Valence Band Photoemission Study of
the Kondo Insulator CeNiSn

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The electronic structure of the Kondo insulator CeNiSn has been investigated by using photoemission spectroscopy. A satellite feature is observed in the valence band spectrum about 6 eV below the Ni $3d$ main peak, indicating a strong Ni $3d$ Coulomb correlation in CeNiSn. The Ce $4f$ partial spectral weight exhibits three peak structures, including one due to the $4f^1 \rightarrow 4f^0$ transition, another near E_F, and the other which overlaps the Ni $3d$ main peak. We interpret the peak near E_F as reflecting mainly the Ce $4f$/Sn $5p$ hybridization, whereas that around the Ni $3d$ main peak as reflecting both the Ce $4f$/Ni $3d$ and Ce $5d$/Ni $3d$ hybridization. Yield measurements across the $4d \rightarrow 4f$ threshold indicate the Ce valence to be close to $3+$. The prominent Fermi edge suggests a metallic ground state in CeNiSn.

1. Introduction

CeNiSn is considered to be a valence-fluctuating compound with an anomalous ground state [1-5]. CeNiSn is classified as a Kondo insulator since transport and magnetic measurements on CeNiSn indicate the energy gap formation in the non-magnetic ground state below $T_g \approx 6$ K (T_g: the gap formation temperature). The characteristic Kondo temperature T_K is estimated to be 40-80 K [6]. In addition, temperature(T)-dependent gap developments and an anisotropic energy gap were observed in the tunneling spectroscopy measurements [7]. The estimated energy gap (10 K) [2, 7] is an order of magnitude smaller than those of valence-fluctuating Sm and Yb compounds [8]. Therefore, much interest has been focused on how such a small energy gap is caused by strong correlations in the Kondo lattice.

Despite extensive studies on CeNiSn, there are several unresolved issues. First, the origin of the energy gap formation is not understood yet. This gap is considered to be formed within the narrow Ce $4f$ states, but there has been no commonly accepted explanation [9, 10]. CeNiSn does not order

magnetically [11], but there is an evidence of the existence of a quasi-one dimensional anti-ferromagnetic correlation [12]. The role of anti-ferromagnetic spin fluctuations on the energy gap formation has not been fully understood. Secondly, a question on the intrinsic ground state of CeNiSn has been recently raised, because of the finding of the metallic-like T-dependent electrical resistivity in a purified single crystal of CeNiSn [5, 13]. This work has brought on a controversy between the metallic and insulating intrinsic ground state of CeNiSn, and also suggested the importance of experiments on high quality single crystals.

To resolve the above issues on CeNiSn, it is important to investigate its electronic structure. Band structure calculations predict CeNiSn to be a semi-metal or a small-gap insulator with an anisotropic hybridization gap state [14, 15]. Only a few experimental studies have been reported on its electronic structure. Based on valence band and core level photoemission spectroscopy (PES) measurements on polycrystalline CeTSn (T = Ni, Pd, Pt) [16], it has been argued that the valence of Ce is close to trivalent and that the Ce 4f states are strongly hybridized with the Sn 5p states in CeNiSn.

In this paper we report valence band PES measurements on a high quality single crystalline CeNiSn. We have also performed yield measurements near the Ce 4d absorption edge to determine the bulk Ce valence more accurately.

2. Experimental Details

Single crystals of CeNiSn were grown by the Czochralski pulling method by using a tungsten crucible in an rf furnace. The ingot sample was purified by the technique of solid-state electro-transport [5]. Photoemission experiments were carried out at the Ames/Montana ERG/Seya beamline at the Synchrotron Radiation Center. The samples were cleaved in vacuum with a base pressure better than 4×10^{-11} Torr. Temperature was controlled by placing the samples in direct contact with a cryostat cooled down to 20 K using a closed cycle He refrigerator. The Fermi level E_F and the overall instrumental resolution of the system were determined from the valence band spectrum of a sputtered Pt foil near E_F. The total instrumental resolution [FWHM : full width at half maximum] was about 150 meV at hv = 20-70 eV and 250 meV at hv $\approx$ 120 eV. The photon flux was monitored by the yield from a gold mesh and all the spectra reported are normalized to the mesh current.

3. Results and Discussion

Figure 1 shows the valence band energy distribution curves (EDCs) of CeNiSn in the photon energy hv range of 14-121 eV, including both the Ni 3p and Ce 4d absorption thresholds ($\sim$68 eV and $\sim$120 eV, respectively). As hv varies, the line shape of the valence band spectrum changes, which is mainly due to the change in the relative photoionization cross sections of different electronic states [17]. hv = 121 eV and hv = 115 eV correspond to the on-and off-resonance energies, respectively, corresponding to the Ce $4d \rightarrow 4f$ absorption [18]. Therefore the emission between E_F and about 3 eV in binding energy (BE) which is enhanced at hv = 121 eV is identified with the Ce $4f$ emission, whereas the off-resonance spectrum at hv = 115 eV is dominated by the Ni 3d emission. The line shape does not change from hv $\approx$ 115 eV down to hv = 63 eV, indicating that Ni 3d emissions dominate in this photon energy range. hv = 68 eV and hv = 63 eV correspond to the Ni $3p \rightarrow 3d$ on- and off-resonance energies, respectively. At hv = 68 eV, the main peak around 1.4 eV in BE and the satellite peak around 6 eV below the main peak can be roughly assigned to the $3d^9 c^{m-1}$ and $3d^8 c^m$ final state configurations, respectively, as in pure Ni metal (c : conduction or ligand electrons) [19]. The satellite structure associated with the Ni 3d bands is not explained by one electron band theory, and it is taken to arise from the Ni 3d Coulomb correlation. At low hv's (14-30 eV), besides the Ni 3d main peak at 1.4 eV in BE, three other weak structures are observed at E_F, $\sim$ 0.8 eV, and $\sim$2.2 eV in BE, which diminish with increasing hv. Since the Sn 5p and Ce 5d cross sections become larger with re-

spect to that of the Ni 3d electrons at these lower hv's than at higher hv's, these three weak structures seem to have the Sn 5p and Ce 5d characters. This conclusion implies that the Sn 5p and Ce 5d states in CeNiSn are spread over the whole valence band, i.e., from E_F to $\sim$4 eV below.
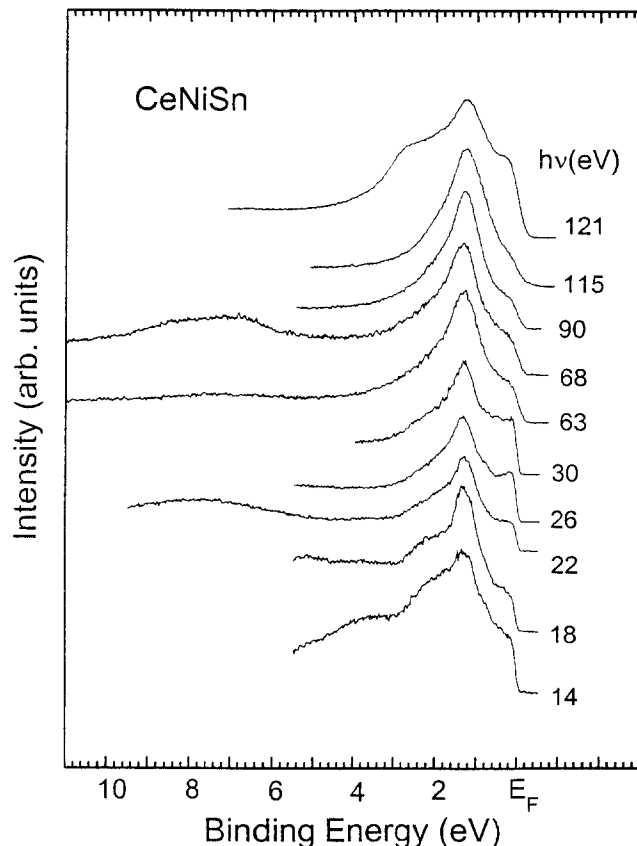

Fig. 1. Valence band photoemission spectra of CeNiSn over a wide photon energy hv range.

A shoulder-like structure is observed near E_F in all the spectra for hv's in 14-121 eV. Such a structure has not been observed in Ref. [16], which reflects a better energy resolution and a better quality of the sample employed in this study. The intensity at E_F relative to that of the Ni 3d main peak (1.4 eV in BE) remains essentially the same from hv $\sim$ 60 eV to hv = 115 eV, indicating the presence of Ni 3d states near E_F. In contrast, the intensity close to E_F becomes enhanced at hv $\approx$ 26 eV, suggesting the presence of the Sn 5p and Ce 5d states [17]. Besides these electronic states, there are also the Ce 4f states near E_F, which will be shown in Fig. 2. Thus the Fermi edge in CeNiSn seems to have a mixed character, i.e., a mixture of the Sn 5p/Ce 5d, Ce 4f, and Ni 3d characters. This interpretation is consistent with the theoretical prediction [15, 20].

Figure 2 presents the extracted Ce 4f partial spectral weight (PSW) distribution (dots), and the subtraction procedure of the Ce $4d \rightarrow 4f$ off-resonance spectrum (dashed line) from the on-resonance spectrum (solid line). The hv = 115 eV spectrum has

been scaled by a factor $\alpha = 0.93$ to account for the hv dependence of the Ni $3d$ cross section [17]. The difference curve exhibits three prominent features at about 0.3 eV ("A"), 1.4 eV ("B") in BE, and 2.7 eV ("C") in BE. It is still necessary to separate out the Ce $4f$ bulk emission from the Ce $5d$ emission. The Ce $5d$ emission is known to resonate at the $4d$ absorption edge as well [21], and so at least some portion of the difference curve (dots) should be identified with the Ce $5d$ emission. As will be discussed later, a substantial contribution from the Ce $5d$ PSW lies under the structure "B".
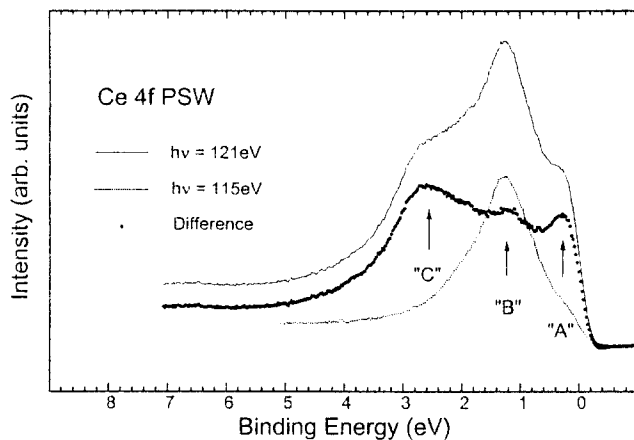

Fig. 2. The extracted Ce $4f$ spectrum (dots) of CeNiSn. The subtraction of the Ce $4d \rightarrow 4f$ off-resonance spectrum (dashed line) from the on-resonance spectrum (solid line) is also shown.

The peaks "A" and "C" are reminiscent of the well-known double-peak structures observed in Ce metal and Ce compounds. The peak "C" corresponds to the $4f^1 \rightarrow 4f^0$ transition [22]. The $4f$ spectral intensity close to E_F ("A") is known to reflect the strength of the hybridization between Ce $4f$ and conduction band electrons, corresponding to the $4f^1 c^{m-1}$ final state [18, 23-25]. In terms of the Gunnarsson/Schönhammer (G/S) theory [23], based on the degenerate impurity Anderson Hamiltonian (IAH) assuming Ce $4f$ electrons to be essentially localized, the spectral feature "A" close to E_F corresponds to the tail of the Kondo resonance and it originates from the hybridization interaction between Ce $4f$ and conduction band electrons and the on-site Coulomb interaction between Ce $4f$ electrons. In the band theoretical view, the peak near E_F is interpreted as the ground state Ce $4f$ band, corresponding to the fully relaxed $4f^1 c^{m-1}$ final states [24].

Even though the detailed origin of the near E_F peak is still controversial, the substantially large intensity of the peak "A" suggests large hybridization, as discussed below. The average separation between Ce sites in CeNiSn ($d = 3.82$ Å) is larger than the Hill limit (3.3-3.5 Å), corresponding to the local moment formation, and even larger than that in γ-Ce and α-Ce ($d(\gamma - Ce) = 3.65$ Å and $d(\alpha - Ce) = 3.39$ Å), suggesting the direct interaction between near neighbor Ce $4f$ electrons to be negligible in CeNiSn. Thus the interac-

tion between Ce $4f$ electrons should be mediated by the hybridization between Ce $4f$ electrons and conduction electrons, mainly with Sn $5p$ or Ni $3d$ electrons. Further the Ce $4f$/Sn $5p$ hybridization seems to be the major origin of the near-E_F peak "A" in the Ce $4f$ PSW because the intensity of the peak "A" is comparable to that of the peak "B", whereas in the Ni $3d$ PSW the main Ni $3d$ peak (at 1.4 eV in BE) is much stronger than the peak near E_F.

Note that the peak "B" exists in the $4f$ derived PSW of CeNiSn, in addition to the well-known two peak structures, which indicates a good quality of data in this study. The location of the peak "B" is very close to that of the Ni $3d$ main peak, suggesting that it originates from the hybridization of the Ni $3d$ electrons with the Ce $4f$ or $5d$ electrons. This interpretation is consistent with the fact that no feature like "B" has been observed in the Ce $4f$ PSW of CeSn$_3$ [26] which reveals only two peaks, corresponding to "A" and "C" above, respectively. Interestingly, the three peak structures in the difference spectrum of CeNiSn (Fig. 2) are very similar to those of CeBe$_{13}$ [21]. In the case of CeBe$_{13}$, the Be s/p PSW has two peaks near E_F and at about 1.5 eV in BE, with the latter located around the middle peak in the difference spectrum. This middle peak in CeBe$_{13}$ has been assigned mainly due to Ce $5d$ contribution. Further, the Ce $5d$ wave functions have a larger overlap with the Ni $3d$ wave functions than the Ce $4f$ wave functions both in space and energy, and so the Ce $5d$/Ni $3d$ hybridization would have a stronger contribution to the peak "B" than the Ce $4f$/Ni $3d$ hybridization. Therefore it is likely that the feature "B" in CeNiSn has a substantial contribution from the Ce $5d$ PSW (probably 30-50 %).

Figure 3 shows the yield spectra taken in the constant-final-state (CFS) and constant-initial-state (CIS) modes across the $4d \rightarrow 4f$ threshold. The spectra have been scaled to have the same magnitude at the peak. E_i values in the CIS spectra denote initial state energies. The well-known Fano-like resonance in the Ce $4f$ cross section is clearly observed in this figure. The line shapes of the Ce $4f$ CIS and CFS yield spectra in CeNiSn are very similar to those of Ce metal [27], for which the Ce valence is close to $3 +$. Moreover, the line shape of the Ce $4f$ CIS in CeNiSn is essentially the same for different values of E_i over the Ce $4f$ PSW, indicating that the $4f$ emission does not have separate contributions from different valence states. However, drawing a quantitative conclusion on the valence of Ce in CeNiSn requires a detailed theoretical analysis of the $4f$ CIS [28-30].

A finite metallic density of states has been observed at E_F above T_g in CeNiSn [31] (measured temperature $T_{msr} \approx 20$ K $> T_g \approx 6$ K), suggesting that CeNiSn is likely to be metallic in the ground state or that the gap is anisotropic. To be consistent with the recent report of the metallic ground state, this feature of a finite density of states at E_F should persist even below T_g. To investigate the anisotropic electronic
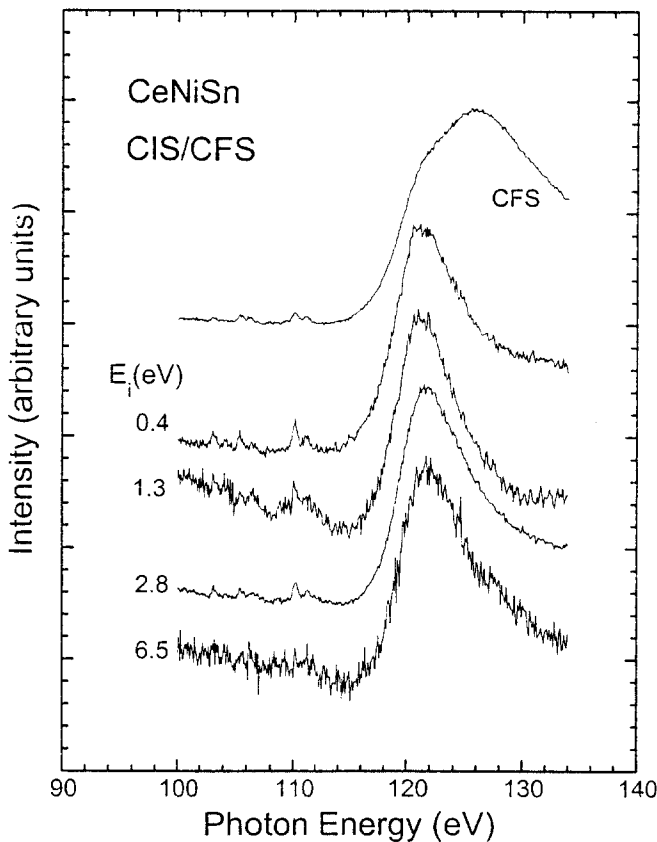
Fig. 3. Constant-initial-state (CIS) yield spectra of CeNiSn taken at initial state energies E_i of $E_i = 0.4$, 1.3, 2.8, and 6.5 eV in BE's, respectively. A constant-final-state (CFS) yield spectrum taken at the kinetic energy E_K of 2 eV is also shown.

structure of CeNiSn more rigorously, it is required to perform ARPES measurements along different symmetry directions and to determine experimental band structures from the data.

4. Conclusions

The electronic structure of the Kondo insulator CeNiSn has been investigated using photoemission spectroscopy (PES). The extracted Ce $4f$ PSW exhibits three peak structures, including the well-known double-peak structures and a new peak located at the position of the Ni $3d$ main peak. The peak near E_F in the two peak structures seems to reflect mainly the Ce $4f$/Sn $5p$ or Ce $4f$/Ce $5d$ hybridization, whereas an extra structure located around the Ni $3d$ main peak reflects the Ce $4f$/Ni $3d$ or Ce $5d$/Ni $3d$ hybridization. In the valence band spectrum taken at the Ni $3p \rightarrow 3d$ on-resonance energy, a satellite feature is observed about 6 eV below the Ni $3d$ main peak, indicating a strong Ni $3d$ Coulomb correlation. CIS and CFS yield spectra across the $4d \rightarrow 4f$ threshold with several initial states over the Ce $4f$ PSW are found to be very similar to those of Ce metal, indicating that the Ce valence is close to $3+$. The Fermi edge spectra also indicates a finite metallic density of

states at E_F above T_g.

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