

Electronic and magnetic properties of CeAl₂ nanoparticles

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Abstract

We presented the X-ray magnetic circular dichroism (XMCD) and X-ray absorption spectroscopy (XAS) studies of heavy fermion compound CeAl₂ bulk and 8 nm nanoparticles, performed at the Ce *M*_{4,5}- and *L*₃- absorption edges. XMCD and XAS revealed that Ce in bulk CeAl₂ exhibits localized 4f¹ character with magnetic ordering. The Ce in nanoparticles, on the other hand, shows a small amount delocalized 4f⁰ character with non-magnetic Kondo behavior. By applying general sum rules, an estimation of the orbital and spin contribution to those Ce 4f moments can be obtained. Our results also demonstrated that the magnetic behavior in CeAl₂ is very sensitive to the degree of localization of the 4f electrons.

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1. Introduction

The nature of 4f electrons in rare-earth compounds have been the subject of numerous theoretical and experimental studies in recent years [1]. One of the interesting properties of Ce-based compounds is the disappearance of the magnetic moment of the 4f shell under pressure. It has been shown that in Ce compounds may exhibit an analogous transition, if the Ce–Ce interatomic spacing is less than ~3.3 Å [2,3]. The heavy fermion compound CeAl₂ has been found to have the magnetic 4f¹ state at ambient pressure in bulk form [4]. Since the Ce–Ce in CeAl₂ ~3.5 Å is close to the suggested critical distance for the magnetic–nonmagnetic transition, such a transition may take place at moderate pressure. The reduction of the Ce moment was observed in bulk [5] CeAl₂ under pressure or in the CeAl₂ nanoparticles [6]. The antiferromagnetic transition observed in bulk CeAl₂ was not shown in the nanoparticles [7]. The loss of magnetism was attributed to changes of the electronic structure induced by the reduced

particle size. In order to explore the effect of the electronic structure on the magnetic behavior, we have performed XAS and XMCD on nanoparticles and bulk CeAl₂.

2. Experimental

Bulk CeAl₂ was prepared by arc melting the high-purity constituent elements Ce (99.95%) and Al (99.999%) in 1:2 atomic ratios in an argon atmosphere. The structure were confirmed by X-ray diffraction and exhibits cubic Laves structure with a lattice constant *a*₀ = 8.06 Å which is consistent with that of previous report [8]. Nanoparticles of 8 nm CeAl₂ were then fabricated on a liquid-nitrogen cold trap by thermal evaporation of bulk CeAl₂ in a 0.1 Torr helium atmospheres. The details of the sample preparation and characterization of the samples have been reported elsewhere [7]. X-ray absorption studies were performed at 17C and EPU beamline, around Ce *L*₃-edge and Ce *M*_{4,5}-edge in NSRRC, Taiwan. The XMCD were measured at EPU beamline and spectra were obtained by the difference between the absorption spectra recorded for two opposite directions of the magnetic field.

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3. Results and discussions

X-ray absorption spectroscopy at the L_3 -edge has been widely used to study rare-earth containing materials. To have an insight of the influence of size variation into the electronic configuration, we present Ce L_3 -edge absorption spectra in Fig. 1. The large number of unoccupied 5d orbitals in rare-earth atoms produces ($2p$ – $5d$ transition) a prominent L_3 white line (A_1) and additional feature (B_1), correspond to Ce^{3+} and Ce^{4+} , respectively [9]. This clear spectral evolutions evidence the valence higher than 3 in 8 nm is seen. The Ce valence can be evaluated by the relative weight of the separate Ce^{3+} and Ce^{4+} features using the method described by Röhler [10], i.e., $v = (3I_3 + 4I_4)/(I_3 + I_4)$, where I_3 and I_4 are associated with the valence state +3 and +4, respectively. As shown in bottom of Fig. 1, the valence is estimated to be 3.07 for nanoparticles, which can be translated into 4f occupancy ~ 0.93 by $n_f = 4 - v$.

Fig. 2 presented the Ce $M_{4,5}$ -edge absorption and XMCD spectra. The XAS line shape of bulk is similar to γ -Ce, which implies the valence in bulk is mainly +3. The spectrum of nanoparticles shows enhanced features A_2 and B_2 and additional features A_2' and B_2' . These absorption

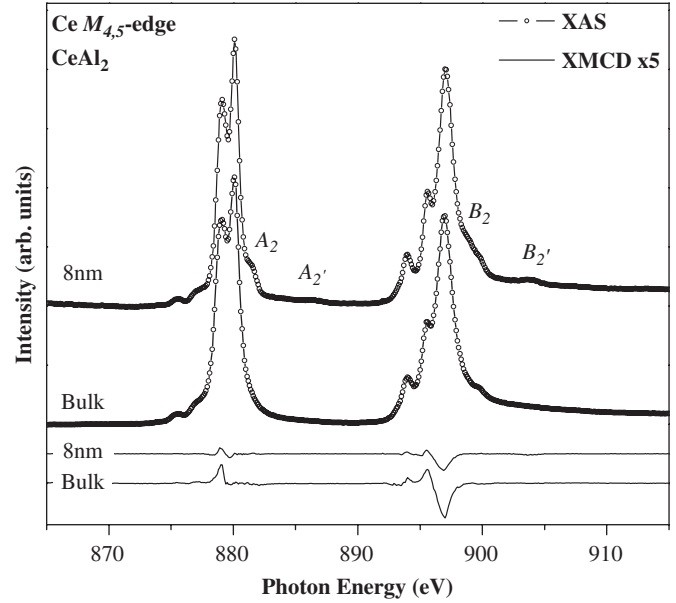


Fig. 2. Ce $M_{4,5}$ -edge XAS and XMCD spectra of 8 nm and bulk $CeAl_2$.

features coincide with the energy position of the main features of Ce^{4+} and can be assigned to $3d^9 4f^1$ final states. This indicates that the nanoparticles exhibits the mixture of $4f^1$ and $4f^0$ configurations in ground state, which is consistent with the observation from Ce L_3 -edge. The growth of peak A_2 , B_2 , A_2' , and B_2' in nanoparticles indicate stronger interaction of the 4f level and conduction band with respect to the bulk. XMCD combines site and orbital selectivity. Moreover, the application of the sum rules gives access to the orbital and spin contributions to the magnetic moment [11,12]. The use this sum rules in this case of $M_{4,5}$ -edge is much easier because the isotropic absorption cross-section can be obtained using a standard procedure for subtracting the rather weakness transitions towards the continuum. The number of f holes can be derived from the Ce L_3 -edge spectrum [13,14].

In order to get a quantitative analysis, we adopt the sum rules proposed by Carra and Thole [11,12]. First, we consider the orbital sum rule. At the spin-orbit-split $M_{4,5}$ absorption edges;

$$\rho_o = \int_{M45} (\mu^+ - \mu^-) dE / \int_{M45} (\mu^+ + \mu^- + \mu^0) dE = (-1/3(14 - n)) \langle L_z \rangle,$$

where μ^+ , μ^- , and μ^0 denote the absorption coefficient for left, right, and linearly polarized light, n is the occupancy of the 4f shell ($n = 1$ for Ce^{3+}), and $\langle L_z \rangle$ is the orbital magnetic moment of the 4f shell in the initial state. Thus, the $\langle L_z \rangle$ are estimated to be 0.23 and 0.19 for bulk and 8 nm nanoparticles.

Now we turn to spin contributions. The dichroic signal of bulk we described in XMCD spectrum is given by $J = 5/2$ state [15]. It has been stressed that the ratio $\langle L_z \rangle / \langle S_z \rangle$ is -8 for $J = 5/2$ [15]. Therefore, the $\langle S_z \rangle$ is estimated to be -0.0288 for bulk. It has been proposed that the spin sum

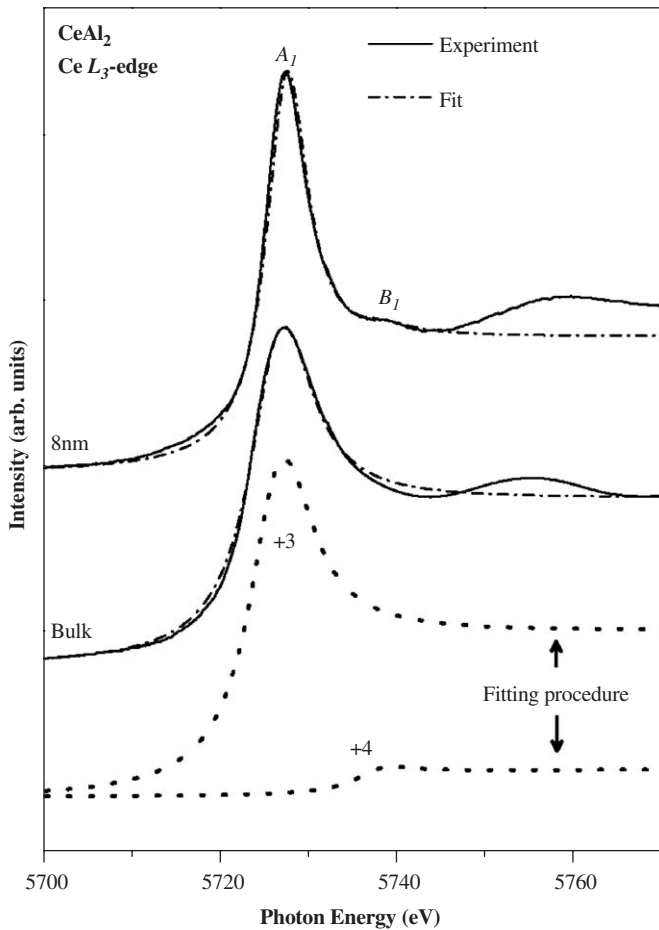


Fig. 1. Ce L_3 -edge XAS spectra of 8 nm and bulk $CeAl_2$. The separated Ce^{3+} and Ce^{4+} contributions are also shown.

rule is invalid for Ce and cannot be used to deduce the spin contribution to the 4f moment. However, a calculation for trivalent ions from Ce to Tm obtained recently from M_{45} -edge in the spin sum rule made by Jo [16] indicates that minor correction is necessary for the spin moment. In the case of Ce^{3+} , $X_I = 1.6X_E$, where X_I was defined as

$$X_I = \int_{M5} (\mu^+ - \mu^-) dE - (3/2) \times \int_{M4} (\mu^+ - \mu^-) dE / ((3/2) \int_{M45} (\mu^+ + \mu) dE),$$

and X_E was defined as $X_E = (2/3)(14-n)\langle S_z \rangle + (2/(14-n))\langle T_z \rangle$. The $\langle T_z \rangle$ is rather small compared to $\langle S_z \rangle$ and $\langle L_z \rangle$ in 3d, 4f, 5f systems with symmetric structure [17,18]. By neglecting $\langle T_z \rangle$ will simplify the calculation. After including these corrections, it yields the $\langle S_z \rangle = -0.03$ and -0.04 for bulk and 8 nm. The $\langle L_z \rangle / \langle S_z \rangle$ is then estimated to be -7.67 for bulk. This calculated value is in good agreement with the $\langle L_z \rangle / \langle S_z \rangle = -8$. On the other hand, the small ratio $\langle L_z \rangle / \langle S_z \rangle \sim -4.75$ (far away from -8) for 8 nm, is the result of the 4f electron delocalization character [19].

Let us consider a total 4f magnetic moment of Ce, M_{4f} are $0.2\mu_B$ for bulk and $0.15\mu_B$ for nanoparticles. The loss of the magnetism is related to the different 4f electronic configurations. Furthermore, in the earlier work, the loss of magnetic entropy in 8 nm nanoparticles compared to bulk is about 30%. Our XMCD results revealed that only 75% left in nanoparticles. The deviation of the magnetic Ce presumably originated from the M_{5d} origin.

4. Conclusions

We reported the XAS and XMCD studies of $CeAl_2$ bulk and 8 nm nanoparticles. The XAS revealed the Ce in bulk exhibits the mostly trivalent ($4f^1$) in contrast to a small

portion of tetravalent Ce ($4f^0$) is found in nanoparticles. The XMCD analysis confirmed that the smaller $\langle L_z \rangle / \langle S_z \rangle$ for 8 nm, is the result of the 4f electron delocalization in 8 nm nanoparticles. Our results also demonstrated that the magnetic behavior in $CeAl_2$ is very sensitive to the degree of localization of the 4f electrons.

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