Temperature Dependent Lattice Distortion in La$_{1-x}$Ce$_x$Ru$_2$ by Ru K-edge Absorption Spectroscopy

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Abstract. X-ray absorption near edge structure (XANES) spectroscopy has been used to investigate local lattice and electronic structure of the intermetallic La$_{1-x}$Ce$_x$Ru$_2$ system. Origin of different features is explored by one electron multiple scattering calculations. The experimental and theoretical analysis demonstrate that the Ce doping in La$_{1-x}$Ce$_x$Ru$_2$ has direct influence on the states at the Fermi level and hence the hybridization between the f and d states induced by doping.

INTRODUCTION

X-ray absorption near edge structure (XANES) was introduced as a tool to investigate intermediate short-range 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 mean free path is large, it decreases rapidly with increasing the energy of the final state since it is strongly scattered by the many body electronic excitations and its mean free path becomes 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 [2-4].

The hybridization of localized f electrons (magnetism) and itinerant d electrons (superconductivity) drives intermetallics towards the border line between magnetic and metallic systems. Among these intermetallic systems, LaRu$_2$ provides an interesting case [5-8] since it is formally a 4f$^0$ system showing a superconducting transition at 4.4 K. Systematic studies of Ce substitution in La$_{1-x}$Ce$_x$Ru$_2$ have shown an anomalous evolution of the superconducting transition temperature from $T_c \sim 4.4$ K at $x = 0.0$ to $T_c \sim 0.3$ K at $x \sim 0.5$. The lattice parameters are found to show a

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continuous evolution with substitution of Ce indicating an average compression of the unit cell [5]. The cooling of the sample introduces a further compression of the unit cell showing overall flexibility of the lattice structure. The anomalous lattice flexibility of CeRu2 was shown by ultrasonic technique measuring elastic stiffness that shows significant lattice softening without structural transition in the normal state [9]. Furthermore, the importance of lattice in the electronic properties has been indicated by an abnormal pressure dependence of the superconducting transition temperature of the La1-xCe,Ru2 system [10]. This unusual effect of pressure on Tc indicates interesting evolution of the electron-lattice interactions in the La1-xCe,Ru2 superconductor. It is still to be understood whether the decrease of the Tc in La1-xCe,Ru2 is due to increasing magnetic interaction or due to change in the local electronic density of states and/or local lattice distortions.

Here we have exploited capabilities of XANES spectroscopy and made high-resolution Ru K-edge XANES measurements to study the effect of Ce in the La1-xCe,Ru2 intermetallic 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. Multiple scattering calculations are made to identify origin of different XANES features [11]. The results suggest that the Ce substitution in place of La in the LaRu2 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 may be due to scattering with localized f electrons injected by the mixed valent Ce.

![Normalized absorption](image)

**FIGURE 1.** Normalized Ru K-edge XANES spectrum of the LaRu2 and its derivative. The spectrum was measured at 290K on LaRu2 in the fluorescence yield mode and is shown normalized to the atomic absorption.
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Here we have exploited capabilities of XANES spectroscopy and made high resolution Ru K-edge XANES measurements to study the effect of Ce in the La$_{1-x}$Ce$_x$Ru$_2$ intermetallic 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. Multiple scattering calculations are made to identify origin of different XANES features [11]. 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 may be due to scattering with localized f electrons injected by the mixed valent Ce.

**FIGURE 1.** Normalized Ru K-edge XANES spectrum of the LaRu$_2$ and its derivative. The spectrum was measured at 200K on LaRu$_2$ in the fluorescence yield mode and is shown normalized to the atomic absorption.
LaRu$_2$ is a laves phase with a face-centered cubic (MgCu$_2$-type) structure [13]. We have calculated real-space multiple scattering of the photoelectron excited from the Ru 1s-state to the atoms surrounding the central Ru for a cluster of atoms. Fig. 2 shows the calculated spectrum for a cluster of five-shells containing all atoms within 5 Å from the central Ru. The experimental spectrum is also plotted for comparison. A good agreement between the two spectra suggests that a cluster of about five shells is sufficient to describe the characteristic XANES features of the LaRu$_2$ system.

From the cluster dependence of the XANES multiple scattering peaks we have found that the peak A is associated with the unoccupied states made of mixed Ru p-d states, i.e., central Ru 4p 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 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 6 Ru atoms. The details of the calculations are published elsewhere [11].

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. 3 shows the absorption differences between the spectra measured at different temperatures. We do not observe any appreciable temperature dependence down to $\sim$ 140 K as evident from the absorption difference between the spectra measured at 140 K and 200 K. On the contrary, there is a large change in the main absorption features by lowering the temperature down to 15K that could be seen in the absorption difference between the spectra measured at 15 K and 200 K showing a maximum of $\sim$ 4% of the normalized absorption. The peaks in the derivative spectrum

**FIGURE 3.** Absorption differences revealing temperature dependence (note that the upper difference curve is artificially displaced by 0.02 ).
(α, β, γ) appears almost at the same energy positions (see, e.g. Fig., 2) where the absorption 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 LaRu₂ lattice.

Now we turn towards the influence of Ce doping on the local electronic density of states and the local lattice displacements in the La₁₋₄Ce₄Ru₂. Fig. 4 shows the absorption difference between the spectrum measured on La₀.₆Ce₀.₄Ru₂ and LaRu₂ at 200 K (symbols). We observe a sharp decrease of the unoccupied density of states at the Fermi level (α) and a complex variation of the spectral features in energy range up to ~ 50 eV. In order to understand the spectral variations we have calculated the XANES spectra taking into account the compression of the crystalline lattice (from 7.7 Å to 7.63 Å as given in [5]) and the substitution of La by Ce in the native LaRu₂, i.e., considering the nominal composition La₀.₅Ce₀.₅Ru₂ where the compression (Ce is smaller than La) and the electronic configuration of Ce are taken into account. The absorption difference between the calculated spectra on the La₀.₅Ce₀.₅Ru₂ and the LaRu₂ is plotted in Fig. 4 (solid line). The agreement in the experiment and calculations is quite good and we can reproduce the variation of the peaks in the energy range 10 - 50 eV, however, we are not able reproduce the peak at the Fermi level (see arrow). This suggests that the substitution of Ce in place of La does not change the one-electron density of states at the Fermi level as shown by the multiple scattering calculations. Therefore the disagreement between the calculated and experimental differences is presumed to be related to a re-normalization of quasi particles.

![Absorption difference graph](image)

FIGURE 4. Absorption differences revealing effect of Ce in La₁₋₄Ce₄Ru₂. The differences are made between the measured spectrum of La₀.₅Ce₀.₅Ru₂ and LaRu₂ measured at 200 K (symbols) and calculated (solid line). The derivative of the absorption spectrum is shown as a reference (dashed line).
In summary, we have made temperature dependent Ru K-edge XANES measurements on for LaRu2 system and studied effect of Ce doping on the local lattice and electron density of states. A real space multiple scattering approach has been used to identify the XANES features and a comparison of experimental and calculated spectra have been made. We have found that the temperature dependence of local density of states is mainly controlled by a compression of the LaRu2 lattice by lowering the temperature. On the other hand, the effect Ce substitution in the LaRu2 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 may be renormalized due to quasi-particle scattering with magnetic excitations introduced by localized and itinerant Ce 4f electrons. The suppressed spectral density of states at the Fermi level could be one of the possible reasons to the decrease of the superconducting transition temperature in the La0.5Ce0.5Ru2.

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