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Heavy-Fermion Behavior in $CeAl_2$ Nanoparticles

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In order to examine the quantum size effects on the properties of heavy fermion compounds, we have performed measurements of the low-temperature specific heats for T=0.4 K - 35 K of $CeAl_2$ nanoparticles with average particle size $\approx$ 80 A. The magnitude of γ of $CeAl_2$ changes from 150 mJ/K^2 f.u. to a magnitude as high as 1370 mJ/K^2 f.u. at T=0.4 K as sample size decreases to a certain extent such as nanometer scale. The anti-ferromagnetic order with T_N = 3.8 K in bulk $CeAl_2$ is no longer shown in $CeAl_2$ nanoparticles, whereas a Kondo anomaly with $T_K \approx$ 0.5 K appears at low temperatures and exhibits a large value of γ as mentioned. Obviously the limited geometric size and the less degeneracy of the density of states of conduction electrons $D(\varepsilon_F)$ in nanoparticles hinder the formation of the long-range RKKY interaction among Ce ions and thus their magnetic order. Both magnitudes of the entropy integrated from Kondo anomaly and the experimental γ are about 40% of Rln2 and 3700 mJ/K^2 f.u. of the-theoretical value respectively. The small fraction in magnitude implies incomplete Kondo interactions, indicating either a small portion of Ce ions or only a partial success of interaction involved in the heavy-fermion (Kondo)behavior. The smaller Kondo temperature $T_K \approx JD(\varepsilon_F)\exp(-1/JD(\varepsilon_F))$ of nanoparticles as compared to 5 K of the bulk is conceptually acceptable if $D(\varepsilon_F)$ is small in nanoparticles. Clearly the quantum size effects have larger effect on the RKKY interaction than on Kondo interactions, i.e., the suppress of magnetic order reveals the heavy-fermion behavior. A conclusion is made that $CeAl_2$ can become a very heavy fermion if its magnetic order is suppressed properly by the quantum size effects.

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PACS. 71.28.+d – Narrow-band systems; intermediate-valence solids.
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I. Introduction

About two decades ago nanoparticles were widely studied by scientists and mechanic engineers mostly by the reason of their general physical properties and engineering applications [1-4]. Lately the study of nanoparticles is focused on the subject of electronic quantum size effects in metal particles [5-7]. By virtue of their simplicity and ease of preparation most of these studies are made on pure elements such as Pd [8] and Ag and are not very much done on compounds. The physical properties of nanoparticles are affected directly by their limited geometric sizes. In addition to the effect of geometric size confinement itself, there are also two other size-generated effects-the phonon quantum size effect and the electronic quantum size effect. The former is associated to the addition of new low-frequency surface modes and the truncation of large wave-vector limit in lattice vibrational spectrum, and the latter is related to the increase of the energy level spacing and the decrease of density of states of conduction electrons at Fermi level $D(\varepsilon_F)$ [5].

In order to examine these quantum size effects on the physical properties, such as crystal field effect, RKKY interaction and heavy-fermion (Kondo) behavior in heavy fermion compounds, we have prepared bulk $CeAl_2$ and 80 Å-$CeAl_2$ nanoparticles and performed their measurements of the low-temperature specific heats for T=0.4 K to 35 K.

II. Experimental details

To fabricate $CeAl_2$ nanoparticles, $CeAl_2$ bulk were first prepared by arc melting the high-purity constituent elements Ce(99.9%) and A1(99.9999%) in an argon atmosphere. The ingot of $CeAl_2$ were then powdered for X-ray diffraction examination, no second phase within the detection limit (3%) instruments was found. The cubic Laves structure with lattice constant a=8.06 Å is determined and is consistent with that of early reports [9]. $CeAl_2$ nanoparticles were then fabricated on a liquid-nitrogen-cooled cold trap by thermal evaporation of $CeAl_2$ powder in He atmospheres of 0.1 torn. $CeAl_2$ nanoparticles were also examined by X-ray diffraction spectrum to confirm the same structure as the bulk. No detectable Ce oxidation CeO_2 was found. The average particle size of $CeAl_2$ nanoparticles was calculated from the distribution of particle sizes obtained by transmission electron microscopy. $CeAl_2$ nanoparticles were then compressed into pellets for the specific heat measurements using a thermal-relaxation micro-calorimeter described in early report [8].

III. Results and analysis

In Fig. 1 The X-ray diffraction spectrum of nanoparticles of $CeAl_2$ is shown. The cubic Laves phase of $CeAl_2$ (space group Fd3m) was confirmed and no second phase was detected. The estimated lattice constant of nanoparticles is 8.09 Å which is about 3.7% larger than that of the bulk. The specific heat per formula unit of bulk $CeAl_2$ is plot as C/T versus T in Fig. 2. At low temperatures, an anti-ferromagnetic order pecked at 3.8 K is observed and a broad maximum centered at 35 K over the background of lattice phonons is attributed to the contribution of a crystal field with $T_{CF} \approx 110$ K. We account for the data by the contributions of conduction electrons, lattice phonons, magnetic correlation and crystal field (the sixfold degeneracy of Ce^{3+} with $J=5/2$ splits into a quartet Γ_8 and a doublet Γ_7 in the cubic symmetry). The associated parameters derived from the curve fit with these contributions are given as γ = 150 mJ/K^2 f.u., Debye temperature θ = 325 K and crystal field T_{CF} = 110 K. The magnetic specific heat C_m=C-C_{ph}-C_{cry} yields the integrated entropy of about 0.9 Rln2, where C_{ph} is the specific heat of lattice phonons and C_{cry} is the specific heat of crystal field. The 10% loss of entropy of Rln_2 might be attributed to the Kondo demagnetization. This postulate was also given by C. D. Bred1 *etc.* [8], they asserted that the magnetic ordering in $CeAl_2$ works with 90% success as T $\rightarrow$ 0. This

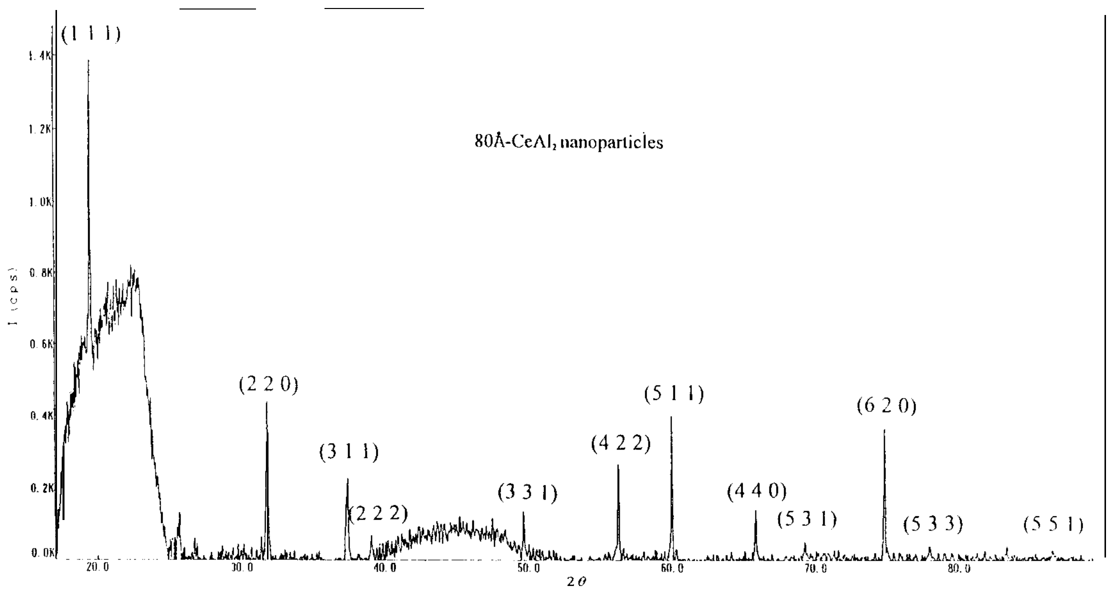

FIG. 1. The X-ray diffraction spectrum of nanoparticles of $CeAl_2$ is shown. The cubic Laves phase of $CeAl_2$ (space group Fd3m) is confirmed and no second phase is detected. The broad -pecks at $2\theta \approx 22°$ and $45°$ are from the grease using in sample attachment.

speculation is consistent with the results drawn from the specific heat measurements on nanoparticles later. In Fig. 3, we plot the specific heat per formula unit of 80 Å-$CeAl_2$ nanoparticles as C/T versus T. The anti-ferromagnetic order in $CeAl_2$ bulk is no longer observed, instead a Kondo anomaly at very low temperatures appears. Similarly way we fit this data by the contributions of lattice phonons, crystal field and Kondo interactions (replacing the anti-ferromagnetic correlation). The associated parameters gained from this curve fit are θ = 212 K (or equivalent sound velocity v=1925 m/s), T_{CF} = 130 K, $T_K \approx$ 0.5 K, γ = 1370 mJ/K^2 f.u. (at 0.4 K).

Since the crystal field is very dependent on the inter-distance of Ce ions, the 18% increase of crystal field in nanoparticles is undoubtedly related to the 3.7% lattice expansion in nanoparticles. This consequence is qualitatively in good agreement to the early pressurized resistivity measurements of $CeAl_2$ made by M. Niclas-Francillon etc. [9] in which the crystal field indeed decreases with the lattice compression by external pressures. The disappearance of magnetic order observed in the bulk indicates that the limited geometric size and the less $D(\varepsilon_F)$ in nanoparticles hinder the formation of the long-range RKKY interaction among Ce ions and their magnetic order. Although the value of γ is as large as 1370 mJ/K^2 fu. at 0.4 K, it is only about 40% of 3700 mJ/K^2 f.u. of the theoretical value expected by V. T. Rajain [12] at same temperature. The Kondo interactions affected by the limited geometric size is also reflected in the calculation of the magnetic entropy. The magnitude of entropy integrated from Kondo anomaly C_m=C-C_{ph}-C_{cry} is also about 40% of Rln2. Both of the low temperature Kondo anomaly and the large value of γ obviously

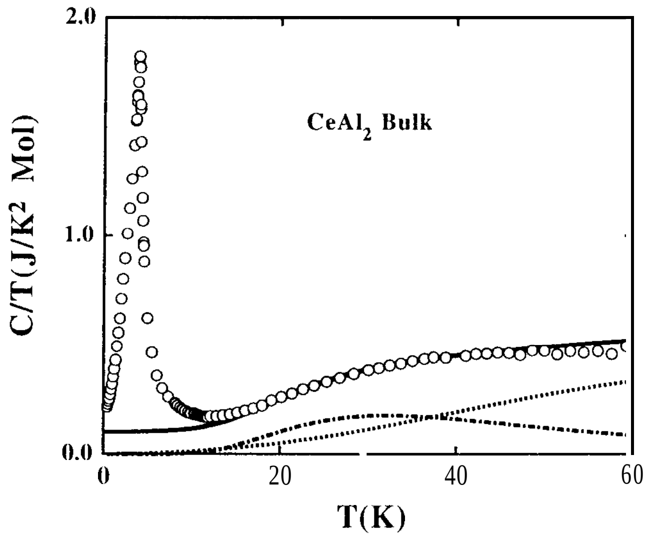

FIG. 2. The specific heat per formula unit of bulk $CeAl_2$ is plot as C/T versus T (open circles). The dotted line represents the specific heat of lattice phonons with θ=325 K and the dot-dashed line represents the specific heat of crystal field with T_{CF}=110 K. The solid line is the sum of all above contributions and the specific heat of conduction electrons with γ=150 mJ/K^2 f.u.

reflects that the quantum size effects have larger impact on the RKKY interaction than on the Kondo interactions, i.e., the suppress of magnetic order reveals a obvious heavy-fermion (Kondo) behavior. The smaller T_K in nanoparticles as compared to 5K of the bulk is qualitatively acceptable through the equation $T_K \sim JD(\varepsilon_F)\exp(-1/JD(\varepsilon_F))$ if $D(\varepsilon_F)$ is smaller in nanoparticles. The incomplete Kondo interactions implie that either a small portion of Ce ions involved in Kondo interactions or only a partial success of Kondo interactions occurred in nanoparticles.

V. Conclusion

We have observed the quantum size effects play important roles in affecting the physical properties of nanoparticles. The suppress of magnetic order reveals obvious Kondo interactions and heavy fermion behavior in $CeAl_2$. The linear coefficient of specific heat γ is increased from 150 mJ/K^2 f.u. of the bulk value to a magnitude as large as 1370 mJ/K^2 f.u. at T=0.4 K in 80 Å-$CeAl_2$ nanoparticles. Especially for T $\rightarrow$ 0 the value of $\gamma(0)$ is expected to be 9000 mJ/K^2 f.u. estimated through the equation $T_K = \pi R/6\gamma(0)$ in 80 Å-$CeAl_2$ nanoparticles. Both magnitudes of the entropy integrated from Kondo anomaly and the experimental γ are about 40% of Rln2 and 3700 mJ/K^2 f.u. of the theoretical value respectively, indicating either a small portion of Ce ions or only a partial success of interaction involved in the heavy-fermion (Kondo) behavior in nanoparticles. The smaller T_K in nanoparticles as compared to 5 K of the bulk is qualitatively acceptable through the

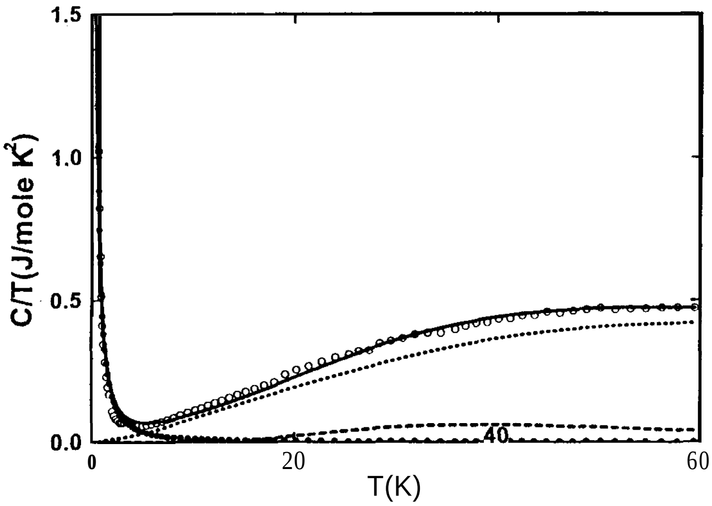

FIG. 3. The specific heat per formula unit of 80 Å-$CeAl_2$ nanoparticles is plot as C/T versus T (open circles). The dotted line represents the specific heat of lattice phonons with $\theta=212$ K (or equivalent sound velocity v=1925 m/s) and the dashed line represents the specific heat of crystal field with $T_{CF}=130$ K. The solid circles represent Kondo anomaly with $T_K=0.5$ K. The solid line is the sum of all above contributions.

equation $T_K \sim JD(\varepsilon_F) \exp(-1/JD(\varepsilon_F))$ if the density of states of conduction electrons $D(\varepsilon_F)$ is smaller in nanoparticles. A conclusion is made that $CeAl_2$ can become a very heavy fermion if its magnetic order is suppressed properly by the quantum size effects.

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