

Temperature-dependence of Kondo resonance in CeSi₂ studied by bulk-sensitive resonant photoemission

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Abstract

We performed temperature-dependent bulk-sensitive resonant photoemission spectroscopy and Ce M_{4,5} X-ray absorption spectroscopy (XAS) of CeSi₂. The XAS data clearly show the increase of the f-level occupancy number n_f as the temperature is raised, which is consistent with the non-crossing approximation calculation in the Kondo scenario. In addition, the bulk-sensitive resonant photoemission of the 4f spectral weights shows that the height of the Kondo resonance at the Fermi level relative to that of the $f^1 \rightarrow f^0$ emission peak is reduced as the temperature is raised. The Gunnarsson-Schönhammer calculation fit gives generally good agreement with the valence band spectra, and the n_f values derived from the fit shows the same temperature dependence as predicted by the Kondo scenario.

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1. Introduction

In the photoemission community, CeSi₂ has been known as a simple standard Kondo system which is suitable to test the validity of the single impurity Anderson model (SIAM) [1,2] in the analysis of Ce compound valence band spectra. Its Kondo temperature T_K is estimated to be between 35 and 132 K [3–5], which is easily accessible by a standard photoemission apparatus. The magnetic susceptibility shows a breakdown of the Curie–Weiss law at low temperatures without any indication of ordering [6]. Heat-capacity measurements exclude magnetic ordering or crystal-field transitions below 70 K down to 0.1 K and yield a linear coefficient of the specific heat $\gamma(T \rightarrow 0) \approx 100$ mJ/K² mole [6]. These facts indicate that the Kondo effect dominates the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction, thereby favoring a non-magnetic ground state. $\gamma(T \rightarrow 0)$ is strongly enhanced when compared with normal metals, but is still one order of magnitude smaller than those of extreme

heavy-electron compounds [7]. In Ce-based heavy Fermion systems, the Kondo energy scale, δ , typically ranges between 0.1 and 50 meV and for CeSi₂, δ ranges between 3 and 10 meV.

This parameter for CeSi₂ still sets extremely severe resolution conditions in photoemission studies. Only ultraviolet photoemission (UPS) can reach this resolution limits currently. The most commonly used method to extract the 4f spectral weights in UPS is the use of the conventional increase of the 4f cross-section between the photon energies 21.2 eV (He_I) and 40.8 eV (He_{II}) and this method has also been used to investigate the temperature evolution of 4f spectral weights in CeSi₂. The results of these investigations were interpreted as demonstrating the essential characteristics of the spectral functions based on the SIAM [3,8,10]: the scaling of the Kondo peak intensity with T_K , and its nonconventional temperature dependence. However, some groups questioned this interpretation of the photoemission spectra and proposed that a conventional density-of-states (DOS) model provides a sufficient explanation [4,9]. The main point of the latter groups was that the temperature or the material dependence of the 4f spectral weights near the Fermi level, which had been interpreted as the tail of the

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Kondo resonance, did not exactly follow the Kondo scenario and the non-crossing approximation (NCA) calculation [11], but their temperature dependence could be explained sufficiently by such mundane, conventional effects as phonon broadening.

The most powerful technique for the extraction of the 4f states from the band states consists of the exploitation of synchrotron radiation to take advantage of the huge 4f cross-section resonance at Ce 3d(4d) \rightarrow 4f absorption edge [12]. Since the surface effect is significant in UPS technique and the resonance photoemission (RPES) technique at the Ce 4d edge, Ce 3d edge RPES has a great advantage in that it can probe more bulk-like spectra. In fact recent technical improvements in synchrotron radiation beamline instrumentation enable us to extract reliable bulk Ce 4f spectral weights with improved resolution [13]. In this study, we report the temperature-dependent bulk-sensitive Ce 3d \rightarrow 4f resonant photoemission study of CeSi₂ to test the applicability of SIAM and especially the temperature dependence of the Kondo resonance.

2. Experimental

The sample of CeSi₂ was polycrystalline made by argon arc-melting method followed by annealing. The crystal structure of the sample was checked by X-ray diffraction and it shows the expected tetragonal α -ThSi₂ structure. CeSi₂ is known as the silicide with the highest melting temperature within the binary Ce–Si system. Temperature-dependent RPES at Ce M₅ absorption edge and Ce M_{4,5} XAS were performed at the beamline BL25SU of SPring-8 in Japan [13]. The energy resolution of the photon source for Ce

3d RPES was about 80 meV (full width at half maximum: FWHM) and the overall experimental resolution for RPES was about 120 meV FWHM using Scienta SES200 electron spectrometer [14]. The XAS measurements were also done by the total yield mode normalized by the mesh current. The pressure in the vacuum chamber was below 3×10^{-10} mbar during the measurements. Temperature was controlled by a closed-cycle He cryostat and a heater. The measuring temperature ranged between 20 and 270 K. Sample surface was cleaned by scraping with a diamond file in situ and every time the cleanness of sample surface was checked with the O 1s core-level spectrum. The Fermi level E_F of the sample was referred to a scraped Pd metal attached to the sample holder.

3. Results and discussions

The Ce M_{4,5} XAS data of CeSi₂ at low temperature ($T = 20$ K) are shown in Fig. 1. In this figure, the photon energies for several multiplet peaks are given and the inelastic background is represented by the dashed line. Since there are no confirmed theories which describe the background generation in the XAS measurement, we use the tangent hyperbolic functions for the background. In the inset, we show the comparison of the photoemission spectra of CeSi₂ taken at the on-resonant ($h\nu = 882.15$ eV) and off-resonant ($h\nu = 870$ eV) photon energies. We can see the drastic change of the intensity and shape of the valence band spectra due to the following resonance effect at the Ce M₅ absorption edge.

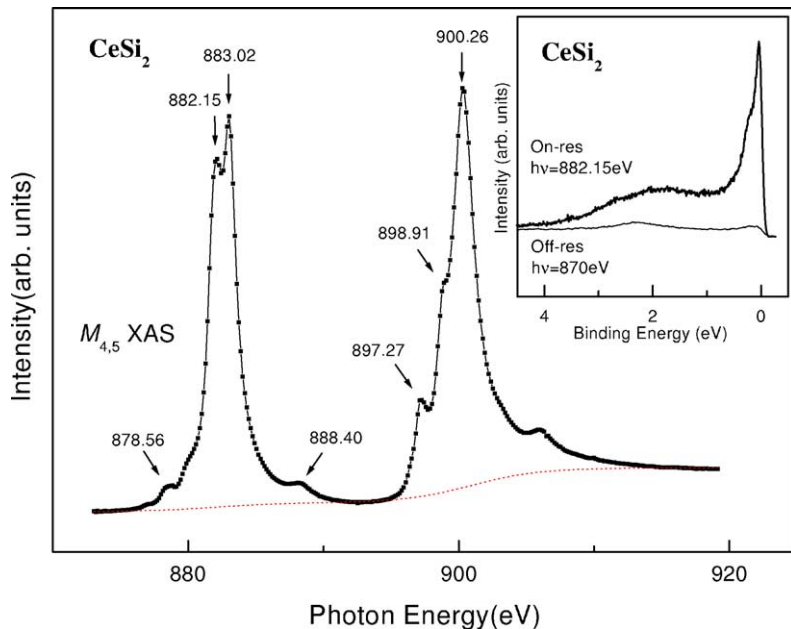
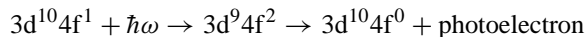


Fig. 1. Ce M_{4,5} XAS data of CeSi₂ taken at $T = 20$ K. The photon energies for several peaks are also given. The dashed line indicates the inelastic background. The inset shows off- and on-resonance photoemission data of CeSi₂ valence band. We used the photon energy $h\nu = 882.15$ eV for RPES.

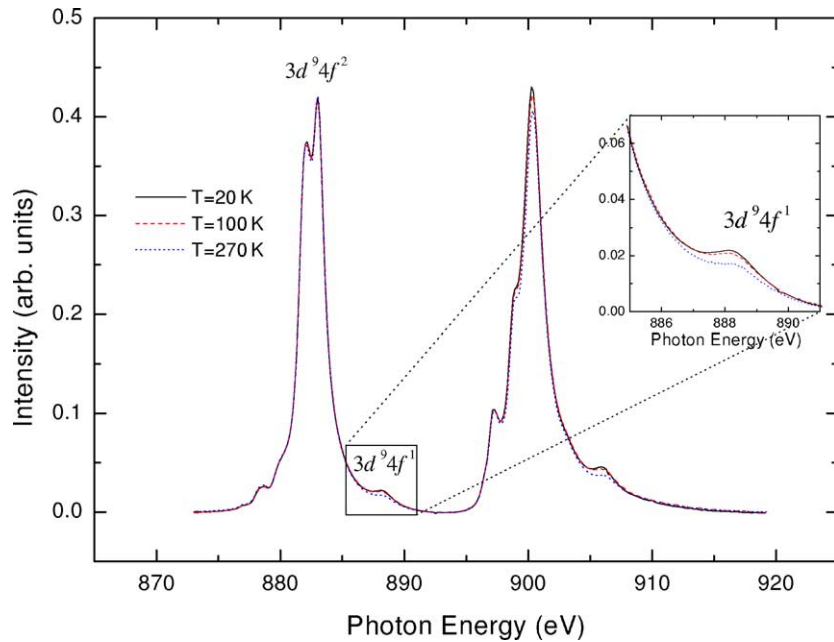


Fig. 2. Ce $M_{4,5}$ XAS data taken at $T = 20, 100, 270$ K. The background was subtracted for a clear comparison. The inset shows the parts corresponding to the $3d_{5/2}^9 4f^1$ final state configuration in more detail.

The Ce $M_{4,5}$ XAS data of CeSi₂ show apparent temperature dependence as displayed in Fig. 2, especially at the states corresponding to the $3d_{5/2}^9 4f^1$ final state configuration (see inset). The intensity reduction of peaks of $3d_{5/2}^9 4f^1$ configuration implies that the 4f-level occupancy number n_f increases as temperature increases and this is just as predicted by the Kondo scenario and NCA calculation [11,15].

To see the temperature dependence of the Kondo resonance explicitly, we took the RPES spectra as a function of

temperature. For these RPES measurements, we used the incident photon energy $h\nu = 882.15$ eV, which corresponds to the lowest multiplet structure of the Ce $3d_{5/2}^9 4f^2$ configuration in the absorption spectra, since the spectra taken at the maximum peak position are often found to be contaminated by incoherent Auger emissions [16]. The Ce 3d-4f RPES data of CeSi₂ thus obtained at $T = 20, 50, 200, 250$ K are shown in Fig. 3. In previously reported UPS data [17,18] and Ce 4d-4f RPES data [4,12], the surface contributions were

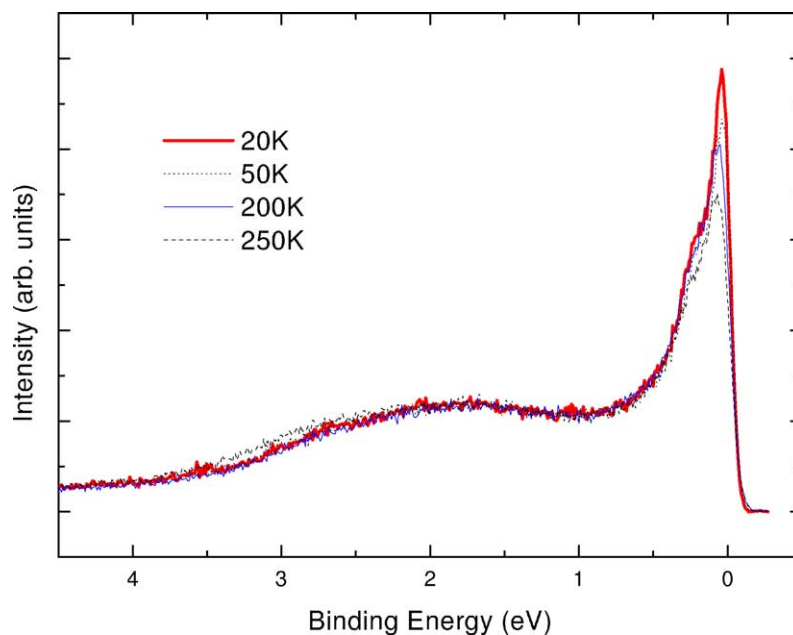


Fig. 3. Ce 3d-4f RPES data of CeSi₂ taken at $T = 20, 50, 200, 250$ K. The temperature-dependence of the Kondo resonance near E_F is apparent.

significant due to the short escape depth of photoelectrons with these kinetic energies, and the bulk Ce 4f spectral features could not be clearly identified. In the present Ce 3d-4f RPES data, on the other hand, it is estimated that the surface contribution is less than 20% to the total spectral weights, and the very different shape of the present 3d-4f RPES data from the previously published 4d-4f RPES data reflects this effect.

We can see in Fig. 3 that the height of the large peak near the Fermi level E_F (the Kondo resonance) is reduced relative to that of the $f^1 \rightarrow f^0$ emission peak as the temperature is raised. This is consistent with the NCA calculation [11], which predicts similar change of the relative peak height between the f emission near E_F and the $f^1 \rightarrow f^0$ emission with the temperature. However, to our knowledge, this effect has not been directly verified with experimental data up to now due to the high surface contribution in the UPS and Ce 4d-4f RPES studies. In the case of the previous Ce 3d-4f RPES studies [19], poor photon energy resolution hinders direct verification, since the photon energy dependence of RPES spectra is significant due to the overlapping incoherent Auger emissions [16]. With the improved energy resolution of the present study at the Ce 3d-edge, we can now obtain reliable Ce 3d-4f RPES data and compare them with the NCA predictions directly and confirm this theoretical prediction. This relative change between f spectral weight of the Kondo resonance and the $f^1 \rightarrow f^0$ emission in RPES is reminiscent of the similar change of f spectral weights between the Kondo resonance and the $f^1 \rightarrow f^2$ transition in the inverse photoemission (IPES) of CeSi₂ [20]. However, since in the NCA calculation, the f-f Coulomb interaction U_{ff} is set to be infinite, the NCA results cannot be directly compared with IPES spectra. In the RPES spectra, the $f^2 \rightarrow f^1$ emission contribution is small, though not negligible, and the direct comparison is possible in principle. However, it is still difficult to make quantitative comparison between our RPES data and NCA calculation, because the $f^1 \rightarrow f^0$ emission peak is too wide and there is some uncertainty as to the amount of inelastic background emissions.

We also performed the Gunnarsson–Schönhammer (GS) fit of the whole valence band of the CeSi₂ bulk-sensitive RPES data. For the GS calculation, the lowest order f^0 , f^1 , f^2 , and the second-order f^0 states were employed as basis states, and the spin–orbit splitting and crystal electric field splitting of the 4f level were included. It was shown that the crystal field splitting should not be neglected in the NCA calculation in order to estimate a realistic T_K [21] and we confirmed that the crystal field splitting should be included also in the GS calculation. It is well known that in the case of Ce-transition metal compounds, it is quite essential to employ realistic hybridization strength $|V(\epsilon)|^2$ in GS calculation in order to fully interpret experimental spectra and fit the thermodynamic quantities, since transition metal d-bands are fairly localized and interact strongly with Ce 4f states. $|V(\epsilon)|^2$ can be written as the conduction density

of state $\rho(\epsilon)$ and the average hopping matrix element squared $|v(\epsilon)|^2$.

$$|V(\epsilon)|^2 = \rho(\epsilon)|v(\epsilon)|^2$$

In the simplest approximation, the $|v(\epsilon)|^2$ is assumed to be constant and then $\rho(\epsilon)$ is obtained from non-4f spectral weight, that is, off-resonant spectra in RPES studies. This approach is successful in many previous photoemission studies [22–24].

However, in sp valence band compounds such as CeSi₂, the wavefunctions of sp valence bands are spread out and interact weakly with Ce 4f states and therefore it may be better to employ semi-elliptical $|V(\epsilon)|^2$ as in the case of free electron approximation than the $|V(\epsilon)|^2$ from off-resonant spectra (for the discussion on the hybridization strength and the off-resonance spectra, see [25]). We tried to make a fit by employing both types of $|V(\epsilon)|^2$.

$$|V(\epsilon)|^2 = \begin{cases} |V_1(\epsilon)|^2 & \text{semi-elliptical} \\ = A\sqrt{B^2 - (\epsilon - \epsilon_0)^2} & \\ |V_2(\epsilon)|^2 & \text{off-resonant spectra} \end{cases}$$

and found that the semi-elliptical $|V(\epsilon)|^2$ ($|V_1(\epsilon)|^2$) gives better agreement with experimental data in our CeSi₂ case. We represent the resulting GS calculation results in Fig. 4 along with the GS fit with $|V_2(\epsilon)|^2$ from off-resonant spectra in the inset. We choose $B = 5$ eV since the bottom of the valence band can be considered to be located there from off-resonant spectra and choose $\epsilon_0 = E_F$. We summarize our fitting parameter values for the GS calculation with the semi-elliptical $|V(\epsilon)|^2$ in Table 1, along with the resulting n_f values.

The values of T_K and n_f deduced from the lowest temperature ($T = 20$ K) valence band fitting are somewhat different from those deduced in the previous UPS and Ce 4d-4f RPES studies. The estimated $T_K = 169$ K is higher and $n_f = 0.949$ is smaller than those of the previous UPS and Ce 4d-4f RPES studies ($T_K \approx 40$ K, $n_f \approx 0.97$) [3,8,26]. However, another bulk-sensitive and direct estimation of n_f

Table 1

The GS fitting parameters of CeSi₂ valence band obtained from Ce 3d-edge RPES and the resulting 4f-level occupancy number n_f

Temperature (K)	Δ (eV)	n_f
20	0.075	0.949
50	0.070	0.979
200	0.067	0.997
250	0.065	1.008

The semi-elliptical $|V(\epsilon)|^2$ is used. For all temperatures, the 4f level binding energy ϵ_f is set to -1.55 eV, the spin–orbit splitting of the 4f level is set to 0.28 eV and the crystal-field splittings of the 4f level are set to 0.025 and 0.048 eV [28], respectively. f-f coulomb interaction U_{ff} is set to 6.2 eV as determined from photoemission and inverse photoemission spectra [20]. The derived T_K value from the lowest temperature ($T = 20$ K) data is 169 K.

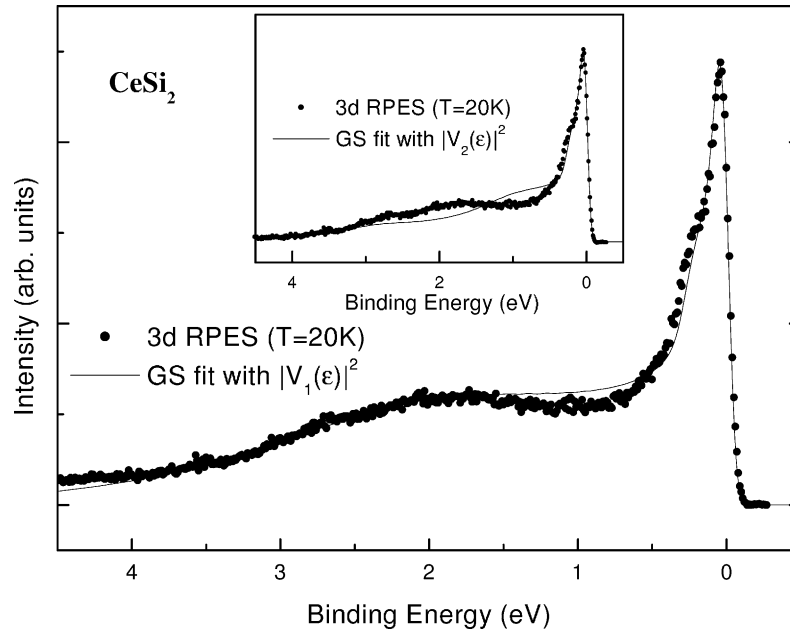


Fig. 4. The GS calculation fit for Ce 3d-4f RPES data of CeSi_2 taken at $T = 20\text{ K}$ with the semi-elliptical $|V(\epsilon)|^2$ ($|V_1(\epsilon)|^2$). The fitting parameter values are summarized in Table 1. The inset shows the GS calculation fit with $|V_2(\epsilon)|^2$ from the off-resonant spectra.

has been reported previously using the Ce L_3 XAS [27] and their n_f value ($n_f = 0.9$ below 40 K) is much smaller than those from the UPS and Ce 4d-4f RPES studies, and the n_f value derived from our study lies between the two. This can be considered partly to reflect the bulk-sensitivity of our data. The temperature dependence of the obtained n_f values from our study is again just as predicted by the Kondo scenario.

We can also estimate the zero-temperature magnetic susceptibility $\chi_m(0)$ from the parameter values for the lowest temperature data (20 K) and it came out to be 2.0×10^{-3} emu/mol. This value is close to the experimentally measured susceptibility $\chi_m^*(0)$ (4.2×10^{-3} emu/mol) [5], although the T_K and n_f values derived from our 3d-4f RPES differ from those of the previous UPS and Ce 4d-4f RPES studies. Therefore, we suppose that our fitting results are consistent with the transport measurement and our bulk sensitive RPES data can be well interpreted within the Anderson impurity model scheme. One possible reason for the difference of parameter values between our present study and the previous UPS and Ce 4d-4f RPES studies is the strong contribution of the surface components in previous photoemission studies.

4. Conclusions

We have studied the bulk-sensitive electronic structure of CeSi_2 by performing temperature-dependent resonant photoemission spectroscopy and Ce $M_{4,5}$ X-ray absorption spectroscopy. In the bulk-sensitive resonant photoemission, we can see that the Kondo resonance is reduced in height relative to the $f^1 \rightarrow f^0$ emission peak as the temperature

increases, and this is consistent with the prediction of the NCA calculation although the experimental limitation prevents the quantitative analysis. We fit the whole valence band spectra using the GS calculation and it gives general good agreements. Although the n_f values derived from the GS calculation show some discrepancy from those from Ce L_3 XAS and from the previous UPS and Ce 4d-4f RPES studies, the estimated zero-temperature magnetic susceptibility is close to the experimentally measured value. The n_f values derived from our spectra of the resonant photoemission and the X-ray absorption have the same temperature dependence as predicted by the Kondo scenario. We conclude that our data can be well interpreted within the Anderson impurity model scheme and the Kondo scenario.

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