

# Variation of electronic structures of CeAl<sub>2</sub> thin films with thickness studied by X-ray absorption near-edge structure spectroscopy

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## Abstract

We report the X-ray absorption near-edge structures (XANES) of CeAl<sub>2</sub> thin films of various thickness, 40–120 nm, at Al K-, Ce L<sub>3</sub>-, and Ce M<sub>4,5</sub>-edges. It is found that the threshold of near-edge absorption features at the Al K-edge shifts to the higher photon energy as film thickness decreases, implying that Al loses p-orbital charge and the valence of Ce increases slightly as revealed from the XANES features at Ce L<sub>3</sub>- and M<sub>4,5</sub>-edges. Above observations suggest that there is charge transfer from Al to Ce as the surface to bulk ratio is varied. This induces change in the electronic structures of CeAl<sub>2</sub> thin films. The Ce 4f electrons are surface sensitive in nanoparticles compared to thin films. This work also shows that 4f electronic states of Ce ions are sensitive to the reduction of the coordination number induced by surface effects that would change their hybridization.

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## 1. Introduction

The subject of finite size effects on nanoparticle has attracted tremendous interests in the recent years due to their applications in the emerging nanotechnology [1,2]. They exhibit properties different from those of the bulk related geometric structure, electronic band structure, and magnetism essentially because of a symmetry breaking and/or of a lower dimensionality. The concept of surface to bulk ratio plays a very important role in understanding of these materials. Thus, nanomaterials are characterized by a large number of atoms with very low coordination number on the surface, at corners and edges. From an electronic structure point of perspective, particle shape, size distribution, and surface to bulk ratio of nanomaterials are crit-

ical. The absence of three-dimensional symmetry at surface changes the electronic structure and the magnetic properties. In many cases, unique properties of nanoparticles arise because of the competition between surface magnetic properties and core magnetic properties. Two major factors determine the electron energy levels of nanoparticles, the increased surface area and the reduced coordination. The former tends to broaden the band while the latter tends to narrow the band [3]. Direct measurement of the electronic structure of nanocrystalline materials using X-ray spectroscopic techniques revealed various interesting effects [3–5]. In a recent work [5], it was reported that decrease of 4f occupancy and narrower line-width in 8 nm nanoparticle of CeAl<sub>2</sub> were attributed to surface effects caused by the small particle size, including lower coordination number and higher surface pressure. In order to understand the effect of different surface to bulk ratio in electronic state of CeAl<sub>2</sub>, thin films of different thickness were investigated. As the thickness of the film enters the nanoscale regime, the electronic structure

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gets modified which in turn affects the electronic properties of the materials dominated progressively by surface effects. The Ce intermetallics are known to exhibit a variety of interesting behaviours such as kondo lattice, intermediate valency, heavy fermionic superconductivity, and magnetism. In these alloys, 4f states exhibit atomic character and sometimes exhibit a more delocalized nature meaning 4f wave function mixes with the extended states of the solid. X-ray absorption near-edge structure (XANES) is the modulation of the absorption signal due to electronic transition from core level to outer unoccupied electronic states. Therefore, XANES offers as one of the possible means to understand the variation in the electronic structure when the surface to bulk ratio is changed. It may be noted that XANES is bulk sensitive. In this study, we report the XANES spectra of  $\text{CeAl}_2$  at various thickness, 40–120 nm, and understand the changes in the electronic structure as the thickness is increased.

## 2. Experimental

Bulk  $\text{CeAl}_2$  alloys were prepared by arc melting the high-purity constituent elements in an argon atmosphere. Details are described elsewhere [5,6]. The nanoparticles and thin films of  $\text{CeAl}_2$  were prepared by evaporating bulk  $\text{CeAl}_2$  and the difference was essentially the use of a cold trap in 0.1 Torr helium for the preparation of nanoparticles. No such cooling was used for the preparation of the thin films of  $\text{CeAl}_2$ . The reason for such cooling during preparation of nanoparticles was to reduce the energy of particles and prevent particles from interacting with each other and ensure that they remain as particles and not to form films. The major disadvantage of this method was that only 8 nm nanoparticles can be successfully obtained. Thus, we prepared the thin films of various thickness: 40, 65, 80, 100, and 120 nm to investigate the effect of different surface to bulk ratio in electronic structure of  $\text{CeAl}_2$ . The X-ray diffraction for all these samples including nanoparticles show similar features that of bulk,  $\text{CeAl}_2$ . There were no traces of  $\text{CeO}_2$  within the resolution (3%) of X-ray diffractometer. X-ray absorption measurements were performed at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The XANES at Ce  $L_3$ -edge spectra were taken at Wiggler 17C beamline using fluorescent mode at room temperature. The XANES spectra at Ce  $M_{4,5}$ - and Al K-edges were recorded at beamline 20A (also known as HSGM) using total electron yield and fluorescent mode, respectively. The energy resolution of wiggler 17C was better than 0.4 eV, and the HSGM beamline was about 0.2 eV. It is commonly found that many cerium compounds are very sensitive and get oxidized even in vacuum. Surprisingly, these  $\text{CeAl}_2$  compounds are found to be very stable and not easy to oxidize even in the air.

## 3. Results and discussion

The samples were characterized by X-ray diffraction and there were no impurity phases including  $\text{CeO}_2$ . Fig. 1 shows the normalized XANES Al K-edge spectra of  $\text{CeAl}_2$  thin films having different thickness, varying from 40 to 120 nm, along with bulk  $\text{CeAl}_2$  and pure Al metal foil. The spectral features of

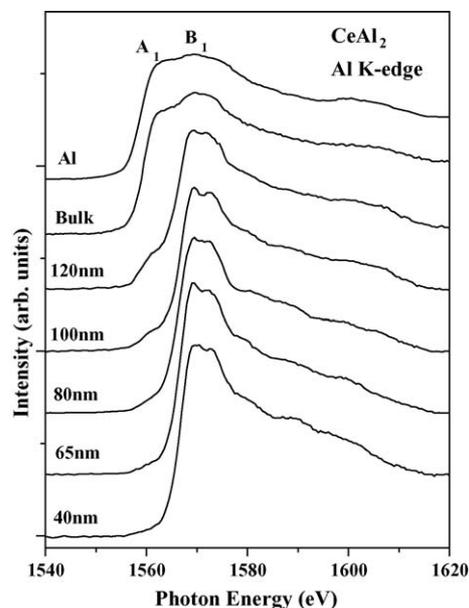


Fig. 1. Normalized XANES spectra of various  $\text{CeAl}_2$  thin films (40, 65, 80, 100, and 120 nm), bulk  $\text{CeAl}_2$ , and pure Al metal at Al K-edge.

Al K-edge XANES spectra of the  $\text{CeAl}_2$  films are very similar but differ significantly from that of bulk  $\text{CeAl}_2$  and pure Al. The intensities of the leading features of  $\text{CeAl}_2$  thin films are significantly enhanced and the inflection point of the threshold clearly shifts towards the higher energy relative to that of bulk  $\text{CeAl}_2$  and pure Al. According to the dipole-transition selective rules the leading feature in Fig. 1 is due to transitions from 1s core state to unoccupied Al 3p derived states that hybridize strongly with Ce 4f–5d states in the  $\text{CeAl}_2$ . The intensity of feature  $A_1$ , 1555–1563 eV, is significantly reduced and feature  $B_1$  (located at around 1570 eV) is enhanced in the  $\text{CeAl}_2$  thin films. As evident from Fig. 2(top panel), the edge shifts to higher energy while the intensity of the feature  $B_1$  decreases when thickness is increased from 40 to 120 nm. This result suggests that Al loses more p orbital charge to the Ce and has a more attractive electrostatic potential when the thickness of the thin films are reduced [7]. This reduction of the p-state charge results in lessening the screening of the Al nuclear charge and thus lowers the Al 1s energy level. Also observed is the increase of the Al 3p holes with reducing thickness, determined by the difference of the densities of Al 3p states for  $\text{CeAl}_2$  films and pure Al just above the Fermi level. In the earlier report [8], the density of states (DOS) for Al unoccupied states with s, p, and d characters spread up to  $\sim 60$  eV. Thus, the normalization procedure is conducted in the energy range between 1610 and 1620 eV. The relative intensity of the area under feature  $A_1$  and  $B_1$  with respect to pure Al, which is obtained by integrating the spectral difference ( $\delta A_1 + \delta B_1$ ) between each film and the pure Al, is plotted in the lower panel of Fig. 2. The integrations of ( $\delta A_1 + \delta B_1$ ) yield 1.56, 2.85, 4.14, 6.61, and 9.32 for 120, 100, 80, 65, and 40 nm films. This comparison indicates the integration ( $\delta A_1 + \delta B_1$ ) is increasing as thickness decreases, implying Al loses p-orbital charge which is in accordance with the suggesting indicated by the shift of the edge of spectra.

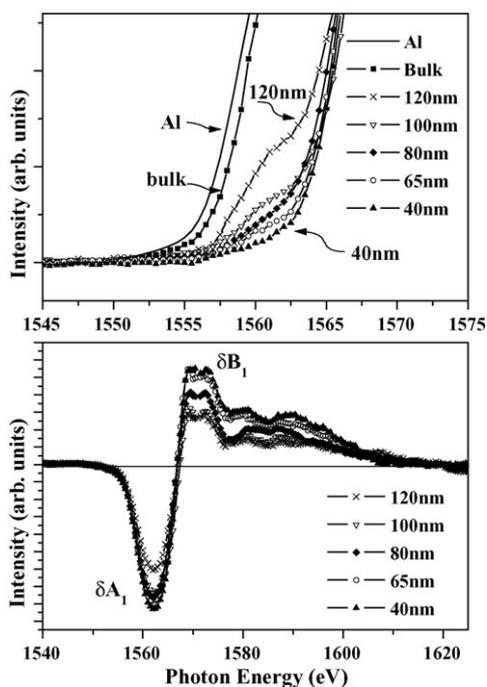


Fig. 2. The magnified leading features at the threshold of XANES spectra at Al K-edge are shown. Note that edges for films shift towards the higher energy side with the decrease in thickness of the films. The lower panel shows the difference spectra of CeAl<sub>2</sub> thin films obtained after subtracting pure Al K-edge spectra.

Before understanding these results, we define surface to bulk ratio.

It is known that solid possesses surface tension,  $\gamma$ , and bulk cohesive energy,  $G$ . While the surface energy is defined as  $\gamma A$ , the bulk cohesive energy is defined by  $GV$ , where the quantities  $A$  and  $V$  represent, respectively, the surface area and volume of the solid. The relative magnitude between the surface tension and the bulk cohesive energy of the material that builds up the solid defines the surface to bulk ratio, while the surface tension is caused by the attraction between the molecules due to various intermolecular forces and bulk cohesion is the energy required to separate the atoms of the solid into isolated atomic species. Thus, the surface to bulk ratio can be simply defined as the surface atoms compared to the number of bulk atoms. For a spherical object, the surface and the volume, respectively, are  $V = (4/3)\pi r^3$  and  $A = 4\pi r^2$  and yield the ratio  $A/V \sim 1/r$ . Similarly for a cubical object, the ratio of surface ( $A = 24r^2$ ) to volume ( $V = 8r^3$ ) also yields  $A/V \sim 1/r$ . Above understanding can be extended in terms of surface atoms and bulk atoms. The lattice constant for CeAl<sub>2</sub> is  $\sim 8 \text{ \AA}$ . The dimensions of the films investigated were of  $5 \text{ mm} \times 5 \text{ mm} \times \text{thickness}$  and the number of the atoms on the probing surface is  $\sim 5 \text{ mm}/8 \text{ \AA} \times 5 \text{ mm}/8 \text{ \AA}$  atoms and resulting in the total layers as  $\sim \text{thickness}/8 \text{ \AA}$ . Thus, the surface atoms to bulk atoms ratio is  $\sim 1/\text{thickness}$  which is related to the factor  $\sim 1/r$ . Consequently, above analysis of surface to bulk ratio is useful in understanding the electronic structures of these materials of various thickness. For large solids, the physical and chemical properties are determined primarily by the bulk volume and for small ones, the properties are influenced primarily by the surface area. Although the surface of CeAl<sub>2</sub> films looked

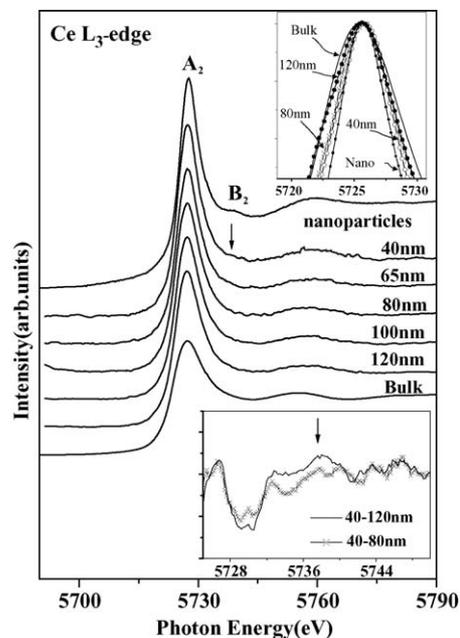


Fig. 3. XANES spectra at Ce L<sub>3</sub>-edge for various thickness of CeAl<sub>2</sub> thin films along with bulk and CeAl<sub>2</sub> nanoparticles. Note that the intensity of the feature assigned to Ce<sup>4+</sup> is significantly high (marked as B<sub>2</sub>) in nanoparticles compared to thin films.

like shining and mirror-like, the surface of the film was not perfectly flat. Since the thickness of the film from one edge to the other was about  $\pm 5\%$ , it is likely that the small clustered surfaces were formed during sample preparation. The formation of the small clusters will further enhance the surface to bulk ratio. It may be noted that the surface to bulk ratio is 0.025, 0.0154, 0.0125, 0.01, and 0.0083 nm<sup>-1</sup> for 40, 65, 80, 100, and 120 nm, respectively. The relation between the integration ( $\delta A_1 + \delta B_1$ ) and surface to bulk ratio as a function of film thickness will be shown later in Fig. 4. This implies the charge transfer is closely related to the surface to bulk ratio.

To understand the changes in the electronic structure of Ce site, XANES measurements were carried out at Ce L<sub>3</sub>- and Ce M<sub>4,5</sub>-edges. Often, Ce L<sub>3</sub>-edge XANES spectroscopy has been used as one of the methods for the quantitative determination of the ratio of the Ce<sup>3+</sup> and Ce<sup>4+</sup>, since both these species exhibit unique and distinguishable absorption peaks. Fig. 3 shows the XANES Ce L<sub>3</sub>-edge spectra for different thickness of CeAl<sub>2</sub> thin films, together with the bulk and nanoparticles. The spectral features of CeAl<sub>2</sub> (bulk) are very much similar to spectra reported by Chaboy et al. [9]. The main peak A<sub>2</sub>  $\sim 5727 \text{ eV}$  corresponds to trivalent Ce in CeAl<sub>2</sub> with  $4f^1(5d6s)^3$  configuration, and a weak feature B<sub>2</sub> on the higher energy side at  $\sim 5738 \text{ eV}$  corresponds to tetravalent Ce in CeAl<sub>2</sub> with  $4f^0(5d6s)^4$  configuration [10] marked by an arrow is observed in nanoparticles and rather weak in 40 nm film. The general line shapes in Ce L<sub>3</sub>-edge of thin films display similar profiles. It is obvious that all films show strong trivalent peak, whereas the tetravalent peak has low intensity and it is almost merged into the trivalent peak. This indicates that the variation of the  $4f^0$  contribution is rather very small. At a closer inspection, two consequences are revealed. First, the line-width reduces as the film thickness decreases, as

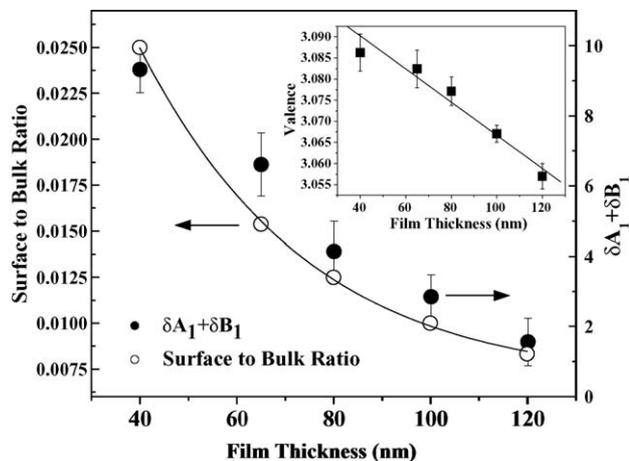


Fig. 4. Relationship between the integrated area under Al K-edge, and the surface to bulk ratio as a function of film thickness is shown along with the inset of the average valence of Ce as a function of the film thickness.

shown in upper inset of Fig. 3. This effect of reduced line-width, which is similar to the effect observed from the nanoparticles [5], may be due to the lower density of states at the Fermi level as a result of the higher surface to bulk ratio [2].

Both transition matrix element and density of states are important to reproduce the XANES spectra. Without theoretical calculations, one could understand the spectral features in qualitative way. Thus, the effect of reduced line-width, which is similar to the effect observed from the nanoparticles, may be due to the narrowing the 4f band as a result of the low coordination numbers. Second, the evolution of  $Ce^{4+}$  features can be extracted by subtracting the spectrum for each film from the thinnest one (40 nm), as can be seen in the lower inset in Fig. 3. The variation of  $4f^0(5d6s)^4$  state marked by an arrow shows that  $Ce^{4+}$  contribution is increased as thickness decreases. In general, by a standard procedure [12], the  $A_2$  and  $B_2$  features can be isolated by fitting two Lorentzians for the peaks corresponding to  $Ce^{3+}$  and  $Ce^{4+}$  after subtracting the arctangent edge jump from the XANES spectrum. The average Ce valence for the sample can be calculated by summing the weighted 3+ and 4+ contributions ( $v = 3 + (I_{Ce^{4+}} / (I_{Ce^{3+}} + I_{Ce^{4+}}))$ ) [11,12]. It is also evident that in these thin films there is no impurity phase of  $CeO_2$  [13]. Fig. 4 shows the integration ( $\delta A_1 + \delta B_1$ ) as a function of the film thickness. The inset in Fig. 4 plots the average valence as a function of the film thickness. The valence change is interpreted as due to the surface pressure which becomes significant. This surface pressure may raise the 4f level relative to the Fermi level and promote 4f electron to the conduction band [5]. An important point that needs to be noted is that in thinner film, the Al loses more p-orbital charges and Ce exhibits mixed valence. The valence change may also correlate with Ce–Al charge transfer behaviour and surface to bulk ratio.

The XANES spectra at the Ce  $M_{4,5}$ -edges are displayed in Fig. 5. The Ce  $M_{4,5}$ -edge results from the electron transitions from 3d to unoccupied 4f state. The spectrum of bulk  $CeAl_2$  exhibits two main structures at around 880 and 897 eV due to the  $3d_{3/2}$  and  $3d_{5/2}$  multiple structures of the  $3d^9 4f^2$  final state. The line shape is quite similar to that of  $\gamma$ -Ce, and no obvious  $3d^9 4f^1$

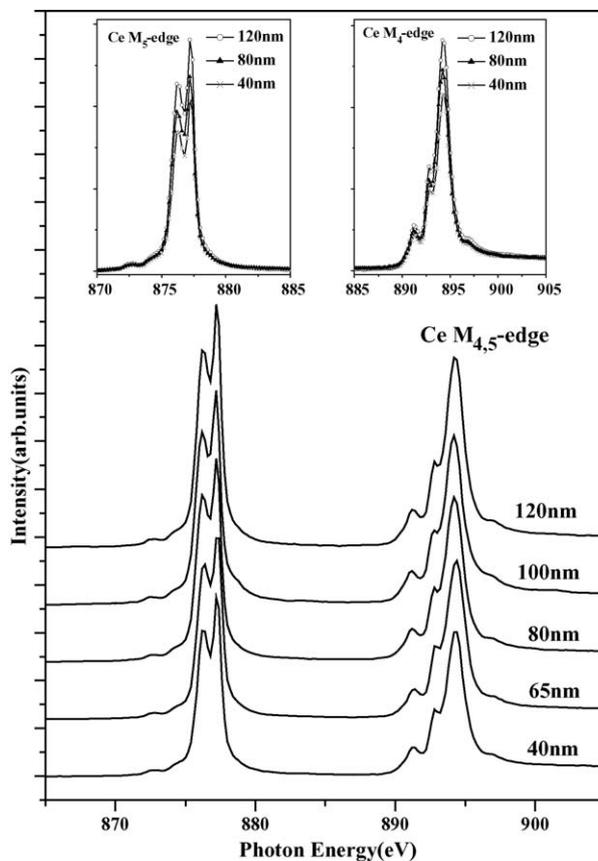


Fig. 5. XANES spectra at Ce  $M_{4,5}$ -edge for various  $CeAl_2$  thin films. Note that there is increase in the intensity of features as the thickness increases.

final state was detected which implies the valence is mainly 3+. More closely comparing the intensities of these samples, as shown in the inset, the reduction of intensity in thinner film implies the gain of charge at the Ce site and consequently the 4f unoccupied states is decreasing.

By comparing the results from Al K- and Ce  $M_{4,5}$ -edges XANES, the charge transfer is from Al 3p to Ce 4f state. This was also proposed in earlier studies using resonant inelastic X-ray scattering and other reports [14,15]. The Ce in bulk  $CeAl_2$  is mostly 3+ state with  $(5d6s)^3$  configuration. In nanoparticles or in the thin films, the charge transfer from Al 3p to Ce 4f state, since the surface pressure raises up the 4f level relative to the Fermi level and causes 4f electron to populate the conduction band  $(5d6s)^4$  configuration. Thus, the results from Ce  $M_{4,5}$ - and Al K-edges suggest the charge transfer from the Al 3p to Ce 4f state, and the 4f electrons are transferred to conduction band and enhance the valence in thinner  $CeAl_2$  films. Thus, the surface to bulk ratio plays a key role and affects the electronic structure of  $CeAl_2$  thin films with various thickness. This observation also verifies that, in nanoparticles, the formation of the non-magnetic tetravalent Ce may be responsible for the reduction of magnetic entropy observed in low temperature specific heat measurements is due to the higher surface area [6,16]. However, from above observation, the change in electronic structure is small but distinct. This cannot be totally attributed to the change in magnetic property described in ref. [16]. Such deviation may

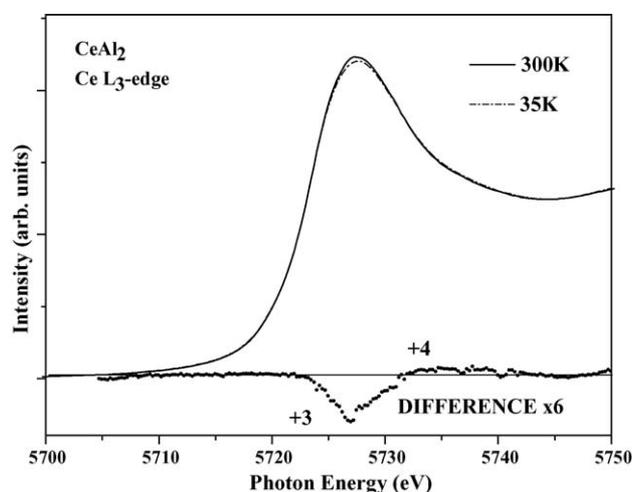


Fig. 6. The temperature dependent XANES spectra for bulk  $\text{CeAl}_2$  at 35 and 300 K. The difference spectrum shown in dotted line indicates the valence is increased at low temperature.

be due to the effect of temperature at which the experiment was performed and the bulk sensitiveness of XANES. Spectroscopic measurements were made at room temperature and the change in magnetic entropy was observed in low temperature specific heat measurements. In order to clarify the temperature effect on the electronic structure, specifically the 4f configuration, we have performed Ce  $L_{3\text{-edge}}$  XANES measurement at various temperatures. Since there is only subtle spectral change due to temperature variations, we have only plotted the spectra in Fig. 6 taken at room temperature and that taken at the lowest temperature 35 K for comparison. The dotted curve at the bottom is the spectral difference obtained by subtracting the room spectrum from the 35 K spectrum. It is evident that as temperature goes down, while the  $\text{Ce}^{3+}$  contribution decreases, the  $\text{Ce}^{4+}$  increases. This shows that Ce 4f electronic states are at the borderline between localization and itinerancy. In other words, the degree of mixing of the 4f and conduction electron states is determined by surface to bulk ratio effects. In films of small thickness, the surface effects dominate and induce changes in 4f configuration due to the reduction of the coordination. These are also consistent with the results obtained in Sm nanoparticles [3]. It may be noted that two major factors are likely to determine the final electronic configurations for nanoparticles: (i) band broadening induced by surface pressure and (ii) band narrowing as a result of reduced coordination numbers. The band narrowing was observable in Ce  $L_{3\text{-edge}}$  XANES as the white-line-width is reduced for nanoparticles. The surface pressure is likely to make band broader and it is proposed as the mechanism for raising the 4f levels relative to the Fermi level and resulting 4f electron transfer to the conduction band. Thus, these competing factors are important in this study and responsible in the shift of the 4f energy levels close to Fermi level. Understandably, the small particles favor the 4+ configuration ( $4f^0(5d6s)^4$ ). This shows that the electronic structure of a solid at the surface may be different from that in the bulk due to the reduced coordination number and different atomic geometry. In the case of core levels,

it can manifest itself as the phenomena of the surface core-level shift and the surface valence transition [17].

#### 4. Conclusion

Present XANES study on thin films of  $\text{CeAl}_2$  at the Al K-, Ce  $L_{3\text{-}}$ , and Ce  $M_{4,5}$ -edges provides evidence that Ce ions are in mixed valent state when surface to bulk ratio is high. The spectral features assigned to  $\text{Ce}^{4+}$  increase with the decrease of thickness of the thin films. Such variations are attributed to the changes in the electronic state of Ce ions due to charge transfer from Al ions. Additionally, the valence change evidenced by Ce  $L_{3\text{-edge}}$  is due to transfer of the 4f electrons to the conduction band. The variation in the electronic structure (from  $4f^1$  to  $4f^0$  configuration) of Ce can be understood as the charge transfer from Al 3p state to Ce 4f state, and results in lowering of energy between 4f and 5d orbital, followed by the promotion of the 4f electron to 5d state.

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