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Physica B 284–288 (2000) 1738–1739

PHYSICA B

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Size dependence of heavy-fermion behavior in $CeAl_2$

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Abstract

Heavy-fermion compound $CeAl_2$ has a Kondo temperature T_K of 5 K and a *Neel* temperature T_N of 3.8 K. As the dimensions of specimen decrease, the size effect was shown as the suppression of T_K and the magnitude of anti-ferromagnetic anomaly in specific heat. For 80 Å nanoparticles the magnitude of γ extrapolates to 9500 mJ/K^2 mole at absolute zero, whose value falls in the highest range ever reported for heavy-fermion systems. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heavy fermion; Kondo effect; Specific heat

1. Introduction and experiment

In a bulk form, $CeAl_2$ is a well-known Kondo system with $T_K = 5$ K [1]. It also undergoes an anti-ferromagnetic ordering at $T_N = 3.8$ K. Since the RKKY interaction and Kondo interaction of the 4f moments involve the participation of conduction electrons, the change in particle size should bring significant consequences. This report describes a calorimetric study . Bulk $CeAl_2$ sample was first prepared by arc melting. Evaporating the bulk $CeAl_2$ in a helium atmosphere produced 80 Å particles, whereas 9000 and 17 000 Å were fabricated through ball milling. The particle size distributions were characterized by TEM, HRTEM and SEM. The microscopic images reveal better spherical shape and a narrower size distribution in 80 Å $CeAl_2$ than those from ball milling. Powder X-ray diffraction for all these different size specimens yields a single phase of cubic Laves structure and lattice constant a_0 from 8.06 to 8.09 Å with a consequence of a slight lattice expansion for the finest specimen of 80 Å $CeAl_2$. The characteristic chemical reactivity of nanoparticles, particularly the high oxidation susceptibility of Ce, could likely lead to a thin layer of CeO_2 on the surface of fine particles. It is of interest to note that the surface oxidation layer can actually prevent a given nanoparticle from making electronic contact with its neighbors, thus upholding finite size effects, if any.

2. Results and discussion

The temperature dependence of specific heat for all specimens are shown in Fig. 1. For bulk $CeAl_2$ a well-defined peak reveals the previously known anti-ferromagnetic ordering at $T_N = 3.8$ K with an associated entropy of $R\ln 2$ as expected for the ground state doublet of Ce^{3+} ions. At well below T_N, $C = \gamma T + \beta T^3$ with $\gamma \approx 150$ mJ/K^2 mol.

The magnitude of the anti-ferromagnetic peak decreases as the particle size decreases, but T_N remains practically the same. Meanwhile, a Kondo-type anomaly prevails at much lower temperatures. Apparently, the portion of Ce ion involved in Kondo interaction increases as particle size decreases. The total magnetic entropy are $R\ln 2$ for all specimens except 80 Å $CeAl_2$ in which only about 70% of $R\ln 2$ is accountable. The shortage is attributed to the relatively large portion of surface non-magnetic Ce ions in these finest particles. The constant T_N may reflect a constant magnetic exchange integral J of the same lattice structure. When the

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PII: S0921-4526(99)02905-1

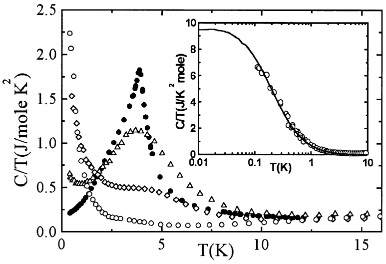

Fig. 1. $C(T)/T$ versus T for bulk and various size $CeAl_2$ (●: bulk, △: 17 000 Å, ◇: 9000 Å, ○: 80 Å). Inset: The specific heat of 80 Å $CeAl_2$ at lowest temperatures (see text).

particle diameter becomes smaller, however, the coherence length of the spin fluctuations can reach a point not large enough to sustain a true phase transition. The existence of CeO_2 can account for some 5% of the missing magnetic Ce ions for 80 Å $CeAl_2$. The major portion must be related then to the appreciable number of surfaces or outer-shell ions in a nanoparticle. The surface ions for 80 Å $CeAl_2$ within a thickness of $0.5a_0$, would occupy $\approx 27\%$ of the total volume, but for larger particle diameter up to a few thousands of Å, this surface effect is negligible. To ascertain that the lower temperature anomaly is of the Kondo origin, further calorimetric measurements were made on 80 Å $CeAl_2$ in external magnetic fields of 2.6 and 6.5 T, respectively. The profile of the anomaly and its response to magnetic fields are in reasonable agreement with the theoretical curves for a Kondo ion ($J = \frac{1}{2}$) derived by Sacramento [2] for bulk $CeAl_2$, except that the peak positions occur at slightly higher temperatures. The difference between bulk and nanoparticle is attributed to the size effect.

After the lattice and Schottky contributions being subtracted at the lowest temperatures, specific heat of 80 Å $CeAl_2$ in the inset of Fig. 1 can be fitted to the Kondo model with $J = \frac{1}{2}$ and $T_K = 0.65$ K with a reduction factor 0.7 (represented by a solid line). The significant reduction in T_K as compared to the bulk value of 5 K can be attributed only partially to lattice expansion. The major difference must be caused, therefore, by the electronic quantum size effect. In nanoparticles, the discreteness of energy levels δ becomes more pronounced. The larger δ in turn lowers the density of states at Fermi level, $D(\varepsilon_F)$. Meanwhile, $T_K \approx \epsilon_F \exp[-1/D(\epsilon_F)]$ and the reduced $D(\epsilon_F)$ yields a smaller T_K.

Finally, the most impressive finding of this work is the magnitude of the coefficient γ of the linear term in specific heat. At zero field, this parameter has already reached a quite large value of almost 7000 mJ/K^2 mol at $T = 0.11$ K, the lowest temperature of measurements. Based on the Kondo model with $J = \frac{1}{2}$, it is extrapolated to 9500 mJ/K^2 mol at absolute zero (see inset in Fig. 1), which falls in the highest range ever reported for heavy fermion systems.

Acknowledgements

This work was supported by the National Council of the Republic of China under Grants No. NSC88-2112-M-001-026.

References

[1] F. Steglich, C.D. Bredl, M. Loewenhaupt, K.D. Schotte, J. Phys. Colloq. 40 (1979) C5-301 and references therein.
[2] P.D. Sacramento, P. Schlottmann, Phys. Rev. B 40 (1989) 431.