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HEAVY-FERMION BEHAVIOR IN $CeAl_2$ NANOPARTICLES

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Abstract--*In order to examine the quantum size effects on the heavy-fermion behavior in $CeAl_2$, we have performed measurements of the low-temperature specific heats for $CeAl_2$ nanoparticles with average particle size 80Å for temperature down to 80mK. For 80Å - nanoparticles the magnitude of γ of $CeAl_2$ can be as high as $3600mJ/K^2 f.u.$ at $T=80mK$ with $T_K \approx 0.65K$. Compared with the sharp anti-ferromagnetic order ($T_N=3.8K$) in bulk $CeAl_2$ only a blurred peak at same temperatures is observed in $CeAl_2$ nanoparticles. Due to the suppression of the long-range magnetic order by the limited geometric size and the less degeneracy of the density of states of conduction electrons $D(\varepsilon_F)$ the enhanced heavy-fermion behavior (in terms of γ) and the disappearance of magnetic order in $CeAl_2$ nanoparticles are attributed to the quantum size effects in nanoparticles. ©1999 Acta Metallurgica Inc.*

INTRODUCTION

About two decades ago nanoparticles were widely studied by scientists and mechanical engineers mostly for the reason of their general physical properties and engineering applications (1-4). Lately due to more interesting basic physical properties found in nanoparticles, such as the quantum size effects, the research on nanoparticles again becomes an important field (5-7). There is no doubt that the physical properties of nanoparticles can be affected directly by the confinement of limited geometric sizes. In this report these quantum size effects on magnetic interactions, such as crystal field effect, RKKY interaction and Kondo behavior were examined by thermodynamic measurements on bulk $CeAl_2$ and 80Å-$CeAl_2$ nanoparticles.

EXPERIMENTAL DETAILS

$CeAl_2$ nanoparticles were fabricated on a liquid-nitrogen-cooled cold trap by thermal evaporation of bulk $CeAl_2$ in He atmosphere (99.99%) of 0.1 torr. The structures and phase purities of bulk $CeAl_2$ and nanoparticles were examined by powder X-ray diffraction in Fig. 1.

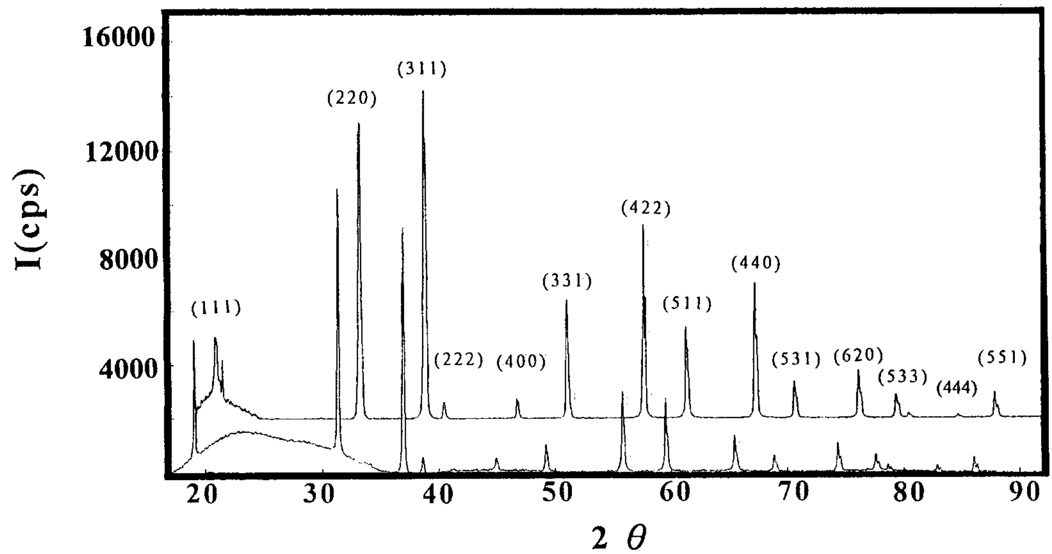

Fig. 1 The X-ray diffraction spectra of 80Å-$CeAl_2$ nanoparticles (bottom) and bulk $CeAl_2$ (top). The top one is slightly shifted to right for easy observation. The broad peaks seen at $2\theta \approx 22°$ and at 45° are from the grease used in sample attachment.

In bulk $CeAl_2$ the single phase of cubic Laves structure with lattice constant a= 8.06Å is determined and is consistent with that of early reports (8); in 80Å-$CeAl_2$ the X-ray diffraction shows the same structure as that of the bulk except a slight (≈0.37%) lattice expansion with a= 8.09Å. No second phase is detected for either specimen. A couple of different batches of 80Å-$CeAl_2$ were prepared, some of them showed no visible Ce oxidation (Fig. 1) whereas some ones did show minor CeO_2 phase (main diffraction peak at 2θ =28.56° for Cu Kα line). Although all the measurements in the report were done on our best quality specimens in Fig. 1, but due to the limitation of X-ray diffraction resolution it is possible that a very light layer of Ce oxidation especially on surface of nanoparticle is not detected.

The 80Å of average diameter of $CeAl_2$ nanoparticles was calculated from the distribution of particle sizes obtained by transmission electron microscopy (TEM). For specific heat measurements an assemble of $CeAl_2$ nanoparticles was collected and was very lightly pressed into a pellet with a pressure much less than the strength that can possibly transform $CeAl_2$ nanoparticles into a bulk. After being pressed no visible change on the color of nanoparticles is observed and the density of the pellet is estimated about 10-15% of the bulk by re-melting a pellet of nanoparticles into a bulk. The measurements of specific heat were performed using a thermal-relaxation micro-calorimeter which was described in an early report (9).

RESULTS AND ANALYSIS

The specific heat C(T) for bulk $CeAl_2$ is plotted as C/T versus T in Fig. 2. In bulk $CeAl_2$

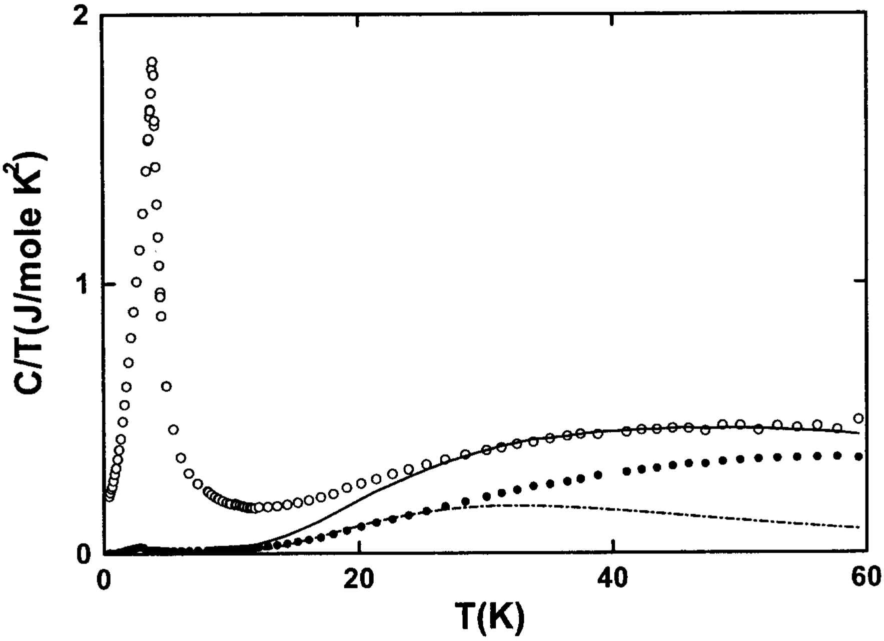

Fig. 2 The specific heat data, plotted as C/T versus T, for bulk $CeAl_2$ (open circles) and $LaAl_2$ (closed circles). The specific heat of $LaAl_2$ represents the contribution of lattice phonons. The peak at 3.2K in $LaAl_2$ corresponds to a superconducting transition. The dot-dashed line represents the theoretical specific heat due to the crystal field with T_{CF}= 110 K. The solid line is the sum of contributions of lattice phonons and the crystal field.

an anti-ferromagnetic order peaked at 3.8K is observed and a broad maximum centered at 35K over the background of lattice phonons is attributed to the contribution of a crystal field. Since for temperatures below T_N the anti-ferromagnetic specific heat is proportional to T^3, the low-temperature specific heat is fit to equation $C = \gamma T + a T^3$ with a value of $\gamma \approx$150mJ/ mole K^2. The magnitude of γ is only about one sixth of the single ion value 900 mJ/ mole K^2 calculated from equation ($T_0 = \pi R/6\gamma$, T_K=1.29 T_0) for Kondo temperature T_K=5K (10). An explanation for this observation was given by C.D. Bredl etc (10) who asserted that only a small fraction of the conduction band states is involved in the Kondo effect and works on weakening of the magnetic moments. We account for the specific heat of bulk $CeAl_2$ by the contributions of lattice phonons C_{ph}, magnetic correlation C_m and crystal field C_{cry}(the six-fold degeneracy of Ce^{3+} with J=5/2 splits into a quartet Γ_8 and a doublet Γ_7 in the cubic symmetry). To estimate the contribution of specific heat of lattice phonons, an iso-structure non-magnetic $LaAl_2$ is measured and shown as closed circles in Fig.2. After the subtraction of lattice phonons the specific heat of $CeAl_2$ fits well to that of a magnetic contribution C_m and a crystal field C_{cry} with T_{CF} =110K. The entropy integrated from C_m reaches Rln2 at T=17K. The specific heat C(T) for 80Å-$CeAl_2$ is plotted as C/T versus T in Fig. 3. In nanoparticles the sharp anti-ferromagnetic transition peak seen in $CeAl_2$ bulk is no longer observed, instead only a small blurred bump is found at same temperature region. An observation of a linear term with

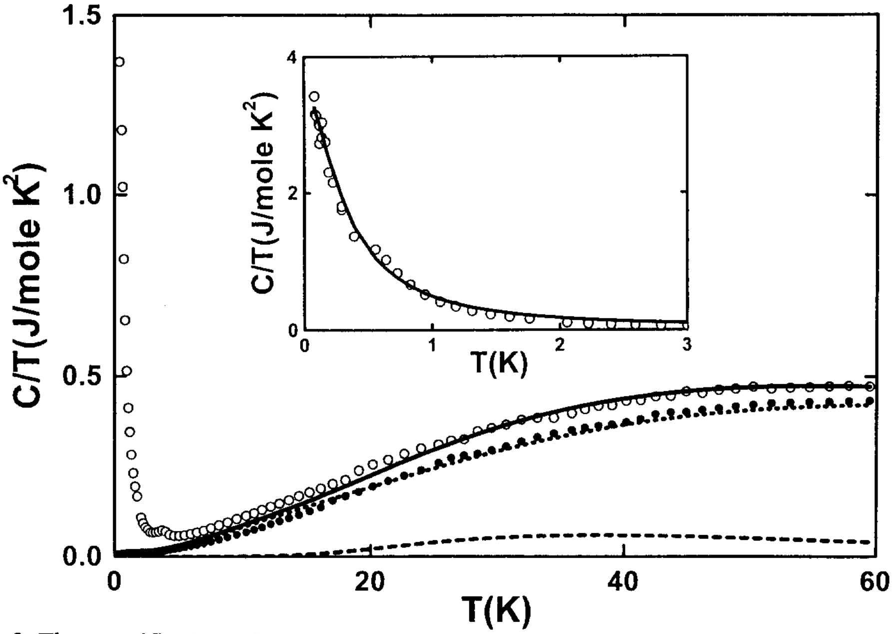

Fig. 3 The specific heat data, plotted as C/T versus T for 80Å-$CeAl_2$ nanoparticles (open circles) and 80Å-$LaAl_2$ (closed circles). The dotted line represents the specific heat of lattice phonons calculated for 80Å-$CeAl_2$ and the dashed line represents the 40% of specific heat of crystal field with T_{CF} = 130K. The solid line is the sum of all above various contributions. In inset the low temperature region is shown and the solid line is the fit for a 40% specific heat of Kondo anomaly with T_K = 0.65K.

a value of γ as high as 3600mJ/ mole K^2 as T $\rightarrow$ 0 indicates a characteristic Fermi-liquid behavior (see inset in Fig. 3). This γ is about twenty-four times of its bulk value ($\approx$150mJ/ mole K^2). The small blurred bump at 3.8K (with an equivalent entropy about $\approx$1.5% of Rln2) is due to a residual anti-ferromagnetic transition as seen in the bulk as the long-range RKKY interaction is suppressed by the limited geometric size and the smaller $D(\varepsilon_F)$. After the subtraction of lattice phonons taken from 80Å-$LaAl_2$, the specific heat at high temperatures fits to a 40% of the contribution of crystal field with T_{CF}= 130K, while the specific heat at low temperatures fits to a 40% of Kondo anomaly with T_K = 0.65K. The smaller Kondo temperature $T_K \approx \varepsilon_F \exp(-1/JD(\varepsilon_F))$ of nanoparticles in comparison to 5K of the bulk is conceptually acceptable if nanoparticle exhibits a smaller value of $D(\varepsilon_F)$ owing to the electronic quantum size effect. Using the model treating small particles by Baltes and Hilf (9,11) a theoretical calculation for lattice phonon of 80Å-$LaAl_2$ is shown as dotted line in Fig. 3. The calculated result with sound velocity v=1950 m/s (corresponding to a Debye temperature θ_D= 212K) fits well to the experimental data of 80Å-$LaAl_2$. The smaller value of Debye temperature θ_D =212K of lattice phonon as compared to 325K of the bulk is due to the phonon softening in nanoparticles. Since the crystal field is very dependent on the inter-distance of Ce ions, the 20% increase of crystal field might be related to the 0.37% of lattice expansion in nanoparticles. This consequence is qualitatively consistent with the earlier pressurized resistivity measurements of $CeAl_2$ made by M. Nicoas-Francillon etc. (8) in which the crystal field indeed decreases with the lattice compression by external pressures. Although the value of γ is as large as 3600mJ/ mole K^2 for $T\rightarrow 0$, it is only about 40% of 9000mJ/ mole K^2 of the theoretical value for T_K=0.65K expected by the model of V.T. Rajain (12). The magnitude of entropy integrated from the Kondo anomaly C_m is about 40% of Rln2. The reduced γ and entropy reflect the possibility that there are only 40% magnetic Ce ions left in 80Å-$CeAl_2$ nanoparticles and the rest of 60% of Ce ions are non-magnetic. The possible existence of non-magnetic Ce in the form of CeO_2 can account 5-10% non-magnetic Ce ions. Since the surface ions in nanoparticle occupy a large fraction of its volume, and usually have different magnetic behavior from that of core ions, this might account for the rest of the loss of magnetic Ce ions.

CONCLUSION

We have found a very large value of γ in 80Å-$CeAl_2$ nanoparticles and observed the quantum size effects in affecting the physical properties of heavy fermion compound. The linear coefficient of specific heat γ increases from 150mJ/ mole K^2 for the bulk material to a magnitude as large as 3600mJ/ mole K^2 for $T\rightarrow 0$ in 80Å-$CeAl_2$ nanoparticles. It is shown that the existing heavy-fermion behavior is revealed after the suppression of the long-range RKKY interaction. In addition to the 40% of crystal field fit to the high-temperature specific heat, the magnitude of the entropy below the Kondo anomaly is only about 40% of the theoretical value of Rln2; indicating the loss of 60% of magnetic Ce ions presumably on the surfaces of nanoparticles. The smaller T_K in nanoparticles as compared to 5K of the bulk is qualitatively acceptable owing to a smaller value of $D(\varepsilon_F)$ in nanoparticles. A conclusion is made that $CeAl_2$ can become a heavy fermion compound if its magnetic order can be suppressed properly by the quantum size effects.

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