We report the electronic structure study of intermetallic CeCo$_2$ nanothin films of various thicknesses by X-ray absorption near-edge structure (XANES) spectroscopy at Ce L$_3$-, Co K-, and L$_2,3$-edges. The Ce L$_3$-edge absorption spectra reveal that the contribution of tetravalent Ce component increases with the film thickness, and all investigated nanothin films exhibit intermediate valence nature. Variation of the spectral intensities observed at the Co K-edge threshold implies modification in the Co 3d states and the enhancement of 3d-4f hybridization. The Co 3d and Ce 4f occupation numbers were estimated from these spectroscopic results. The present study brings out how the surface-to-bulk ratio and the charge transfer between Ce and Co ions affect the electronic structure of nanothin films.

1. Introduction

Nanometer scale thin films (or nanothin films) of thickness from 10 to a few hundred nanometers are of great interest for understanding fundamental questions such as how surface properties develop into bulk properties and how their electronic structure modifies during the process of such change over. Among rare-earth-based intermetallics, cerium (Ce)-based compounds fascinate materials scientists because of their puzzling electronic properties such as kondo effects, long-range magnetic ordering, coexistence of heavy-fermionic behavior, and superconductivity. These unusual properties are commonly attributed to hybridization of the 4f electrons with the conduction electrons. Most Ce compounds in their stable trivalent state, [Xe] 4f$^1$ configuration of the 4f electrons with the conduction electrons. Most Ce compounds are essentially nonmagnetic in this compound. The CeCo$_2$ system modifies during the process of such change over. Among rare-earth-based intermetallics, cerium (Ce)-based compounds the electronic properties develop into bulk properties and how their electronic structure modifies during the process of such change over. Among rare-earth-based intermetallics, cerium (Ce)-based compounds, the electronic properties such as kondo effects, long-range magnetic ordering, coexistence of heavy-fermionic behavior, and superconductivity. These unusual properties are commonly attributed to hybridization of the 4f electrons with the conduction electrons. Most Ce compounds in their stable trivalent state, [Xe] 4f$^1$ configuration of the 4f electrons with the conduction electrons. Most Ce compounds are essentially nonmagnetic in this compound. The CeCo$_2$ system modifies during the process of such change over. Among rare-earth-based intermetallics, cerium (Ce)-based compounds, the electronic properties such as kondo effects, long-range magnetic ordering, coexistence of heavy-fermionic behavior, and superconductivity. These unusual properties are commonly attributed to hybridization of the 4f electrons with the conduction electrons. Most Ce compounds in their stable trivalent state, [Xe] 4f$^1$ configuration of the 4f electrons with the conduction electrons. Most Ce compounds are essentially nonmagnetic in this compound.

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CeCo$_2$: a single-peak profile in the case of CeAl$_2$ and double-peak profile for CeCo$_2$ that arise primarily as a result of the difference in their electronic configurations.

2. Experimental Details

The bulk CeCo$_2$ sample was prepared by the arc-melting method from high-purity constituent elements Ce (99.95%) and Co (99.95%) in 1:2 atomic ratios in an argon atmosphere (99.999%). In order to obtain a homogeneous phase of CeCo$_2$, melting was repeated five times and annealed at 900 °C for a week. The CeCo$_2$ nanothin films of thickness 30, 40, 75, 110, and 140 nm were fabricated on to a glass substrate without cooling by flash evaporation of bulk CeCo$_2$ ingot. All the “as-prepared” nanothin films were annealed at 900 °C for the duration of 1 week. The structure and phase purity were determined by X-ray diffraction, and these films were found to be in cubic Laves structure with a lattice constant of $a_0 = 7.160$ Å.

X-ray absorption measurements were performed at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The XANES spectra at Ce L$_3$- and Co K-edges were carried out at Wiggler beamline 17C using fluorescent mode at room temperature. The monochromator Si (111) crystals were used at Wiggler beamline 17C with an energy resolution $\Delta E / E$ better than $2 \times 10^{-4}$. The energy resolution at 5723 eV (Ce L$_3$-edge) was about 0.3 eV, and for the Co K-edge, it was $\sim 0.4$ eV. In order to eliminate the effect of the self-absorption, all measurements were done in normal incidence geometry. Since pure Ce gets oxidized very easily, the energy scale was calibrated by using vanadium thin film (V K-edge at 5465 eV). The Ce L$_3$-edge has an absorption energy of 5723 eV, which is $\sim 160$ eV above the V K-edge. The compound CeF$_3$ was used as a reference for the Ce L$_3$-edge, which shows a single peak profile at 5727.1 eV. Apart from this, the experimental setup allows one to simultaneously measure the reference sample CeF$_3$ behind the CeCo$_2$, CeCo$_2$ nanothin films. The signal of this reference sample was noisy because of the X-rays that cannot totally transverse the substrate. However, the first-differential point of raising absorption edge still allowed us to check the energy. The XANES spectra at Co L$_2$,3-edges were recorded at HSGM beamline 20A using total electron yield mode. The energy resolution was set to 0.2 eV.

3. Results and Discussion

Figure 1 shows Ce L$_3$-edge XANES spectra of CeCo$_2$ nanothin films along with bulk CeCo$_2$. The large number of unoccupied Ce 5d orbitals, via 2p to 5d transition, results in two prominent L$_3$ white lines, marked as A$_1$ and B$_1$. The ground state of the Ce atom has the electronic configuration of [Xe] 4f$^4$5d$^6$6s$^2$. In Ce intermetallics, the 5d$^6$6s$^2$ electrons participate in bonding and form a part of the valence band. The 4f electron occupancy is primarily determined by the chemical environment. This can be visualized as two configurations, 4f$^3$ (Ce$^{3+}$ state) and 4f$^0$ (Ce$^{4+}$ state), which result in two different spectral structures (A$_1$ and B$_1$) in Ce L$_3$-edge XANES. The double-peak spectral shape at the L$_3$-edge is known to be the signature of the intermediate valence nature.

In general, Ce L$_3$-edges of strongly correlated systems, such as cerium-based oxides, display three characteristic contributions associated with 4f$^0$, 4f$^3$L and 4f$^0$ configurations when Ce ions are in +3 and +4 states. For such systems, there is strong hybridization of the Ce states with O 2p states, which give rise to ligand holes represented as 4f$^0$L configurations. As to the intermetallic compound, CeCo$_2$, the ligand hole state is absent and should result in two contributions at the threshold of the Ce L$_3$-edge spectra. The inset shows the profile of the line-width of the spectral feature A$_1$ and the thickness of the nanothin films. As evident from Figure 1, there is a clear spectral evolution indicating a change in the valency and line-widths depending on film thickness. These parameters are likely to provide better understanding of the intermetallics. Enhancement of the 4f$^0$ state implies an increase of 4f electron occupancy at Ce site as the thickness decreases.

In Figure 1, all spectra show trivalent and tetravalent Ce valence states as shown in the fitting procedure (deconvoluted) marked by dashed lines at the bottom of the figure. Each valence state can be decomposed into a Gaussian function and an arctangent edge jump function. The former function describes the localized 5d final states, which reflect the Ce$^{3+}$ or Ce$^{4+}$ valence states, and the latter represents the transition to continuum states above $E_C$. The open circles represent the fitting curve by summing the weighted Ce$^{3+}$ and Ce$^{4+}$. The fitting curves are found to be in good agreement with the experimental results. Subsequently, the average valency of Ce was evaluated by following a standard procedure, $\gamma_{av} = 3 + \frac{I_{Ce^{3+}}}{I_{Ce^{3+}} + I_{Ce^{4+}}}$, where $I_{Ce^{3+}}$ and $I_{Ce^{4+}}$ are associated with the integrated intensities of the trivalent and tetravalent Ce contributions. The estimated valencies of Ce for bulk, 140, 110, 70, 40, and 30 nm nanothin films are, respectively, 3.30, 3.30, 3.28, 3.27, 3.24, and 3.22. It clearly shows that the valency increases with thickness of nanothin films. There is minor a discrepancy

![Figure 1. XANES spectra at Ce L$_3$-edge for bulk and various thicknesses of CeCo$_2$ nanothin films. Note the change in spectral features A$_1$ and B$_1$ with the thickness of the film. Inset shows the line-width of spectral feature A$_1$, which changes with the film thickness.](image-url)
from the fitting around 5720 eV due to the contribution of the dipole-forbidden 2p to 4f transitions.

Two major factors determine the electron energy levels in nanoscale materials: the increased surface area, and the reduced coordination number. The former broadens the band, while the latter tends to narrow the band.\(^{(16)}\) The band narrowing is observed in Ce L\(_2\)-edge XANES as the thickness is decreased (shown in the inset of Figure 1), indicating the reduced coordination number. This observation is also consistent with results of CeAl\(_2\) thin films and CeCo\(_2\) nanoparticles.\(^{(17)}\) In CeAl\(_2\) nanoparticles, the valency change is explained by the stronger surface pressure lifting the 4f level up close to the conduction band.\(^{(16)}\) However, the present result does not support this statement since there is no shift in the Ce 4f levels relative to the E\(_f\), otherwise the valency should enhance as the thickness of the CeCo\(_2\) thin film is increased. Apparently, in addition to the modification of the Ce 4f level position due to the increase of the valency, there should be other competing mechanisms that dominate the valency change in the CeCo\(_2\) system.

The physical and chemical properties of solid-state matter are determined primarily by the bulk volume. In the case of nanomaterials, these properties could be influenced significantly by the surface area. The surface-to-volume ratio is a useful parameter when studying the transition from bulk to nanomaterials. Surface tension (\(\gamma\)) and cohesive energy (\(G\)) are two important physical quantities that determine the growth and thermal stability of the materials. While surface tension is caused by the attraction between the molecules due to various intermolecular forces, the bulk cohesion is the energy required to separate the atoms of the solid into isolated atomic species. Since \(\gamma\) refers to the surface energy per unit area and \(G\) is the attractive energy per unit volume, one can represent the surface energy as \(\gamma A\) and the bulk cohesive energy as \(GV\) where the quantities \(A\) and \(V\) represent the surface area and volume of the solid, respectively. In nature, materials attempt to balance surface energy and bulk cohesive energy (i.e., \(\gamma A = GV\)). Thus the surface-to-bulk ratio is defined as the ratio of the number of surface atoms to the number of bulk atoms and reflects the relative magnitude between the surface tension and bulk cohesive energy of the material. In other words, the surface-to-bulk ratio directly refers to the surface-to-bulk energy ratio (\(A/V = G/\gamma\)) and is inversely proportional to the radius or thickness of the solid if the shape has a perfect geometry. The analysis of the surface-to-bulk ratio is useful in understanding the electronic structures of these nanofilm thin films. The dimensions of the nanofilm thin films in this study were \(\sim 5 \text{ mm} \times 5 \text{ mm} \times \text{thickness}\). The surface layer is about few atomic monolayers, and it is assumed that the thickness of surface layer is \(d\). Thus the surface area should be regarded as a very thin layer of \(\sim 5 \text{ mm} \times 5 \text{ mm} \times d\). If the contribution of the side wall of the film is neglected, the surface-to-bulk ratio is solely determined by the ratio of \(\text{layer}_{\text{surface}} / \text{layer}_{\text{total}}\), and thus the surface-to-bulk ratio results as \(\sim d / \text{thickness}\). Consequently, the thickness plays an important role in the surface-to-bulk ratio of nanofilm thin films, and the values of surface-to-bulk ratio are estimated to be 0.0333, 0.0251, 0.0133, 0.0091, and 0.0071 for 30, 40, 75, 110, and 140 nm, respectively. These results along with the valency as a function of thickness are shown in Figure 2. This analysis of surface-to-bulk ratio appears to be adequate. In short, for solids, the physical and chemical properties of solids are determined by the bulk, and, for nanofilm thin films, the properties are influenced primarily by the surface.

To understand the origin of variation of Ce valency and the correlation at the Co site, we measured XANES at Co K- and L\(_{2,3}\)-edges. Taking advantage of the orbital and site selectivity offered by X-ray absorption process, by tuning the photon energy near Co K- and L\(_{2,3}\)-edges, one can investigate the electronic structure at the Co site and valency change. The normalized XANES spectra at the Co K-edge are presented in Figure 3. For Co K-edge absorption, where the inner 1s electron is excited to the final state, the 4p orbital reflects the density of unoccupied 4p states above the Fermi level, thus the Co K-edge mainly probes the unoccupied 4p states. However, the pre-edge peak structure is attributed to 3d character due to the hybridized Co 4sp-Co 3d states as well as the hybridized Ce 4f-5d-Co 3d states.\(^{(18)}\) As a result, the prepeak comprises mixed states, and its intensity does not directly reflect the change of the Co 3d state alone.


Ce (4f, 5d) and those of Co (3d). Thus, the modification of the stronger hybridization between the conduction states of it becomes more convenient to count the "unoccupied 3d states" contributions to the DOS at band and Co 3d band. This calculation further reveals that the spectra at the Co L 2,3-edge. The integrated intensity across unoccupied 3d states. Figure 4 shows the normalized XANES from 2p to 3d states and give direct information about the state configuration for the complete "3d occupancy" is 3d 10. So A 3 may reflect the change of the hybridization strength and variation of the density of empty 3d states. 19,20 Thus, the modification of A 3 intensity with decreasing E takes account of the Co ions atomic ratio in CeCo 2, the variation of Co 3d occupancy is consistent with that of Ce 4f occupancy. This experimental observation suggests there is charge transfer between Ce and Co, thus the charge transfer is another factor in addition to the surface effect that influences the Ce valency.

When the thickness of CeCo 2 film decreases, the relatively reduced hybridization and charge transfer results in less charge distribution in the 3d orbital. As a result, the 3d band moves up toward the Ef. 26,27 This is consistent with the recent calculation that predicts that the 3d band of surface Co atom becomes narrower and pushed up slightly toward the Ef in comparison with the bulk. 28 As the band is pushed toward the Ef, the hybridization should be increased without affecting the Ce 4f levels. However, this argument conflicts with the XANES result, which shows small hybridization in thinner nanofilms. Consequently, the influence of the Ce site has to be taken into account. Possible explanations are that (i) the narrowing of Ce 4f band, 29 in accordance with the result from the line-width shown in Figure 1, by ν = 4 – ν. It shows that the occupation of the Co 3d states decreases with a corresponding increased Ce 4f occupation as the thickness reduces. It is noted that the variation of Ce 4f occupancy is about ~11%, and the estimated variation of 3d occupancy is about ~5%. If one takes account of the Co ions atomic ratio in CeCo 2, the variation of Co 3d occupancy is consistent with that of Ce 4f occupancy.

![Graph showing the occupancy of Ce –4f and Co3d at different thicknesses.](image)

Figure 5. The graph shows the occupancy of Ce –4f and Co3d at different thicknesses.

using the parameter of “3d occupancy”. One would start with Co metal and bulk CeCo 2 and assume their 3d occupancy numbers to be 7 (Co) and 7.5 (bulk CeCo 2). 23–25 The area under XANES spectra was measured to be 13.9 and 7.9, respectively, for Co metal and bulk CeCo 2. Since the area under the XANES spectra is proportional to the unoccupied state, the 3d occupancy can be estimated. 24,25 Thus, the estimated “3d occupancy” will be 7.093, 7.116, 7.195, 7.237, and 7.245 for nanofilms with thicknesses of 30, 40, 75, 110, and 140 nm, respectively. This is plotted in Figure 5 along with the occupancy of Ce. The Ce 4f occupancy numbers can be translated from the valency, which is estimated from Figure 1, by n = 4 – ν. It shows that the occupation of the Co 3d states decreases with a corresponding increased Ce 4f occupation as the thickness reduces. When the thickness of CeCo 2 film decreases, the relatively reduced hybridization and charge transfer results in less charge distribution in the 3d orbital. As a result, the 3d band moves up toward the Ef. 26,27 This is consistent with the recent calculation that predicts that the 3d band of surface Co atom becomes narrower and pushed up slightly toward the Ef in comparison with the bulk. 28 As the band is pushed toward the Ef, the hybridization should be increased without affecting the Ce 4f levels. However, this argument conflicts with the XANES result, which shows small hybridization in thinner nanofilms. Consequently, the influence of the Ce site has to be taken into account. Possible explanations are that (i) the narrowing of Ce 4f band, 29 in accordance with the result from the line-width shown in Figure 1, or (ii) the shift of the 4f band away from the Ef may reduce the

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overlap of the 3d and 4f bands. The band structure calculations, based on generalized gradient approximation (GGA) in pseudopotential and GGA with the on-site Coulomb energy U (GGA + U) calculation shows the Ce 4f states from the surface layer is shifted away from the $E_F$ by 2 eV. Thus, even though the 3d band is shifted up to the $E_F$, the overlap of wave function from 3d and 4f decreases and also reduces hybridization strength in nanothin films. From the above discussion, the valency change is closely related to the surface-to-bulk ratio, and the charge transfer between Ce and Co has the consequence of the valency change driven by the different surface-to-bulk ratio.

4. Conclusion

The XANES study at the Ce L$_{3}$-edge revealed that Ce ions are in the intermediate valence state, and the contribution of the tetravalent component increases as the thickness of the CeCo$_2$ nanothin films increases. XANES at Co K- and L$_{2,3}$-edges show that the hybridization strength and 3d occupancy also varies with film thickness. It is found that charge transfer from Ce to Co increases with thickness of CeCo$_2$ nanothin films. Both the bulk-to-surface effect and the presence of Co 3d charge transfer modify the Ce 4f electron occupation, resulting in the change of DOS and the valency. The experimental findings suggest that the valency change in CeCo$_2$ is due to the charge transfer driven by the surface-to-bulk ratio effect.

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