Electronic Structure of CeCo₂ Thin Films Studied by X-ray Absorption Spectroscopy

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The nature of 4f electron in rare-earth compound has attracted much attention in recent years. This is due to the f states may possess both localized and band-like character. In this, the electronic and magnetic properties of materials in nanoscale can be different from the bulk. In a recent study of heavy fermion compound CeAl₂, it is demonstrated that the bulk CeAl₂ exhibits magnetic ordering whereas shows nonmagnetic in nanoparticles, which is attributed to the surface effect. On the contrary, CeCo₂ undergoes a nonmagnetic-magnetic transition with size reduction. It would be of interest to investigate how surface effect influences the electronic structure on CeCo₂. From our preparation method, the flash evaporation, only particle size with diameter smaller than ~10nm are successful obtained. In order to verify the surface effect on the electronic state of CeCo₂, by studying samples of different surface to bulk ratio, x-ray absorption near edge structure (XANES) were therefore performed at thin films of different thickness.

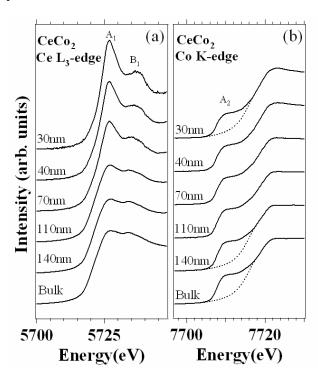


Figure 1. XANES spectra at (a) Ce L_3 -edge and (b) Co K-edge for $CeCo_2$ bulk and thin films.

X-ray absorption spectroscopy at L_3 -ege has been widely used to study rare-earth materials and to determine the valence in mixed-valence materials. X-ray absorption measurements were carried out at beamline 17C at the National Synchrotron Radiation Research Center (NSRRC). Fig. 1(a) shows XANES spectra for Ce L_3 -edge. The large number of unoccupied 5d orbital produces a prominent L_3 white line $A_2 \left(2p^*4f^0(5d6s)^4$ final state) and additional feature $B_2 \left(2p^*4f^0(5d6s)^5\right)$ final state), respectively, correspond to Ce^{3+} and Ce^{4+} states ($2p^*$ denotes a hole in 2p level). This clear spectral evolutions evidence the valence change is seen. The enhancement of $4f^1$ states in thinner films implies the gain of 4f electron in Ce site.

XANES spectra at Co K-edge are presented in Fig. 1(b). For Co K-edge, an electron is excited from inner s orbital to final p orbital. However, The shoulderlike feature A_1 at about 7110 eV primarily reflects the density of empty 3d states through the s-p-d rehybridization. The progressive decreasing of the feature A_1 as reducing thickness evidences the electronic perturbation of the density of state driven by the surface to bulk ratio. This result indicates a less hybridization between conduction states of Ce 4f5d and Co 3d states in thinner films. It is also noted that the unoccupied 3d states vary with the film thickness. By comparing the results from Ce L_3 - and Co K-edge, the charge transfer between Ce and Co may be the consequence of the valence change driven by the different surface to bulk ratio.