Anderson’s impurity-model analysis on CeO$_{1-x}$F$_x$BiS$_2$

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Abstract. We have investigated the impact of F-doing on CeO$_{1-x}$F$_x$BiS$_2$ in terms of the electronic-structural parameters of Anderson’s impurity-model analysis. It was recently reported using Ce $L_3$-edge x-ray absorption spectroscopy (XAS) that CeOBiS$_2$ falls in the Ce valence fluctuation regime and the F-doping drives the system into the Kondo regime. The Ce $L_3$-edge XAS spectra with the various F-doping levels can be reproduced by adjusting the transfer integral in the Anderson’s impurity model. The present analysis indicates that the F-doping to the system corresponds to the decrease of the Ce-Bi transfer integral.

1. Introduction

A superconductor with BiS$_2$ layers has been recently discovered by Mizuguchi et al. [1], and this discovery was followed by active related researches on this new family of superconductors including REO$_{1-x}$F$_x$BiS$_2$ (RE = rare-earth elements) with the BiS$_2$ layers [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. In the REO$_{1-x}$F$_x$BiS$_2$ system, the REO spacer layers partition the electronically active BiS$_2$ layers as illustrated in Fig. 1(a), and the band filling and the superconductivity of the BiS$_2$ layer can be controlled by the F-doping in the REO spacers.

A variety of BiS$_2$-based systems have been synthesized with various spacer layers. Among them, CeO$_{1-x}$F$_x$BiS$_2$ exhibits coexistence of superconductivity and ferromagnetism at low temperature [15] and has been attracting great interest. Moreover, the Ce valence fluctuation in the CeOBiS$_2$ has lately been reported using Ce $L_3$-edge x-ray absorption spectroscopy (XAS) [16]. This XAS study has also revealed the impact of the F-doping on the system; decreasing the Ce valence fluctuation and inducing coexistence of superconductivity and ferromagnetism. In order to understand the interesting interplay between the superconductivity in the BiS$_2$ layer and the ferromagnetism in the CeO layer, one should study the interlayer electronic interaction between the Ce 4f electrons and the Bi 6p conduction electrons. Such information
Figure 1. (Color online) (a) Side view of the crystal structure of CeO$_{1-x}$F$_x$BiS$_2$. The dotted rectangular denotes the unit cell. (b) Ce-S-Bi hopping channel in CeO$_{1-x}$F$_x$BiS$_2$. The local-structural study [21] has revealed that the positions of Ce, S, and Bi move to the directions denoted by the arrows with the F-doping. When the doping amount $x$ reaches more than 0.4, the Ce-S-Bi hybridization is reduced by the increase of the Bi-S bond length.

can be obtained by analyzing the Ce L$_3$-edge XAS spectra. In this context, it is interesting and important to investigate the effects of the F-doping on the XAS spectra in terms of the electronic-structural parameters of the Anderson’s impurity model in order to have a deeper understanding of the system. We have therefore applied Anderson’s impurity-model calculation on this Ce L$_3$-edge XAS results of the CeO$_{1-x}$F$_x$BiS$_2$ system.

In addition to the band filling control by the F-doping, the $T_c$ of REO$_{1-x}$F$_x$BiS$_2$ depends on high pressure annealing. For example, maximum $T_c$ of 10.5 K has been achieved in LaO$_{1-x}$F$_x$BiS$_2$ synthesized by the high pressure annealing [5], suggesting that the F-doping introduces local lattice distortions in the BiS$_2$ and REO layers.

2. Model for the calculation

The model Hamiltonian is given by the standard Anderson Hamiltonian including the Ce 4$f$ electrons, the conduction-band electrons, and the Ce 2$p$ core-level electrons as below.

$$
\mathcal{H}_A = \sum_k \varepsilon_k c_k^+c_k + \varepsilon_f \sum_m f_m^+ f_m + U f \sum_{m'>m} f_{m'}^+ f_{m'} f_m^+ f_m + n_c \varepsilon_c + (1 - n_c)Q f \sum_m f_m^+ f_m + \sum_{m,k} (V_{mk} c_k^+ f_m + V_{mk}^* f_m^+ c_k) 
$$

(1)

Here, $f_m^+$ are creation operators for the Ce 4$f$ electrons with orbital notation $m$, and $c_k^+$ are creation operators for Bloch electrons in the conduction band with wave vector $k$. The parameters $U$ and $Q$ are the on-site repulsive Coulomb interaction between the Ce 4$f$ electrons and the attractive Coulomb interaction between the Ce 4$f$ electron and Ce 2$p$ core hole. Note that the notations $m$ and $k$ include spin. The parameter $V$ describes the transfer integral between the Ce 4$f$ and conduction-band electrons, $\varepsilon_c/n_c$ represent the energy/number of the Ce 2$p$ core-level electron.
In the Ce $L_3$-edge XAS process, the absorption occurs from the Ce $2p$ core level to the Ce $5d$ unoccupied states mixed with the Ce $4f$ states. In the framework of the Anderson’s impurity model, the initial state can be simply given by

$$|i\rangle = \alpha |4f^0 L^2\rangle + \beta |4f^1 L^1\rangle + \gamma |4f^2\rangle$$

where $L$ denotes a conduction-band electron. The conduction band is mainly given by a mixture of Bi $6p$ and S $3p$ orbitals. The final states are given by

$$|f\rangle = \alpha'|2p 4f^0 5d^1 L^2\rangle + \beta'|2p 4f^1 5d^1 L^1\rangle + \gamma'|2p 4f^2 5d^1\rangle.$$  

Using $\alpha$, $\beta$, $\gamma$, $\alpha'$, $\beta'$, and $\gamma'$, the spectral weight is given by $|\alpha \alpha' + \beta \beta' + \gamma \gamma'|^2$. The energy of the $|2p 4f^0 5d^1 L^2\rangle$ state is given by $-Q_d - 2Q_L + U_L + 2U_{dl}$, that of the $|2p 4f^1 5d^1 L^1\rangle$ is given by $\varepsilon_f - Q_f - Q_d - Q_L + U_{dl} + U_{fd}$, and that of $|2p 4f^2 5d^1\rangle$ is given by $2\varepsilon_f - 2Q_f - Q_d + U_f + 2U_{fd}$. The parameter $Q_f$ ($Q_d$ or $Q_L$) is the attractive Coulomb interaction between the Ce $2p$ core hole and the Ce $4f$ (Ce $5d$ or conduction-band) electrons, $U_f$ ($U_L$) is the repulsive Coulomb interaction between the Ce $4f$ (conduction-band) electrons, and $\varepsilon_f$ is the energy level of $4f$ electrons from the Fermi level. $U_{fd}$ ($U_{dl}$) is the repulsive Coulomb interaction between the Ce $4f$ (conduction-band) and Ce $5d$ electrons. The off diagonal terms between $|4f^0 L^2\rangle$ and $|4f^1 L^1\rangle$ (or between $|4f^1 L^1\rangle$ and $|4f^2\rangle$) are expressed by the transfer integral $T$. Considering the distance between Ce and Bi is rather far, this transfer should happen via S (namely, Ce-S-Bi hopping channel) as shown in Fig. 1(b).

Since $U_d$, $U_{fd}$, $U_{dl}$, $Q_d$, and $Q_L$ are substantially small compared with the other parameters, these five parameters are neglected in the present analysis. As a result, the present analysis includes four adjustable parameters; $\varepsilon_f$, $U_f$, $Q_f$, and $T$.

3. Results and discussion

Figure 2 shows the Ce $L_3$-edge XAS results compared with the Anderson’s impurity model calculations. First of all, the Ce $L_3$-edge peak around 5725 eV is accompanied by the clear shoulder structure around 5737 eV for $x=0.0$. The position and the relative intensity of the shoulder structure allows us to determine the four adjustable parameters. The calculated result

![Figure 2](Image)

**Figure 2.** (Color online) Previous Ce $L_3$-edge XAS experimental results on CeO$_{1-x}$F$_x$Bi$_2$ [16] and corresponding impurity-model calculations for various $T$ values. The transfer integral $T$ is dramatically reduced in going from $x=0.2$ to 0.4.
for $\varepsilon_f = -0.66$ eV, $U_f = 10$ eV, $Q_f = 10.7$ eV, and $T= 0.215$ eV can reproduce the shoulder structure as shown in the left panel of Fig. 2. The circles are the reported XAS data [16], and solid lines are our calculation. The peak around 5725 eV is the transition from Ce $2p$ to $5d$ mixed with the Ce $4f^1$ final state whereas the one around 5737 eV is the same transition mixed with the Ce $4f^0$ final state [17, 18, 19, 20]. In the CeO$_{1-x}$F$_x$BiS$_2$ system, the F-doping corresponds to the decrease of the transfer integral $T$, that was reported by the previous extended x-ray absorption fine structure (EXAFS) study [21]. The local changes of the Ce, S, and Bi are schematically shown in Fig. 1(b). As one can see, the F-doping makes the distance between Ce and Bi get further, and the Ce-S-Bi hopping channel is broken when the F-doping reached more than 0.4. This corresponds to the decrease of the transfer integral between conduction electrons and Ce $4f$ electrons. Therefore, only $T$ should be varied to explain the evolution of the XAS result by the F-doping, and we have fixed all the other parameters as $\varepsilon_f = -0.66$ eV, $U_f = 10$ eV, and $Q_f = 10.7$ eV. Since the Ce L$_3$-edge XAS was performed on the CeO$_{1-x}$F$_x$BiS$_2$ with $x =$0.0, 0.2, 0.4, 0.6, 0.8, and 1.0, we have applied the calculation on the same F-doping levels. The results of our impurity-model calculation are shown in Fig. 2. One can see the systematic change due to the F-doping, and our calculation with monotonically decreasing transfer integral have succeeded in reproducing the experimental results by setting $T = 0.215$, 0.165, and 0.05 eV for $x =$0.0, 0.2, and 0.4. The transfer integral $T$ is zero for the system with $x =$0.6, 0.8, and 1.0. This decrease of the transfer integral is also consistent with the recent EXAFS study [21]. The summary of the parameter set obtained by the present analysis is shown in Table 1. The number of Ce $4f$ electrons ($n_f$) are calculated to be 0.71, 0.75, and 0.94 for $x =$0.0, 0.2, and 0.4, respectively. This result is consistent with the crossover from the valence fluctuation regime to the Kondo regime by the F-doping.

4. Summary
We have applied the Anderson’s impurity-model analysis to the Ce L$_3$-edge XAS results of the CeO$_{1-x}$F$_x$BiS$_2$ system, and succeeded in estimating the reasonable parameter set of the system. The Ce L$_3$-edge XAS spectra with the various F-doping levels can be reproduced by adjusting the transfer integral, and we have found that the F-doping to the system corresponds to the decrease of transfer integral between the Ce $4f$ state and the Bi 6p-S 3p conduction band.

### Table 1.

| Doping amount $x$ | 0.0 | 0.2 | 0.4 | 0.6, 0.8, and 1.0 |
|------------------|-----|-----|-----|------------------|
| $T$ (adjusted parameter) | 0.215 | 0.165 | 0.05 | zero |
| $n_f$ | 0.71 | 0.75 | 0.94 |

| Fixed parameters | $\varepsilon_f = -0.66$ eV | $U_f = 10$ eV | $Q_f = 10.7$ eV |

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