Ce $4f$ electronic states of CeO$_{1-x}$F$_x$Bi$_2$S$_2$ studied by soft x-ray photoemission spectroscopy

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We use soft x-ray photoemission spectroscopy (SXPES) to investigate Ce $4f$ electronic states of a new Bi$_2$ layered superconductor CeO$_{1-x}$F$_x$Bi$_2$S$_2$, for polycrystalline and single-crystal samples. The Ce 3d spectrum of the single crystal of nominal composition $x = 0.7$ has no $f^8$ component and the spectral shape closely resembles the ones observed for Ce trivalent insulating compounds, strongly implying that the CeO layer is still in an insulating state even after the F doping. The Ce 3d-$4f$ resonant SXPES for both polycrystalline and single-crystal samples shows that the prominent peak is located around 1 eV below the Fermi level ($E_F$) with negligible spectral intensity at $E_F$. The F-concentration dependence of the valence band spectra for single crystals shows the increases of the degeneracy in energy levels and of the interaction between Ce 4f and S 3p states. These results give insight into the nature of the CeO$_{1-x}$F$_x$ layer and the microscopic coexistence of magnetism and superconductivity in CeO$_{1-x}$F$_x$Bi$_2$S$_2$.

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1. INTRODUCTION

The iron-based superconductors including LnFeAsO$_{1−x}$F$_x$ ($Ln =$ lanthanide) are discovered in the course of exploring a new $p$-type transparent semiconductor with two-dimensional layered structure which consists of a narrow-gap semiconductor sandwiched by wide-gap insulating layers [1,2]. LnCuChO ($Ch =$ chalcogen) is one of such transparent semiconductors, and it is pointed out that it has “natural multiple quantum wells” built into its layered structure [3]. For the compounds containing CeO layers as the “wide-gap” layers, such as CeCuSO ($Ln =$ Ce and $Ch =$ S), one of the key issues is the influence of the implantation of the $4f$ electron into the energy region near the Fermi level ($E_F$) on the electronic and the magnetic properties. The magnetometry measurement shows that stoichiometric CeCuSO is not a mixed-valence compound but is a well-behaved Ce$^{3+}$ compound [4].

When a narrow-gap semiconductor (CuS) layer in CeCuSO is replaced with a metallic layer consisting of transition metal ($T M$) and pnictogen ($P n$) atoms (Ce$T M$P$n$O), the interaction between the metallic $d$ band and Ce $4f$ state leads to diverse variations in the physical properties depending on the strength of the interaction. A typical example is the Ce$T M$PO ($T M =$ Fe, Ru, Os and $P n =$ P) family of compounds: CeFePO with a paramagnetic heavy fermion behavior [5], CeRuPO with a ferromagnetic (FM) order at $T_C =$ 15 K (which is a Kondo lattice system ($T_K$ $\sim$ 10 K)) [6], and CeOsPO with an antiferromagnetic (AFM) order at $T_S =$ 4.4 K [6]. Another important example is CeFeAsO, which is a bad metal and exhibits a structural distortion near 155 K, followed by a commensurate AFM ordering on the Fe sublattice below $\sim$140 K and an AFM transition of Ce$^{3+}$ below 4 K [7,8]. In addition, the F-doped compound (CeFeAsO$_{1−x}$F$_x$) shows superconductivity with high transition temperature (as high as $T_C =$ 41 K for $x =$ 0.16), involved with the suppression of both the structural distortion and the magnetic order [7,8].

CeO$_{1−x}$F$_x$Bi$_2$S$_2$ is one of the newly discovered superconductors LnO$_{1−x}$F$_x$Bi$_2$S$_2$ ($Ln =$ La, Ce, Pr, Nd, Yb) [9,10] where the CeO$_{1−x}$F$_x$ and the Bi$_2$S$_2$ layers are stacked alternatively. The latter layer has no metallic $d$ band and it is a narrow-gap semiconductor. F substitution for O introduces electron carriers to the Bi$_2$S$_2$ layer. Eventually, CeO$_{1−x}$F$_x$Bi$_2$S$_2$ exhibits not only superconductivity but also ferromagnetic-like behaviors.

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Furthermore, it is concluded that the superconducting and the magnetically ordered states coexist for higher $x$ at low temperatures [12–15]. These findings have caused particular interest in this compound and stimulated further investigations of it [16–23]. The phase diagrams, obtained by systematic investigation for nominal F-concentration ($x$) dependence ($x = 0.0–1.0$) of both the magnetic ordering and the superconducting properties of the as-grown polycrystalline samples, show that ferromagnetic-like ordering occurs at slightly higher temperature than the superconducting transition for $x > 0.4$ [21]. For the samples postannealed under high pressure, the superconducting transition temperature $T_c$ increases and exceeds magnetic ordering temperature $T_m$ to a subtle extent ($T_c < T_m$). In contrast, for single-crystal samples, the same trend with the as-grown samples ($T_c < T_m$) is observed. For example, the magnetic ordering temperature $T_m$ is 5.6 K and the superconducting transition temperature $T_c$ (estimated by Meissner effect) is 3.0 K for $x = 0.7$ [19,24]. The Ce $L_3$ edge x-ray absorption spectroscopy (XAS) measurements for polycrystalline samples show a crossover from mixed valence states to the localized $4f$ states under F doping [16]. The extended x-ray absorption fine structure (EXAFS) analysis exhibits that this change in the electronic structure is driven by suppression of the Ce-S-Bi coupling channel due to the local crystal structure deformation, leading to the coexistence of the superconducting BiS$_2$ layer and the ferromagnetic CeO$_{1−x}$F$_x$ layer [16,17]. In contrast, for the CeOBiS$_2$ ($x = 0.0$) single crystal, it is concluded that Ce $4f$ electrons are in a well-localized state split by crystalline-electric-field (CEF) effects, from electrical resistivity, magnetization, and, specific-heat measurements [20].

To reach a comprehensive understanding of these findings, spectroscopic investigation of Ce $4f$ states for single crystals is crucial. Soft x-ray photoemission spectroscopy (SXPS) is known to be a useful experimental technique in order to clarify the nature of Ce $4f$ states [25]. The variety of the physical properties that Ce compounds exhibit (magnetic ordering, heavy fermion, Kondo insulator, mixed valence, and so on) can be explained in terms of the hybridization strength between Ce $4f$ and conduction electrons, which is formulated by single-impurity or periodic-impurity Anderson models. When the hybridization is negligible, Ce $4f$ electrons are localized on the atomic sites and the electronic states of the system can be described with one $4f$ electron ($f^1$) state and conduction band. The system tends to exhibit magnetic ordering at lower temperature due to RKKY interaction between magnetic moments of $4f$ electrons on the different sites via conduction electrons. As the hybridization increases, $4f$ electrons gain itinerancy and the electronic states can be described with the combination of $f^1$ and $f^0$ (no $4f$ electron) states and conduction band. The system can exhibit the Kondo effect and becomes heavy fermions at lower temperature (or insulating behavior, known as a Kondo insulator, because of the formation of the hybridization gap around $E_F$). When the hybridization is further increased, the system does not show any anomaly and the electronic states can be described by a highly hybridized conduction band, which is explained well with band structure calculations. Such a different electron configuration is reflected in the Ce $3d$ core level photoemission and XAS spectra. More importantly, Ce $3d$-$4f$ resonant SXPS can provide Ce $4f$ partial density of states and therefore directly reveal the relation of Ce $4f$ states with conducting properties, although there are few reports on the Ce $3d$-$4f$ resonant SXPS of layered compounds consisting of alternatively stacked CeO and metallic/semiconducting layers so far [26–28]. Recent reports on Ce $4d$-$4f$ resonant SXPS for CeO$_{1−x}$F$_x$Bi$_2$S$_2$ shows that the Ce $4f$ electrons in both $x = 0.0$ and 0.5 systems respectively formed a flat band at 1.0 and 1.4 eV below $E_F$ and there was no contribution to the CeO layer in an insulating state even after the F doping. Ce $3d$-$4f$ resonant SXPS shows that the prominent peak is located around 1 eV below $E_F$ with negligible spectral intensity at $E_F$, different from the typical spectra characteristic of those in the Kondo regime. This indicates that the Ce $4f$ electrons in the F-doped superconductors play a minor role in the superconductivity. The $F$-concentration dependence of the valence band spectra of single crystals ($x = 0.3$ and 0.7) shows the enhancements of the degeneracy in the binding energies and of the interaction between Ce $4f$ and S $3p$ states, which strongly support the interpretation that the Ce-S2-Ce superexchange interaction (S2 is an out-of-plane sulfur atom) between Ce$^{3+}$ sites is responsible for the emergence of the magnetic ordering in the CeO$_{1−x}$F$_x$ layer [16,17,22].

The organization of the paper is as follows. In Sec. II, we describe the sample preparation and the experimental setups. In Sec. III A, we present the Ce $3d$ core level SXPS, and discuss the nature of Ce $4f$ electrons for F-doped compounds. In Sec. III B, we present the resonant SXPS results with Ce $M_{4,5}$ edge XAS spectra and discuss the Ce $4f$ partial density of states. We compare on-resonant SXPS spectra with those of the other systems in Sec. III C. In Sec. III D, we discuss the $F$-concentration dependence of the valence band spectra and discuss it in terms of local structure deformation. Finally, Sec. IV will contain a summary and conclusions.

II. EXPERIMENTAL

Single-crystal samples of CeO$_{1−x}$F$_x$Bi$_2$S$_2$ were grown by a CsCl/KCl flux method at 873–1073 K in a vacuumed quartz tube [18]. The starting materials were Ce$_2$S$_3$, Bi, Bi$_2$S$_3$, Bi$_2$O$_3$, and BiF$_3$. The nominal compositions of F were set to be $x = 0.3$ and 0.7, and the chemical compositions ($y$) were determined to be 0.16 and 0.28 by electron probe microanalysis (EPMA), respectively [24]. For the single crystal of $x = 0.7$, the superconducting transition temperature ($T_c$) was estimated to be 3.2 K (3.0 K) from the zero-resistivity temperature (from the Meissner effect), while the magnetic ordering temperature ($T_m$) of 5.6 K was determined as the temperature at which the zero-field-cooled curve begins to deviate from the field-cooled curve. For the single crystal of $x = 0.3$, neither $T_c$ nor $T_m$ were observed above 2 K. Polycrystalline samples of CeO$_{1−x}$F$_x$Bi$_2$S$_2$...
were prepared with a solid-state reaction and then annealed under high pressure [21]. Starting materials were Bi$_2$O$_3$, BiF$_3$, Ce$_2$S$_3$, Bi$_2$S$_3$, and Bi grains. The nominal composition of F was set to be $x = 0.7$. Details on the sample preparation and characterization are given elsewhere [18,19,21,24].

SXPES and XAS measurements were performed at BL-2A in the Photon Factory (PF), KEK, with an SES2002 electron analyzer. The total energy resolution was set to be 0.2–0.4 eV for PES measurements using photon energies of 870–1200 eV (70 eV). The binding energies were referenced to $E_F$ of gold. The base pressures of the measurement chambers were better than 2×10$^{-9}$ Pa. The samples were fractured (cleaved) for polycrystalline (single-crystal) samples to obtain fresh surfaces at 16 K and kept at the same temperature during the measurements. All SXPES and XAS results reported here were obtained within 8 h after fracturing (cleaving), within which no spectral changes were observed.

III. RESULTS and DISCUSSION

A. Ce 3d SXPES measurement

We start with Ce 3d SXPES in order to obtain insight into the nature of Ce 4$f$ electrons in CeO$_{1−x}$F$_x$ layers of CeO$_{1−x}$F$_x$Bi$_2$S$_2$. Figure 1 shows Ce 3d SXPES spectra of single-crystal samples, $x = 0.3$ (light green) and 0.7 (dark green), measured with a photon energy of 1200 eV. The $x = 0.3$ spectrum is composed of several peaks that are attributed to the transitions to the three different 4$f$ final states ($f^0$, $f^1$, and $f^2$) for each spin-orbit partner (3d$_{5/2}$ and 3d$_{3/2}$). In general, the energy of the $f^0$ final state in the Ce 3d photoemission process is well separated from those of the other two final states, and so it is considered that the intensity of the highest-binding-energy peak in each set of three structures is a measure of the $f^0$ component in the initial state [31]. In contrast, the $f^1$ and $f^2$ final states have relatively close energies, which results in relatively strong hybridization between them [32]. With increasing $x$, the intensity of the $f^0$ peak is reduced and the energy positions of the $f^1$ and the $f^2$ peaks show rigid shifts to higher binding energy by 0.3 eV, and the corresponding $f^0$ component for 3d$_{3/2}$ disappears except for a broad structure which may be assigned to a plasmon loss [33]. Here, we cannot completely deny the possibility that the weak $f^0$ components of $x = 0.3$ originate from the CeO$_2$-like impurities as discussed in the Supplemental Material [34]. However, we can safely describe an important overall spectral feature, which is not affected by the possible inclusion of CeO$_2$-like signals which induce the $f^0$ component; that is, the two-peak structures of $f^1$ and $f^2$ components closely resemble the spectra observed for Ce trivalent insulating compounds, such as CeO$_2$ [35] and CeCl$_3$ [33], but they do not resemble well those for the Ce trivalent metallic compounds such as CeSe [36] and CePd [31] where the $f^2$ components are weak. These findings strongly imply that the CeO layer is still in an insulating state even after the F doping. For the shoulder structure at ~907 eV, the same structure is observed for CeCl$_3$ [33] and the origin is unclear at present.

The inset shows the magnified spectra of the $f^1$ and $f^2$ components for 3d$_{5/2}$ where the spectra are normalized to the integrated intensities and the spectrum for $x = 0.7$ is shifted by −0.3 eV to match the peak positions with the ones for $x = 0.3$. It is clear that the width of the spectra are almost the same but the intensity ratio of the two components changes. We will discuss this difference later in Sec. III D, from the viewpoint of the F-concentration dependence of the electronic states.

B. Ce 3d-4$f$ resonant SXPES measurement

A more direct and powerful way to access and reveal the occupied Ce 4$f$ states is to use the Ce 3d-4$f$ resonant SXPES measurement [30,37,38]. This method is selective in chemical states of the target element, and a resonant enhanced spectrum is therefore less influenced by contaminations, especially near the $E_F$ region. In Fig. 2, we show off- and on-resonance spectra of the $x = 0.7$ single-crystal and polycrystalline samples measured at two photon energies, 870 eV (A) and 881.7 eV (B) in XAS spectra near the Ce $M_5$ edge shown in the inset. Each spectrum is magnified by the scale factor denoted on the right side of the figure.

1. Off-resonant spectra

The off-resonant spectrum (thin curves) for the single-crystal sample of $x = 0.7$ in Fig. 2(a) has dominant structures from 1.5 to 6.5 eV with smaller intensities near the $E_F$ region. The 4$f$ contribution around 1.4 eV (see below) almost vanishes. It should be noted here that this strong reduction
remains. Resistivity measurements exhibit semiconducting behavior still although a known unresolved problem that the electrical a single crystal of results are consistent with the recent ARPES measurement for more structureless spectral shape with a Fermi edge. These polycrystalline sample of $x$ states $[41,43]$. In Fig. 2(b), the off-resonant spectrum for the F-doped polycrystalline sample of $x$ = 0.7 exhibits the same spectral shape as the one in (a), indicating that the on-resonance spectrum for the single crystal in (a) can be regarded as the $f$ pDOS, though normally it reflects the $f$-derived electronic structure which is integrated only for a limited region in the Brillouin zone (BZ). The absence of the strong enhancement just below the $E_F$ region for both samples indicates that the hybridization of Ce $4f$ electrons and the non-$f$ valence states near the $E_F$ is negligible $[44]$. This result suggests that Ce $4f$ electrons hardly contribute to the states near the $E_F$ and therefore give a negligible contribution to the superconductivity. This result is, furthermore, consistent with the recent resonant photoemission result for single-crystal CeO$_{0.5}$F$_{0.5}$BiS$_2$ using 4$d$-$4f$ resonant photoemission $[29]$. is due to the Fano profiles and, therefore, can be interpreted as “antiresonance phenomena” $[39,40]$. The major intensity distributions indicate the partial density of states (pDOS) of O 2$p$ and S 3$p$ multiplied photoemission cross sections. Actually, the spectral shapes closely resemble the valence band spectra reported for the polycrystalline LaO$_{1-x}$F$_x$BiS$_2$ which has no $f$ electron $[41]$. The band calculation for LaO$_{1-x}$F$_x$BiS$_2$ shows that the DOS of the occupied valence states in the lower binding energy region mainly consists of S 3$p$ and that in the higher binding energy region mainly originate from O 2$p$ $[42]$. In the magnified off-resonant spectra of near the $E_F$ region in Fig. 2(a), one observes that it has a clear Fermi edge, which is considered that mainly derived from Bi 6$p$ states $[41,43]$. In Fig. 2(b), the off-resonant spectrum for the polycrystalline sample of $x$ = 0.7 also shows a similar but more structureless spectral shape with a Fermi edge. These results are consistent with the recent ARPES measurement for a single crystal of $x$ = 0.7 which shows a clear Fermi surface $[23]$, although a known unresolved problem that the electrical resistivity measurements exhibit semiconducting behavior still remains $[19,24]$.

2. On-resonant spectra

For the on-resonant spectrum (thick curves) in Fig. 2(a), the intensity around 1.4 eV shows a drastic increase while the intensity just near the $E_F$ region stays lower. The on-resonant spectrum for the F-doped polycrystalline sample of $x$ = 0.7 in Fig. 2(b) exhibits the same spectral shape as the one in (a), indicating that the on-resonance spectrum for the single crystal in (a) can be regarded as the $f$ pDOS, though normally it reflects the $f$-derived electronic structure which is integrated only for a limited region in the Brillouin zone (BZ). The absence of the strong enhancement just below the $E_F$ region for both samples indicates that the hybridization of Ce $4f$ electrons and the non-$f$ valence states near the $E_F$ is negligible $[44]$. This result suggests that Ce $4f$ electrons hardly contribute to the states near the $E_F$ and therefore give a negligible contribution to the superconductivity. This result is, furthermore, consistent with the recent resonant photoemission result for single-crystal CeO$_{0.5}$F$_{0.5}$BiS$_2$ using 4$d$-$4f$ resonant photoemission $[29]$.

C. Comparison of on-resonant spectra with those for other systems

Comparison of the Ce $4f$ electronic states of CeO$_{1-x}$F$_x$BiS$_2$ with other compounds can give further information on the origin of the physical properties. Figure 3 shows the comparison of the on-resonant spectrum in Fig. 2 with the ones (black solid curves) of polycrystalline CeFeAsO$_{0.85}$F$_{0.15}$, single-crystal CeRhIn$_5$, and single-crystal CeFe$_4$P$_{12}$, which are taken from Refs. $[27, 45]$, and $[46]$, respectively. The energy resolutions used for these spectra have the same order of magnitude $(0.2 \sim 0.3$ eV) as the one in this study. The spectra are normalized to the integrated intensities, and the intensity of the CeFeAsO$_{0.85}$F$_{0.15}$ spectrum is enlarged twice for the sake of clear comparison.

For the single crystal and polycrystalline samples of CeO$_{0.5}$F$_{0.5}$BiS$_2$, the peak positions of the main peaks are 1.38 and 1.34 eV, respectively, and the full widths at half maximum (FWHM) of the main peaks $(\Delta E_{f,1F})$, indicated by arrows) are 0.73 eV and 0.81 eV, respectively. The observed spectral shapes for these two CeO$_{0.5}$F$_{0.5}$BiS$_2$ samples have a flat portion with a low intensity from about 2 to 6 eV added to the main peak at 1.3–1.4 eV. The spectral edges around 6 eV have almost the same energy positions with those of the off-resonant spectra (see Fig. 2).

1. Comparison with CeFe$_4$P$_{12}$ and CeRhIn$_5$

The observed on-resonant spectra for CeO$_{0.5}$F$_{0.5}$BiS$_2$ resemble the one for semiconducting skutterudite CeFe$_4$P$_{12}$ $[46]$, although the binding energy of the main peak for CeFe$_4$P$_{12}$ is smaller (at 0.7 eV) and the width of the flat portion in the higher binding energy region is narrower (from 1.5 to 3 eV). The width of the main peak $(\Delta E_{f,1F} = 0.88$ eV) is slightly broader than the ones for CeO$_{0.5}$F$_{0.5}$BiS$_2$. The reason for the small $f$ derived structure $(f^4)$ near $E_F$ of CeFe$_4$P$_{12}$ was attributed to the existence of hybridization gap at $E_F$ $[46]$. This is not the case for the metallic CeO$_{1-x}$F$_x$BiS$_2$.

For CeRhIn$_5$, which consists of a metallic Ce layer (CeIn$_3$) and a RhIn$_2$ layer $[45]$, the on-resonant spectrum shows a two-peak spectral structure at $E_F$ and 2 eV in binding.
FIG. 3. Comparison of the on-resonance spectra in Fig. 2 with the ones (black solid curves) of polycrystalline CeFeAsO$_{0.89}$F$_{0.11}$, single-crystal CeRhIn$_5$, and single-crystal CeFe$_4$P$_{12}$, which are taken from Refs. [27], [45], and [46], respectively. They are normalized to the integrated intensities, and the CeFeAsO$_{0.89}$F$_{0.11}$ spectrum is enlarged twice for the sake of clarity.

energy, and the total width of the two-peak spectral shape is about 3.1 eV. This feature is clearly different from that of the on-resonant spectra for CeO$_{1-x}$F$_x$. CeRhIn$_5$ is regarded as a metallic system with nearly localized 4\textit{f} and exhibits magnetic ordering at 3.8 K at ambient pressure. The above observation exhibits that the electronic structure of CeO$_{1-x}$F$_x$BiS$_2$ is different from that of a metallic Ce layer system with a localized 4\textit{f} state, though the two compounds have a similar $\gamma$ values: 58.1 mJ/mol K$^2$ for the CeO$_{0.5}$F$_{0.5}$BiS$_2$ polycrystalline sample [11] and 52 mJ/mol K$^2$ for CeRhIn$_5$ [47]. This spectral difference also suggests that the magnetic ordering of CeO$_{1-x}$F$_x$BiS$_2$ may not be due to RKKY interaction.

2. Comparison with CeFeAsO$_{0.89}$F$_{0.11}$

Regarding CeFeAsO$_{0.89}$F$_{0.11}$, it has a more similar crystal structure to that of CeO$_{1-x}$F$_x$BiS$_2$, consisting of CeO$_{1-x}$F$_x$ layers between FeAs layers. In Fig. 4, the spectrum of CeFeAsO$_{0.89}$F$_{0.11}$ has a broad peak around 1.8 eV in binding energy with smaller intensity near $E_F$, suggesting the negligible hybridization between Ce 4\textit{f} and the states near $E_F$. Compared to those of CeO$_{1-x}$F$_x$BiS$_2$, that of CeFeAsO$_{0.89}$F$_{0.11}$ has similar features (a main peak and a flat portion) except that the main peak has a higher binding energy ($\sim$1.7 eV) and the whole spectrum is much broader than those of the CeO$_{1-x}$F$_x$BiS$_2$ samples. The width of the main peak $\Delta E_{4f}$ is 3.1 eV for CeFeAsO$_{0.89}$F$_{0.11}$, and it is about 4 times larger than those of CeO$_{1-x}$F$_x$BiS$_2$ samples. These differences in the on-resonant spectra between the two compounds imply that the hybridization strengths between Ce 4\textit{f} and other valence states are different in the two compounds, and they seem not to be attributed to differences in the local structures, especially a difference in the Ce-O distances between the two compounds and/or a difference between the Ce-S2 and the Ce-As distances as follows (S2 are out-of-plane sulfur atoms in the BiS$_2$ layer).

The Ce $L_3$ edge EXAFS analysis for polycrystalline CeO$_{1-x}$F$_x$BiS$_2$ [17] and the neutron scattering analysis for polycrystalline CeFeAsO$_{1-x}$F$_x$ [8] have revealed that, for nondoped samples, the Ce-O distances in both compounds are 2.34 Å and the Ce-S2(Ce-As) distance is 3.08 Å (3.34 Å). The Ce-O distances are almost the same as the one of CeO$_2$, 2.36 Å.
above, the Ce-S (Ce-As) distance is about 7% (10%) longer than the Ce-S (Ce-As) distance in a rocksalt CeS (CeAs), 2.89 Å (3.04 Å) \[ 49,50\]. These facts suggest that the Ce-O interactions are the same order of magnitude as the Ce-S (Ce-As) distance, which is about 7% (10%) longer than the Ce-S (Ce-As) distance. Here, we can obtain valuable information from the valence electronic structure of the rocksalt CeS and CeAs, that is, the electronic structure of the rocksalt CeS and CeAs. This information is crucial in understanding the Ce-O interactions in the view points of the bond length. Therefore, the bond length difference seems not to be a main factor in the hybridization strength between Ce 4f and other valence states in the two compounds. Furthermore, upon F-doping to CeO1.6F0.4BiS2, the Ce-(O, F) and Ce-S2 distances in the CeO1.6F0.4BiS2 show relatively large increase (+0.15 Å) and decrease (−0.08 Å), respectively, causing a shift and a broadening in the Ce 4f spectrum as discussed later. These changes are, however, small compared with the differences in the on-resonant spectra between CeO1.6F0.4BiS2 and CeFeAs0.89F0.11. Incidentally, the Ce-(O, F) and the Ce-As distances in CeFeAsO0.89F0.11 exhibit just small changes (less than 0.02 Å) under F doping.

It is therefore considered that the other factor, that is, the energy level alignment between the Ce 4f and the S 3p (As 4p), has a more important role in the observed differences between the on-resonant spectra of the two compounds. Here one can obtain valuable information from the valence electronic structure of the rocksalt CeS and CeAs, that is, the Ce 4f states in a rocksalt CeS are mostly separated from both S 3p and Ce 5d bands and reside in the energy gap between them \[ 51\] while the Ce 4f states in a rocksalt CeAs are degenerate energetically with the As 4p band and merge with it to some extent \[ 52\]. This difference between rocksalt CeS and CeAs seems to be a common feature observed between Ce monochalcogenides and monopnictides \[ 51,52\]. Similarly, the degeneracy in energy levels between Ce 4f and S 3p bands in CeO1.6F0.4BiS2 is weak, as shown in Fig. 3 where the overlaps between the main peak of the on-resonant spectra and the off-resonant spectra are small, while the occupied states of Ce 4f in CeFeAs0.89F0.11 are energetically degenerate with a relatively large part of occupied states of As 4p bands as shown by the band calculation and the XES measurements in Ref. \[ 38\]. It is therefore considered that, as a result of the above difference in the energy level alignment features, the interaction between the CeO1.6F0.4F2 and the BiS2 layers in CeO1.6F0.4BiS2 is weaker than that between the CeO1.6F0.4F2 and the FeAs layers in CeFeAs0.89F0.11. This conclusion will be one of the key ingredients to understand the differences in the magnetism and the superconductivity between the two compounds as a whole.

D. F-concentration dependence of the valence band spectra

Finally, we discuss the relation between the structural deformation and the changes in the valence band electronic structure including the Ce 4f states caused by the F doping. As noted above, the Ce L3 edge EXAFS analysis for polycrystalline CeO1.6F0.4BiS2 shows that the F doping of x = 0.7 results in an increase of the Ce-(O,F) distance by 0.15 Å and a decrease of the Ce-S2 distance by 0.08 Å, accompanied with a decrease of the spacing between the adjacent BiS2 layers and atomic disorder in the BiS2 layer \[ 17\]. The x-ray diffraction analysis for CeO1.6F0.4BiS2 single crystals exhibits that crystals with higher F content have a nearly flat Bi-S plane and that the Ce-(O,F) distance decreases from 2.38 to 2.41 Å and the Ce-S2 distance decreases from 3.11 to 3.08 Å under the increase of the F concentration from x = 0.3 to 0.7 \[ 19,24\]. These trends in the local structural deformations for both polycrystalline and single-crystal samples are consistent with each other.

To elucidate the influences of these local structural deformations on the valence electronic structure precisely, we show the F-concentration dependence of the valence band spectra of single crystals in Fig. 4(a), which are measured with photon energy of 1200 eV and angle-integrated for acceptance angle of 11 degrees along the Γ-X line in the BZ centered at the Γ point (about 200% of BZ along Γ-X line). The use of 1200 eV spectra has an advantage that the Ce derived states and O, S derived states show comparable intensities, which makes it easier to analyze the data, as described below. The nominal concentrations of F (x) are 0.3 and 0.7, respectively, which enable us to link the obtained results with the physical properties. The highest peaks in the spectra correspond to the main peaks in the on-resonant spectra, which means that they are mainly derived from the Ce 4f states. In addition, the structures in the higher binding energy region are consistent with the antiresonant spectrum in Fig. 2(a) and attributed to O 2p and S 3p states. The peaks around 9 eV originate from the F 2s. These assignments are also confirmed in the second derivative intensity map of the energy distribution curves of the ARPES spectra measured along the Γ-X direction for x = 0.7 with photon energy of 70 eV, as shown in Fig. 4(b) where the negatively intense signals show the peak positions of the ARPES spectra. The thick arrow indicates the 4f-derived band, which is not observed in the ARPES data measured for LaO0.5F0.4BiS2 [53]. The thin arrow shows the electron pocket band derived mainly from Bi 6p \[ 41,43\].

Under the increase of the F concentration from x = 0.3 to 0.7, the spectrum does not show a complete rigid shift, as seen in Fig. 4(c) (where the spectra are normalized to the integrated intensities). The most intense peak (Ce 4f) shifts by 0.3 eV which corresponds to the shift of the Ce 3d spectrum (see Fig. 1), while the other structures in the higher binding energy region (including S 3p, O 2p, and F 2s) shift by 0.2 eV. The latter shift is almost rigid, suggesting a close relation with the chemical potential shift due to the carrier doping. As a result of the additional shift of the Ce 4f peak (0.3−0.2 = 0.1 eV), the peak-to-peak energy separation between the most and the second most intense peaks (ΔEpp) changes from 1.5 eV to 1.4 eV. Simultaneously, the valence-band width (ΔEVB), which is the energy width of the whole band (including Ce 4f, O 3p, and F 2p) at the half maximum of the higher binding energy edge indicated by arrows, also decreases from 5.6 eV to 5.4 eV. In contrast, the width of the most intense peak (ΔE1f) increases slightly from 0.73 eV to 0.77 eV, which is confirmed by the fitting procedure with Gaussian functions as shown in Fig. 4(a). This small broadening of ΔE1f may related to the increase of the adjacent F atoms which will modify the potential energy on the Ce site, producing the site variation of the 4f states. This site variation may affect also the width and shape of the Ce 3d spectra, although the changes will be expected to be small because of the small changes in ΔE1f. Actually, the Ce 3d spectra in Fig. 1 shows almost the same width with each other. The intensity ratio of
the $f^1$ and $f^2$ components, however, exhibits clear difference as mentioned in Sec. III A. According to the results obtained by the Ce-ligand cluster model calculation [32], this kind of change in the intensity ratio of the $f$ states under the F doping. This increase of the interaction between $p$ and $\Delta E_1$ of the valence bands. These changes are observed as the additional shift of the Ce 4$f$ peak (the decrease of $\Delta E_{pp}$ and the reduction of $\Delta E_{VB}$). Here we present an interpretation which can explain the derivation of these changes in the valence bands as a whole, in the view point of the structural deformation resulting from the increase of the F concentration; the increase of the Ce-(O, F) distance upon F doping weakens the interaction between Ce 4$f$ and O 2$p$ states, and it causes a decrease of the energy separation of bonding and antibonding states consisting of them, leading to the decreases of the $\Delta E_{pp}$ and $\Delta E_{VB}$. The decrease of the $\Delta E_{pp}$ then, enhances the interaction between Ce 4$f$ and S 3$p$ states together with the decrease of the Ce-S2 distance under the F doping. This increase of the interaction between Ce 4$f$ and S 3$p$ states possibly results in just a slight increase of the $\Delta E_{4f}$ as observed, since the interaction between Ce 4$f$ and S 3$p$ states is relatively weak due to the 7% longer Ce-S distance than that of a rocksalt CeS. These F-concentration dependencies of the valence bands are depicted schematically in Fig. 5. It should be noted here that the observed increases of the degeneracy in energy levels and of the interaction between Ce 4$f$ and S 3$p$ states strongly support the interpretation that the Ce-S2-Ce superexchange interaction between Ce$^{3+}$ sites is responsible for the emergence of the magnetic ordering in the CeO$_{1-x}$F$_x$ layer, explaining the absence ($x = 0.3$) and presence ($x = 0.7$) of the magnetic ordering [16,17,22]. In addition, the Ce 4$f$ peak shifting from the $E_F$ under F doping suggests that the magnetic ordering and the superconductivity are disconnected in this system. We hope that the present results motivate further theoretical investigation to confirm this scenario for the magnetic ordering and the superconductivity.

IV. CONCLUSIONS

We have performed Ce 3$d$ core level SX-PES, Ce $M_{4,5}$ edge XAS, and Ce 3$d$-4$f$ resonant SX-PES to study electronic structure of Ce 4$f$ electrons for CeO$_{1-x}$F$_x$BiS$_2$ polycrystalline ($x = 0.0$ and 0.7) and single-crystal samples ($x = 0.3$ and 0.7). The Ce 3$d$ spectrum of the single crystal of $x = 0.7$ has no $f^0$ component and the spectral shape closely resembles the ones observed for Ce trivalent insulating compounds, strongly implying that the CeO layer is still in an insulating state even after the F doping. From 3$d$-4$f$ resonant SX-PES, negligible Ce 4$f$ contribution to states at $E_F$ is observed, indicating that Ce 4$f$ plays a minor role in metallic/superconducting properties. The very different spectral shape of CeO$_{1-x}$F$_x$BiS$_2$ compared to that of a Ce compound having localized Ce 4$f$ and exhibiting magnetism suggests that the origin of the magnetic ordering in CeO$_{1-x}$F$_x$BiS$_2$ may not be due to RKKY interaction. The comparison of the on-resonant spectra with the one for CeFeAsO$_{0.39}$F$_{0.11}$ shows that the interaction between the CeO$_{1-x}$F$_x$ and the BiS$_2$ layers in CeO$_{1-x}$F$_x$BiS$_2$ is weaker than that between the CeO$_{1-x}$F$_x$ and the FeAs layers in CeFeAsO$_{0.39}$F$_{0.11}$. The F-concentration dependence of the valence band spectra of single crystals ($x = 0.3$ and 0.7) shows the increases of the degeneracy in energy levels and of the interaction between Ce 4$f$ and S 3$p$ states under F doping, which strongly support the interpretation that the Ce-S2-Ce superexchange interaction between Ce$^{3+}$ sites is responsible for the emergence of the magnetic ordering in the CeO$_{1-x}$F$_x$ layer. These results give insight into the nature of the CeO$_{1-x}$F$_x$ layer and the microscopic coexistence of magnetism and superconductivity in CeO$_{1-x}$F$_x$BiS$_2$.

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In general, there is a possibility that one can observe different resonant behaviors for the different final states. For Ce compounds classified into a Kondo system, however, the Kondo effects are not observed at the several photon energies (not shown).

We have observed the maximum intensity for the spectrum measured at the $3d$ state of the main structure of the Ce $5f$ edge XAS spectrum, since both of the intermediate states of the Kondo resonance peak and the final state of the main structure of the Ce $5f$ edge XAS spectrum are classified into a Kondo system. However, the Kondo effects are not observed at the several photon energies (not shown). To see the presence or absence of a Kondo resonance, it is important to measure the spectrum at the photon energy of the maximum resonance enhancement. We have observed the maximum intensity for the spectrum measured at the photon energy $B$ among the resonance spectra measured at several photon energies (not shown).

In general, there is a possibility that one can observe different resonant behaviors for the different final states. For Ce compounds classified into a Kondo system, however, the Kondo resonance peak of the Ce $4f$ state is observed with the maximum intensity at the photon energy corresponding to one of the main peaks in their Ce $M_5$ edge XAS spectrum, since both of the intermediate states of the Kondo resonance peak and the final state of the main structure of the Ce $M_5$ edge XAS spectrum are classified into a Kondo system. To see the presence or absence of a Kondo resonance, it is important to measure the spectrum at the photon energy of the maximum resonance enhancement. We have observed the maximum intensity for the spectrum measured at the photon energy $B$ among the resonance spectra measured at several photon energies (not shown).

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