

Pressure and temperature dependence of the Ce valence and c - f hybridization gap in CeTIn_5 ($T = \text{Co, Rh, Ir}$) heavy-fermion superconductors

H. Yamaoka,^{1,*} Y. Yamamoto,² E. F. Schwier,³ F. Honda,⁴ Y. Zekko,^{2,†} Y. Ohta,^{2,‡} J.-F. Lin,^{5,6} M. Nakatake,^{3,§} H. Iwasawa,³ M. Arita,³ K. Shimada,³ N. Hiraoka,⁷ H. Ishii,⁷ K.-D. Tsuei,⁷ and J. Mizuki²

¹*RIKEN SPring-8 Center, Sayo, Hyogo 679-5148, Japan*

²*Graduate School of Science and Technology, Kwansai Gakuin University, Sanda, Hyogo 669-1337, Japan*

³*Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-0046, Japan*

⁴*Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan*

⁵*Department of Geological Sciences, The University of Texas at Austin, Austin, Texas 78712, USA*

⁶*Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China*

⁷*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan, Republic of China*

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Pressure- and temperature-induced changes in the Ce valence and c - f hybridization of the Ce115 superconductors have been studied systematically. Resonant x-ray-emission spectroscopy indicated that the increase of the Ce valence with pressure was significant for CeCoIn_5 , and moderate for $\text{CeIr}(\text{In}_{0.925}\text{Cd}_{0.075})_5$. We found no abrupt change of the Ce valence in the Kondo regime for $\text{CeIr}(\text{In}_{0.925}\text{Cd}_{0.075})_5$, which suggests that valence fluctuations are unlikely to mediate the superconductivity in this material. X-ray-diffraction results were consistent with the pressure-induced change in the Ce valence. High-resolution photoelectron spectroscopy revealed a temperature-dependent reduction of the spectral intensity at the Fermi level, indicating enhanced c - f hybridization on cooling.

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The BCS theory that explains superconductivity (SC) based on Cooper pair formation due to the electron-phonon interaction often fails to describe the SC states observed in heavy-fermion systems. In the case of CePd_2Si_2 , Cooper pair formation mediated by magnetic spin fluctuations (SF) likely explains the SC state [1]. Heavy-fermion compounds such as CeCu_2Si_2 and CeCu_2Ge_2 , on the other hand, are known to show two pressure-induced superconducting regimes SC1 and SC2 [2,3]. Interestingly, the superconducting transition temperature (T_c) of SC2 is higher than that of SC1. In the SC1 regime, it has been considered that the superconductivity is mediated by the SF. Based on the extended periodic Anderson model with repulsion between f and conduction electrons within a slave-boson mean-field theory [4,5], the valence-fluctuation (VF) mediated superconductivity has been proposed theoretically for the SC2 regime. Candidates of the valence-fluctuation mediated superconductor are $\text{CeCu}_2(\text{Si,Ge})_2$, $\beta\text{-YbAlB}_4$, and Ce115 (CeIrIn_5 , CeRhIn_5) [5]. Another scenario for the origin of the SC2 region is the orbital-fluctuation (OF) mediated pairing mechanism in which the c - f hybridization of the excited level plays an important role in the origin of the superconductivity in the system [6,7]. It has been shown experimentally that superconductivity can be induced in the d -wave channel of Ce-based materials [3]

implying the significance of the c - f hybridization in the occurrence of the SC state. A pressure dependence of the Ce valence change has been reported for CeCu_2Si_2 [8]. While the results seemingly do not support the VF-SC scenario, the authors did not deny its viability [8]. These facts motivated us to measure the Ce valence of CeCu_2Ge_2 (pressure dependence) and $\text{Ce}(\text{Cu}_{1-x}\text{Ni}_x)\text{Si}_2$ (x dependence) [9]. However, neither compound exhibited a sudden valence change around the transition to SC2.

In the case of CeCoIn_5 , hole-doping with Cd or Hg (Refs. [10,11]) induced an antiferromagnetic (AFM) ground state, while electron-doping with Sn (Refs. [11,12]) either suppressed T_c or recovered a Fermi liquid ground state. Among the Ce115 systems, CeCoIn_5 is considered to be located near the quantum critical point (QCP), and the AFM SF-SC scenario is likely. However, the origin of the superconductivity in CeIrIn_5 and $\text{CeIr}(\text{In}_{0.925}\text{Cd}_{0.075})_5$ is still under debate [13–17].

In CeIrIn_5 , thermal transport properties observed in a rotating magnetic field [13], NMR measurements [14], and the doping-induced AFM state near the quantum critical point [15] were consistent with the magnetic pairing mechanism. Recent resistivity and heat-capacity measurements of 1% Cd-doped CeIrIn_5 under pressure also showed a common magnetic mechanism [16]. Meanwhile, nuclear quadrupole (NQR) experiments showed a large residual spin-lattice relaxation rate $1/TT_1$ that behaves linearly well below T_c as well as a change in the pressure-induced NQR frequency at the superconducting region, pointing to a possible valence change of Ce [17]. The temperature dependence of $1/TT_1$ showed the same trend for both CeIrIn_5 and Cd-doped CeIrIn_5 . These behaviors can be explained by the VF-SC scenario; however, no direct measurement of the Ce valence in Ce115 under pressure has been reported so far. The origin of superconductivity in CeIrIn_5 and Cd-doped CeIrIn_5 remains an unresolved puzzle.

* Author to whom all correspondence should be addressed: yamaoka@spring8.or.jp

† Present address: Yokohama R & D Center, Nissin Incorporated, 1-18-2 Hakusan, Midori-ku, Yokohama 226-0006, Japan.

‡ Present address: Department of Physics, Osaka University, 1-3 Yamadaoka, Suita 565-0871, Japan.

§ Present address: Aichi Synchrotron Radiation Center, Seto, Aichi 489-0965, Japan.

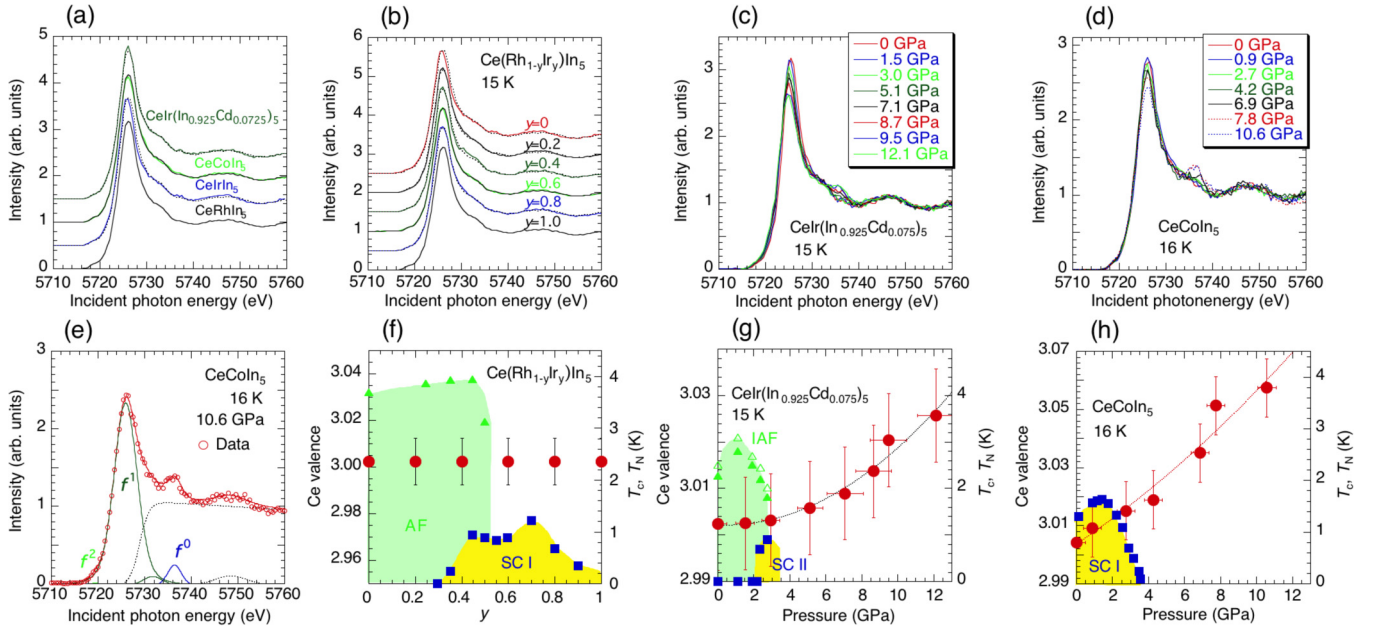


FIG. 1. (Color online) (a) and (b) Chemical composition dependence of the PFY-XAS spectra at 15 K. Dotted lines, superposed in (a) and (b) for comparison, correspond to the spectra of CeRhIn₅ and CeIrIn₅, respectively. (c) and (d) Pressure dependence of the PFY-XAS spectra for CeIr(In_{0.925}Cd_{0.075})₅ at 15 K and CeCoIn₅ at 16 K. (e) PFY-XAS spectrum (circles) of CeCoIn₅ at 16 K and 10.6 GPa with a fitting curve (red solid line), assumed f^2 (light-green solid line, very weak), f^1 (green solid line), and f^0 (blue solid line) components, and background and other residual components (dashed lines). (f) Change in the Ce valence as a function of y for Ce(Rh_{1-y}Ir_y)In₅. (g) and (h) Pressure dependence of the Ce valence (closed circle) for CeIr(In_{0.925}Cd_{0.075})₅ and CeCoIn₅. In (f), (g), and (h), the transition temperatures of the antiferromagnetic order (AF, closed triangle) and superconducting region (SC, closed square) are also shown [17,31,40]. IAF is inhomogeneous AF [17].

The AFM-SF involving f electrons may generate an attractive Cooper pairing interaction in the d -wave channel. Below the Kondo temperature, the c - f hybridization becomes stronger, resulting in the development of the hybridization gap. Further decreases in the temperature may cause the superconducting gap to open below T_c [18]. Therefore, in the SF mediated superconductors, the c - f hybridization gap correlates with the SC. Signatures of the hybridization gap have been observed by optical spectroscopy [19,20] and scanning tunneling spectroscopy (STM) [21–23]. These results call for direct and bulk sensitive measurements of the c - f hybridization gap formation by low photon energy high-resolution photoelectron spectroscopy (PES).

The purpose of this study is to clarify the pressure- and temperature-induced change in the Ce valence and c - f hybridization of the Ce115 superconductors systematically. High-quality single crystals of CeCoIn₅, Ce(Rh_{1-y}Ir_y)In₅ ($y = 0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0$), and CeIr(In_{0.925}Cd_{0.075})₅ were prepared. Resonant x-ray-emission spectroscopy (RXES) with x-ray-absorption spectroscopy (XAS) in the partial fluorescence mode (PFY-XAS) at the Ce L_3 edge was employed to directly observe small valence changes. The valence transition is often correlated to a change in the unit-cell volume. Therefore, x-ray-diffraction (XRD) measurements were performed under high-pressure conditions. The combination of these results allowed us to make a precise quantitative estimation of the temperature and pressure (T - P) dependences of the valence and its correlation to the volume change. Our results show that neither the Ce valence nor the unit-cell volume exhibit any sudden changes in the observed pressure range, which is incompatible with the VF-SC scenario. PES for CeCoIn₅,

CeIr(In_{0.925}Cd_{0.075})₅, and Ce(Rh_{1-y}Ir_y)In₅ at $h\nu = 8.37$ eV (Xe I line) and 6.36 eV (Laser) was also performed to directly clarify the temperature dependence of the hybridization gap formation. Note that photoelectrons with a kinetic energy of ~ 2 eV tend to have a longer inelastic mean free path of ~ 10 nm [24,25]. Details regarding the experimental techniques can be found in the Supplemental Material [26].

Figure 1(a) shows the PFY-XAS spectra for CeCoIn₅, CeIrIn₅, CeRhIn₅, and CeIr(In_{0.925}Cd_{0.075})₅ at 15 K. The differences among these spectra are very small, indicating a similar Ce valence state in these compounds at ambient pressure. The chemical composition dependence of the PFY-XAS spectra for Ce(Rh_{1-y}Ir_y)In₅ is shown Fig. 1(b). To obtain the mean Ce valence, we evaluated the spectral intensity ratios of the f^2 , f^1 , and f^0 components in the PFY-XAS spectra [27,28]. Figure 1(c) shows an example of a fit to the CeCoIn₅ PFY-XAS spectrum measured at 16 K and 10.6 GPa. Figure 1(f) shows the y dependence of the mean Ce valence with the transition temperatures to the superconducting (T_c) and AFM states (AF, T_N). No apparent y dependence of the electronic structure and the Ce valence is observed within experimental errors. The absence of the sudden change of the Ce valence at the phase boundary clearly indicates that the VF-SC scenario is not likely for these compounds.

Figures 1(c) and 1(d) show the pressure dependence of the PFY-XAS spectra of CeIr(In_{0.925}Cd_{0.075})₅ and CeCoIn₅ at low temperatures. In Fig. 1(g), the Ce valence in CeIr(In_{0.925}Cd_{0.075})₅ does not show significant changes up to 3 GPa, and it gradually increases above 5 GPa. Similar behavior has been observed in other Ce superconductors such as CeIrSi₃ (Ref. [27]) and CePd₂Si₂ (Ref. [28]). In

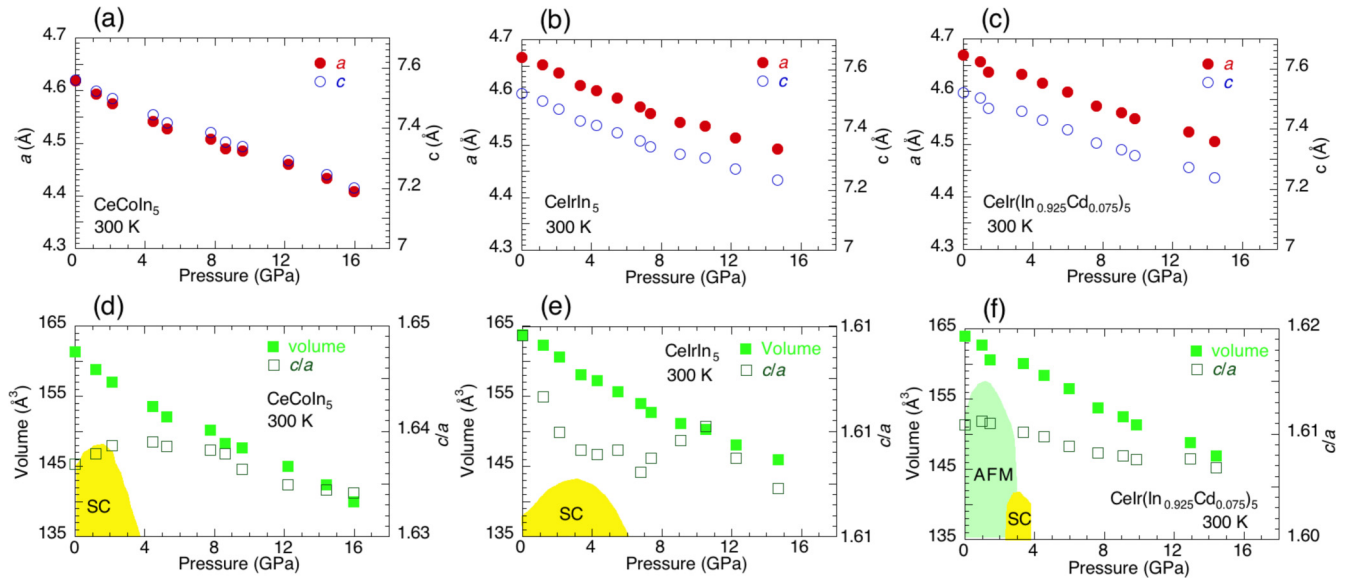


FIG. 2. (Color online) Pressure dependence of the lattice constants of a (closed circle) and c (open circle) for (a) CeCoIn_5 , (b) CeIrIn_5 , and (c) $\text{CeIr}(\text{In}_{0.925}\text{Cd}_{0.075})_5$. Pressure dependence of the volume (closed square) and the ratio of c/a (open square) are shown in (d) CeCoIn_5 , (e) CeIrIn_5 , and (f) $\text{CeIr}(\text{In}_{0.925}\text{Cd}_{0.075})_5$, respectively. In (d), (e), and (f) the superconducting and AFM ranges are also shown, where the vertical full scale corresponds to 4 K [17,31,40].

general, Ce-based systems tend to change from Kondo to valence fluctuation regimes upon increasing pressure, which is well understood based on the single-impurity Anderson model [28,29]. The Ce valence in CeCoIn_5 , on the other hand, increases rapidly to the valence fluctuation region with pressure, as shown in Fig. 1(h). This is reasonably understood because the volume of CeCoIn_5 is already smaller than that of CeIrIn_5 at ambient pressure, and the compressibility of CeCoIn_5 is larger than that of the other two compounds, as shown in Fig. 2.

The Ce valence showed a negligible temperature dependence according to the previous XANES study of $\text{CeIr}_{1-x}\text{Rh}_x\text{In}_5$ at 20–300 K (Ref. [30]) and our XAS study of Ce122 systems at 9–300 K (Ref. [9]). Although the present high-pressure study has been performed at temperatures higher than T_c , the previous XANES and XAS results suggest that the Ce valence in Ce115 and Ce122 systems does not have a significant temperature dependence.

Figures 2(a)–2(f) show the pressure dependence of the lattice constants, volume, and the ratio of c/a at room temperature. The lattice constants decrease with pressure monotonically. At ambient pressure, the volume of CeCoIn_5 is the smallest among the compounds while its compressibility is the largest. In the case of CeIrIn_5 , the substitution of 7.5%-Ir for Cd does not show a significant change in the pressure dependence of the volume.

A strong correlation between c/a and T_c has been suggested [31]. While the volume decreases monotonically in these compounds, the c/a ratio shows the maximum value to be around 5 GPa for CeCoIn_5 and 11 GPa for CeIrIn_5 , which are larger than the superconducting pressure range. The 7.5%-Cd-doped sample, on the other hand, has no such peak structure in the ratio of c/a . These compounds showed no structural transition in the measured pressured range, supporting no rapid change in the Ce valence. No difference between the basic

crystallographic properties of the c/a ratio and bulk modulus between 300 and 10 K has been reported [32]. Therefore, we assume that the above properties are retained down to low temperatures.

The VF-SC scenario predicted a rapid change in the Ce valence just before the maximum T_c in the T - P phase diagram [4]. This scenario was expected to explain the superconductivity in $\text{CeIr}(\text{In}_{0.925}\text{Cd}_{0.075})_5$ in the SC2 phase [17]. Our results, however, indicate that the Ce valence does not change rapidly as predicted by the VF-SC scenario below 3 GPa within the experimental errors. Therefore, the VF-SC scenario cannot be compatible with the results for $\text{CeIr}(\text{In}_{0.925}\text{Cd}_{0.075})_5$. Note that the SF-SC scenario appears to be more appropriate than the VF-SC scenario to explain the transport and thermodynamic properties of $\text{CeIrIn}_{5-x}\text{Hg}_x$, $\text{CeIrIn}_{5-x}\text{Sn}_x$, and $\text{CeIr}_{1-x}\text{Pt}_x\text{In}_5$ [15]. Additionally, neutron scattering experiments of CeRhIn_5 showed the magnetic fluctuation and magnons [33,34].

Figures 3(a) and 3(b) show the temperature dependence of the valence-band photoelectron spectra of CeIrIn_5 and CeCoIn_5 , respectively. The corresponding density of states (DOS) is shown in Figs. 3(c) and 3(d), which indicate a reduction of the intensity at the Fermi level (E_F) upon cooling, i.e., the formation of the c - f hybridization gap. The result agrees with the prediction of dynamical mean field theory (DMFT) [35], which also explained the scanning tunneling spectroscopy results [21,22] and the two-channel cotunneling model. The DMFT calculations of CeIrIn_5 also reproduced the temperature dependence of the optical conductivity data [36], where the development of the hybridization gap was suggested. Our measurements show direct proof of the development of the hybridization gap.

The c - f hybridization competes with the magnetic order or spin fluctuation, and thus the hybridized band may be modified partly by the appearance of the superconducting state [18,23]. Interestingly, in angle-resolved PES of CeCoIn_5

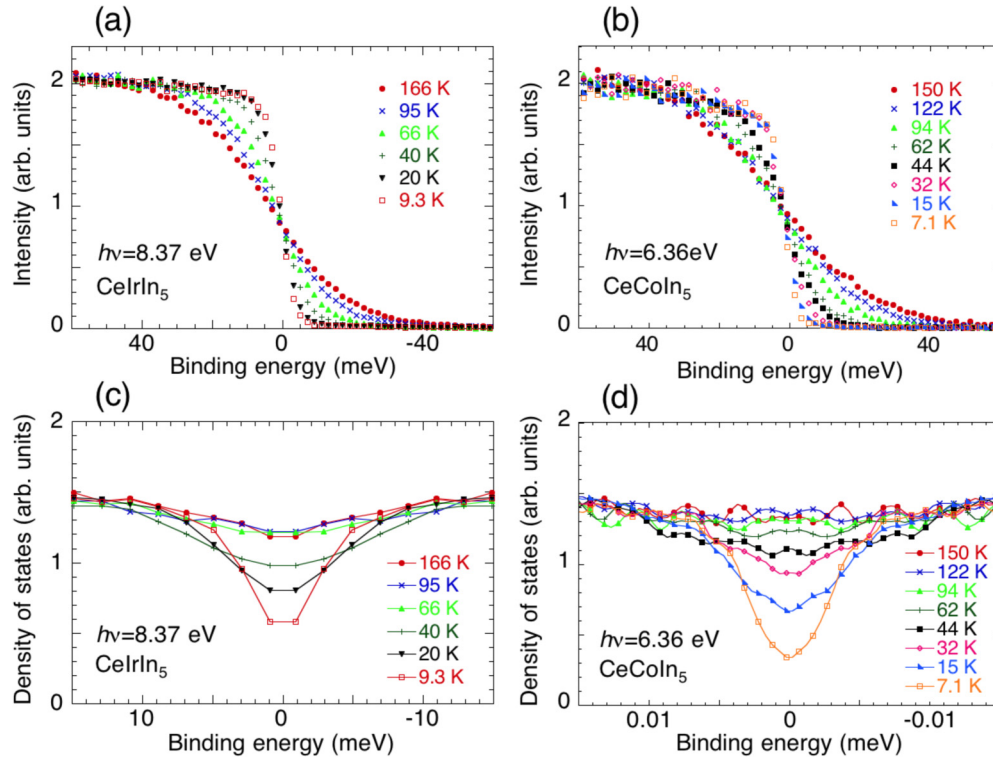


FIG. 3. (Color online) Parts (a) and (b) show the temperature dependences of the valence-band spectra near the Fermi level for CeIrIn₅ and CeCoIn₅, respectively. Parts (c) and (d) show spectra symmetrized with respect to E_F to recover the temperature-dependent DOS.

at 1.7 K, the weakest hybridization was found in the highly two-dimensional bands [37]. It should be noted that CeRhIn₅, which does not show superconductivity at ambient pressure, has weaker c - f hybridization strength than CeIrIn₅ [38]. In Fig. 3, the onset temperatures of the hybridization gap formation are not so different between CeCoIn₅ (44–62 K) and CeIrIn₅ (40–60 K). On the other hand, the electronic specific-heat coefficient of CeCoIn₅ is nearly half that of CeIrIn₅. The results of both the XAS and the PES did not show a significant difference of the hybridization strength between CeCoIn₅ and CeIrIn₅ within the experimental accuracies.

In conclusion, the Ce valence of CeIr(In_{0.925}Cd_{0.075})₅ showed a smooth change with pressure from the Kondo to valence fluctuation regions, suggesting that the VF-SC is not likely. The pressure-induced change in the Ce valence for CeCoIn₅ was larger than that for CeIr(In_{0.925}Cd_{0.075})₅, which may correspond to larger compressibility in CeCoIn₅. The PFY-XAS spectra were similar for CeCoIn₅, CeIrIn₅, CeRhIn₅, and CeIr(In_{0.925}Cd_{0.075})₅ samples at ambient pressure and at 15 K. The superconductivity easily disappeared at high pressures where the system moves to the valence fluctuation regime with stronger c - f hybridization. Note that recent nonresonant inelastic x-ray scattering has indicated an absence of the orbital rotation in CeCu₂Ge₂ [39], which is not compatible with the OF scenario predicted by the theory based

on the DMFT [6]. So far, the SF-SC scenario is compatible with the reported experimental results at least for the Ce115 systems. The XRD study indicated that the volume changed smoothly with pressure and no structural transition existed for CeCoIn₅, CeIrIn₅, and CeIr(In_{0.925}Cd_{0.075})₅, consistent with the PFY-XAS results. CeCoIn₅ showed the largest compressibility among these compounds. High-resolution PES showed development of the c - f hybridization gap at low temperatures in CeIrIn₅ and CeCoIn₅.

The experiments were performed at SPring-8 Taiwan beamlines BL12XU and BL12B1 (under SPring-8 Proposals No. 2013B4128, No. 2013B4258, No. 2014A4256, and corresponding NSRRC Proposal No. 2013-3-008) and at HiSOR beamlines BL-1 and BL-9A, and Laser PES station (Proposals No. 13-A-1 and No. 14-A-5) in Hiroshima University. We thank the N-BARD, Hiroshima University for supplying the liquid helium. This work is partly supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science in Japan (Proposal No. 15K05194). J.F.L. acknowledges support from HPSTAR. E.F.S. acknowledges financial support from the JSPS postdoctoral fellowship for overseas researchers as well as the Alexander von Humboldt Foundation (Grant No. P13783).

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