Role of valence fluctuations in the superconductivity of Ce122 compounds

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Pressure dependence of the Ce valence in $CeCu_2Ge_2$ has been measured up to 24 GPa at 300 K and to 17 GPa at 18-20 K using x-ray absorption spectroscopy in the partial fluorescence yield. A smooth increase of the Ce valence with pressure is observed across the two superconducting (SC) regions without any noticeable irregularity. The chemical pressure dependence of the Ce valence was also measured in $Ce(Cu_{1-x}Ni_x)_2Si_2$ at 20 K. A very weak, monotonous increase of the valence with x was observed, without any significant change in the two SC regions. Within experimental uncertainties, our results show no evidence for the valence transition with an abrupt change in the valence state near the SC II region, challenging the valence-fluctuation mediated superconductivity model in these compounds at high pressure and low temperature.

Study of heavy-fermion superconductivity has been motivated by the discovery of superconductivity in $CeCu_2Si_2$ [1]. The BCS theory predicts the suppression of superconductivity by a small amount of magnetic impurities. Therefore, Ce-based heavy-fermion superconductors have been considered to be unconventional superconductors because their valences are close to the magnetic Ce^{3+} state. Superconductivity in these compounds is widely believed to be mediated by antiferromagnetic spin fluctuations. Furthermore, in the Ce-based heavy-fermion systems which exhibit superconductivity under pressure, the superconducting (SC) transition often occurs in the vicinity of the quantum critical point (QCP), leading to scenarios which attribute superconductivity to the occurrence of the spin fluctuations around the QCP. As illustrated in Fig. 1 (in SC I and SC II [2–4]), the SC phase diagrams of $CeCu_2Si_2$ and $CeCu_2Ge_2$, where T_C is the SC critical temperature, show two dome-shaped SC regions. Both SC dome structures of $CeCu_2Si_2$ and $CeCu_2Ge_2$ appear to be identical after pressure scaling. Similar anomalies in transport properties of these compounds have been reported [5, 6].

The phase diagram of $CeCu_2Ge_2$ phase diagram shows an overlap between SC I and antiferromagnetism (AFM), suggesting a possible antiferromagnetic spin fluctuation mediated pairing interaction. On the other hand, the separation between the onset of the second region SC II, which corresponds to the sharp increase in T_C around 12 GPa, and the disappearance of the AFM order around 8 GPa indicates to a different mechanism for the emergence of the SC II phase. Based on the expanded periodic Anderson model with the slave-boson mean-field theory, valence fluctuations (VF) were proposed as a possible pairing mechanism for the appearance of the SC II region [5, 7–9]. A theoretical orbital transition between two different levels has also been suggested as a mechanism for the occurrence of the superconductivity in the SC II region that is far away from the AFM QCP [10, 11].

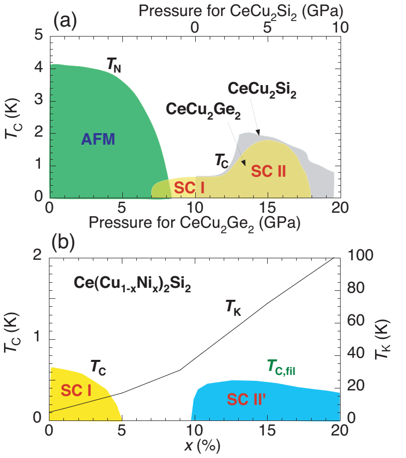

FIG. 1. (Color online). (a) Schematic view of pressure-temperature phase diagram of $CeCu_2Ge_2$ and $CeCu_2Si_2$. [3] Pressure for $CeCu_2Si_2$ is shifted by 10 GPa (upper horizontal axis) to be consitent with that of $CeCu_2Ge_2$. Superconducting region consists of SC I and SC II. Antiferromagnetic (AFM) order is only observed in $CeCu_2Ge_2$. (b) Pressure-temperature phase diagram of $Ce(Cu_{1-x}Ni_x)_2Si_2$ as a function of x [14]. Kondo temperature (T_K) is also shown for comparison.

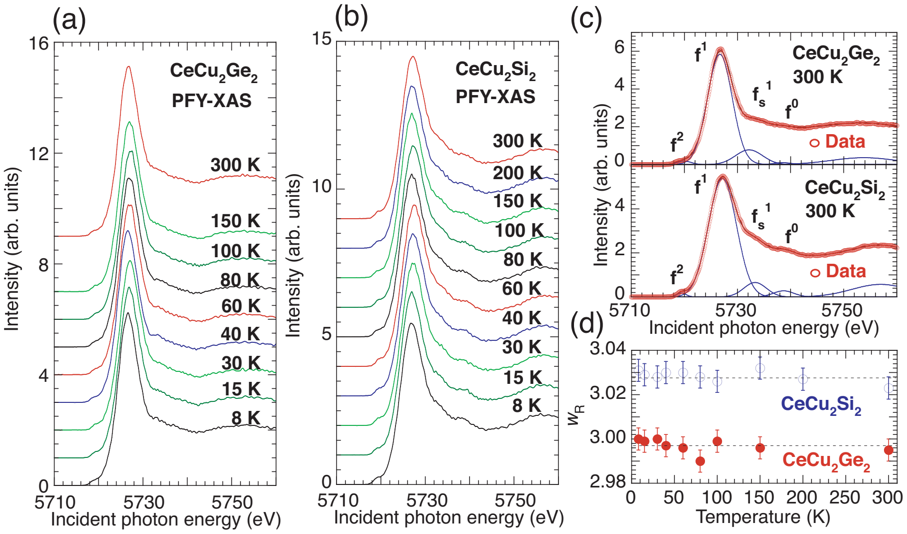

FIG. 2. (Color online) Temperature dependences of PFY-XAS for (a) $CeCu_2Ge_2$ and (b) $CeCu_2Si_2$. (c) Examples of the fits for $CeCu_2Ge_2$ and $CeCu_2Si_2$. (d) Derived ratios for the PFY-XAS spectral weight of the compounds as a function of temperature.

Transport properties of $CeCu_2Ge_2$ such as T-linear resistivity can be explained by the theory of the critical valence fluctuation scenario for the superconductivity in the SC II region (VF mediated superconductivity) [5]. The pressure dependence of the unit-cell volume also showed an anomalous contraction around the maximum T_C ($T_{\rm Cmax}$), suggesting a valence instability and providing further evidence for a pairing mechanism mediated by VF [12]. However, recently results from detailed measurements of the unit cell volume at 12 K were unable to confirm the occurrence of the anomalous volume contraction [13]. This calls for a direct measurement of the pressure dependence of the Ce valence in $CeCu_2Ge_2$.

It has been recently observed that Ni-substitution for Cu sites in $CeCu_2Si_2$ also generates two similar SC domes, although the second SC region shows filamentary superconductivity (SC II') [14]. Ni-substitution for Cu in $CeCu_2Si_2$ induces chemical pressure, which results in a changeover from a heavy-fermion state to an intermediate valence regime via an increase in the Kondo temperature (T_K). $Ce(Cu_{1-x}Ni_x)_2Si_2$ in the paramagnetic region shows similar anomalies in resistivity such as T-linear behavior in $CeCu_2Si_2$. Therefore, the SC II' region in $Ce(Cu_{1-x}Ni_x)_2Si_2$ possibly has the same origin as that in the parent compounds of $CeCu_2Si_2$ and $CeCu_2Ge_2$.

In this letter we report the first direct measurement of the Ce valence in $CeCu_2Ge_2$ as a function of pressure, using x-ray absorption spectroscopy (PFY-XAS) in the high-resolution partial fluorescence yield mode [15–17]. The measured high-resolution x-ray absorption spectroscopy permits reliable derivations of small changes in the Ce valence which cannot be otherwise detected using the normal XAS [18]. The PFY-XAS is a photon-in and photon-out spectroscopic technique that was conducted through the Be gasket of the high-pressure diamond anvil cell. To avoid the destruction of the brittle Be gasket at low temperatures, the maximum pressure achieved was limited to less than 17 GPa. We also measured the temperature dependence of the Ce valence for both $CeCu_2Ge_2$ and $CeCu_2Si_2$, as well as the dependence as a function of x in $Ce(Cu_{1-x}Ni_x)_2Si_2$ up to $x \sim 0.2$. Our results show a smooth increase of the Ce valence as a function of hydrostatic pressure for $CeCu_2Ge_2$ and chemical pressure (Ni-concentration) for the Ni-doped $CeCu_2Si_2$.

The temperature dependence of the PFY-XAS spectra is shown in Figs. 2(a) for $CeCu_2Ge_2$ and 2(b) for $CeCu_2Si_2$. Examples of the fits are shown in Fig. 2(c). The spectra of these compounds mainly consist of the $4f^1$ (Ce^{3+}) component with small fractions of $4f^0$ (Ce^{4+}) and $4f^2$ (Ce^{2+}). The intensity of $4f^0$ is stronger in $CeCu_2Si_2$ than that in $CeCu_2Ge_2$. These results agree with a previous photoemission study [20]. In Fig. 2(d) the estimated spectral weight ratios (w_R) are shown as a function of temperature. We define this ratio as w_R=3+$\{I(f^0)$-$I(f^2)\}/\{I(f^0)+I(f^1)+I(f^2)\}$, where $I(f^n)$ is the intensity of the f^n component in the PFY-XAS spectra. The absolute value of w_R is not strictly equivalent to the Ce valence in the ground state because the $4f^2$ component can partly stem from the core-hole effect in the final state of the PFY-XAS process [21, 22]. Because no variation in the intensity of $4f^2$ is found as a function of temperature and pressure, the changes of the w_R and ground-state valence can be considered nearly identical. The experimental errors mainly originate from the statistics of the data and spectral fitting. In the Ni-doped systems the spectral uncertainty is the main contributor. However, since we systematically fitted the spectra, relative errors in the pressure dependence as well as x-dependence should be small.

No temperature dependence of the valence is observed for either compound, contrary to the predicted temperature dependence of the Ce valence derived from the temperature dependence of the lattice parameters [23]. The magnitude of the crystal electric field (CEF) is 191 K for $CeCu_2Ge_2$ (Ref. 24), and 140 and 364 K for $CeCu_2Si_2$ (Ref. 25), while the Kondo temperature is 6 K for $CeCu_2Ge_2$ and 4.5-10 K for $CeCu_2Si_2$. A much smaller T_K than the CEF may explain the absence of the temperature dependence in both compounds [26]. Another clear feature in our study is that w_R is always higher in $CeCu_2Si_2$ than in $CeCu_2Ge_2$, indicating a strong c-f hybridization in $CeCu_2Si_2$. The mean w_R, averaged over the measured temperature range, is estimated to be 2.99±0.01 for $CeCu_2Ge_2$ and 3.02±0.01 for $CeCu_2Si_2$, which is confirmed by the analyses of the resonant x-ray emission spectra as a function of the incident photon energy [17]. The weaker hybridization in $CeCu_2Ge_2$ is consistent with the larger atomic radius of Ge compared to Si; the substitution resulted in larger lattice constants for $CeCu_2Ge_2$ [13, 23].

We note that the Ce valence normally increases with pressure because of the increase of c-f hybridization. In other words, volume contraction may increase the hybridization, resulting in the increase of the Ce valence. In $CeCu_2Si_2$ a volume contraction of about 13% occurs with pressure up to 9 GPa, while in $CeCu_2Ge_2$ the volume contraction of about 11% requires a pressure increase of approximately 20 GPa [13]. Thus the compressibility of $CeCu_2Si_2$ is much larger than that of $CeCu_2Ge_2$, indicating larger monotonic valence changes with pressure. Therefore it is difficult to find a sudden Ce valence crossover hidden in a larger background of the monotonic pressure-induced valence change if the sudden change in volume at the valence crossover point is relatively small. Studying both $CeCu_2Ge_2$ and $Ce(Cu_{1-x}Ni_x)_2Si_2$ has an advantage in that the amplitude of the external and chemical pressure-induced volume changes is much smaller than that of $CeCu_2Si_2$. An anomalous small jump in the valence would therefore be easier to detect.

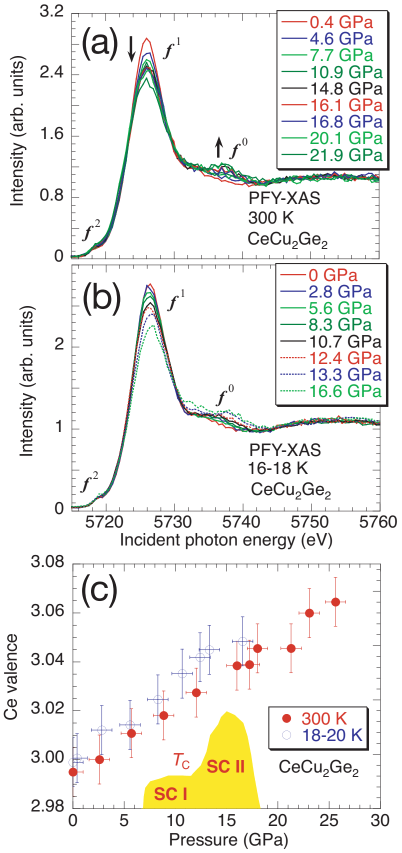

FIG. 3. (Color online). PFY-XAS spectra of $CeCu_2Ge_2$ as a function of pressure at (a) 300 K and (b) 16-18 K. (c) Estimated spectral weight ratio from the fit to the PFY-XAS spectra as a function of pressure at 300 K (Closed circle) and 16-18 K (open circle) with a schematic figure of two superconducting regions.

In Fig. 3 we show the pressure dependence of the PFY-XAS spectra measured at (a) 300 K and (b) 16-18 K. With increasing pressure the intensity of $4f^1$ decreases, while the intensity of $4f^0$ increases, showing a monotonic increase of the Ce valence. The Ce valence at low temperature is slightly higher than at 300 K, reflecting the increase of hybridization at low temperatures. The theory of the VF-mediated superconductivity predicts a change in the valence greater than an order of 0.01 at the critical valence crossover pressure just after T_{Cmax} [27]. Here we construe the valence crossover as a relatively rapid relative change in the valence without a first-order transition. However, within experimental errors, we only observe a smooth increase of the Ce valence with pressure without any noticeable changes in spectral features across the two SC regions at both room and low temperatures. Another distinct feature is the significantly smaller pressure dependence of the Ce valence in $CeCu_2Ge_2$ than in $CeCu_2Si_2$ [28]. This may correspond to the smaller compressibility of $CeCu_2Ge_2$ [13].

We also measured the Ce valence as a function of the Ni concentration x in $Ce(Cu_{1-x}Ni_x)_2Si_2$. Increasing x results in a monotonic decrease of the volume at room temperature [14]. A specific heat measurement revealed that low-lying antiferromagnetic quantum fluctuations around the AFM QCP are notably suppressed by the Ni substitution, and that the Fermi liquid state recovers in the Ni-rich region at approximately $x > 0.12$ [14]. A T-linear dependence of the resistivity was observed at $x \approx 0.1$ together with an indication of superconductivity, which is similar to the SC II region of $CeCu_2Si_2$ in Fig. 1(b). Figure 4(a) shows representative PFY-XAS spectra of

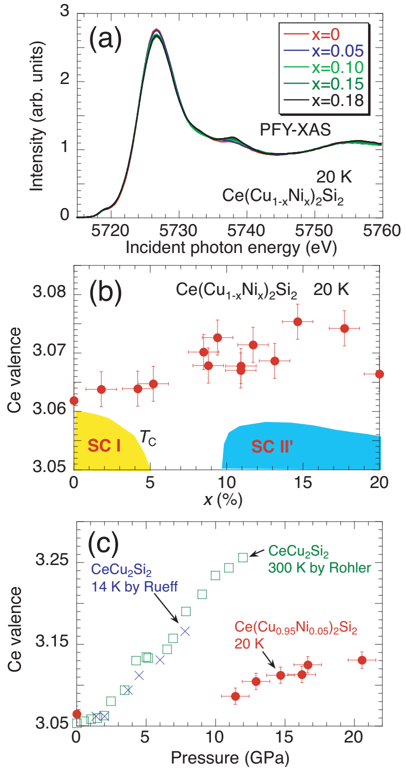

FIG. 4. (Color online). (a) PFY-XAS spectra of $Ce(Cu_{1-x}Ni_x)_2Si_2$ as a function of x at 20 K. (b) Ce valence (spectral weight ratio) estimated from the fit to the PFY-XAS spectra with a schematic figure of two superconducting regions. (c) Pressure-induced change in the Ce valence for $Ce(Cu_{0.95}Ni_{0.05})_2Si_2$ with the data of $CeCu_2Si_2$ from the literatures [28, 29].

$Ce(Cu_{1-x}Ni_x)_2Si_2$ at 20 K. Chemical composition dependence of the spectra is very small although the Kondo temperature increases with x. However, a small increase of $4f^1$ and a decrease of $4f^0$ are clearly observed due to the high statistics of the spectra. The x dependence of the Ce valence is shown in Fig. 4(b) for $x < 0.12$. Our results indicate a very weak and progressive x dependence of the Ce valence without any discontinuous change. The small amplitude of the change in the valence can be explained by the fact that the volume change between $x = 0$ and 0.2 is only ∼1% [14]. The pressure dependence of the valence for the $x = 0.05$ sample is actually remarkably small as well, as shown in Fig. 4(c), compared with previous results for $CeCu_2Si_2$, suggesting the possibility that a small amount of Ni substitution results in a decrease in the compressibility. We note that the sample containing $x = 0.05$ has a reduced critical pressure of ~ 2.8 GPa for the T-linear resistivity as compared with that of ~ 4 GPa for $CeCu_2Si_2$. The result shown in Fig. 4(c) is surprising because 5% Ni substitution can greatly affect the pressure dependence of the Ce valence.

In the theory of the VF mediated superconductivity, the Coulomb repulsion U_{fc} between f and conduction (c) electrons was included, causing a valence transition with pressure [7, 8], where the first-order valence transition which terminates the d-wave superconductivity was found to be enhanced. This can be seen as a d-wave pairing mechanism generated by the Coulomb repulsion. Experimentally, one would expect to observe a valence transition with an abrupt valence-change just after T_{Cmax}. In $CeCu_2Si_2$, a smooth valence increase was observed under pressure across the SC domes at both low [28] and room [29] temperatures. Rueff *et al.* concluded a possible valence fluctuation mediated superconductivity based on these results. However, such a gradual valence increase is actually consistent with what is normally observed in compressed Ce compounds [30], in which the valence fluctuation mediated superconductivity is not theoretically expected. In these Ce compounds, a pressure-induced transition occurs from Kondo to valence fluctuation regions, resulting in a gradual increase of the Ce valence as well as an increase of the Kondo temperature. Theoretically the mechanism for the appearance of the superconductivity in the SC II region of $CeCu_2Ge_2$ is the same as that in $CeCu_2Si_2$. We note that the pressure-induced change in the Ce valence is very different in two Ce compounds; the change in the Ce valence for $CeCu_2Ge_2$ is much less than that in $CeCu_2Si_2$. The theory of the VF-mediated superconductivity showed that a larger change in the Ce valence induces a larger T_{Cmax}. Thus, if the large pressure-induced background change in the Ce valence results in the valence fluctuation mediated superconductivity, T_{Cmax} of $CeCu_2Si_2$ should be much larger than that of $CeCu_2Ge_2$. However, T_{Cmax} of both compounds is the same order as shown in Fig. 1(a).

To verify the theory based on the valence fluctuation scenario, we should find an abrupt change in the valence on the background of the gradual change in the Ce valence. In $CeCu_2Si_2$ pressure-induced change in the Ce valence was large primarily due to larger compressibility described above, inducing a large background of monotonic increase in the Ce valence. In $Ce(Cu_{1-x}Ni_x)_2Si_2$, even a small substitution of Ni for the Cu site would strongly affects the pressure-induced change in the Ce valence. Thus our Ce122 systems may be serve as better candidates for observations of the small valence crossover. Within experimental uncertainties at both room and low temperatures, our results also show a smooth increase of the Ce valence as a function of pressure for $CeCu_2Ge_2$ and as a function of x for $Ce(Cu_{1-x}Ni_x)_2Si_2$, without any anomalous jump just after T_{Cmax}. Since $Ce(Cu_{1-x}Ni_x)_2Si_2$ has been observed to show the filamentary superconductivity, the relationship between the bulk superconductivity and the Ce valence at high pressures and low temperatures remains to be further investigated in the future.

Another proposed scenario for the origin of the SC II region is the orbital fluctuation mediated pairing mechanism [10, 11]. In the theoretical model by Hattori [10] two localized f orbitals were assumed and their occupancy changed discontinuously with pressure, resulting in the increase of the orbital fluctuations at a critical end point. However, the orbital fluctuations coupled with charge fluctuations, resulting in a valence transition coinciding with the orbital crossover. Thus this scenario contrasts our results. Pourovskii *et al.* suggested that the change of orbital occupancy of the two levels, split by the crystal field as a function of temperature or pressure, affects the $4f$ density of states in the vicinity of the Fermi level [11]. This theory based on the orbital fluctuations showed a possible change in the non-resonant inelastic scattering spectra due to the orbital fluctuation and direct observations of the orbital fluctuation remains to be investigated in the future. Finally, we emphasize in our clear experimental findings that there is no apparent sign of the valence crossover within our experimental errors. Our results here call for a reconsideration of the valence fluctuation scenario to account for the unconventional superconductivity in Ce(Cu,Si)$_2$Ge$_2$ heavy fermion compounds.

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Supplemental information

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I. EXPERIMENT

Single crystals of $\mathrm{CeCu_2X_2}$ (X = Ge, Si) were synthesized by the Czochralski method in a tetra-arc furnace. PFY-XAS and RXES measurements were performed at the Taiwan beamline BL12XU at SPring-8. The undulator beam was monochromatized by a pair of Si(111) crystals and focused to a size of 30(horizontal)×20(vertical) $\mu\mathrm{m}^2$ at the sample position using a toroidal and K-B mirrors. Incident photon energies were calibrated by using metal K-absorption edges of V and Cr. The incident photon flux was estimated to be about 7-8$\times10^{11}$ photons/s at 5.46 keV. A Johann-type spectrometer equipped with a spherically bent Si(400) crystal (radius of about 1 m) was used to analyze the Ce $L\alpha_1$ ($3d_{5/2}\rightarrow2p_{3/2}$) emission line with a solid state detector (XFlash 1001 type 1201). The overall energy resolution was estimated to be about 1.5 eV around the emitted photon energy of 4.8 keV. The intensities of all spectra were normalized by the incident beam intensity monitored just before the sample. A closed-circuit He cryostat was used for the low-temperature measurements down to 16 K. The high-pressure conditions were accomplished using a diamond anvil cell (DAC) with a Be-gasket. At low temperature a membrane-controlled DAC was used. Silicone oil at room temperature and a Methanol-ethanol mixture at low temperature were used as pressure-transmitting mediums. The pressure was measured based on the Raman shift of the fluorescence from tiny ruby fragments in the DAC.

II. PHYSICAL PROPERTIES

In Table I we summarize the physical properties of $\mathrm{CeCu_2Ge_2}$ and $\mathrm{CeCu_2Si_2}$. $\mathrm{CeCu_2}X_2$ (x = Ge, Si) has $\mathrm{ThCr_2Si_2}$-type tetragonal crystal structure with space group of $I4/mmm$. Here T_C, T_K, T_N, μ, P_C, γ, and CEF are superconducting transition temperature, Kondo temperature, Néel temperature, paramagnetic moment in unit of μ_B (Bohr magnetron), critical pressure where superconductivity occurs, and crystal electric field, respectively. In Table I, we show the Kondo temperature T_K = 4 K for $\mathrm{CeCu_2Ge_2}$ and 7 K for $\mathrm{CeCu_2Si_2}$, that were estimated from defining T_K as double the value where S reaches $1/(2R\ln 2)$. T_K of $\mathrm{CeCu_2Ge_2}$ is lower than that of $\mathrm{CeCu_2Si_2}$, although the estimation may involve some uncertainties mainly caused by the extrapolation of the experimental values from the lowest temperature data point to 0 K.

III. RESONANT X-RAY EMISSION SPECTRA AT AMBIENT PRESSURE

Figures 1(b) and 1(f) show the resonant x-ray emission spectroscopy (RXES) spectra measured on $\mathrm{CeCu_2Ge_2}$ and $\mathrm{CeCu_2Si_2}$, respectively, at 300 K, as a function of the incident energy across the Ce L_3 edge. The vertical offset of the RXES spectra is scaled to the incident energy axis of the PFY-XAS spectrum (Figs. 1(a) and 1(e)). Figures 1(c) and 1(g) reveal the contour intensity images of the RXES spectra. Energy transfer is defined as the difference between the incident photon (E_{in}) and the emitted photon energies. Both contour images are very similar. Each RXES spectrum is fitted with three components corresponding to the Raman Ce^{2+} ($4f^2$), Ce^{3+} ($4f^1$), and the fluorescence, assuming two Voigt functions for $4f^n$ components[25–27]. We estimated the spectral weight ratio by using the formula v_R=3+$\{I(f^0)$-$I(f^2)\}/\{I(f^0)+I(f^1)+I(f^2)\}$, where $I(f^n)$ is the intensity of the f^n component. The valences are estimated to be v_R=2.989±0.01 and 2.988±0.01 for $\mathrm{CeCu_2Ge_2}$ and $\mathrm{CeCu_2Si_2}$, respectively. We ignore the $4f^0$ component in the fits of the RXES spectra because it is too weak to be discriminated from the intense fluorescence peak. Therefore the values of v_R are less than 3. We are, however, able to extract the $4f^0$ component in the PFY-XAS spectra as shown in the paper, which results in slightly different values of v_R compared with RXES. In the fit of the PFY-XAS spectra there is uncertainty due to the overlap of the $2p\rightarrow5d$ peaks with the arctan-like part corresponding to the excitations towards the continuum. We note that although this uncertainty may affect the absolute value of the valence, the estimation of the relative

TABLE I. Physical parameters of $\mathrm{CeCu_2Ge_2}$ and $\mathrm{CeCu_2Si_2}$.

	$\mathrm{CeCu_2Ge_2}$	$\mathrm{CeCu_2Si_2}$
Lattice at RT	$a = 4.143\text{Å}^a$ $b = 10.156\text{Å}^a$	$a = 4.096\text{Å}^b$ $b = 9.911\text{Å}^b$
T_C	0.6 K^c	0.64 K^d
T_K	4 K^e	7 K^f
T_N	4 K (0 GPa)^g	0.8 K for A-phase
Weiss temperature	20 K^h	140 K^i
μ_eff (μ_B)	2.51^j	2.48^k
P_C	7.7 GPa^l	0 GPa^m
γ (mJ/mol K^2)	200^n	700-1100^o
CEF (K)	197, 212^p	140, 363^q

a: Ref. 1, b: Refs. 2, 3, c: Ref. 4, d: Ref. 5, e: Ref. 6, f: Refs. 7, 8, 9, 10, 11, g: Refs. 1, 6, 12, 13, h: Ref. 12 i: Refs. 12, 14, 15, j: Ref. 16 k: Ref. 15 l: Ref. 17, m: Ref. 18, n: Ref. 19, o: Ref. 20, p: Refs. 21, 22 q: Refs. 23, 24

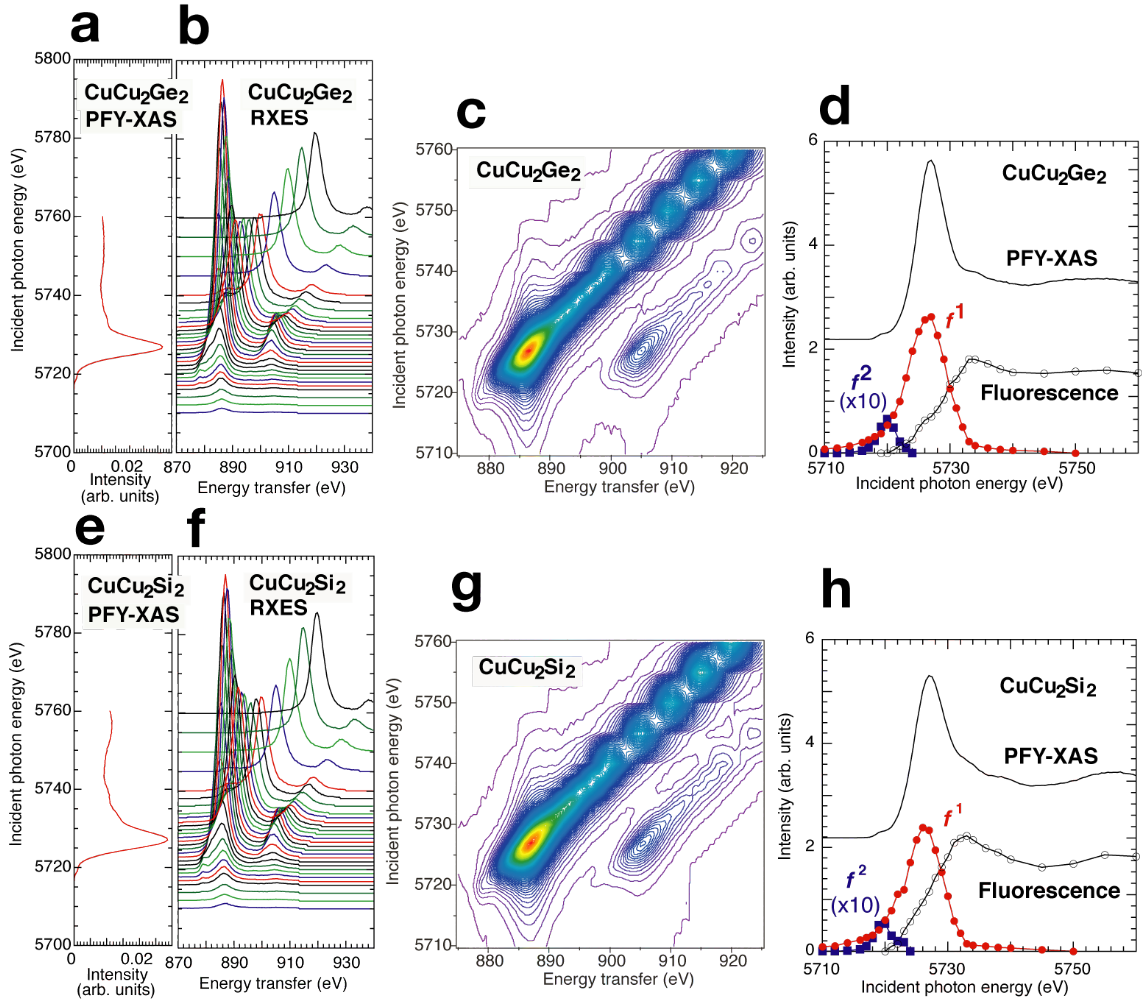

FIG. 1. (Color online). (a) and (e): PFY-XAS spectra for $\mathrm{CeCu_2Ge_2}$ and $\mathrm{CeCu_2Si_2}$ at 300 K. (b) and (f): RXES spectra as a function of the incident photon energies. The vertical position of the each RXES spectra corresponds to the E_{in} of PFY-XAS spectrum they were measured at in the panels (a) and (e), respectively. (c) and (g): Contour images of the RXES spectra. (d) and (h): Analyzed results of the Raman and fluorescence components as a function of the incident photon energies by the fitting procedure with the PFY-XAS spectra. Closed circles, closed squares, and open circle correspond to the Ce^{2+}, Ce^{3+}, and fluorescence components, respectively.

changes as a function of temperature or pressure remains reliable.

IV. PRESSURE DEPENDENCE

For the f^2 component it is difficult to conclude the general trend because of the very weak intensity. Here we note that the presence of the f^2 component is primarily related to a final-state effect with a core-hole in the $3d_{5/2}$ level,[28,29] whereas in the ground state the weight of the f^2 component should be negligibly small[30,31]. Accordingly, the value of the v_R ratio is not exactly the same as the ground state Ce-valence v_g. Especially, since the v_R is smaller than 3 due to the presence of the Ce^{2+} component as described above, similar to that of $CeRu_2Si_2$[32].

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