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On the change of electronic states at the Fermi level by Ce doping in the intermetallic $LaRu_2$

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Abstract

Variation of electronic structure at the Fermi level in superconducting $LaRu_2$ intermetallic system has been studied by X-ray absorption near edge structure (XANES) spectroscopy. The high resolution Ru K-edge XANES have been measured by fluorescence yield method using multi-element solid state detector assembly allowing to reach a signal to noise ratio of the order of $\Delta\alpha/\alpha \sim 10^{-4}$. The results show that a doping by mixed valence Ce in place of La in the $LaRu_2$ directly modifies the electronic states at the Fermi level leading to a decrease of the superconducting transition temperature.

Keywords: Fluorescence XANES; $LaRu_2$ superconductor; *f* electron systems; Itinerant and localized carriers

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1. Introduction

X-ray absorption near edge structure (XANES) was introduced as a tool to investigate intermediate short-range structural order and electronic structure in complex materials [1]. The X-ray absorption coefficient $\mu(E)$ is given by the product of the matrix element and the joint density of states for the electronic transitions from the initial to final states. The dipole matrix element from the initial state, the core level of well defined symmetry, selects the partial density of final states for the allowed electronic transitions. The XANES spectroscopy probes the final states in an energy range of about 50 eV above the chemical potential. While at the Fermi level the photoelectron mean free path is very large, it decreases rapidly with increasing the energy of the final state due to strong scattering by the many body electronic excitations resulting in the mean free path to become of the order of 5 Å. Therefore the XANES spectra can be solved in the real space describing the final state as an outgoing spherical wave which interferes with the waves backscattered from the neighbouring atoms within a cluster of atoms in the intermediate range of the order of 5 Å [2–6].

The $LaRu_2$ intermetallic superconductor constructs an interesting case [7–10] being formally a $4f^0$ system. The Ce in $LaRu_2$ at the La site is found to suppress the superconducting transition temperature from $T_c \sim 4.4$ K for $LaRu_2$ to $T_c \sim 0.3$ K for $La_{0.5}Ce_{0.5}Ru_2$. The T_c increases if Ce is further increased in the system reaching a maximum T_c of 6.2 K for the $CeRu_2$ [7,8]. The origin of this abnormal superconducting behavior is one of the debated questions. Indeed, it is the hybridization of localized *f* electrons and itinerant *d* electrons which drives these intermetallic superconductors towards an exotic phase of matter lying at the border line between magnetic and metallic systems. It is not clear, whether the unusual behavior of T_c in $La_{1-x}Ce_xRu_2$ is solely due to magnetic interaction or due to change in the local electronic density of states and/or local lattice distortions or due to competing behaviour of the magnetic and electronic interactions as the Ce enters in the system as a mixed valent with an average valence of ~3.3. In fact, several spectroscopic experiments revealed Ce to be mixed valent with significant weight of *f* states at the Fermi level [11–14].

Here we have exploited capabilities of XANES spectroscopy to study the effect of Ce in the $La_{1-x}Ce_xRu_2$ intermetallic system to probe the electronic density of states at the Fermi level. We have made high resolution Ru

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K-edge XANES measurements to further enlighten the understanding of the unusual superconductivity in the system. The advantage of the high photon flux at the ESRF synchrotron facility and fluorescence detection by a multi-element solid state detector has been taken to measure the absorption spectra with very high signal to noise ratio in order to explore the small changes due to Ce substitution. Multiple scattering calculations are made to identify origin of different features of the Ru K-edge [15]. The results suggest that the Ce substitution in place of La in the $LaRu_2$ introduce large change in the density of states at the Fermi level and hence modify the hybridization between the *f* and *d*. The decrease in the superconducting transition appears to be related with change in the density of states because of scattering with localized *f* electrons injected by the mixed valent Ce.

2. Experimental

Fluorescence yield (FY) Ru K-edge absorption measurements on well characterized powder samples of $La_{1-x}Ce_xRu_2$ were made at the beamline BM29 of European Synchrotron Radiation Facility (ESRF), Grenoble. Si(311) double crystal monochromator was used to get high resolution, in addition to the high photon flux available in the range of Ru K-edge. The Ru K_α fluorescence photons were collected using multi-element Ge X-ray detector system covering a large solid angle of the X-ray fluorescence emission. Several absorption scans were recorded to ascertain the reproducibility of the experimental data and to obtain spectra with very high signal-to-noise ratio. The samples were cooled by a closed cycle He refrigerator and the temperature was controlled by a PID controller and monitored with an accuracy of ± 1 K.

3. Results and discussion

Fig. 1 shows the fluorescence yield spectrum representing the raw absorption data measured on the $LaRu_2$ at 200 K. The Ru K_α fluorescence count is shown along with the relative errors. The Ru K-edge X-ray absorption near edge structure (XANES) spectrum shows at least three well-resolved features denoted by A, B and C. The peak positions were precisely determined by the second derivative of the XANES spectrum. The pre-peak A appears near the threshold of the Ru K-edge while the peak B and C appear at about 12 eV and about 38 eV above the threshold.

It has been shown by multiple scattering calculations for the Ru K-edge that the pre-peak A is associated with the unoccupied states made of mixed Ru *p–d* states, i.e., central Ru 4*p* states hybridized with *d* orbitals of outer Ru shell. The Ru *p–d* states are also mixed-up with higher-shell La-*d*/*f* orbitals. Therefore the peak A contains

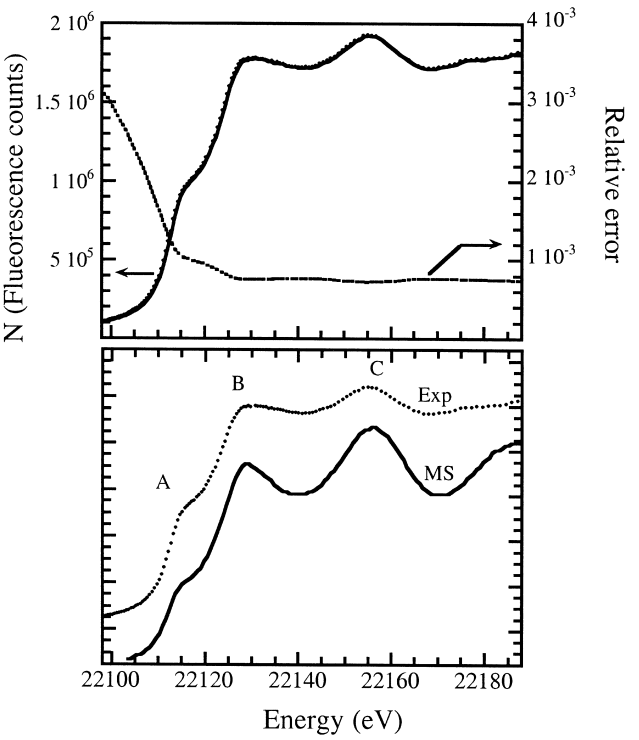

Fig. 1. (upper) Fluorescence yield spectrum representing the Ru K-edge X-ray absorption near edge structure (XANES) spectrum measured at 200 K on $LaRu_2$. The absolute Ru K_α fluorescence count (*N*) is shown along with the relative errors $1/\sqrt{N}$ (dotted line); (lower) The calculated XANES spectrum (MS) compared with the experimental spectrum (Exp.).

information on the density of states at the Fermi level in the $LaRu_2$ system. On the other hand, the peak B is assigned to the $1s \rightarrow 4p$ transition. In the real space, the feature B is attributed to multiple scattering within the Ru atomic shell while the peak C is dominantly due to single-scattering events between absorber and the shell of six Ru atoms. We have shown the multiple scattering calculations along with the experimental spectrum to show the agreement in respect to the intensity and the energy positions of different XANES features (Fig. 1b). The details of the calculations are published elsewhere [15].

We have measured the Ru K-edge XANES spectra on the $LaRu_2$ at several temperatures to investigate the effect on the local lattice and local density of states at the Fermi level. Fig. 2 shows the absorption differences between the spectra measured at different temperatures along with the absorption spectrum and its derivative. We do not observe any appreciable temperature dependence down to ~140 K as evident from the absorption difference between the spectra measured at 140 and 200 K. On the contrary, there is a large change in the main absorption features by lowering the temperature to 15 K that could be seen in the absorption difference between the spectra measured at 15 and 200 K showing a maximum of ~4% of the normalized absorption. The peaks in the derivative spectrum (α, β, γ) appears at the same energy positions where the absorption

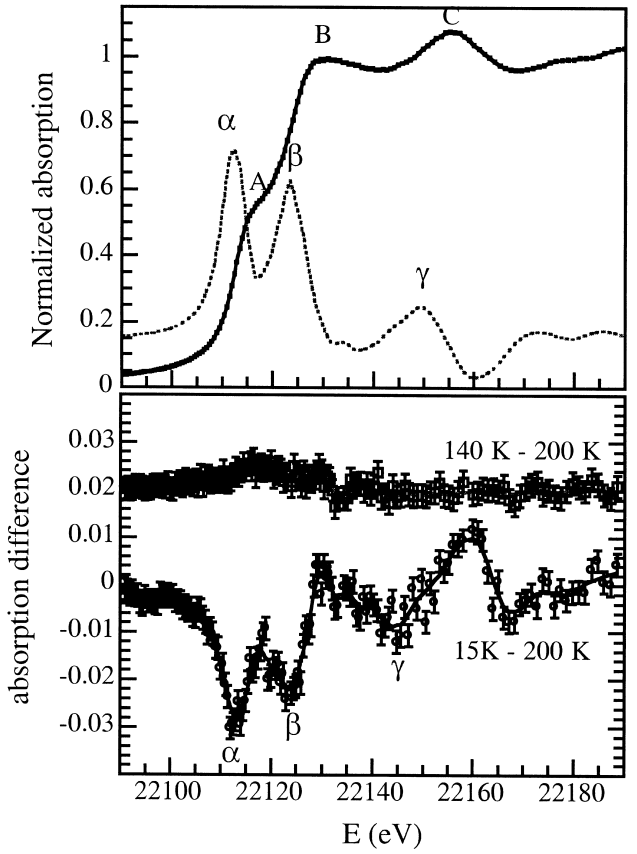

Fig. 2. (upper) Normalized Ru K-edge XANES spectrum of the $LaRu_2$ and its derivative; (lower) absorption differences between the spectra measured at different temperatures (note that the upper difference curve is artificially displaced by 0.02).

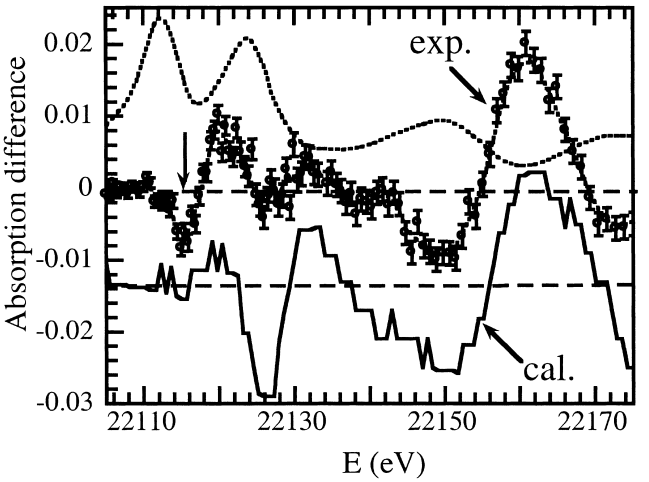

Fig. 3. Absorption difference between the spectrum measured on $La_{0.5}Ce_{0.5}Ru_2$ and $LaRu_2$ at 200 K (symbols). The derivative of the absorption spectrum is shown as a reference (dotted line). The Difference between calculated spectrum for $La_{0.5}Ce_{0.5}Ru_2$ and $LaRu_2$ is also shown (solid line).

difference shows peaks, suggesting that the temperature dependence is mainly due to an energy shift and it appears to be related to an overall contraction of the $LaRu_2$ lattice. A similar kind of lattice flexibility has earlier been shown for the $CeRu_2$ by ultrasonic measurements [16].

Let us now turn to the effect of Ce doping on the absorption spectrum of the $LaRu_2$. In Fig. 3 we have plotted the absorption difference between the spectrum measured on $La_{0.5}Ce_{0.5}Ru_2$ and $LaRu_2$ at 200 K. The derivative of the absorption spectrum is also shown as a reference. The substitution of the Ce in the $LaRu_2$ lattice appears to have dual effect; change in the lattice (energy shift towards higher energy indicating a compression of the native lattice) and change in the density of states at the Fermi level. Indeed the difference spectrum shows that there is a sharp decrease of the unoccupied density of states at the Fermi level and a complex variation of the spectral features in the energy range up to ~50 eV. The spectral variations in the energy range 10–50 eV could be satisfactorily reproduced in the multiple scattering calculations [15] for the nominal composition $La_{0.5}Ce_{0.5}Ru_2$ considering a marginal compression of the lattice due to Ce doping, however, the variation in the density of states at the Fermi level could not be reproduced. Therefore the hybridization between Ru 4*p*–4*d* orbitals with *f* states of La/Ce appears to be playing vital role and it seems that Ce in place of La does not change simply the one-electron density of states at the Fermi level. Thus the decrease of density of states at the Fermi level by Ce substitution in the $La_{0.5}Ce_{0.5}Ru_2$ should be related to a re-normalization due to the quasi-particle scattering with magnetic excitations introduced by localized and fluctuating Ce 4*f* electrons at the Fermi level.

In summary, we have reported temperature dependent high resolution Ru K-edge XANES measurements on $LaRu_2$ system and studied effect of Ce doping on the local electron density of states. We have found that the temperature dependence of local density of states is simply controlled by a compression of the $LaRu_2$ lattice by lowering the temperature. On the other hand, the effect Ce substitution in the $LaRu_2$ is two-fold; the lattice shows an overall compression and suppression of density of states at the Fermi level. The suppression of the density of states does not seem to be related with variation of single particle density of states but it is renormalized due to quasi-particle scattering with magnetic excitations introduced by localized and itinerant Ce 4*f* electrons. The suppressed spectral density of states at the Fermi level could justify the decrease of the superconducting transition temperature in the $La_{0.5}Ce_{0.5}Ru_2$.

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