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Electronic structure of $CeCo_2$ thin films studied by X-ray absorption spectroscopy

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Abstract

We present an X-ray absorption near-edge structure (XANES) study at Ce L_3-, and Co K-edges of $CeCo_2$ thin films with the thickness varying from 30 to 140 nm. Ce L_3-edge spectra exhibit the mixed valence nature and the tetravalent contribution increases with the thickness of $CeCo_2$. The variation in the spectral intensity observed at Co K-edge threshold indicates that there is a change in 3d occupancy and also in 3d–4f–5d hybridization. This study shows the effect of surface to bulk ratio and how it influences the charge transfer between Ce and Co ions and hence the electronic structure of $CeCo_2$ thin films.

Keywords: XANES; Mixed valence; Surface; Thin film

1. Introduction

$CeCo_2$ is a superconducting compound with transition temperature T_c of 1 K [1]. It has been considered that Ce in $CeCo_2$ is in an intermediate valence state due to the collapsed volume and both Ce and Co are essentially nonmagnetic [1,2]. The intriguing behavior of 4f electrons in rare-earth compounds is that it possesses both localized and band-like characters. It becomes clear that the electronic and magnetic properties of materials in nanoscale are different from the bulk even though their chemical composition being the same. Recent study on $CeAl_2$, it has demonstrated that the bulk $CeAl_2$ exhibits magnetic ordering while $CeAl_2$ nanoparticles show nonmagnetic nature [3]. This phenomenon has been attributed to the effect of surface to bulk ratio [4]. On the contrary, $CeCo_2$ exhibits the opposite behavior [2]. It would be of interest to investigate how bulk to surface effect influences the electronic structure on $CeCo_2$. X-ray absorption near edge structure (XANES) has been a favored experimental tool to study the core level changes and understand the electronic structure with thin films of different thickness.

2. Experimental

The $CeCo_2$ thin films of thickness 30, 40, 70, 110 and 140 nm were prepared by flash evaporation of bulk $CeCo_2$ ingot onto a liquid nitrogen cold trap in a 0.1 Torr of high purity helium and the thickness of these films were monitored by a quartz crystal oscillator during the evaporation process. Details are given elsewhere [3]. X-ray absorption measurements were carried out at beamline 17C at the National Synchrotron Radiation Research Center (NSRRC), Taiwan, in fluorescence mode at room temperature.

3. Results and discussions

Fig. 1(a) shows XANES spectra at Ce L_3-edges of $CeCo_2$ thin films. The unoccupied Ce 5d orbital produces two

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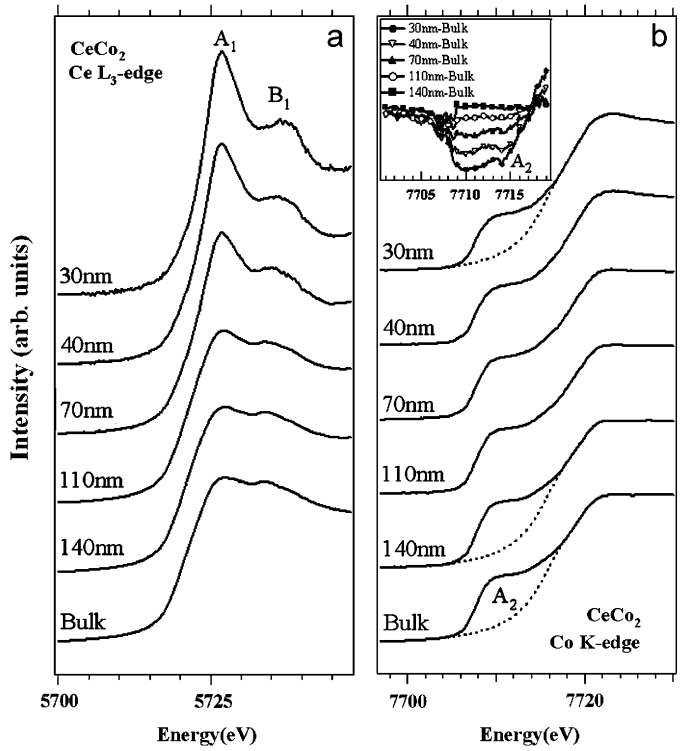

Fig. 1. XANES spectra for bulk $CeCo_2$ and thin films at (a) Ce L_3-edge and (b) Co K-edge. Inset in (b) is obtained after subtracting the spectrum of bulk $CeCo_2$.

prominent L_3 white lines, marked as A_1 and B_1 which are ascribed, respectively, to $2p^*4f^1(5d6s)^4$ and $2p^*4f^0(5d6s)^5$ final states, corresponding to Ce^{3+} and Ce^{4+} states [5]. The 2p* denotes a hole in 2p level. As evident from the figure, there is a clear spectral evolution indicating the valence change with thickness. The enhancement of $4f^1$ states in very thin films implies the increased 4f electron occupancy of Ce atoms.

XANES spectra at Co K-edge are presented in Fig. 1(b). The absorption feature A_2 at ~7110 eV primarily reflects the density of empty 3d states through the s–p–d rehybridization [6]. The systematic reduction of the feature A_2 with thickness shows the electronic perturbation of the density of state resulting from the surface to bulk ratio. The inset of Fig. 1(b) obtained after subtracting the bulk spectra, shows that the hybridization between conduction states of Ce 4f5d and Co 3d states increases with film thickness. It is also noted that the unoccupied 3d states increase as film thickness decrease. By comparing the results from Ce L_3- and Co K-edges, the charge transfer between Ce and Co may be the consequence of the valence change driven by the different surface to bulk ratio.

4. Conclusions

The XANES study at Ce L_3-edge revealed the mixed valence nature of Ce ions and the contribution of Ce^{4+} is reducing as thickness decreases [5]. On the other hand, the XANES at Co K-edge provides evidence that the 3d occupancy varies with film thickness [7]. These results suggest that the valence change is due to the charge transfer driven by the surface to bulk ratio effect.

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