Available online at www.sciencedirect.com
SCIENCE DIRECT
Physica B 359–361 (2005) 497–499
PHYSICA B
www.elsevier.com/locate/physb

Superconductivity in $CeCo_2$ nanoparticles

Y.Y. Chen[a], S.-J. Jang[b], C.R. Wang[c], H.D. Yang[d,*]

[a]Institute of Physics, Academia Sinica, Taipei, Taiwan, ROC
[b]Center for Teacher Education and Graduate School of Education, Chung Yuan Christian University, Chung-Li, Taiwan, ROC
[c]Department of Physics, Tunghai, Taichung, Taiwan, ROC
[d]Department of Physics, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, ROC

Abstract

Both Ce and Co are essentially nonmagnetic in Pauli-paramagnetic $CeCo_2$, which undergoes a superconducting transition near 1 K. When made into 58-Å nanoparticles, the compound becomes paramagnetic. Meanwhile, based on heat capacity measurements, the nanoparticles remain to be nonsuperconducting down to 0.4 K but exhibit a low-temperature Kondo anomaly with $C/T \sim 350\,\mathrm{mJ/mol\,K^2}$ at 0.4 K. Such intriguing effects are consequences of the competition between superconducting gap and electronic spectrum's mean level spacing.

PACS: 65.80.+n; 82.60.Qr; 72.15.QM

Keywords: Superconductivity; Kondo anomaly; Nanoparticles

1. Introduction

When the physical dimension of a given material is reduced towards nanoscale, various physical properties including superconducting and magnetic characteristics can often be drastically altered. More recently, a size-induced crossover from magnetic ordering to a Kondo magnetism was observed in $CeAl_2$, Ce_3Al and Ce_3Al_{11} [1]. This study was carried out, therefore, on another Ce-based compound, $CeCo_2$. Bulk $CeCo_2$ undergoes a superconducting transition near 1 K. Its extremely low magnetic susceptibility indicates that both Ce and Co are essentially nonmagnetic [2]. The zero magnetization of Ce indicates an electronic state $\langle [Xe]4f^0 5d^2 6s^2 \rangle$ of Ce^{4+} without localized 4f electrons, eventhough a large electronic specific heat coefficient $\gamma \approx 34\,\mathrm{mJ/mol\,K^2}$ seems to suggest a tendency to localization.

2. Experimental details

Experimentally, bulk $CeCo_2$ was first synthesized under argon by arc-melting thoroughly

*Corresponding author. Tel.: +886 2 2789 6725; fax: +886 2 2783 4187.
E-mail address: cheny2@phys.sinica.edu.tw (Y.Y. Chen).

0921-4526/$ - see front matter
doi:10.1016/j.physb.2005.01.126

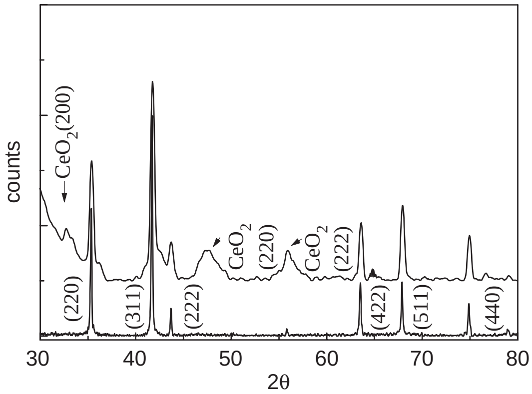

Fig. 1. X-ray diffraction patterns of bulk (the bottom) and nanoparticle (the top) $CeCo_2$.

mixed Ce (99.95%) and Co (99.95%) in a 1:2 atomic ratio. The expected cubic Laves-phase crystal structure was confirmed by X-ray diffraction (XRD) (Fig. 1). Nanoparticles were then fabricated on a liquid-nitrogen cooled surface by flash evaporation of bulk ingots in a helium atmosphere. High-resolution transmission electron microscopy (HRTEM) was employed to directly observe the nearly spherical particles and their size distribution, yielding an estimated average size of 58 Å (Fig. 2). According to the XRD spectra, the structure and lattice constant a (7.171 Å) is practically the same as those of the parent bulk material, except some line broadening.

3. Results and analysis

The main phase of the nanoparticles appears to be paramagnetic. To more relevantly elucidate the difference in electronic properties between bulk and nanoparticle $CeCo_2$, a calorimetric study was made at 0.4–15 K, using a thermal-relaxation micro-calorimeter in a ^{3}He cryostat. The temperature dependence of specific heat for $CeCo_2$ samples is shown in Fig. 3. For bulk $CeCo_2$, a well-defined superconducting transition occurs at $T_c \sim 1$ K as previously reported. The normal-state data can be fitted by $C/T = \gamma + \beta T^2$, which yields the electronic specific heat coefficient $\gamma = 37\,\mathrm{mJ/mol\,K^2}$, and a Debye temperature $\Theta_D = 200$ K based on the lattice specific heat coefficient $\beta = 0.00075\,\mathrm{J/f.u.\,K^4}$. At zero magnetic field, the nanoparticles clearly do not undergo a superconducting transition at 1 K or down to 0.4 K. Instead, an anomaly was seen at low temperatures and is identified below as a Kondo behaviour. The upturn in C/T reaches $350\,\mathrm{mJ/mol\,K^2}$ at 0.4 K. The observed suppression of superconductivity could be a consequence of the increase of electronic energy level spacing by size reduction. As suggested by Anderson [3], superconductivity would no longer be possible when the particle diameter d becomes small enough and the electronic spectrum's mean level spacing δ becomes larger than the superconducting gap Δ of the bulk.

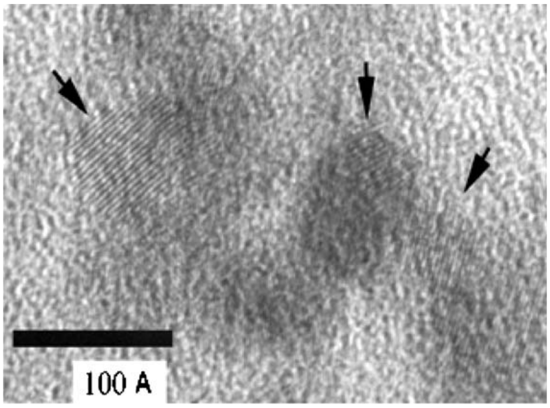

Fig. 2. HRTEM image of nanoscaled $CeCo_2$ sample reveals several well-crystallized particles showing clear lattice arrays.

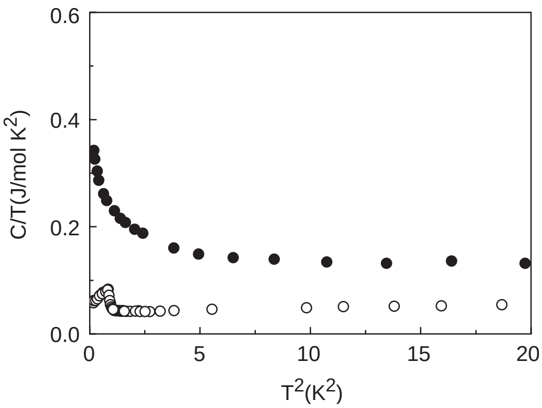

Fig. 3. C/T versus T^2 for bulk and nanoparticle $CeCo_2$ represented by closed and open circles, respectively.

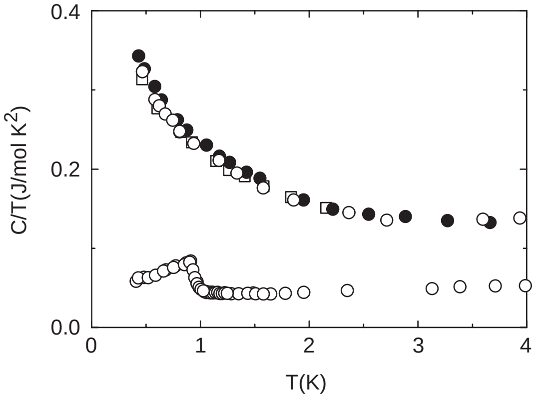

Fig. 4. Comparison for field-dependent specific heat for $H = 0$, 0.2 and 0.4 T represented by solid circles, open circles and squares, respectively.

To ascertain the lack of a superconducting transition and the Kondo origin of the low-temperature specific heat anomaly, further calorimetric measurements were made in magnetic fields H from 500 G up to 4 T. Even if the superconducting transition spreads over a wide temperature range owing to particle size distribution, the specific heat near 1 K should be suppressed as field increases to the critical field H_{c2}~0.275 T for $CeCo_2$. To avoid the confusion from the suppression of Kondo singlets under magnetic field, specific heat data for $H = 0$, 0.2 and 0.4 T are compared in Fig. 4. However, apart from a slight shift of magnetic effects on Kondo singlets, no change to reflect superconductivity was observed.

Acknowledgement

This work was supported by the National Research Council of the Republic of China under Grant no. NSC 93-2112-M-001-075.

References

[1] Y.Y. Chen, Y.D. Yao, C.R. Wang, W.H. Li, C.L. Chang, T.K. Lee, T.M. Homg, J.C. Ho, S.F. Pan, Phys. Rev. Lett. 84 (2000) 4990.
[2] T.M. Seixas, J.M. Machado Silva, Physica B 269 (1999) 362.
[3] P.W. Anderson, J. Phys. Chem. Solids 11 (1959) 26.