High-resolution photoemission study of $Ce_{1-x}La_xRhAs$: a collapse of the energy gap in the Kondo semiconductor

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Abstract

High-resolution resonance-photoemission spectroscopy has been performed on the $Ce_{1-x}La_xRhAs$ ($0 \le x \le 0.05$) single crystal to elucidate a collapse of the energy gap in the Kondo semiconductor CeRhAs by La substitution. With increasing x, the spectral intensity of the Ce $4f^1$ derived states near the Fermi level decreases and new 4f derived spectral feature appears at a higher binding energy. The Rh 4d-derived states, on the other hand, are not significantly changed by the substitution. New 4f-derived states have incoherent nature, which is responsible for the collapse of the semiconducting state for $x > \sim 0.02$.
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The orthorhombic CeRhAs, known as a Kondo semiconductor, has attracted much interest for its unusual energy-gap formation associated with the successive first-order-structural-phase transitions [1]. Recently La-substituted $Ce_{1-x}La_xRhAs$ single crystals have been synthesized [2]. It has been found that a semiconducting behavior almost disappears with a La concentration as low as $x \sim 0.02$ [2]. In order to elucidate how the energy gap in CeRhAs collapses by the La substitution, we have conducted a high-resolution resonance-photoemission spectroscopy (PES) study of $Ce_{1-x}La_xRhAs$ ($0 \le x \le 0.05$).

Single crystals of $Ce_{1-x}La_xRhAs$ (x=0, 0.003, 0.02, 0.05) were grown by the Bridgman method [1,2]. The 3d-4f resonance PES experiments ($h\nu$=870-881 eV) were done at the beamline BL23SU of SPring-8 [3], and the 4d-4f resonance PES experiments ($h\nu$=122 eV) at the beamline BL-1 of HiSOR [4]. The sample temperature was kept at 10-20 K, and the overall energy resolution was set at ΔE=20 meV ($h\nu$=122 eV) and 100 meV ($h\nu$=870-881 eV). Clean sample surfaces were obtained by fracturing the sample in the ultrahigh vacuum.

Figure 1 shows on-resonance PES spectra of $Ce_{1-x}La_xRhAs$ at $h\nu$ = 881 eV and 122 eV. Due to large resonance enhancement, one can regard these spectra as the Ce 4f partial spectra. We have normalized these spectra to the area for the binding energy (E_B) range of $E_B \sim 0$-9 eV. A peak structure near E_F for the x=0 sample at $h\nu$=881 eV corresponds to the $Ce4f^1$ final state, which exhibits a hybridization gap of ~100 meV. Our previous measurements indicate that the energy gap is originated from As4p, Rh4d and Ce4f hybridization [4,5], in agreement with the band-structure calculation [6]. A broad spectral feature at ~2.5 eV is derived from the Ce $4f^0$ final

state and partly from the Rh 4d states. As the Ce is replaced by La from x=0 to 0.003, the intensity of the peak near E_F is reduced. From x=0.003 to x=0.02, a drastic change has been observed; the peak intensity is shifted to the higher binding energy of E_B~0.4 eV. From x=0.02 to 0.05, the overall spectral features are the same, but the spectral weight of the Ce $4f^1$ state with respect to the Ce $4f^0$ state is reduced. These behaviors cannot be explained by the rigid-band model. Note that the spectra for x=0.02 and 0.05 near E_F are similar to the spectrum at hν=122 eV, where the localized electronic states at surface form a peak structure at ~0.4 eV. This suggests that a localized 4f state appears in the bulk upon La substitution. We assume that the new state has incoherent nature and does not participate in the hybridization-gap formation. This leads to the collapse of the insulating state of CeRhAs. As there is a significant modification of the spectral features between x=0.003 and 0.02, there should exist a critical concentration x_c for the semiconductor-to-metal transition. On the basis of the transport properties [2], x_c is closer to 0.02.

Figure 2 shows the off-resonance spectra at hν=870 eV, which mainly reflect Rh 4d states. One cannot recognize significant x dependence of the spectral features. This indicates that the overall Rh4d states remain unchanged for x<0.05.

In summary, high-resolution resonance PES study of $Ce_{1-x}La_xRhAs$ (x=0, 0.0003, 0.02, 0.05) single crystals has been done. While the Rh 4d derived states were not influenced by the La substitution, the Ce 4f derived states were significantly modified between x=0.003 and 0.02: the intensity of the coherent peak near E_F is reduced and new spectral feature appears at E_B~0.4 eV. The new 4f derived state has incoherent nature, which is responsible for the collapse of the insulating state for x>~0.02.

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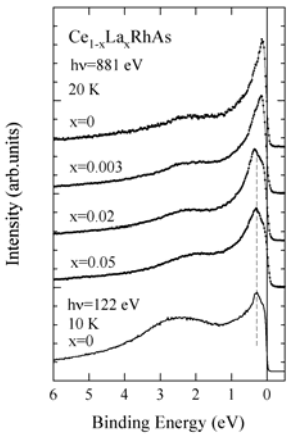

Fig. 1. High-resolution on-resonance photoemission spectra of $Ce_{1-x}La_xRhAs$ single crystal at hν = 881 eV and 122 eV.

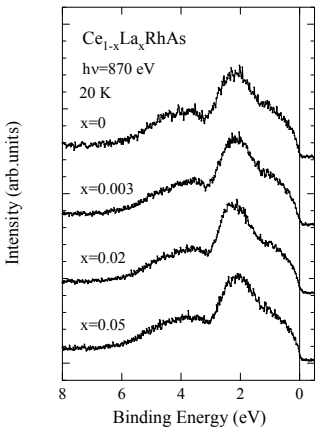

Fig. 2. High-resolution off-resonance photoemission spectra of $Ce_{1-x}La_xRhAs$ single crystal at hν = 870 eV.