Role of valence changes and nanoscale atomic displacements in BiS$_2$-based superconductors

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Superconductivity within layered crystal structures has attracted sustained interest among condensed matter community, primarily due to their exotic superconducting properties. EuBiS$_2$F is a newly discovered member in the BiS$_2$-based superconducting family, which shows superconductivity at 0.3 K without extrinsic doping. With 50 at.% Ce substitution for Eu, superconductivity is enhanced with $T_c$ increased up to 2.2 K. However, the mechanisms for the $T_c$ enhancement have not yet been elucidated. In this study, the Ce-doping effect on the self-electron-doped superconductor EuBiS$_2$F was investigated by X-ray absorption spectroscopy (XAS). We have established a relationship between Ce-doping and the $T_c$ enhancement in terms of Eu valence changes and nanoscale atomic displacements. The new finding sheds light on the interplay among superconductivity, charge and local structure in BiS$_2$-based superconductors.

Superconductivity in quasi-two-dimensional crystal structures has attracted sustained interest in the past decades. The most outstanding examples include high-$T_c$ cuprates with CuO$_2$ superconducting layers and Fe-based superconductors with a Fe-square lattice. Very recently, superconductivity of BiS$_2$-based compounds which have similar layered crystal structure as those of cuprates and Fe-based materials has been reported. The first member of the BiS$_2$-based superconducting family is Bi$_2$O$_2$S$_3$, with a $T_c$ of 8.6 K. It was found that the characteristic BiS$_2$ layers are responsible for the superconductivity. So far, several ReBiS$_2$O$_{1-x}$F$_x$ (Re = La, Ce, Pr and Nd) and doped SrBiS$_2$F superconductors have been discovered with the highest $T_c$ of 10.6 K. Band structure calculations indicate that the undoped parent compounds such as LaBiS$_2$O and SrBiS$_2$F are insulators with an energy gap of 0.82 and 0.80 eV, respectively. Upon electron doping, both compounds exhibit metallic conducting behavior and a superconducting transition at low temperatures. On the other hand, recent works demonstrate that the isostructural compounds EuBiS$_2$F and Eu$_3$Bi$_2$S$_4$F$_4$ are metallic, and they even exhibit superconductivity without extrinsic doping, at temperatures below 0.3 K and 1.5 K respectively. It was suggested that the Eu valence is essentially divalent in Ce-doped system. On the contrary, the average Eu valence with respect to the parent compound increases with the Se doping in Eu$_3$Bi$_2$S$_6$Se$_2$F$_8$ which has the highest $T_c$ of 3.35 K. How the Eu valence changes and its consequence on superconductivity in the parent and doped BiS$_2$-based superconductors still remain unresolved.

Moreover, one of the important problems in the layered systems is the inter- and intra-layer interactions. Similar to Fe-based superconductors, the interactions between superconducting BiS$_2$ layers and blocking layers can be revealed via the nanoscale atomic displacements. Hence, in order to understand the origin of superconductivity, it is critical to investigate the Eu valence and the local atomic displacements in the parent and doped Eu-containing BiS$_2$-based superconductors.

The X-ray absorption spectroscopy (XAS), consisting of the X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy, is an ideal technique to retrieve...
the substantial information of both valence transition and nanoscale atomic displacements, thus XAS has been widely applied in physics and chemistry\textsuperscript{19–21}. For example, based on the “fingerprint effect”, Eu \( L_3 \)-edge XANES for Eu\textsubscript{Fe\textsubscript{2}}As\textsubscript{2} presents the visually experimental evidence for the pressure-induced valence changes of Eu ions\textsuperscript{22}. In addition, Bi \( L_3 \)-edge EXAFS were performed to probe the local atomic structure of Bi\textsubscript{S\textsubscript{2}}-based systems\textsuperscript{18}. In this contribution, we investigated the local structure of EuBi\textsubscript{S\textsubscript{2}}F-based system as a function of Ce-doping by XAS, providing the atomic site-selective information of valence changes and nanoscale atomic displacements.

**Results**

**Role of Eu valence changes in the parent and Ce-doped EuBi\textsubscript{S\textsubscript{2}}F.** For the Eu-containing superconductors, detailed investigations of the Eu valence change may provide valuable information on the electronic structure, which is fundamental for a better understanding of their superconductivity\textsuperscript{22,23}. Figure 1a shows normalized Eu \( L_3 \)-edge XANES data for EuBi\textsubscript{S\textsubscript{2}}F and Eu\textsubscript{0.5}Ce\textsubscript{0.5}Bi\textsubscript{S\textsubscript{2}}F. The main peak (6975 eV) and the other feature (6983 eV) in the Fig. 1a are associated respectively to Eu\textsuperscript{2+}(4f\textsuperscript{7}) and Eu\textsuperscript{3+}(4f\textsuperscript{6})\textsuperscript{22}.

Now we determine quantitatively the valence of Eu for the parent and Ce-doped EuBi\textsubscript{S\textsubscript{2}}F by fitting the XANES spectra to an arctangent step function and a Lorentzian peak for each valence state. The mean valence was determined by using a widely used method\textsuperscript{24,25}:

\[
v = 2 + \frac{I^{2+}}{I^{2+} + I^{3+}}
\]

where \( I^{2+} \) and \( I^{3+} \) is integrated intensity of peaks corresponding to Eu\textsuperscript{2+} and Eu\textsuperscript{3+} on XANES spectrum. Based on the best curve fit in Fig. 1, we estimated the mean valence of Eu ions in EuBi\textsubscript{S\textsubscript{2}}F and Eu\textsubscript{0.5}Ce\textsubscript{0.5}Bi\textsubscript{S\textsubscript{2}}F. The main peak (6975 eV) and the other feature (6983 eV) in the Fig. 1a are associated respectively to Eu\textsuperscript{2+}(4f\textsuperscript{7}) and Eu\textsuperscript{3+}(4f\textsuperscript{6})\textsuperscript{22}.

In Fig. 1 we focus on the normalized Ce \( L_3 \)-edge XANES data for Eu\textsubscript{0.5}Ce\textsubscript{0.5}Bi\textsubscript{S\textsubscript{2}}F, in which three main structures A, B and C can be identified. The first peak A around 5728 eV is associated to the transition from the Ce 2p core level to the vacant Ce 5d state mixed with the Ce 4f\textsuperscript{1} final state, i.e. Ce\textsuperscript{4+} state\textsuperscript{26}. On the other hand, the weak feature B around 5745 eV is a characteristic feature of layered rare-earth systems\textsuperscript{26}, and its intensity is generally sensitive to the F atom order/disorder in the Eu/CeF layers. The third peak C is the so-called continuum resonance, providing the information on the local lattice structures. It should be noted that the energy difference between
the characteristic Ce$^{3+}$ (4$f^1$) and Ce$^{4+}$ (4$f^0$) absorption peaks is approximately 12 eV, which is independent and is mainly determined by the Ce 2p-4f Coulomb interaction. But in Fig. 2 we found no obvious evidence of Ce$^{4+}$ feature around 5740 eV, demonstrating that the Ce valence in the Eu$_{0.5}$Ce$_{0.5}$BiS$_2$F sample is essentially trivalent. Considering the valence of Eu, 50 at.% Ce-doping could cause an increment of mean valence for Eu/Ce ions, which increases from +2.16 of parent EuBiS$_2$F to +2.53 of Ce-doped system. Consequently, additional 17% charges were induced upon Ce-doping in EuBiS$_2$F, which is believed to be crucial for the superconductivity enhancement.

**Nanoscale atomic displacements in EuBiS$_2$F and Eu$_{0.5}$Ce$_{0.5}$BiS$_2$F.** As is well known, material properties are in a close relationship with its nanoscale atomic structure. Analogous to cuprates and Fe-based superconductors, Ce impurity could alter the local atomic displacements of both blocking layers and BiS$_2$ superconducting layers. Therefore, to gain an insight into the atomic displacements induced by Ce-doping, we have undertaken detailed structural study by means of Eu and Bi $L_3$-edge EXAFS measurements. Figures 3 and 4 display the Fourier transform (FT) magnitudes of the EXAFS oscillations providing real space information at Eu and Bi $L_3$-edge, respectively. We have to underline that the positions of the peaks in the FT are shifted a few tenths of Å from the actual interatomic distances because of the EXAFS phase shift. In the BiS$_2$ layer the in-plane and out-of-plane S atoms are denoted as S1 and S2, respectively. The Eu atom is coordinated with four nearest F atoms at ~2.52 Å and four S2 atoms at ~3.04 Å. Therefore, the broad structure ($R = 1.5$–3.0 Å) in the FT of Eu $L_3$-edge EXAFS corresponds to the contributions of Eu-F and Eu-S2 bonds. On the other hand, the near-neighbor of Bi atoms are one out-of-plane S2 atom at ~2.50 Å and four in-plane S1 atoms at ~2.87 Å. Therefore, the broad structure ($R = 1.4$–2.6 Å) in Fig. 4 contains information on the Bi-S2 and Bi-S1 bonds. Obviously, large changes in the FTs of both Eu and Bi $L_3$-edge can be seen with Ce-doping, indicating the atomic displacements in blocking layers and also in the electronically active BiS$_2$ layers.

The EXAFS amplitude depends on several factors and is given by the following general equation:

$$
\text{Amplitude} = \sum \frac{\sigma^2}{\sigma^2 + R^2}
$$
where $N_j$ is the number of neighboring atoms at a distance $R_j$, $S_0^2$ is the passive electron reduction factor, $f_j(k, R_j)$ is the backscattering amplitude, $\lambda$ is the photoelectron mean free path, $\delta_j(k)$ is the phase shift and $\sigma_j^2$ is the correlated Debye-Waller factor.

In order to obtain quantitative results, we firstly fit the peaks of EXAFS spectra at Eu $L_3$-edge involving contributions of four Eu-F and four Eu-S$_2$ bonds, which were isolated from the FTs with a rectangular window. The range in $k$ space was 3–12 Å$^{-1}$ and that in $R$ space was 1.5–3.0 Å. Considering the absorption energy at Eu $L_3$ (6977 eV) and $L_2$-edge (7617 eV), the maximum wave-vector $k$ for Eu $L_3$-edge EXAFS is up to 12 Å$^{-1}$. The spatial resolution $\Delta = \pi R_{k_{\text{max}}}/2$ is about 0.13 Å with the $k_{\text{max}}$ = 12 Å$^{-1}$, which is sufficient to distinguish between Eu-F and Eu-S$_2$ bonds. For the least-squares fits, average structure measured by diffraction on EuBiS$_2$F system$^{13}$ is used as the starting model. The backscattering amplitudes and phase shift were calculated using the FEFF code$^{29}$. Only the radial distances $R_j$ and the corresponding $\sigma_j^2$ were allowed to vary, with coordination numbers $N_j$ fixed to the nominal values. The passive electrons reduction factor $S_0^2$ and photoelectron energy zero $E_0$ were also fixed after fit trials on different scans. The best values for the $S_0^2$ were found to be 0.9 and fixed to this value for all the shells. The number of independent parameters which could be determined by EXAFS is limited by the number of the independent data points $N_{\text{ind}}$=($2\Delta k\Delta R$)/$\pi$, where $\Delta k$ and $\Delta R$ are respectively the ranges of the fit in the $k$ and $R$ space$^{28}$. In our case, $N_{\text{ind}}$ is 8 ($\Delta k$=9 Å$^{-1}$, $\Delta R$=1.5 Å), sufficient to obtain all parameters.

As shown in Table 1, upon Ce-doping the distance of Eu-S$_2$ bond is essentially unchanged within the errors, while the Eu-F distance becomes slightly elongated from 2.51(1) Å to 2.54(1) Å, suggesting a thicker EuF layer induced by Ce-doping.
which were isolated from the FTs with a rectangular window. The range in k-space was 3~15 Å

together, the anomalously large diffraction thermal factor of in-plane S1 atom33. Upon Ce-doping, the

valence information retrieved from our XANES data.

using XAS measurements. First of all, the valence of Eu ions in EuBiS2F is estimated to be about

displacements can be revealed by Eu and Bi

L3

+2.05(1) and that of Ce ions are essentially trivalent. The main effect of Ce-doping is to provide

strating the self-electron-doping nature without any extrinsic doping. Upon 50 at.% Ce-doping, the mean valence

using the IFEFFIT program package34.

were collected with several scans in transmission mode at room temperature. Data reduction was performed

result in an increase of

T

value are

+2.05(1) and that of Ce ions are essentially trivalent. The main effect of Ce-doping is to provide

strating the self-electron-doping nature without any extrinsic doping. Upon 50 at.% Ce-doping, the mean valence

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Acknowledgements

This work was partly supported by the National Natural Science Foundation of China (NSFC 11405089 and U1532128), the Natural Science Foundation of Jiangsu Province of China (No. BK20130855), the “Six Talents Peak” Foundation of Jiangsu Province (2014-XCL-015), the Nanotechnology Foundation of Suzhou Bureau of Science and Technology (ZXG201444) and the Scientific Research Foundation of Nanjing University of Posts and Telecommunications (NY213053).

Author Contributions

J.C. performed the experiment and analyzed the data. Y.W. and W.X. provided the support for the data collection and analysis. G.H.C and H.F.Z. provided the samples and discussed the results. J.C. and S.L.L. wrote the paper. All of the authors reviewed on the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Cheng, J. et al. Role of valence changes and nanoscale atomic displacements in BiS₂-based superconductors. Sci. Rep. 6, 37394; doi: 10.1038/srep37394 (2016).

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