Role of the Ce valence in the coexistence of superconductivity and ferromagnetism of CeO$_{1-x}$F$_x$BiS$_2$ revealed by Ce L$_3$-edge x-ray absorption spectroscopy

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We have performed Ce L$_3$-edge x-ray absorption spectroscopy (XAS) measurements on CeO$_{1-x}$F$_x$BiS$_2$, in which the superconductivity of the BiS$_2$ layer and the ferromagnetism of the CeO$_{1-x}$F$_x$ layer are induced by the F-doping, in order to investigate the impact of the F-doping on the local electronic and lattice structures. The Ce L$_3$-edge XAS spectrum of CeOBiS$_2$ exhibits coexistence of 4f$^1$ (Ce$^{3+}$) and 4f$^0$ (Ce$^{4+}$) state transitions revealing Ce mixed valency in this system. The spectral weight of the 4f$^0$ state decreases with the F-doping and completely disappears for $x > 0.4$ where the system shows the superconductivity and the ferromagnetism. The results suggest that suppression of Ce-S-Bi coupling channel by the F-doping appears to drive the system from the valence fluctuation regime to the Kondo-like regime, leading to the coexistence of the superconducting BiS$_2$ layer and the ferromagnetic CeO$_{1-x}$F$_x$ layer.

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Since the discovery of the high-$T_c$ superconductivity in the layered Fe pnictides,$^1$ tremendous research efforts have been dedicated to explore new superconductors in various pnictides and chalcogenides with layered structures. Very recently, a new family of superconductors with the BiS$_2$ layer has been discovered by Mizuguchi et al.$^2$ and the discovery followed by the extensive research activities on the related systems including REO$_{1-x}$F$_x$BiS$_2$ (RE = rare-earth elements) with the BiS$_2$ layer.$^3,17$ In the REO$_{1-x}$F$_x$BiS$_2$, the electronically active BiS$_2$ layers are separated by the REO spacers, and the band filling and the superconductivity of the BiS$_2$ layer can be controlled by the F-doping in the REO spacers. The maximum $T_c$ of 10.5 K has been achieved in LaO$_{1-x}$F$_x$BiS$_2$ synthesized by high pressure annealing$^6$ whereas that synthesized at ambient pressure tends to be non-superconducting. In addition, high pressure studies on optimally doped LaO$_{0.5}$F$_{0.5}$BiS$_2$ (synthesized at ambient pressure) have revealed that $T_c$ increases up to the maximum value of 10.1 K at 1-2 GPa followed by a gradual decrease with increasing pressure.$^{18-20}$ These experiments indicate that the superconductivity in BiS$_2$-based superconductors is highly sensitive to the local atomic displacements.

While various BiS$_2$-based systems have been synthesized with different spacer layers, the particular case of CeO$_{1-x}$F$_x$BiS$_2$ with coexistence of superconductivity and ferromagnetism at low temperature is interesting.$^2,21$ In fact, CeO$_{1-x}$F$_x$BiS$_2$ shows superconductivity and ferromagnetism with a maximum $T_c$ of 6 K. While BiS$_2$-based superconductors have been considered as conventional superconductors with electron-phonon coupling, the coexistence of superconductivity and ferromagnetism provokes further studies to understand interaction of different electronic degrees of freedom and the role of spacer layers in these materials. In addition, the ferromagnetism and the superconductivity are enhanced in the samples synthesized by high pressure annealing, indicating high sensitivity to the local atomic displacements.

Ce L$_3$ x-ray absorption spectroscopy (XAS) is a direct probe of the local structure around a selected absorbing atom and distribution of the valence electrons, with the final states in the continuum being due to multiple scattering resonances of the photoelectron in a finite cluster.$^{22}$ In this work, we have exploited Ce L$_3$ XAS to investigate the impact of the F-doping on the electronic and lattice structures of CeO$_{1-x}$F$_x$BiS$_2$ system synthesized differently, i.e. as grown (AG) and high pressure (HP) annealed. Since it is difficult to prepare clean surfaces using the available polycrystalline CeO$_{1-x}$F$_x$BiS$_2$ samples, the bulk-sensitive Ce L$_3$-edge XAS taken in the transmission mode is the most reliable tool to evaluate the Ce valence. The Ce L$_3$-edge XAS spectrum of CeOBiS$_2$ exhibits the transitions to the 4f$^1$ and 4f$^0$ final states, indicating the Ce$^{3+}$/Ce$^{4+}$ valence fluctuation that should be related with the Ce-S-Bi coupling channel. Namely, the Ce$^{3+}$ (4f$^1$) and Ce$^{4+}$ (4f$^0$) states are mixed in the ground state due to the hybridization between the Ce 4f orbitals and the Bi 6p conduction band. The spectral weight of the 4f$^0$ states
decreases with the F-doping and disappears completely for \( x > 0.4 \) where the system shows the coexistence of the superconductivity and ferromagnetism at low temperature. The F-doping is expected to break the Ce-S-Bi coupling channel and induce crossover from the valence fluctuation regime to the Kondo-like regime.

Ce \( L_3 \)-edge XAS measurements were performed on polycrystalline samples of CeO\(_{1-x}F_x\)BiS\(_2\) prepared by the solid-state reaction method. Both AG and HP annealed samples were used for the measurements. All the samples were well characterized for their transport and average structural properties prior to the absorption measurements. Details on the sample preparation and characterization are given elsewhere.\(^{21}\) The X-ray absorption experiments were performed at the XAFS beamline of the Elettra Synchrotron Radiation Facility, Trieste, where the synchrotron radiation emitted by a bending magnet source was monochromatized using a double crystal Si(111) monochromator. The measurements were taken at room temperature in transmission mode using three ionization chambers mounted in series for simultaneous measurements on the sample and a reference. As a routine experimental approach, several absorption scans were collected on each sample to ensure the reproducibility of the spectra, in addition to the high signal to noise ratio.

Figure 1 displays the Ce \( L_3 \)-edge XAS spectra of AG (Fig. 1 (a)) and HP (Fig. 1 (b)) CeO\(_{1-x}F_x\)BiS\(_2\) \(( x = 0.0, 0.2, 0.4, 0.6, 0.8, \) and \( 1.0 \)). The spectra are normalized with respect to the atomic absorption estimated by a linear fit to the high energy part of the spectra. Three main structures around 5725 eV, 5737 eV, and 5758 eV can be identified on the Ce \( L_3 \)-edge XAS spectra. The first peak around 5725 eV is the absorption white line corresponding to the transition from the Ce 2\( p \) core level to the vacant Ce 5d state mixed with the Ce 4f\(^1\) final state.\(^{23-26} \) On the other hand, the second peak around 5737 eV corresponds to the transition from the Ce 2p core level to the vacant Ce 5d state mixed with the Ce 4f\(^0\) final state. The 4f\(^1\) and 4f\(^0\) final states are the so-called well-screened and poorly-screened states and provide information on the Ce valence states. Presence of both 4f\(^1\) and 4f\(^0\) states suggest the Ce\(^{3+}\)/Ce\(^{4+}\) valence fluctuation. On the other hand, the energy difference between the 4f\(^1\) and 4f\(^0\) absorption peaks, which is approximately 12 eV\(^{23-25} \) is mainly determined by the Ce 2p - Ce 4f Coulomb interaction and is expected to be independent of the F-doping. One can see a systematic change due to the F-doping in the 4f\(^1\) and 4f\(^0\) peak intensity. The third peak around 5758 eV includes the information on the local lattice structures. This peak is so-called continuum resonance (CR), likely to be due to Ce-Bi scattering with a contribution from the Ce-Ce scattering, reflecting evolution of the Ce-Bi/Ce bond length. In addition, there is a weak feature around 5742 eV. This feature is a characteristic feature of layered rare-earth systems, and its intensity is generally sensitive to the O/F atom order/disorder in the CeO/F layer.

In order to qualify the electronic states, we have estimated the spectral weight of 4f\(^1\) and 4f\(^0\) absorption peaks using the following procedure. A constant background estimated by an arctangent function was subtracted from the XAS spectra (inset of Fig. 1). The background-subtracted spectra were fitted by Gaussian functions, reproducing all the main peaks, i.e., 4f\(^1\) + 4f\(^0\) as shown in Fig. 2. As for the 4f\(^1\) peak, we utilized three Gaussian functions to reproduce the asymmetric line shape, while a symmetric Gaussian function was enough to describe the 4f\(^0\) peak. The 4f\(^0\) peak is found to decrease monotonically with the F-doping. The fit of the weak peak (peak around 5742 eV, characteristic feature of layered structures) is fixed for all the fits since this feature is independent of the F-doping. The weak peak was used in the fit in order to ensure the proper area estimation of the 4f\(^0\) peak. The CR was not considered in the fit. The fit for all the samples are shown along with the experimental results.

The intensity of the main peaks 4f\(^1\) + 4f\(^0\) depends on the amount of additional background from the grain boundaries and the hybridization between the Ce 4f and Ce 5d orbitals which can be changed by the F-doping and
FIG. 2. (Color online) Multi-curve fitting results on Ce $L_3$-edge XAS spectra in CeO$_{1-x}$F$_x$BiS$_2$ with (a) $x$ = 0.0, (b) $x$ = 0.2, (c) $x$ = 0.4, (d) $x$ = 0.6, (e) $x$ = 0.8, and (f) $x$ = 1.0. The experimental data of AG and HP are shown as triangles and circles, respectively. The fitted results are shown by solid lines on the HP and AG experimental data. Each component of the fitting lines is shown only for the HP experimental data. The tiny peak around 5742 eV is fixed for all the cases from (a) to (f).

FIG. 3. (Color online) The relative spectral weight of $4f^0$ states for both AG and HP samples.

FIG. 4. (Color online) (a) The crystal structure of CeO$_{1-x}$F$_x$BiS$_2$. The dashed box represents the unit cell. (b) The local structure of CeO$_{1-x}$F$_x$BiS$_2$ for $x < 0.4$ and (c) for $x > 0.4$. The bond length of Ce-S$_2$ decreases and that of Bi-S$_2$ increases when $x > 0.4$ as depicted.

The experimental data of AG and HP are shown as triangles and circles, respectively. The fitted results are shown by solid lines on the HP and AG experimental data. Each component of the fitting lines is shown only for the HP experimental data. The tiny peak around 5742 eV is fixed for all the cases from (a) to (f).

The high pressure synthesis. Therefore, we employ the relative spectral weight $4f^0/[4f^1 + 4f^0]$, which is obtained by integrating the Gauss functions and is shown in Fig. 3, in order to discuss the Ce valence. The relatively large $4f^0/[4f^1 + 4f^0]$ value in CeOBiS$_2$ indicates that the Ce$^{4+}$ state with $4f^0$ electronic configuration is coexisting with the Ce$^{3+}$ state with $4f^1$ electronic configuration. The existence of the $4f^0$ peak, namely, the valence fluctuation between the Ce$^{3+}$ and Ce$^{4+}$ states in CeOBiS$_2$ is in sharp contrast to the pure Ce$^{3+}$ state in iron-based CeOFeAs pnictides. The $4f^0/[4f^1 + 4f^0]$ value decreases with the F-doping both in the AG and HP samples. The $4f^0/[4f^1 + 4f^0]$ value of the AG sample is slightly larger than the HP sample at $x$=0.6, which is located between the Ce$^{3+}$/Ce$^{4+}$ valence fluctuation regime and the Ce$^{3+}$ Kondo-like regime. The small $4f^0/[4f^1 + 4f^0]$ value at $x$=0.6 in the HP sample would be consistent with the fact that the superconductivity and ferromagnetism tend to be enhanced in the HP samples. However, the difference in $4f^0/[4f^1 + 4f^0]$ is very subtle, suggesting that some additional factors such as inhomogeneity play important role in the difference between the AG and HP samples.

Recalling the atomic structure, the layered structure of CeOBiS$_2$ contains BiS$_2$ layer intercalated with CeO layer. The in-plane S atoms in the BiS$_2$ layer (S1 as in Fig. 4(a)) are located at a distance of about 2.8 Å from Bi atoms while the out-of-plane S (S2 as in Fig. 4(a)) atom linking the spacer layer with the BiS$_2$ plane is located at a distance of about 2.6 Å. By the F-substitution, the Bi-S2 distance increases ($\Delta R_{\text{max}} \sim 0.12\text{Å}$) while
the Ce$^{4+}$ ferromagnetism. Therefore, instead of the direct Ce-Ce exchange interaction, the Ce-S-Ce superexchange interaction as in Fig. 4 (c) between Ce$^{3+}$ sites is expected to be responsible for the ferromagnetism of the CeO$_{1-x}$F$_x$ layer. For $x > 0.4$, the ferromagnetic CeO$_{1-x}$F$_x$ layer is expected to be insulating just like the LaO$_{1-x}$F$_x$ layer, and is decoupled from the superconducting BiS$_2$ layer.

Above arguments are consistent with the structural changes observed in the same experiment through the CR peak. The CR peak is due to the Ce-Bi scattering with a contribution from the Ce-Ce. Fig. 5 shows a zoom over of the CR peak for the two series of CeO$_{1-x}$F$_x$BiS$_2$ samples, with the peak position evolving with the F-doping. The decrease of energy separation between the white line and the CR peak suggests that the Ce-Bi distance is getting elongated following the empirical rule for the CR ($\Delta E \propto 1/d^2$). The elongation of the Ce-Bi bond length would contribute to the reduction of the Ce-Bi coupling through Ce-S-Bi channel. Namely, the hybridization between the Ce 4f orbital and the Bi 6p conduction band decreases with the F-doping and the Ce$^{3+}$/Ce$^{4+}$ valence fluctuation is suppressed. This is consistent with the decrease of the 4f$^0/[4f^1+4f^0]$ value by the F-doping.

In conclusion, the Ce L$_3$-edge XAS results on CeO$_{1-x}$F$_x$BiS$_2$ shows that the superconductivity and ferromagnetism are suppressed for $x < 0.4$ in the valence fluctuation regime evidenced by the 4f$^1$ and 4f$^0$ states. The peak position of the CR depends on the F-doping and indicates the Ce-Bi bond length increases with the F-doping. The present experimental results show that CeOBiS$_2$ has the Ce$^{3+}$/Ce$^{4+}$ valence fluctuation due to the Ce-Bi coupling through Ce-S-Bi channel and that the superconductivity of the BiS$_2$ layer tends to be suppressed by the Ce-Bi coupling. The Ce-S-Bi coupling channel is broken by the F-doping. Consequently, the system undergoes a crossover from the valence fluctuation regime for $x < 0.4$ to the Kondo-like regime for $x > 0.4$ in which superconducting BiS$_2$ layer and the ferromagnetic CeO$_{1-x}$F$_x$ layer are decoupled and hence coexist. The results provide important information on the role of Ce valence in the coexisting superconductivity and ferromagnetism in the CeO$_{1-x}$F$_x$BiS$_2$ system.

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1. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
2. Y. Mizuguchi, H. Fujihisa, Y. Gotoh, et al., Phys. Rev. B 86, 220510(R) (2012).
3. S. K. Singh, A. Kumar, B. Gahtori, et al., J. Am. Chem. Soc. 134, 16504 (2012).
