOS(E_F) and $\mu_{eff}(T)$ of $CeFe_4P_{12}$ show a suppression of about ∼70% with reduction from $T = 294$ to $T = 14$ K.

Moreover, unlike $CeOs_4Sb_{12}$, there is no kink in the data to suggest the onset of reduction in the two quantities. This is consistent with the discussion above that $CeFe_4P_{12}$ is a large gap Kondo semiconductor with the gap closing above the temperature range of the present data. The same reasoning may apply to explain the large difference in the room temperature effective moment values of the two materials. Thus the similarity between the temperature dependence of the μ_{eff} and DOS(E_F) further substantiates the Kondo character of the charge gaps in $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$.

In table 1, we compile a list of the charge gaps Δ_C of Ce-based Kondo semiconductors obtained from a comparison of photoemission and optical spectroscopy, along with the single ion Kondo temperature T_K and spin gaps (Δ_S) as

Table 1. Charge gap and its scaling with T_K in various Ce-based Kondo semiconductors.

Kondo semiconductors	T_K meV (K)	Δ_S meV (K)	Δ_C meV (K)	Δ_C/k_BT_K
$Ce_3Bi_4Pt_3$	21[a] (240)	20[b] (230)	∼40–45[a] (460–520)	∼1.9–2.1
CeRhSb	31[c] (360)	35[d] (406)	∼60–70[e] (700–810)	∼1.9–2.2
CeRhAs	132[f] (1530)	150[g] (1740)	∼180–200[e] (2090–2320)	∼1.4–1.5
$CeRu_4Sb_{12}$	26[h] (300)	30[g] (348)	∼45–50[i] (520–580)	∼1.7–1.9
$CeOs_4Sb_{12}$	26[g] (300)	27[g] (313)	∼50–60[j] (580–700)	∼1.9–2.3
$CeFe_4P_{12}$	∼120[k] (1400)	—	∼220–240[k] (2550–2785)	∼1.8–2.0

[a] Reference [46]. [b] Reference [50].
[c] Reference [47]. [d] Reference [51]. [e] Reference [31].
[f] Reference [52]. [g] Reference [8b]. [h] Reference [53].
[i] References [7, 45]. [j] Present study and [19].
[k] Present study and [23].

reported in the literature. T_K is determined from the magnetic susceptibility for all the materials, except for $CeFe_4P_{12}$ for which the magnetic susceptibility above room temperature has not been reported. For $CeOs_4Sb_{12}$, it is noted that $T_K \sim 100$ K as estimated from spectroscopy parameters is lower than that from magnetic susceptibility ($T_K \sim 300$ K). Accordingly, for $CeFe_4P_{12}$, we have used T_K as determined from the spectroscopy parameters as a lower estimate and further studies of the high-temperature susceptibility are required to confirm the same. The spin gap (Δ_S) values, as determined from reported inelastic neutron scattering results [8b], showed a direct correlation of Δ_S and T_K given by $\Delta_S \sim k_BT_K$. For this universal behaviour to be valid, the T_K was estimated as $3T_{max}$, where T_{max} is the temperature corresponding to a broad maximum seen in the magnetic susceptibility, as discussed in the introduction. It is noted that alternative estimates of T_K for CeRhSb [47] and $CeOs_4Sb_{12}$ [15] lead to smaller values of $T_K \sim 100$ K, and lead to deviations from the universal behaviour. A similar situation also holds for $CeRu_4Sb_{12}$, which is classified as a non-Fermi liquid and not a semiconductor [48], but we include it here as it shows a temperature-dependent pseudogap opening in photoemission and optical spectroscopy measurements with coupled changes in transport properties. Given the photoemission and optical spectroscopy results, we have made a careful check to correctly determine the Δ_C for each of the materials. In particular, for $CeOs_4Sb_{12}$, Δ_C from photoemission (∼50 meV) and optical spectroscopy (∼60–70 meV) is found to be comparable, while for all other materials the photoemission value is found to be half the optical value. Importantly, a comparison of Δ_C and T_K leads to a simple scaling given by $\Delta_C \sim 2k_BT_K$ for all materials, except CeRhAs. This discrepancy is attributed to the fact that recent studies on single crystal CeRhAs have revealed three successive transitions (at $T_1 = 370$ K, $T_2 = 235$ K and $T_3 = 165$ K) in electrical resistivity, magnetic susceptibility and structure [52], while the photoemission studies carried out on polycrystals did not show these transitions.

Since Kondo semiconductors are defined in terms of the binding energy of a local singlet formed by hybridization between conduction electrons and a localized f electron with a magnetic moment, it has been expected that the spin and charge gaps should scale with T_K. Thus, a scaling of the form $\Delta_S \sim k_B T_K$ as shown from inelastic neutron studies and $\Delta_C \sim 2k_B T_K$ as obtained in the present work confirm that the spin and charge gaps have a universal behaviour. While the T_K determines the charge gap size based on the SIAM [24, 44], the temperature at which the pseudogap opening begins to occur has been attributed to a signature of coherence associated with a lattice of Kondo singlets or, in other words, indicates the importance of the symmetric ALM [25–28, 49]. While gap opening starts around $T_O \sim 150$ K for $CeOs_4Sb_{12}$ and seems to match the symmetric ALM calculations that predicted $T_O \sim (0.6–0.4)T_K$ [25, 26], we have tried to check for systematics in the known data for other Kondo semiconductors. Unfortunately, the data do not indicate a systematic trend, with the experimental values showing a spread of $T_O \sim (0.1–0.6)T_K$. Thus, the question of a universal coherence energy scale associated with a periodic array of the localized f electron sites, each with a single ion Kondo temperature T_K, is considered to be a more formidable issue that will require further work.

4. Conclusions

In conclusion, our photoemission study shows that $CeOs_4Sb_{12}$ and $CeFe_4P_{12}$ exhibit a temperature-dependent pseudogap in the occupied DOS of ∼50 meV and ∼110 meV, respectively. The XPS Ce 3d core level data and SIAM calculations also suggest a Kondo picture, yielding corresponding f electron counts of 0.97 and 0.86, showing that $CeFe_4P_{12}$ is strongly hybridized compared to $CeOs_4Sb_{12}$. The temperature dependence of the DOS(E_F) for both materials follows a systematic reduction which matches the quenching of the effective magnetic moment on reducing the temperature, thus confirming the Kondo-physics origin of the pseudogap opening. A compilation of measured pseudogaps using photoemission and optical spectroscopy identifies the charge gaps Δ_C for Ce-based Kondo semiconductors and provides a direct relation with T_K given by $\Delta_C \sim 2k_B T_K$. In conjunction with the known behaviour of the spin gaps $\Delta_S \sim k_B T_K$, the results establish the coupled energy scaling of the spin and charge gaps in Kondo semiconductors.

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