

# Valence state of CeAl<sub>2</sub> nanoparticles studied by Ce L<sub>3</sub>-edge x-ray absorption spectroscopy

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(Received 1 November 1999; accepted for publication 5 January 2000)

We report measurements of the Ce L<sub>3</sub>-edge x-ray absorption near-edge structure on CeAl<sub>2</sub> nanoparticles with average diameters of 80 Å. The Ce exhibits a mixed valence with a small amount of tetravalent Ce, which is in contrast to the purely trivalent Ce observed in bulk CeAl<sub>2</sub>. A shift in the absorption edge to higher energy and a narrower linewidth are also observed in the nanoparticle samples. These spectral differences are attributed to surface effects caused by the small particle size, including a lower coordination number and higher surface pressure. The observation of nonmagnetic tetravalent Ce with the 4f<sup>0</sup> configuration is in good agreement with the small values of magnetic entropy seen in low temperature specific heat measurements. © 2000 American Institute of Physics. [S0021-8979(00)05207-5]

## INTRODUCTION

The study of physical properties of nanocrystalline materials has become an active area of research in recent years. Such research has been primarily motivated by potential technological applications, especially the future demand for ultrasmall devices for the electronics industry.<sup>1</sup> The electronic structure of nanocrystalline materials is of fundamental importance to the understanding of these materials.<sup>2</sup> In a recent study<sup>3</sup> of the specific heat of 80 Å nanoparticles, it was deduced that cerium atoms on the nanoparticle surface are nonmagnetic. In addition, the antiferromagnetic transition ( $T_N=3.8$  K) which is seen in bulk CeAl<sub>2</sub> was not observed in the nanoparticles. The loss of magnetism was attributed to changes in the electronic structure due to reduced particle size. In order to further explore the effect of particle size on the electronic properties, we have performed Ce L<sub>3</sub>-edge x-ray absorption near edge structure (XANES) studies on CeAl<sub>2</sub> nanoparticles and on the bulk sample for comparison. In the 80 Å nanoparticle sample we observed a small contribution by Ce<sup>4+</sup> corresponding to the 4f<sup>0</sup> configuration, while in the bulk sample only Ce<sup>3+</sup> (4f<sup>1</sup> configuration) features are present.

## EXPERIMENT

Nanoparticles of CeAl<sub>2</sub> were fabricated on a liquid-nitrogen cold trap by flash evaporation of the bulk CeAl<sub>2</sub>, which was prepared by arc melting the high-purity constituent elements in an argon atmosphere. Details of the procedure are described elsewhere.<sup>4</sup> X-ray absorption measurements were performed at beamline 15B of the Synchrotron Radiation Research Center (SRRC), Taiwan, using a Si(111) double-crystal monochromator with an energy resolution of about 1/6000. The x-ray absorption spectra were collected in

transmission mode using gas-ionization chambers as detectors. A single layer of the nanoparticles (or fine powder of the bulk sample) was put onto Scotch tape and the appropriate sample thickness was obtained by stacking multiple layers of the tapes for the XANES measurements.

Since bulk CeAl<sub>2</sub> is very stable in air, we detected no trace of CeO<sub>2</sub> within the resolution limit of our x-ray diffraction (XRD) apparatus (3%) for the nanoparticle sample on which we performed XANES measurements.

## RESULTS AND DISCUSSION

Figure 1 plots Ce L<sub>3</sub>-edge x-ray absorption spectra for bulk and 80 Å nanoparticle samples of CeAl<sub>2</sub>. Both spectra are normalized to the absorption step above 5780 eV. It is well known that Ce is trivalent in bulk CeAl<sub>2</sub> with a 4f<sup>1</sup>(5d6s)<sup>3</sup> configuration.<sup>5</sup> The corresponding feature for trivalent Ce is the single peak at 5727 eV. For the nanoparticle sample, on the other hand, we observe an additional feature at about 5738 eV which is marked by the vertical arrow. This peak corresponds to tetravalent Ce with a 4f<sup>0</sup>(5d6s)<sup>4</sup> configuration.<sup>6,7</sup>

The Ce<sup>4+</sup> feature observed in the nanoparticle indicates that the Ce becomes a mixed valent as a result of reduced particle size. The small intensity of the Ce<sup>4+</sup> feature compared to that of the nearby Ce<sup>3+</sup> feature makes it impractical to estimate the average Ce valence by quantitative curve fitting. It was reported that the Ce valence in bulk CeAl<sub>2</sub> becomes mixed 3+/4+ at pressures above 65 kbars.<sup>8</sup> A mixed valent Ce is also observed in CeAl<sub>2</sub> when it is chemically compressed by doping with Sc.<sup>6,9</sup> In nanoparticles, a relatively large number of atoms are at the surface. The surface pressure becomes significant which causes the 4f levels to raise relative to the Fermi level and results in a transfer of a 4f electron to the conduction band.<sup>10</sup> Although the effect of reduced particle size on the valence change is comparable to that of applied pressure,<sup>11</sup> the volume collapse which accom-

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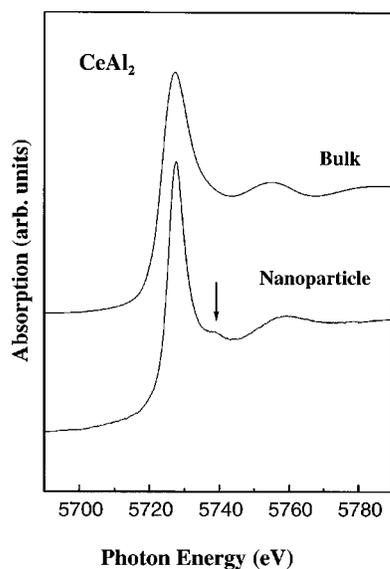


FIG. 1. Ce  $L_3$ -edge XANES spectra for bulk and 80 Å nanoparticle samples of  $CeAl_2$ . Both spectra are normalized to the absorption step well above the edge. The arrow indicates the tetravalent feature in the nanoparticle spectrum.

panies the application of pressure in bulk samples is not observed in our 80 Å nanoparticle sample. We interpret this in terms of the particle size of our sample. A volume collapse due to reduced grain size was observed in 40 Å Eu and 30 Å Yb.<sup>12</sup> We assume that such a volume collapse can take place in  $CeAl_2$  if the particle size is much less than 80 Å. Moreover, the Ce  $L_3$ -edge absorption energy of the spectrum of the nanoparticle is shifted 0.4 eV towards higher energy relative to that of the bulk. This effect was also observed in nanoparticles of rare earths<sup>12</sup> and various metals.<sup>13</sup> The energy shift of the absorption edge was interpreted as due to a size dependent initial state electronic structure, specifically the changes in the number of  $d$  electrons.<sup>14</sup>

By comparing our nanoparticle spectrum with that of  $Ce_{0.3}Sc_{0.7}Al_2$ , reported in Ref. 4, we find that the Ce  $L_3$ -edge absorption spectral line shapes are very similar in the two

cases except for the linewidth of the trivalent peak which is much narrower in the nanoparticle sample (see Fig. 1). This effect of reduced linewidth is attributed to the lower density of states at the Fermi level, possibly resulting from the higher surface area.<sup>15</sup>

In summary, we have observed a size dependent valence change in nanoparticles of  $CeAl_2$  that is due to the promotion of  $f$  electrons to the conduction band. This effect is similar to that which results from the application of pressure. The formation of nonmagnetic tetravalent Ce due to the reduced particle size is presumably responsible for the small values of magnetic entropy observed in low temperature specific heat measurements.<sup>3,4</sup>

## ACKNOWLEDGMENTS

The authors wish to thank Dr. H. H. Hung and T. E. Dann of SRRC for their skillful and generous assistance in performing these experiments. This work was supported by the National Science Council of the Republic of China under Grant No. NSC 88-2112-M-032-012.

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