ANISOTROPIC THERMOELECTRIC PROPERTIES OF CeRhAs WITH SUPERSTRUCTURES*

T. Takabatake, T. Suemitsu, T. Sasakawa, J. Kitagawa, K. Umeo

Department of Quantum Matter, ADSM, Hiroshima University
Higashi-Hiroshima 739-8530, Japan

M. Nakajima, K. Iwasa and M. Kohgi

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

(Received July 10, 2002)

We report thermoelectric, magnetic and structural properties of the so-called Kondo semiconductor CeRhAs. The resistivity $\rho(T)$ along the three principal axes exhibits step-like anomalies at $T_1 = 370$, $T_2 = 235$ and $T_3 = 165$ K, respectively, and increases by two orders of magnitude on cooling to 1.5 K. Below T_1 an abrupt drop in the magnetic susceptibility along all the axes is associated with the cell doubling along the b- and c-axes, suggesting a charge-density-wave transition. Below T_3 the increase in the thermopower is strongest along the a-axis with a maximum of 186 μV/K at 35 K. The thermoelectric figure of merit becomes largest along the c-axis with the maximum value of 1.0×10^{-3}/K, being comparable with that of $CePd_3$.

PACS numbers: 75.30.Mb, 71.27.+a, 72.15.Jf

Formation of a narrow pseudogap in the so-called Kondo semiconductors such as CeNiSn, CeRhSb, $Ce_3Bi_4Pt_3$ and YbB_{12} has been the subject of intense research in the field of strongly correlated f-electron systems [1]. The origin of the gapping at the Fermi level in heavy-electron bands was attributed to anisotropic hybridization of $4f$ wave functions with a half-filled conduction band [2,3]. Recently, it has been proposed that the presence of a narrow pseudogap may satisfy the requisite for a high figure of merit for thermoelectric application [4]. In fact, these compounds exhibit rather large thermopower of 40-150 μV/K at temperatures below the gap formation temperature [5,6].

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

CeRhAs shares with the Kondo semimetals CeNiSn and CeRhSb the same orthorhombic ε-TiNiSi-type structure [7]. It was classified into a valence-fluctuating system because the magnetic susceptibility exhibits a broad maximum at 450 K. The maximum value of 1×10^{-3} emu/mol is several times smaller than those for CeNiSn and CeRhSb. This fact indicates the hybridization between the $4f$ electron and the conduction band in CeRhAs to be much stronger than in CeNiSn and CeRhSb. Furthermore, the semiconducting behavior of the electrical resistivity with activation energy of 80 K placed this compound in the class of Kondo semiconductor [7].

Recently, we have succeeded in growing single crystalline samples of CeRhAs by using Bridgman technique [8]. X-ray diffraction experiments have revealed three phase transitions. Below $T_1 = 370$ K, a superlattice reflection appears at q_1=(0 1/2 1/2). This means that the unit cell of the orthorhombic structure is doubled along the b- and c-axes. At $T_2 = 235$ K, much weaker reflections appear at q_2=(0 1/3 1/3) and q_3=(1/3 0 0) [9], the indexes of which are based on the ε-TiNiSi structure. The latter intensity suddenly increases below $T_3 = 165$ K, where the zig-zag chain along the a-axis shrinks and the resistivity along the three principal axes strongly increase. These observations suggested that the gap formation is intimately related to the structural transformations with lattice modulations [8].

We report here the anisotropic behavior in the electrical resistivity ρ, thermopower S and thermal conductivity κ of single crystal CeRhAs in relation to the magnetic and structural properties. It is found that the transport properties are highly anisotropic although the magnetic susceptibility χ is essentially isotropic. The methods of the crystal growth and of the transport and magnetic measurements are reported elsewhere [8].

The simultaneous occurrence of superlattice formation and distinct anomalies in $\chi(T)$ is demonstrated in Fig. 1. There are three anomalies in χ at T_1, T_2, and T_3, respectively, and an upswing below 30 K. On cooling from T_1 to 30 K, the decrease of χ in all the directions amounts to 30% of the value at the maximum. The abrupt decrease at T_1 is a clear indication of the onset of the gap formation in the electronic density of states. It is noteworthy that the gap formation is associated with the development of the superlattice reflection at q_1. The $\chi(T)$ has a terrace in the temperature range between T_2 and T_3, where this reflection stops growing. On cooling from T_3 to 30 K, the gradual decrease in $\chi(T)$ well corresponds to the re-increase of the intensity of the superlattice reflection. This good correspondence corroborates the idea that the cell doubling along both the b- and c-axes is responsible for the gapping in the electronic density of states. For the phase transition at T_1, the sudden decrease in the electronic density of states associated with the superlattice formation is characteristic of a charge-density-waves (CDW's) transition. Although three-dimensional structures are unfavorable to the

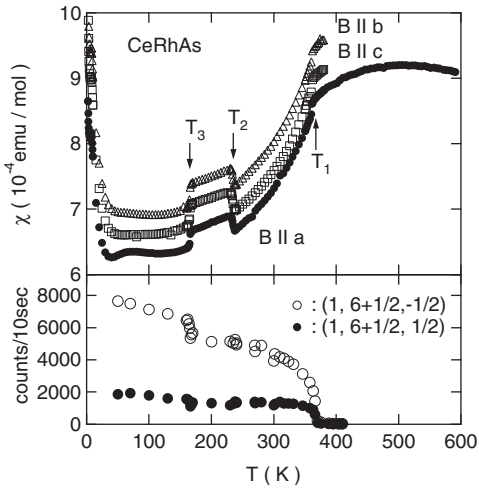

Fig. 1. Temperature dependence of magnetic susceptibility and superlattice reflections corresponding to cell doubling along the b- and c-axes of single crystal CeRhAs.

formation of CDW's, a few compounds such as CuV_2S_4 and $Er_5Ir_4Si_{10}$ have been reported to undergo CDW transitions [10, 11].

In Fig. 2 we show temperature variations of ρ, S, and κ of CeRhAs along the principal axes. Three step-like anomalies in $\rho(T)$ are observed at T_1, T_2, and T_3, respectively. An important observation is the strong anisotropy in $\rho(T)$; ρ_a is several times larger and exhibits different behavior than ρ_b and ρ_c. The relation, $\rho_a > \rho_b$ and ρ_c, is opposite to the case of CeNiSn, where ρ_a is smallest at low temperatures. At T_3, ρ_a jumps but ρ_c drops, which is caused by the vanishment of the lattice modulation characterized with $q_2 = (0\ 1/3\ 1/3)$ [8]. From the activated energy E_a in the range $110 < T < 150$ K, the gap values $E_g = 2E_a$ are estimated to be 282, 158, 156 K, respectively, along the a, b and c axes.

The three curves of $S(T)$ exhibit a two-peak structure in addition to the anomalies at T_1, T_2, and T_3. The two-peak structure resembles that of $S(T)$ for CeRhSb, where the higher- and lower-temperature peaks were ascribed to the incoherent Kondo effect and gap formation, respectively [5]. As T is decreased across T_3, $S(T)$ jumps and rises to a huge maximum of 186, 70, and 125 μV/K, respectively, along the a, b, and c axes at round 35–45 K. The steady increase of $S(T)$ for $50 < T < 100$ K can be expressed by using the equation, $S(T) = k_B(E_F - E_V)/|e|k_BT$, which is applicable for a non-degenerate p-type semiconductor with a top of the valence band at E_V below the Fermi level E_F [12]. A fit to the data of $S_a(T)$ gives a value of 130 K for $2(E_F - E_V)$, being comparable with the gap energy estimated from the activation energy of the resistivity.

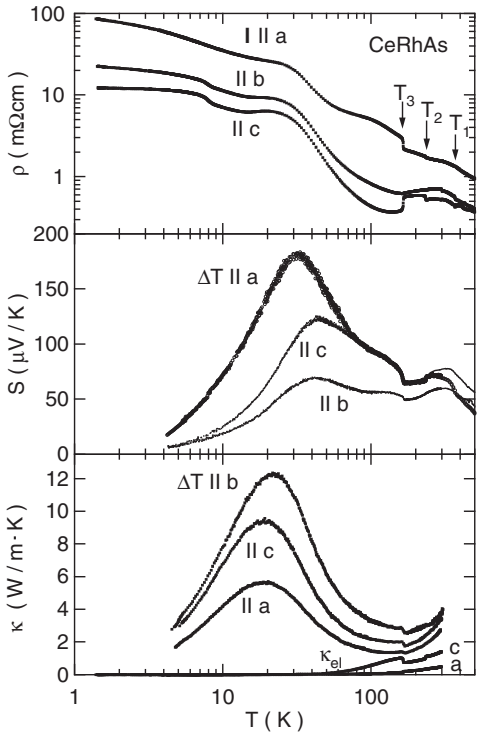

Fig. 2. Temperature dependence of the electrical resistivity, thermopower and thermal conductivity for single crystals of CeRhAs.

The thermal conductivity κ of intermetallic compounds is in general assumed as a sum of the electronic contribution $\kappa_{\rm el}$ and lattice contribution $\kappa_{\rm ph}$. We estimated $\kappa_{\rm el}$ using the Wiedemann–Franz law, $\kappa_{\rm el} = L_0 T/\rho$, where L_0 is the Sommerfeld value of 24.5 nWΩ/K^2. In the lowest frame of Fig. 2, we plot thus calculated $\kappa_{\rm el}(T)$, which is less than 40% of κ at 300 K and rapidly decreases on cooling. Although the size of jump in κ_c at T_3 is comparable with that in $\kappa_{{\rm el},c}$, the jump in κ_a contradicts the drop in $\kappa_{{\rm el},a}$. Therefore, both the jump in κ_a and the significant enhancement of $\kappa(T)$ along the three axes for $T < T_3$ are attributed to the enhancement of $\kappa_{\rm ph}$. It should be recalled that much weaker enhancement of $\kappa(T)$ was observed for CeNiSn and CeRhSb below the gap formation temperature, 15 and 20 K, respectively [13, 14]. The enhancement was attributed to the prolonged phonon lifetime due to the reduction of the electron-phonon scattering rate as a result of the decrease in the electron density of states. More pronounced enhancement of $\kappa(T)$ in CeRhAs reflects the much lower density of charge carriers in the gapped state. In fact, the carrier density in CeRhAs at 4 K is 1.8×10^{-4}/f.u. [8], being one order of magnitude smaller than that in CeNiSn and CeRhSb. Then, the phonon-mean-free-path in

the gapped state of CeRhAs would be determined by the phonon-phonon scattering, whereas that in CeNiSn and CeRhSb possessing residual charge carriers is still governed by the electron-phonon scattering. The calculation of $\kappa(T)$ by taking account of the effect of gap formation on the electron-phonon scattering rate will be given in a separate paper [15]. To explain the reason why $\kappa_a(T)$ is smaller than $\kappa_b(T)$ and $\kappa_c(T)$, we need to take account of the phonon scattering by stacking faults perpendicular to the a axis in the crystal used for the present study.

From the knowledge of $\rho(T)$, $S(T)$, and $\kappa(T)$, we have evaluated the thermoelectric figure of merit $Z = S^2/\rho\kappa$ along the three principal axes. The results of $Z(T)$ are presented in Fig. 3. The smallest value for $\rho(T)$ along the c-axis leads to the largest value of Z with a maximum of 1.0×10^{-3} K^{-1} at 120 K. This value is comparable with that of the typical valence fluctuating Ce compound $CePd_3$ [16,17]. If partial substitution of constituent elements in CeRhAs could reduce the resistivity with keeping the large thermopower intact, then the figure of merit would be further increased.

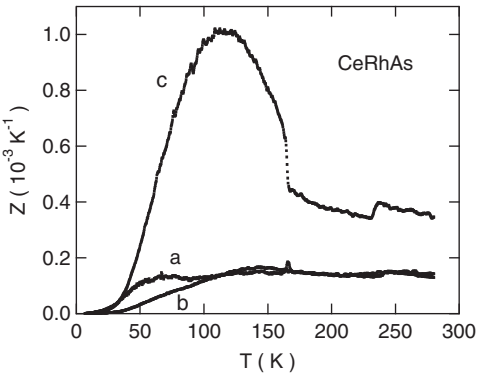

Fig. 3. Temperature dependence of thermoelectric figure of merit of CeRhAs.

In summary, we have found the sudden decrease in the magnetic susceptibility of CeRhAs along all the directions on cooling below $T_1 = 370$ K. This phase transition originates from the doubling of the unit cell along the b- and c-axes. Below $T_3 = 165$ K, the transport gap manifests itself in the strong increase in $\rho(T)$, $S(T)$ and $\kappa(T)$. The increase in $\rho(T)$ and $S(T)$ is most significant along the chain of Ce atoms. These observations indicate that the gap formation in CeRhAs is a phase transition driven by the instability of both the lattice and electronic structure. The sharp transition is essentially different from the crossover from a metallic state to a semimetallic state found in the Kondo semiconductors CeNiSn and CeRhSb. Further studies are necessary to elucidate the relation between the structural instability and the possible nesting of the Fermi surface of the hybridized band in CeRhAs.

This work was supported in part by a Grant-in Aid for Scientific Research (COE Research 13CE2002) of MEXT, Japan and a NEDO International Joint Research Grant.

REFERENCES

[1] T. Takabatake *et al.*, *J. Magn. Magn. Mater.* **177-181**, 277 (1998).
[2] G. Aeppli, Z. Fisk, *Comments Condens. Matter Phys.* **16**, 155 (1992).
[3] H. Ikeda, K. Miyake, *J. Phys. Soc. Jpn.* **65**, 1769 (1996).
[4] G.D. Mahan, J.O. Sofo, *Proc. Natl. Acad. Sci. USA* **93**, 7436 (1996).
[5] T. Takabatake *et al.*, *Phys. Rev.* **B50**, 623 (1994).
[6] T. Takabatake *et al.*, Proc. Inter. Conf. ICT2001, 8-11 June, Beijing, p. 266.
[7] S. Yoshii *et al.*, *Physica B* **223&224**, 421 (1996).
[8] T. Sasakawa *et al.*, *Phys. Rev.* **B**, in press.
[9] M. Nakajima *et al.*, in this proceedings.
[10] R.M. Fleming *et al.*, *Phys. Rev.* **B24**, 2850(1981).
[11] F. Galli *et al.*, *Phys. Rev. Lett.* **85**, 158 (2000).
[12] K. Seeger, *Semiconductor Physics*, Springer, Heiderberg 1989.
[13] Y. Isikawa *et al.*, *J. Phys. Soc. Jpn.* **60**, 2514 (1991).
[14] M. Sera *et al.*, *Phys. Rev.* **B55**, 6421 (1997).
[15] J. Kitagawa *et al.*, unpublished.
[16] R.J. Gambino, W.D. Grobman, A.M. Toxen, *Appl. Phys. Lett.* **22**, 506 (1973).
[17] K.L. Proctor *et al.*, *J. Phys. Chem. Solids* **60**, 663 (1999).