## Single Impurity Anderson Model versus Density Functional Theory for Describing Ce L<sub>3</sub> X-Ray Absorption Spectra of CeFe<sub>2</sub>: Resolution of a Recent Controversy

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We resolved a recent controversy on the structure of the Ce  $L_3$  x-ray absorption spectra (XAS) of CeFe<sub>2</sub>; i.e., which of the single impurity Anderson model (SIAM) and the first-principles band calculations based on the density-functional theory (DFT) describes more appropriately the Ce 4f states and their contribution to the Ce  $L_3$  XAS? For this purpose, we examined the core-hole effect in Ce  $L_3$  XAS as an application of our new method taking advantage of resonant x-ray emission spectroscopy. Our result clearly shows that the Ce  $L_3$  XAS structure is caused by the mixed valence 4f character revealed by the core-hole potential effect as indicated by SIAM, but denies the possibility that the  $L_3$  XAS structure is caused by the 5d band structure with a very small core-hole effect as predicted by band calculations based on DFT.

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The mixed valence (MV) phenomenon (also denoted by the valence-fluctuation or intermediate valence phenomenon) of rare-earth compounds has been extensively studied as one of the most attractive many-body effects in strongly correlated electron systems. The x-ray absorption spectroscopy (XAS) at the Ce  $L_3$  edge has played an important role in detecting the MV state of various Ce compounds [1]. In the ground state of MV Ce compounds, the energies of Ce  $4f^0$  and  $4f^1$  configurations are located close to each other and mixed by the hybridization V between the 4f and conduction band states. In the final state of the Ce  $L_3$  XAS, however, the energies of the two configurations are considered to be separated by a strong core-hole potential (of the order of 10 eV) acting on the 4f state, so that the XAS spectrum exhibits two peaks as an evidence of the MV state. By analyzing the intensity ratio of the two peaks, the averaged valence number has been estimated for a wide variety of MV Ce compounds.

CeFe<sub>2</sub> is a material of particular interest because of its anomalous ferromagnetism with an unusually low Curie temperature, small magnetic moments, small lattice spacing, and an anomalous doping effect, compared to the other rare-earth iron Laves phase compounds. In order to detect and explain these anomalous behaviors of CeFe<sub>2</sub>, extensive studies have been made both experimentally and theoretically, keeping in mind strong hybridization between the Ce 4*f* and Fe 3*d* states [2–7].

We show in Fig. 1(a) the experimental result of the Ce  $L_3$  XAS of CeFe<sub>2</sub>, which was measured by the conventional total fluorescence yield method. It is seen that this

spectrum exhibits the two features *A* and *B*. Asakura *et al.* [5] analyzed the Ce  $L_3$  XAS spectrum of CeFe<sub>2</sub> with the single impurity Anderson model (SIAM) and showed that the features *A* and *B*, respectively, are caused by the two MV configurations,  $4f^1$  and  $4f^0$  configurations, which are revealed by the core-hole potential in the final state. Their result of the XAS spectrum is very similar to that in Fig. 1(b). Asakura *et al.* [6] also calculated the x-ray magnetic circular dichroism (XMCD) spectra at the  $L_{2,3}$  edges of CeFe<sub>2</sub> which were in good agreement with experimental results by Giorgetti *et al.* [3].

More recently, Antonov and co-workers [8,9] calculated the XAS and XMCD spectra at the  $L_{2,3}$  edges of CeFe<sub>2</sub> by first-principles energy band calculations based on the density-functional theory (DFT) and claimed that the structures *A* and *B* in the XAS spectrum are caused by the structure of Ce 5*d* band density of states (DOS), instead of the two MV configurations revealed by the core-hole potential effect. According to their calculations, the corehole effect in the final state of XAS is too small to produce the main XAS structures. Therefore, the origin of the structures *A* and *B* is a serious problem, which directly examines the applicability of two representative methods, SIAM and DFT, to the calculations of x-ray spectra.

Historically, the SIAM was very successful in analyzing a wide variety of x-ray spectroscopies, such as XAS, photoemission (PE), inverse-photoemission (IPE), x-ray scattering, and so on, of various rare-earth systems including MV Ce compounds [1,10,11]. Recently, however, it has been argued that for Ce compounds with strong



FIG. 1 (color online). (a) Experimental and (b) theoretical results of the conventional XAS and the high-energy-resolution fluorescence detected (HERFD) spectra at the Ce  $L_3$  edge of CeFe<sub>2</sub>. The HERFD spectrum corresponds to a highly resolved version of the conventional XAS spectrum. The origin of the structures *A* and *B* has been an issue of controversy. On the methods of experiments and calculations, as well as the definition of HERFD, see the text.

hybridization between the 4f and other valence electron states, such as CeFe<sub>2</sub> and CeRh<sub>3</sub>, calculations based on DFT may give an equally good or even better description of the PE and IPE spectra, XAS, and XMCD [4,8,9,12]. The SIAM versus DFT descriptions for various Ce compounds have been a subject of strong interest in experimental and theoretical investigations in connection with the MV versus energy band pictures of their ground states [13,14]. From these backgrounds, it is of fundamental interest to examine the origin of the features A and B in the Ce  $L_3$  XAS of CeFe<sub>2</sub>.

Very recently three of the present authors proposed a new powerful method to directly examine the core-hole effect in the final state of  $L_3$  XAS spectra of Ce compounds by taking advantage of the resonant x-ray emission spectroscopy (RXES) [15]. In this method, one should measure and compare two different RXES spectra which are caused by the Ce 3d to 2p x-ray emission (denoted by 3d-RXES) and by the Ce valence to 2p x-ray emission (v-RXES) following the resonant excitation of a 2p electron to the 5d band. The features of the two RXES spectra should be significantly different if the core-hole effect plays an essential role in the XAS final state (so that the structures A and B are caused by the MV effect revealed by the core-hole potential), whereas they should be essentially the same if the core-hole effect is negligibly small. The purpose of this Letter is to perform the follow-up experimental observations of the 3d- and v-RXES spectra of CeFe<sub>2</sub> to settle the controversy, and also carry out theoretical calculations of these RXES spectra with SIAM to explain the measured spectra.

The RXES experiments were performed at beam line ID26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble [16]. The incident energy was selected using the  $\langle 311 \rangle$  reflection of a double Si crystal monochromator. RXES spectra were measured using an x-ray emission spectrometer with sample, crystal analyzer, and photon detector arranged in a vertical Rowland geometry. The RXES spectra were recorded at a scattering angle of 90° in the horizontal plane. A combined (incident convoluted with emitted) energy resolution of 0.7 and 0.8 eV was achieved in the v- and 3d-RXES measurements, respectively. The intensity was normalized to the incident flux. A polycrystalline CeFe<sub>2</sub> sample was prepared with special attention to its oxygen sensitivity. The surface of cerium has been specially scraped in a glove box under constant flow of argon with a diamond file before use. The sample was prepared by triarc melting stoichiometric mixture of pure Ce(4N) and Fe(5N) under purified argon protective atmosphere, and subsequently annealed for one week at 750 °C in a vacuum of  $10^{-6}$  Torr to obtain single phase. The MgCu<sub>2</sub>-type C15 crystal structure and the Curie temperature of CeFe2 were carefully controlled by x-ray diffraction pattern and SQUID magnetometer measurements, respectively. The Curie temperature of the sample was 230 K.

We show the measured 3d- and v-RXES spectra in Figs. 2(a) and 2(b), respectively, as 2D contour maps in the plane of incident and transferred photon energies. It is evident that the spectral features of the 3d- and v-RXES are significantly different. In the 3d-RXES spectra, two or three RXES peaks are arranged in the diagonal direction in the 2D plane, while in the v-RXES spectra, a prominent peak and a much weaker subpeak are arranged in the horizontal direction. The peak width of the v-RXES is much larger than that of the 3d-RXES. Therefore we conclude that the core-hole effect is essential in explaining the structures A and B in the Ce  $L_3$  XAS of CeFe<sub>2</sub>. The features A and B are more clearly separated by measuring high-energy-resolution fluorescence detected the (HERFD) spectrum, which is defined by the cross section of the 2D map of 3d-RXES along the diagonal direction through the maximum RXES peak. The result is shown in Fig. 1(a), which is seen to be a less broadened version of the conventional XAS. Thus, we can assign that A and B, respectively, correspond mainly to the  $4f^1$  and  $4f^0$  configurations which are hybridized in the MV ground state but revealed by the core-hole effect as two different features in the final state of the  $L_3$  XAS.



FIG. 2 (color online). Experimental results of (a) 3d-RXES and (b) v-RXES spectra shown as 2D contour maps in the plane of the incident energy and energy transfer. The intensity scale is arbitrary. For the definitions of 3d-RXES and v-RXES, see the text.

In order to confirm our conclusion more clearly, we calculate the 3d- and v-RXES spectra with SIAM and compare the results to the experimental ones. The model is shown schematically in Fig. 3. We consider a system consisting of the Ce 4f, 3d, 2p states, the Ce 5d conduction band, Fe 3d band, and a high-energy continuum band. The Fe 3d states have f symmetry around the central Ce atom and are mixed with the Ce 4f state by the hybridization matrix element V (= 0.3 eV). The 4f level is located at 0.8 eV below the Fermi level. The valence states, from which the x-ray transition to the 2p state occurs in v-RXES, are the occupied states in the Ce 5d band. We take into account the Coulomb interactions between 4felectrons  $U_{ff}$  (= 6.5 eV), between the 4f electron and a core hole  $-U_{fc}$  (= -10.5 eV for both 3d and 2p core holes), between the 4f and 5d electrons  $U_{fd}$  (= 0.2 eV),



FIG. 3 (color online). Model of theoretical calculations of 3dand v-RXES spectra of CeFe<sub>2</sub>. Vertical arrows represent the xray transitions in these RXES spectra. It is seen that for 3d-RXES the difference between the incident and emitted photon energies is of the order of the binding energy of the Ce 3dcore level, while that for v-RXES is close to zero. Therefore, the energy transfer of 3d-RXES ranges from 880 to 910 eV, while that of v-RXES ranges from 0 to 30 eV.

and between the 5*d* and the core hole  $-U_{dc}$  (= -1.2 eV for both 3*d* and 2*p* core holes). The widths of the occupied part of the Fe 3*d* band and the empty part of the Ce 5*d* band are taken to be 2 and 9 eV, respectively, but the occupied part of the Ce 5*d* band is approximated as a single level for simplicity. The main parameter values of SIAM were roughly known as empirical parameters, and then we made fine adjustments of these values to reproduce the experimental data. The present model is very similar to that used by Asakura *et al.* [5] in their calculations of the Ce  $L_{2,3}$  XAS and XMCD spectra, but here the DOS of the Ce 5*d* band is simply assumed to be of rectangular shape, to exclude the effect of DOS structures of the Ce 5*d* band.

The calculated 3d- and v-RXES spectra are shown in Figs. 4(a) and 4(b), respectively, in the form of the 2D contour maps. In our calculations we do not take into account the elastic scattering process, so that the experimental signal at zero energy transfer in Fig. 2(b) is absent in Fig. 4(b). It is seen that the calculated and experimental spectra are in good agreement with each other. The calculated XAS and HERFD spectra are also shown in Fig. 1(b), and they are in good agreement with experimental results in Fig. 1(a). We estimated the contributions of  $4f^0$ ,  $4f^1$ , and  $4f^2$  configurations to the final states of A and B in the XAS spectrum by putting the boundary between A and B at 5735 eV. As a result, we obtain 0% (0.06% in more detail), 64.6%, and 35.4% contributions, respectively, from  $4f^0$ .  $4f^1$ , and  $4f^2$  configurations to A, and 98.8%, 1.2%, and 0% (0.001% in more detail) contributions from those to B. It is thus confirmed that the features A and B in XAS and HERFD spectra correspond mainly to  $4f^1$  and  $4f^0$  configurations, respectively. The feature A includes a considerable amount of the  $4f^2$  configuration which is dominant



FIG. 4 (color online). Theoretical results of (a) 3d-RXES and (b) v-RXES spectra shown as a 2D contour maps in the plane of the incident energy and energy transfer.

below 5724 eV. A hump in the calculated HERFD spectrum below 5724 eV is caused by the  $4f^2$  configuration and it corresponds nicely to a hump in the measured HERFD spectrum in Fig. 1(a).

In many nominally tetravalent Ce (and Pr) compounds, a double-peak structure is often measured in the  $L_3$  XAS spectra. It should be noted that these compounds are actually in the mixed valence state, as in the case of CeFe<sub>2</sub>, and the low- and high-energy peaks correspond mainly to the  $4f^1$  and  $4f^0$  ( $4f^2$  and  $4f^1$  for Pr) configurations, respectively, which are often referred to as the trivalent and tetravalent components [17,18]. Furthermore, a highenergy  $4f^0$  peak (very weak) and a low-energy  $4f^1$  peak (strong) are observed in heavy fermion Ce compounds [19] and Fe-As based superconductors CeFeAsO<sub>1-y</sub> [20], although the Ce in these materials is not nominally tetravalent but much closer to trivalent. In this Letter, we disregarded the structures in the Ce 5d DOS. Actually, we have also made preliminary calculations of XAS and HERFD spectra by using the Ce 5d DOS which is simulated from the DFT calculations [4,8] and confirmed that the structure of the Ce 5d DOS affects only the fine structures within the features A and B (see the measured HERFD spectrum), instead of giving rise to the structures A and B themselves.

In this connection, it is to be mentioned from the experimental side that the fine structures within A and B in the HERFD spectrum change slightly depending on samples and sample conditions because the CeFe<sub>2</sub> sample is very sensitive to oxidation and also to the radiation damage. After repeating our experiments for some different samples, we confirmed the most important conclusion of this Letter that the features of 3d- and v-RXES spectra are always different significantly as a definitive and qualitative conclusion indicating the essential role of the corehole potential in the final state of XAS, in strong contrast to the DFT results. More details on the fine structures within A and B are beyond the scope of this Letter, but will be studied experimentally by changing the CeFe<sub>2</sub> sample and theoretically by changing the model of Ce 5d DOS and the SIAM parameters, and will be published in the near future.

The applicability of SIAM for CeFe<sub>2</sub> was also discussed very recently by Jaouen *et al.* [21] by measuring XMCD spectra at the Ce  $L_3$  edge of CeFe<sub>2</sub> by resonant inelastic x-ray scattering and by comparing the result with theoretical calculations with SIAM by Asakura *et al.* [6]. They observed a clear evidence for  $4f^2$ ,  $4f^1$ , and  $4f^0$  signals predicted by the SIAM calculations, as an indication of the applicability of SIAM being better than DFT calculations. However, the intensity of the XMCD signal by resonant inelastic x-ray scattering was too weak to compare fine details of experimental and theoretical spectra, and some discrepancies were left to be explained. In comparison with their approach, the present method is much more clear-cut in resolving the SIAM versus DFT controversy.

In summary, as an application of our new method of detecting the core-hole effect in the Ce  $L_3$  XAS, we measured and compared the 3*d*- and *v*-RXES spectra of CeFe<sub>2</sub> and showed that their spectral features are significantly different. This indicates that the core-hole effect plays an essential role in the final state of the Ce  $L_3$  XAS. Theoretical calculations of these spectra were also carried out with SIAM and the results are in good agreement with the experimental ones. We consider that all of these results are enough to settle the controversy on the origin of the structures in the Ce  $L_3$  XAS of CeFe<sub>2</sub>.

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