Size effects on mixed valence CePd$_3$

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Abstract. To study the size effects on mixed-valence state of CePd$_3$, nanoparticles of CePd$_3$, sizes ranging from 5.2 to 9.5 nm, were prepared. The mixed valence increased from 3.3 to 3.5 as particle size reduced from bulk to 5.2 nm. This consequence was illustrated by the enhancements of valence fluctuations and 4f electron hybridization with conduction band through size reduction. Another interesting finding in the nanoparticles is that a certain fraction ~ 25% of the sample becomes trivalent which is evident from the increase of magnetic susceptibility at low temperatures.

1. Introduction
CePd$_3$ is a mixed valence compound due to the mixing interaction between trivalent Ce$^{3+}$: $|4f^{1.5}d^{1}6s^{2}>$ and tetravalent Ce$^{4+}$: $|4f^{0}5d^{2}6s^{2}>$. The valence of CePd$_3$ is intermediate with valence ~ 3.5 [1]. Its resistivity exhibits a maximum at a temperature $T_{\text{max}} = 124$ K. This value corresponds to the inelastic magnetic neutron linewidth $\Gamma$; thus, one can use $2T_{\text{max}}$ to estimate its spin-fluctuation temperature $T_{\text{sf}} \sim 248$ K [2]. The result is fairly consistent with that estimated from the temperature of $\chi_{\text{max}}$ in magnetic susceptibility, based on a single ion model [2, 3]. Previous studies on the Ce L$_{\text{III}}$ x-ray absorption edges (XANES) in CeAl$_3$ films suggested a trivalent electronic configuration in cerium, with a mixture of trivalent and tetravalent cerium ions on the film surfaces [4, 5]. In this study, we investigate size effects on the mixed valence state of CePd$_3$. A series of CePd$_3$ nanoparticles was prepared with various sizes. The valence variation was then examined through the measurements of susceptibility and Ce L$_{\text{III}}$-edge XANES.

2. Experimental
The sample of CePd$_3$ was synthesised through mixing element Ce (99.99% purity) and Pd (99.99% purity) in 1:3 atomic ratio thoroughly, followed by arc melting under a flowing atmosphere of high purity argon. To exclude the possible impurity phase and mechanical stress, the obtained CePd$_3$ was subsequently annealed at 570 $^\circ$C for 7 days. Using this as target, nanoparticles with sizes $d = 5.2, 6.2, 9.5$ nm were fabricated by ArF excimer laser ablation. The nanoparticles were collected on a liquid nitrogen-cooled trap. X-ray diffraction (XRD) patterns reveal the cubic structure of CePd$_3$ bulk and nanoparticles (Fig. 1.). All reflection peaks of bulk and nanoparticles were correctly indexed to that of CePd$_3$; the lattice parameter $a = 4.126$ Å of bulk is in good agreement with those reported in literature.
The morphology of nanoparticles was directly observed by high resolution transmission electron microscopy (HRTEM) (Insets in Fig. 2). The average sizes of nanoparticles were estimated by TEM images and fits the full width at half maximum (FWHM) of the (200) peak to theoretical simulation. The lattice parameters of nanoparticles are about the same as that of the bulk based on GSAS analysis.

Figure 1. The x-ray diffraction patterns of CePd$_3$ bulk, 9-, 6-, and 5-nm nanoparticles at room temperature.

Figure 2. The FWHM of (200) peaks display a measure of the nanoparticle sizes for CePd$_3$ bulk, 9-, 6-, and 5-nm nanoparticles with theoretical simulation (lines). Insets: TEM images of nanoparticles for various sizes.

2. Results and Discussion

Ce L$_{\text{III}}$-edge XANES spectroscopies were performed at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The experiments of Ce L$_{\text{III}}$-edge XANES spectra were carried out at Wiggler 17C beam-line using fluorescent mode at room temperature. The Ce L$_{\text{III}}$-edge XANES spectra exhibit the mixed valence nature for both bulk and nanoparticles. Detailed valence information was evaluated by the spectroscopic analysis. The normalization procedure was conducted in the energy range between 5705 and 5755 eV. After evaluating the area contributed from trivalent and tetravalent Ce ions, peaked at 5726 and 5735 eV respectively, the results revealed the valence $z$ of Ce ion increases with size reduction. The valence $z$ is estimated to be 3.28, 3.31, 3.34 and 3.37 for bulk, 9.5, 6.2 and 5.2 nm nanoparticles respectively (Fig. 3.). Although the absolute values of valence calculated
from Ce L$_{III}$-edge XANES spectra significantly depends on the fitting and background subtraction, nevertheless, the trend in the increase of mix valence with size reduction is clearly observed in nanoparticles.

![Ce L$_{III}$-edge XANES spectra of CePd$_3$ bulk and nanoparticles specimens.](image)

**Figure. 3.** Ce L$_{III}$-edge XANES spectra of CePd$_3$ bulk and nanoparticles specimens.

The temperature dependent susceptibility $\chi(T)$ of CePd$_3$ exhibits a paramagnetic behaviour at temperatures above 300 K, followed by a round shaped transition at 100-300 K (inset (a) in Fig. 4). This is consistent with single-ion scaling at spin-fluctuation temperature $T_{sf} \sim 250$ K [2]. The rise at $T< 50$ K may be correlated to the coherence observed in low temperature resistivity data. For nanoparticles, an enhancement of magnetic susceptibility at low temperatures appeared and smeared out the round shaped transition near 125 K in the bulk specimen (Fig. 4 and inset (b)). Magnetic susceptibility increased at low temperatures with size reduction, this indicates a certain fraction $x$ of Ce ions in the sample becomes trivalent. In order to estimate the value of fraction $x$, Curie constant was estimated from the magnetic susceptibility data.

![The temperature dependence of magnetic susceptibility $\chi$ for CePd$_3$ bulk and nanoparticles.](image)

**Figure. 4.** The temperature dependence of magnetic susceptibility $\chi$ for CePd$_3$ bulk and nanoparticles. Insets: susceptibility $\chi$ for bulk and 6.2 nm CePd$_3$. 
The temperature dependence of inversed magnetic susceptibility $1/\chi$ for CePd$_3$ bulk and nanoparticles is shown in Fig. 5. Since the spin-fluctuation temperature $T_{sf}$ is $\sim 250$ K, it is difficult to extract the values of Curie constant from the data at high temperatures $T = 200$-300 K. For low temperature region, the susceptibility was fitted to the Curie-Weiss law $\chi(T) = \chi_0 + C/(T-\Theta)$ for $T = 2$-10 K, where $\chi_0$ is a constant, and $\Theta$ is Curie-Weiss temperature. From Curie constant, the molar percentage of trivalent cerium ions is obtained. For CePd$_3$ bulk, the Curie constant $C$ at low temperature is 0.007 emu/K f.u. Based on the theoretical values 0.204 emu/K f.u. for $J = 1/2$ ground state of magnetic Ce ions, the percentages of magnetic trivalent cerium in CePd$_3$ bulk is estimated to be near 3% [6].

Assuming the rest of the 97% Ce ions are mixed valence with valence $V$, the actual $V$ can then be estimated from the equation, $z = 3x + (1-x)V$: $z$ being the average valence obtained from Ce L$_{III}$-edge XANES, and $x$ the fraction of trivalent cerium estimated from Curie constant. For the bulk, the mixed valence $V$ is estimated to about 3.3. For nanoparticles, the value of Curie constant $C$ increases as particle size decreases. The values of $x$ calculated from $C$ are 0.262, 0.265, and 0.255 for 9.5, 6.2 and 5.2 nm specimens respectively. The new fraction of trivalent cerium was conjectured from the sample surfaces of nanoparticles. Following similar data analysis as those of the bulk, the valence of mixed valence states of Ce in nanoparticles are obtained as 3.42, 3.46 and 3.50 for 9.5, 6.2 and 5.2 nm specimens respectively.

![Figure 5](image-url)

**Figure. 5.** The temperature dependence of the inverse susceptibility $1/\chi$ for CePd$_3$ bulk and nanoparticles. Inset: $1/\chi$ versus $T$ at low temperatures.

In conclusion, the size effect on valence of Ce was presented in CePd$_3$ nanoparticles by means of magnetic susceptibility and Ce L$_{III}$-edge XANES spectra. As the particle size decreases to the nanoscale, about 25 % of cerium became trivalent from magnetic susceptibility data. Meanwhile, the valence of mixed valence cerium increases from 3.3 to 3.5. The trend in the increase of mixed valence with size reduction indicates that 4f electron hybridization with conduction band in CePd$_3$ nanoparticles was enhanced as particle size decreases. The measurement of magnetic susceptibility and Ce L$_{III}$-edge XANES spectra provides only an average valence of the specimens. Therefore, whether the valence change occurred in the whole particle or just on the surface of nanoparticles is unclear. To answer this question, studies with bulk-surface resolved measurements must be performed.

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