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Disorder-induced Kondo behavior in nanostructured $CeAl_2$

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Abstract

The local structural properties of nanoparticle $CeAl_2$ were studied by X-ray absorption fine structure measurements at the Ce L_3-edge. These studies show that the nanocrystalline material is severely disordered compared to its bulk counterpart and that the bond length of Ce–Al in the nanoparticle is about 0.4 Å shorter than that in the bulk. These observations strongly suggest that in addition to size and surface effects, structural disorder plays a role in determining the Kondo behavior in this nanocrystal.

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Keywords: Kondo effect; Nanoparticle; Disorder; XAFS; Local structure; $CeAl_2$

The effect of particle size on physical and electronic properties has attracted broad interest with many studies reported on this subject, both experimentally and theoretically [1]. The $CeAl_2$ system displays the fascinating property that as its particle size becomes comparable to the nanometer scale, the system transitions from displaying magnetic order to Kondo behavior. This transition has been explained in terms of size and surface effects [2]. However, structural changes in the nanosize crystals may also be relevant. We explored this possibility through local structure measurements of bulk and nanocrystalline $CeAl_2$ using the X-ray absorption fine-structure technique (XAFS) which can detect both the bond length and the disorder of a near-neighbor atomic pair from a selected atom species.

The bulk $CeAl_2$ specimen was fabricated by arc melting and the ∼80 Å diameter nanocrystals were obtained using a liquid-nitrogen cold trap [2]. Transmission Ce L_3-edge XAFS measurements at $T = 20$ K were made at beamline 2–3 of the Stanford Synchrotron Radiation Laboratory (SSRL) using a $\frac{1}{2}$-tuned Si(1 1 1) double monochromator. The XAFS data were analyzed with the UWXAFS package [3] (methods are described elsewhere [4]), using the photoelectron back scattering functions calculated with the FEFF8 code [5].

Fig. 1 shows the magnitude of Fourier transformed XAFS data from bulk and nanostructured samples of $CeAl_2$. Note that the peaks are shifted on the $\tilde{r}$-axis from their true bond lengths due to the phase shift of the back scattered photoelectron. Detailed fits are therefore necessary to obtain quantitative information. In any case, the XAFS measured from the nanocrystal is much weaker in magnitude and the peaks are severely shifted compared with data from the bulk.

Fits to the bulk data start from the C15 Laves structure, allowing the bond length and the Debye–Waller factor (σ^2, including thermal vibrations and static disorder) for each shell below 7 Å to vary. We find that the Ce atoms have 12 Al neighbors at 3.356 ± 0.005Å and four Ce neighbors at 3.503 ± 0.006 Å. The σ^2s are $0.0038 \pm 0.0004 \sim$ Å^2 for the Ce–Al pairs and 0.0021 ± 0.0007 Å^2 for the Ce–Ce pairs, respectively. These small σ^2s suggest that the crystalline structure is well ordered. We derive a lattice constant of

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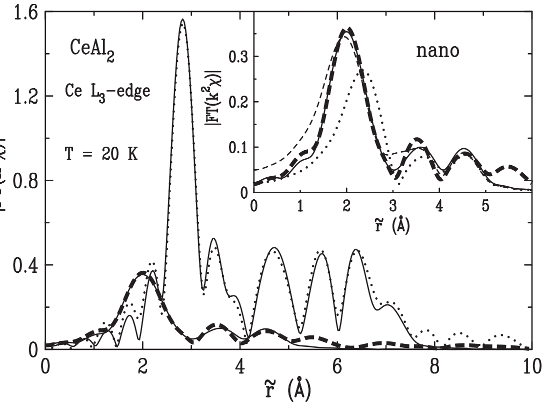

Fig. 1. Magnitude of Fourier transformed XAFS data from a bulk (dotted line) and a nanocrystal (thick-dashed line) of CeAl$_2$ as a function of distance from probe atom Ce. Solid lines are best fits. Inset indicates the XAFS data from the nanostructured CeAl$_2$ and fits with the different models of Al–O mixed (solid line), Al only (dotted line) and O only (thin-dashed line).

8.095 ± 0.015 Å from these data, roughly consistent with the previous X-ray diffraction measurement of 8.054 Å [6].

The nanocrystal fits also start from the bulk model, but reliable results are only obtained from shells shorter than 3.5 Å. The inset shows the various fits assuming that only aluminum, only oxygen, or mixed Al and O occupy the Al site. The models using only Al or only O do not fit the measured data satisfactorily. The fit is considerably improved by including about 10% oxygen into the Al site, although the ratio of the occupancies cannot be accurately determined because of a high correlation between the coordination numbers and the σ^2s in the fit. This observation of oxygen in the Al site agrees with the previous study [2]. In any case, these results strongly suggest that the Al site is partially occupied by oxygen. The best fit shows that the bond lengths are 2.44 ± 0.03 Å and 2.96 ± 0.02 Å for Ce–O and Ce–Al pairs, respectively. The σ^2s in the nanocrystals are 0.044 ± 0.014 Å^2 for 11 ± 5 of aluminum neighbors and 0.005 ± 0.009 Å^2 for 1.3 ± 0.9 of oxygen neighbors. The average σ^2 of the Ce–Al and Ce–O pairs is about an order of magnitude larger than that of the Ce–Al pair in the bulk and the bond length of Ce–Al is about 0.4 Å shorter than the bond length of Ce–Al in the bulk. These measurements indicate that both large distortions and intrinsic disorder exist around Ce in the nanocrystals compared to the bulk.

In summary, we have studied the local structural properties of nanocrystalline CeAl$_2$, comparing with its bulk counterpart. A substantial amount of disorder in the nanocrystals is observed and the Ce–Al bond length is shorter than that in the bulk. Moreover, oxygen is observed in the Al site. These changes in the structural properties should be included in any proper theory of the changes in the physical properties of nanocrystalline CeAl$_2$.

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