ANOMALOUS ORDERED STATE OF FILLED SKUTTERUDITE $CeOs_4Sb_{12}$*

T. Namiki, Y. Aoki, H. Sugawara and H. Sato

Department of Physics, Tokyo Metropolitan University, Tokyo 192-0397, Japan

(Received July 10, 2002)

Preliminary results of specific heat measurement in applied magnetic fields on the filled skutterudite $CeOs_4Sb_{12}$ are presented. Clear anomaly in the specific heat data suggests the existence of an intrinsic phase transition at 0.9 K, accompanied by a gap opening in moderately mass-enhanced quasiparticle bands. Unusual magnetic field effect on the transition temperature, which shifts toward higher temperatures with increasing field, is revealed.

PACS numbers: 75.40.Cx, 71.27.+a, 75.30.Kz, 75.30.Mb

1. Introduction

The filled skutterudites, a series of ternary compounds with the chemical formula RT_4X_{12} (R = rare earth; T = Fe, Ru, or Os; X = P, As, or Sb) crystallizing in a BCC structure, were first reported by Jeitschko and Braun [1]. Since R atoms are surrounded by the 12 X atoms in the crystal structure, it is theoretically expected that $4f$-electrons could be strongly hybridized with p-type conduction electrons [2].

Actually, $CeFe_4X_{12}$ with X=P was reported to have a hybridization gap of $\Delta = 0.11$ eV with clear semiconducting behaviors [3]. When the lattice constant is increased from X=P to As, Δ becomes smaller (0.01 eV [4]), and finally for X=Sb, the gap is closed exhibiting semi-metallic behaviors [5].

Bauer *et al.* [6] reported $CeOs_4Sb_{12}$ to be a narrow-gap semiconductor with $\Delta \sim 9 \times 10^{-4}$ eV, which was estimated from the temperature dependence of the electrical resistivity $\rho(T)$ in $25 < T < 50$ K. They observed a λ-type anomaly at 1.1 K in zero-field specific heat $C(T)$ data and attributed it to an impurity contribution. In this paper, we report that our preliminary results of specific heat measurements on $CeOs_4Sb_{12}$ in applied

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

magnetic fields disagrees with those interpretations. Fermi-liquid like behavior observed in $C(T)$ along with the non-metallic transport property reflects an anomalous electronic state in this compound.

2. Experimental

Single crystals of $CeOs_4Sb_{12}$ were grown by Sb-self-flux method. The raw materials were 3N5 (99.95% pure)-Ce, 3N-Os, and 6N-Sb. X-ray powder diffraction pattern shows that the sample is almost a single phase of $CeOs_4Sb_{12}$ crystallizing in the BCC filled skutterudite structure [7]. Although weak traces of an included Os-metal phase are visible, the maximum peak intensity is only 1.7 % of that of the $CeOs_4Sb_{12}$ phase. Specific heat was measured using a collection of the small single crystals by a quasiadiabatic heat pulse method described in Ref. [8] using a dilution refrigerator equipped with a superconducting magnet.

3. Results and discussions

Figure 1 shows the temperature dependence of specific heat divided by temperature in magnetic fields. For estimation of the phonon contribution ($C_{\rm ph}$), we use data for $LaOs_4Sb_{12}$ [9]. $C_{\rm ph}(T)$, which is shown in Fig. 1, can be described as $9.80 \times 10^{-4} T^3 + 7.19 \times 10^{-5} T^5 - 3.89 \times 10^{-7} T^7$ J/Kmol for $T \leq 8$ K. Negligibly small contribution of $C_{\rm ph}/T$ at low temperatures suggest that the anomaly appearing below 3 K is of electronic origin. An upturn below 0.3 K developing with magnetic field is due to nuclear Schottky contribution (C_N).

In zero field, the data exhibit a prominent sharp peak at $T_x = 0.88$ K. This anomaly was already reported in Ref. [6] with a similar overall temperature dependence [11] and was attributed to an impurity contribution. With increasing field, the anomaly appears to shift to higher temperatures. The position of the anomaly is plotted in a $\mu_0 H$ *vs* T plane (the inset of Fig. 1).

Considering only the C/T *vs* T data in zero field, the curve could be interpreted as the sum of an electronic part of $\gamma \sim 0.18$ J/K^{2}mol [10] and a contribution from an impurity that has a phase transition at 0.88 K as in Ref. [6]. In this case, the data above 3 K in Fig. 1 show that the value of γ is almost field independent. On the other hand, C_e/T below T_x is strongly suppressed by magnetic fields and it reaches less than half of the zero-field value in 4 T. This fact clearly shows that the aforementioned interpretation is incorrect, indicating that the specific heat anomaly should be attributed to an intrinsic phase transition in $CeOs_4Sb_{12}$.

In zero field, the high-T tail of the anomaly above T_x up to $\sim 3T_x$ indicates the existence of short-range correlations. While this tail remains

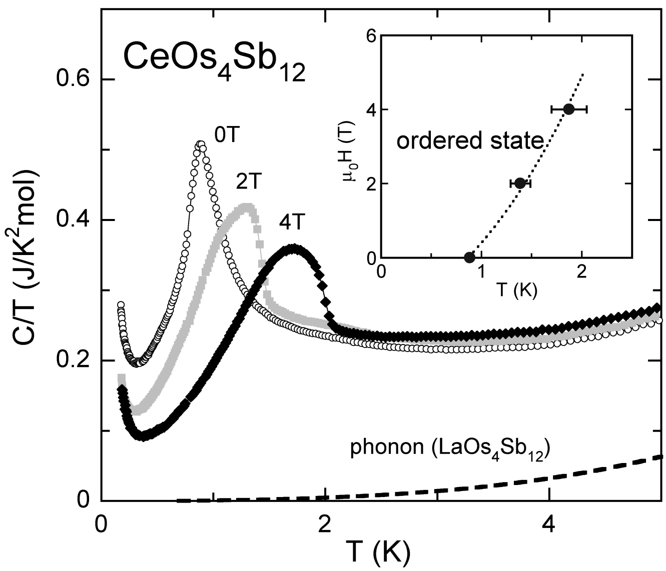

Fig. 1. Specific heat divided by temperature (C/T) *vs* T for a collection of small single crystals of $CeOs_4Sb_{12}$. The broken curve represents the phonon contribution (C_{ph}/T) determined from C/T of $LaOs_4Sb_{12}$ [9]. The inset shows the μ_0H–T phase diagram determined from the specific heat data. The broken line is guide to the eye.

in applied fields, a jump at the phase transition becomes visible in 2 T. Broader transition in 4 T might indicate that each single crystalline grain has a different transition temperature depending on the applied field direction respective to the crystallographic direction. The nature of $dT_x/dH > 0$ itself is reminiscent of the antiferro-quadrupole transition observed in CeB_6 [12] and TmTe [13]. However, the electronic part of the entropy released below T_x is too small ($0.05R\ln 2$ and $0.06\ R\ln 2$ for 0 and 4 T, respectively) to be attributed to such localized f-electron scenario. Taking into account the almost T-independent C_e/T above $\sim 3T_x$ and the depression below T_x, we suggest that the ordering is more likely to be a charge density wave (CDW) or a spin density wave (SDW) of the moderately mass-enhanced quasiparticle band. Probably a gap opening on part of the Fermi surface leads to the suppression of C_e/T and an increase of ρ below T_x [14]. In this scenario, however, the unconventional nature of both the quasiparticle band and the phase transition in $CeOs_4Sb_{12}$ is reflected in the observed $d\rho/dT < 0$ behavior below ~ 50 K [6] and the $dT_x/dH > 0$, which is anomalous for a CDW or SDW transition.

4. Summary

Specific heat measurements performed in magnetic fields on $CeOs_4Sb_{12}$ have clarified the field effect on the clear peak anomaly, which appears at 0.88 K in zero field. Analysis of the data suggests the existence of an intrinsic phase transition, accompanied by a gap opening in moderately mass-enhanced quasiparticle bands. The transition temperature appears to shift toward higher temperatures when magnetic field is increased. The Fermi-liquid-like behavior in the specific heat along with the non-metallic transport properties both observed in the non-ordered state suggest the unconventional nature of the electron state in $CeOs_4Sb_{12}$.

REFERENCES

[1] W. Jeitschko, D. Braun, *Acta Crystallogr.* **B33**, 3401 (1977).

[2] H. Harima, private communication.

[3] H. Sato, Y. Abe, H. Okada, T. D. Matsuda, K. Abe, H. Sugawara, Y. Aoki, *Phys. Rev.* **B62**, 15125 (2000).

[4] F. Grandjean, A. Gérard, D. J. Braun, W. Jeitschko, *J. Phys. Chem. Solids* **45**, 877 (1984).

[5] D. T. Morelli, G. P. Meisner, *J. Appl. Phys.* **77**, 3777 (1995).

[6] E.D. Bauer, A. Ślebarski, E. J. Freeman, C. Sirvent, M.B. Maple, *J. Phys.: Condens. Matter* **13**, 4495 (2001).

[7] D. Braun, W. Jeitschko, *J. Less-Common Met.* **72**, 147 (1980).

[8] Y. Aoki, T. D. Matsuda, H. Sugawara, H. Sato, H. Ohkuni, R. Settai, Y. Ōnuki, E. Yamamoto, Y. Haga, A. V. Andreev, V. Sechovsky, L. Havera, H. Ikeda, K. Miyake, *J. Magn. Magn. Matter.* **177-181**, 271 (1998).

[9] Y. Aoki, T. Namiki, S. Ohsaki, S.R. Saha, H. Sugawara, H. Sato, submitted to *J. Phys. Soc. Jpn.*

[10] This is consistent with photoemission spectroscopy measurements at $\sim$5 K [K. Kanai *el al.*, private communication], which revealed the existence of a finite density-of-states at the Fermi energy. A band structure calculation [H. Harima, private communication] predicts a semimetallic behavior.

[11] The absolute value in Ref. [6] is $\sim$ 50 % smaller than ours.

[12] T. Fujita, M. Suzuki, T. Komatsubara, S. Kunii, T. Kasuya, T. Ohtsuka, *Solid State Commun.* **35**, 569 (1980).

[13] T. Matsumura, S. Nakamura, T. Goto, H. Amitsuka, K. Matsuhira, T. Sakakibara, T. Suzuki, *J. Phys. Soc. Jpn.* **67**, 612 (1998).

[14] H. Sugawara *el al.*, *not published.*