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Original Publication:
http://dx.doi.org/10.1103/PhysRevB.63.075101
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Postprint available at: Linköping University Electronic Press  
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-17467
Electronic-structure investigation of CeB$_6$ by means of soft-x-ray scattering

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(Received 2 June 2000; published 11 January 2001)

The electronic structure of the heavy fermion compound CeB$_6$ is probed by resonant inelastic soft-x-ray scattering using photon energies across the Ce 3$d$ and 4$d$ absorption edges. The hybridization between the localized 4$f$ orbitals and the delocalized valence-band states is studied by identifying the different spectral contributions from inelastic Raman scattering and normal fluorescence. Pronounced energy-loss structures are observed below the elastic peak at both the 3$d$ and 4$d$ thresholds. The origin and character of the inelastic scattering structures are discussed in terms of charge-transfer excitations in connection to the dipole allowed transitions with 4$f$ character. Calculations within the single-impurity Anderson model with full multiplet effects are found to yield consistent spectral functions to the experimental data.

DOI: 10.1103/PhysRevB.63.075101

PACS number(s): 78.70.En, 71.20.Eh, 71.27.+a

I. INTRODUCTION

The electronic structures of Ce heavy fermion compounds has attracted much attention both from an experimental and theoretical point of view since they show a variety of unusual and interesting macroscopic properties. In particular, much interest has been focused on the 4$f$ narrow-band occupancy, and the role of hybridization with the conduction band states which strongly affects the physical properties. It remains a controversy if the localized Ce 4$f$ states are best theoretically described with the single-impurity Anderson model (SIAM) or with density functional theory.

Experimental methods such as x-ray-absorption spectroscopy (XAS) and resonant photoemission spectroscopy (RPES) of the valence-band and core levels have previously proved to be powerful tools for investigating the electronic states, in particular, close to the Fermi level. Recent improvements in the energy resolution of valence-band photoemission spectra with excitation by high-brilliance undulator radiation allow detailed observations of the tail of the so-called Kondo resonance as a very narrow peak in the vicinity of the Fermi level of rather hybridized compounds. However, the predominant surface sensitivity constitutes a serious inherent problem with the use of electron spectroscopies for these kind of studies. Since the 4$f$ states in the Kondo resonance in the surface are very different from those in the bulk, the SIAM approach for RPES has been a subject of controversy.

To further investigate the electronic structures and the bulk properties of heavy fermion materials, we have chosen to study the well known hexaboride CeB$_6$ compound, which is known to exhibit dense Kondo properties. The present measurements were performed using high-resolution resonant inelastic x-ray scattering (RIXS) spectroscopy with selective excitation energies at the Ce 3$d$ and 4$d$ thresholds. A general advantage of using the RIXS technique is the bulk sensitivity, which makes it possible to avoid surface contributions. With the scattering process, the radiative transitions probe the ground and low-lying excited states. Recent valence-band RPES measurements at the 3$d$ and 4$d$ thresholds of CeB$_6$ show two main resonant peak structures: a narrow Kondo peak at the Fermi edge, and a broad structure below the strong elastic peak. The origin and 4$f$ character of the loss structures are discussed in connection to the dipole allowed transitions with 4$f$ character. Calculations including two configurations, these peaks were assigned to the 4$f^1$ and 4$f^0$ final states, respectively.

In general, the identification of the energy positions of the 4$f$ energy-loss structures using the RIXS technique in different Ce compounds is essential for understanding the properties of heavy fermion systems. Although the final states are different in RIXS and RPES, it is useful to compare the energy positions of the peak structures and the validity of the SIAM in both cases for deriving more accurate values of the model parameters. When the excitation energy is tuned on and above the thresholds, the RIXS spectra of CeB$_6$ are found to exhibit interesting resonance behaviors with pronounced energy-loss structures below the strong elastic peak.

II. EXPERIMENTAL DETAILS

The measurements at the Ce 3$d$ edge were performed at beam line BW3 at HASYLAB, Hamburg, using a modified SX700 monochromator. An XAS spectrum at the Ce 3$d$ edge was obtained in total electron yield (TEY) by measur-
ing the sample drain current. The Ce 3d RIXS spectra were recorded using a high-resolution grazing-incidence grating spectrometer with a two-dimensional position-sensitive detector.\textsuperscript{18} During the XAS and RIXS measurements at the Ce 3d edge, the resolutions of the beam line monochromator were about 0.6 eV and 2.0 eV, respectively. The x-ray emission spectrometer had a resolution of about 1.5 eV.

Measurements at the Ce 4d threshold were carried out at beam line 7.0 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The beam line comprises a 89-pole, 5 cm period undulator, and a spherical-grating monochromator.\textsuperscript{19} An XAS spectrum at the 4d threshold region was also obtained in TEY by measuring the sample drain current. During the XAS and RIXS measurements at the 4d edge, the resolution of the monochromator of the beam line was $\sim 0.1$ eV. The X-ray emission spectrometer had a resolution better than 0.2 eV.

All the measurements at the Ce 3d and 4d thresholds were performed at room temperature with a base pressure lower than $5 \times 10^{-9}$ Torr. In order to minimize self-absorption effects, the sample crystal was oriented so that the photons were incident at an angle of about 20° with respect to the sample surface. The emitted photons were recorded at an angle, perpendicular to the direction of the incident photons, with the polarization vector parallel to the horizontal scattering plane. The single crystal of CeB$_6$ was grown by the floating-zone method.\textsuperscript{20}

### III. CALCULATIONAL DETAILS

The Ce 4f$\rightarrow$3d and Ce 4f$\rightarrow$4d RIXS spectra of CeB$_6$ were calculated as a coherent second-order optical process including interference effects using the Kramers-Heisenberg formula.\textsuperscript{21} The Slater integrals, describing 4f-4f, 4f-3d, and 4f-4d Coulomb and exchange interactions, and spin-orbit constants were obtained by the Hartree-Fock method with relativistic corrections.\textsuperscript{22} The reduction ratios of the Slater integrals were $F^4(4f4f)$ 80%, $F^4(3d4f)$ 80%, $G^4(3d4f)$ 80%, $F^4(4d4f)$ 75%, and $G^4(4d4f)$ 66%. Three different configurations were considered: 4f$^0$, 4f$^1$, and 4f$^2$, for the initial and final states, and $d^04f^1$, $d^04f^2$, and $d^04f^3$ for the intermediate states. The weights of the $f^0$, $f^1$, and $f^2$ configurations in the ground state were about 1%, 97%, and 2%, respectively. The effect of electron-hole pair excitations in the conduction band and the crystal-field effects were disregarded for simplicity. The calculations were made at 0 K, so that the ground state was in the Kondo singlet $^1S_0$ bound state due to the effect of hybridization. The scattering angle was fixed to 90° and calculations were made for two different geometries where the scattering plane was either parallel (“depolarized geometry”) or perpendicular (“polarized geometry”) to the polarization vector of the incident photons.

The SIAM\textsuperscript{3} with full multiplet effects was used to describe the system. The parameters were chosen to reproduce the experiment as follows: the 4f level (with respect to the Fermi level $e_F$) $\epsilon_F - \epsilon_F = -2.5$, the occupied conduction bandwidth $W=3.0$, the hybridization strength between the 4f and conduction-band states $V=0.15$, the Coulomb interaction between the 4f electrons $U_{ff}=6.5$, and that between 4f and 3d core electrons $U_{fc}(3d)=8.5$ (in units of eV). The Coulomb interaction between the 4f and 4d core electrons $U_{fc}(4d)$ was taken to be 80% of $U_{fc}(3d)$. The effect of the configuration-dependent hybridization was taken into account with the two reduction factors $R_c=0.8$ and $R_v=0.9$.\textsuperscript{23} The parameters used in the calculations are summarized in Table I. Similar SIAM parameters have previously been used for valence and core level photoemission.\textsuperscript{15}

### IV. RESULTS AND DISCUSSION

Figure 1 shows a set of RIXS spectra of CeB$_6$ recorded at different excitation energies near the Ce 3d$_{5/2}$, 3d$_{3/2}$ thresholds. In the top panel, an XAS spectrum is shown where the excitation energies for the RIXS spectra are indicated by the arrows aimed at the main peaks $A$ ($A'$) and weak satellites $B$ ($B'$) above the thresholds, respectively. The final states of the XAS spectrum are the same as the intermediate states in the RIXS process. The x-ray emission spectra in the lower

![FIG. 1. An XAS spectrum (upper panel) of CeB$_6$ measured at the 3d edge. A set of RIXS spectra (lower panel) for different photon energies around the 3d edge of CeB$_6$ on a photon energy scale. The measurements were made at room temperature at the following excitation energies for the RIXS spectra: 881.2 eV, 884.8 eV, 898.5 eV, and 901.8 eV.](image-url)
The elastic peak, also referred to as Rayleigh scattering, is due to the 3d states having one electron less than in the ground state. The true elastic line, resulting at the weak satellite above the absorption threshold at B, the 4 eV peak is still visible. However, another peak at about 6–7 eV energy loss is now stronger. It should be noted that the 6–7 eV energy-loss feature is not related to a normal 3d5/2 fluorescence line. However, the 3d charge-transfer excitations as a result of electron hopping from delocalized states to a localized state. Weak emission features are also observed in the energy region below 850 and 880 eV photon energy. Similar low-energy-loss structures as those observed at 4 eV and 6–7 eV have previously been assigned to have charge-transfer origin showing a resonant behavior at the thresholds in RIXS spectra of CeO2 and UO2 (Ref. 14) and in electron energy-loss spectra of metallic Ce.24,25 The charge-transfer excitations occur as a result of electron hopping from delocalized states to a localized state. Weak emission features are also observed in the energy region between 850 and 870 eV due to 5p→3d transitions.

Figure 2 shows the results of SIAM calculations of the 3d XAS and RIXS spectra of CeB6. The letters A (A′) and B (B′) denote the same excitation energies as in Fig. 1. The XAS spectrum in the upper panel is made up of the hybridized 3d3/2f1, 3d5/2f2, and 3d5/2f3 manifolds, where the 3d5/2f configuration dominates. The RIXS calculations, shown in the lower panel, are in good agreement with the experimental data in Fig. 1 although contributions from normal fluorescence are not included. Three different kinds of low-energy excited loss structures are observed at 2.5 eV, 4 eV, and 6 eV below the elastic peak. The full lines show the results in the depolarized geometry, i.e., in the same geometry as the experimental results in Fig. 1. In this geometry, the recombination back to the 1S0 ground state is forbidden from geometrical selection rules,26 so that the true elastic line is forbidden. However, 4f3/2 final states with other symmetries give rise to a relatively strong quasielastic peak.

The 4 eV and 6 eV inelastic scattering structures that stay at constant energy loss can be identified in all the simulated RIXS spectra. These structures are almost entirely due to the 4f3/2 final states (f3/2→f5/2 charge-transfer excitations as a result of hybridization), and it is found that the 4 eV peak corresponds mainly to triplet final state terms (3F2,3,4 and 3H4,5,6), while the 6 eV peak is mainly due to singlet final state terms (1I6 and 1D2). The lower energy peak (4 eV) is resonantly enhanced by the intermediate states of the main XAS peaks A (A′), while the higher energy peak (6 eV) is resonantly enhanced by the intermediate states of the XAS satellites B (B′). The dashed lines show the results in the polarized geometry, i.e., when the scattering plane is perpendicular to the polarization vector of the incoming photons. In this configuration, a low-energy excited peak structure of 4f0 character appears at 2.5 eV energy loss from the elastic peak. The f0 final states occur as an indication of the singlet (Kondo) ground state. The transitions to the f0 final states are forbidden in the depolarized geometry due to the 1S0 symmetry of the Kondo ground state.

Figure 3 (top panel) shows an XAS spectrum of CeB6 recorded at the Ce 4d threshold. The large broad structure above threshold in the energy region between 120 and 130 eV, commonly referred to as the giant absorption region, has been observed in many Ce compounds.27 The series of small sharp peaks in the prethreshold region around 102–112 eV have been interpreted as due to transitions to various multiplet states of the excited 4d5/2 configuration.28 The lower panel of Fig. 3 shows a set of RIXS spectra recorded across the Ce 4d threshold of CeB6. The spectra are plotted on an emission photon energy scale and were measured at excitation energies denoted by the letters A–G in the XAS spectrum from 106.0 eV up to 124.5 eV. Pronounced inelastic scattering structures are observed below the strong elastic peaks. The x-ray emission spectra at the 4d edge can basi-
region of the XAS spectrum. These fine structures are related to those in the prethreshold systems with different number of electrons in the final states at 4 eV and 6 eV energy loss in the RIXS spectra when measurements are made in the polarized geometry for temperatures close to or below the Kondo temperature $T_K$. For higher temperatures, the spectra will appear similar to those of a normal Ce$^{3+}$ system, even though the true ground state is the $^1S_0$ Kondo singlet. In the depolarized geometry where the $f^0$ final states are forbidden, the spectra look similar to a normal Ce$^{3+}$ system, even at 0 K. It is interesting to notice that the $f^2$ final states observed at 4 eV and 6 eV energy loss in the RIXS spectra cannot be observed in valence-band RPES but instead appears at 2 eV in inverse photoemission. The difference in the energy position of the $f^2$ peak between the different spectroscopical techniques is a result of probing the systems with different number of electrons in the final states in comparison to the ground state. The RIXS technique is thus shown here to be very useful for detecting the $f^1 \rightarrow f^2$ transitions previously observed in RPES. In the energy region above the $5p$ peaks, several smaller sharp peaks are observed in the spectra. These fine structures are related to those in the prethreshold region of the XAS spectrum.

A comparison to previous RPES measurements of CeB$_6$ (Ref. 29) shows that the $4f$ and $5p$ intensities have a resonance maximum at about 121 eV. The major parts of the resonances are thus expected to appear at the shoulder of the broad absorption structure of the giant band. At somewhat higher photon energies (127 eV), the RPES spectra are instead dominated by the Auger decay, corresponding to normal fluorescence in the radiative channel. In Fig. 3, the normal fluorescence contribution appears below the pronounced 4 eV peak as a broad structure at ~9 eV loss energy in spectrum $G$. A minor contribution to the intensity distribution of the energy-loss features in spectra $D$–$F$ may also be attributed to normal fluorescence, although the major part of the intensity is related to inelastic scattering.

Figure 4 shows the results of SIAM calculations of the 4d XAS and RIXS processes for CeB$_6$. The letters $A$–$G$ denote the same excitation energies as in Fig. 3. The results are in good agreement with the experiment with the exception of the $5p$ emission lines and the normal fluorescence, which are not included in the calculation. The charge-transfer satellites to the $f^2$ final states at 4 eV and 6 eV below the elastic line behave in the simulation in a similar way as at the 3$d$ edge.

The interpretation of the relative peak positions of the low-energy-loss structures in the RIXS spectra are consistent with the results of RPES which show a narrow $f^1$ Kondo peak at the Fermi edge and a broad $f^0$ structure at 2.5 eV binding energy. Due to the configuration interaction between the Ce $4f$ states, the $f^1$ energy-loss structure is located at 0 eV and the $f^0$ structure is predicted to show up at 2.5 eV energy loss in the RIXS spectra when measurements are made in the polarized geometry for temperatures close to or below the Kondo temperature $T_K$. For higher temperatures, the spectra will appear similar to those of a normal Ce$^{3+}$ system, even though the true ground state is the $^1S_0$ Kondo singlet. In the depolarized geometry where the $f^0$ final states are forbidden, the spectra look similar to a normal Ce$^{3+}$ system, even at 0 K. It is interesting to notice that the $f^2$ final states observed at 4 eV and 6 eV energy loss in the RIXS spectra cannot be observed in valence-band RPES but instead appears at 2 eV in inverse photoemission. The difference in the energy position of the $f^2$ peak between the different spectroscopical techniques is a result of probing the systems with different number of electrons in the final states in comparison to the ground state. The RIXS technique is thus shown here to be very useful for detecting the $f^1 \rightarrow f^2$ transitions previously observed in RPES.
inelastic scattering is distinguished from the normal fluorescence.

Changing the incoming photon energy, the contribution from the ground and low-lying states will allow interesting studies of the $f^1\rightarrow f^0$ charge-transfer excitations.

V. CONCLUSIONS

The electronic structure of CeB$_6$ has been measured at the Ce $3d$ and $4d$ absorption thresholds by resonant inelastic soft-x-ray scattering. Due to the bulk sensitivity, the resonant inelastic soft-x-ray scattering technique allows probing the ground and low-lying $4f$ states without surface effects. By changing the incoming photon energy, the contribution from inelastic scattering is distinguished from the normal fluorescence. Pronounced energy-loss structures below the strong elastic peaks are identified as due to charge-transfer excitations to the $4f^2$ state as a result of configurational mixing in the ground and core-excited states. Comparisons to peak structures in model calculations within the single-impurity Anderson model and valence-band resonant photoemission are consistent with the present experimental results.

ACKNOWLEDGMENTS

This work was supported by the Swedish Natural Science Research Council (NFR), the Göran Gustavsson Foundation for Research in Natural Sciences and Medicine. A.L.S. is supported by the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098. T. Takahashi and A. Kotani would like to acknowledge a Grant-in-Aid from the Ministry of Education, Science, Culture and Sports in Japan. The computation in this work has been done using the facilities of the Supercomputer Center, ISSP, University of Tokyo.

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