ELSEVIER

Journal of Alloys and Compounds 317–318 (2001) 302–305

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Magnetic properties and electronic structure of CeB_2C_2

Kazuya Suzuki[a,*], Masatoshi Kato[a], Ryuta Watanuki[a], Taichi Terashima[b]

[a]*Yokohama National University, Graduate School of Engineering, Hodogaya-ku, Yokohama 240-8501, Japan*
[b]*National Research Institute for Metals, Tsukuba 305-0047, Japan*

Abstract

The magnetic properties and the electronic structure of CeB_2C_2 were investigated by magnetic susceptibility, electrical transport and the de Haas van Alphen (dHvA) oscillation measurements. The magnetic susceptibility and heat capacity show successive magnetic transitions at 6.4 and 7.1 K. By an analysis of the crystal field splitting fit to the temperature dependence of the inverse susceptibility, the energy differences of the 4f states were estimated at E_1 ~80 K and E_2 ~300 K. A considerably large cyclotron mass of 9.3 m_0 was found by the temperature dependence of the dHvA oscillation with the frequency of 5470 T along the [100] direction, although the apparent Kondo effect was not found in the transport properties.

Keywords: Inorganic compounds; Magnetic properties; Electronic properties; de Haas van Alphen effect

1. Introduction

Rare earth metal–boron–carbon ternary systems are known to construct various types of low dimensional boron–carbon network structure [1–5]. Among these borocarbides, RB_2C_2 has a layered structure that consists of alternates of rare earth metal sheets and extended boron–carbon sheets. The boron–carbon sheet contains four- and eight-membered rings, and the rare earth atoms are situated in the interstices of the eight-membered rings of successive layers [2]. This structure is derived from the CaB_6-type structure by removing two B atoms at the apexes of the B_6 octahedron in the *c*-direction and by substituting two of four B atoms for C atoms. Recently, it has been revealed through neutron diffraction that the eight-membered ring is formed of the alternation of individual B and C atoms [6,7] as suggested by a band calculation [8]. The band calculation indicates the presence of π-electronic bands in the BC network as in graphite. Survey of the magnetic and transport properties of RB_2C_2 was made [9–11] on polycrystalline samples. In order to elucidate the magnetic properties and electronic structure, we prepared single crystals of CeB_2C_2 and measured the magnetization, heat capacity and electrical resistivity, and the de Haas van Alphen effect.

2. Experimental

Single crystals of CeB_2C_2 were prepared by the Czochralski method using a tetra-arc furnace. Quality of the crystals was examined by X-ray Laue-photographs using imaging plate. The temperature dependence of the magnetic susceptibility was measured by a SQUID magnetometer between 1.8 and 300 K. The magnetic heat capacity was measured by an AC method between 4 to 15 K. The in-plane electrical resistivity was measured for the single crystals between 1.3 and 300 K and the Hall coefficient was measured at 1 T below 20 K. To investigate the electronic state, the de Haas van Alphen effect was measured for CeB_2C_2 by a modulation method, where the magnetic field was applied up to 17.8 T at the temperature as low as 30 mK.

3. Results and discussion

Fig. 1 shows the magnetic susceptibility of the single crystal of CeB_2C_2 below 50 K with the magnetic field *H* parallel and perpendicular to the *c*-axis. The susceptibility shows strong anisotropy with the moments within the layer, suggesting a strong crystal field effect. The susceptibility shows a sharp peak at 7.1 K indicating the occurrence of an antiferromagnetic transition. Fig. 2 shows the magnetization curve of CeB_2C_2 taken at 2 K up to 5 T. The magnetization curve with H // [110] shows a

*Corresponding author.

0925-8388/01/$ – see front matter
PII: S0925-8388(00)01360-8

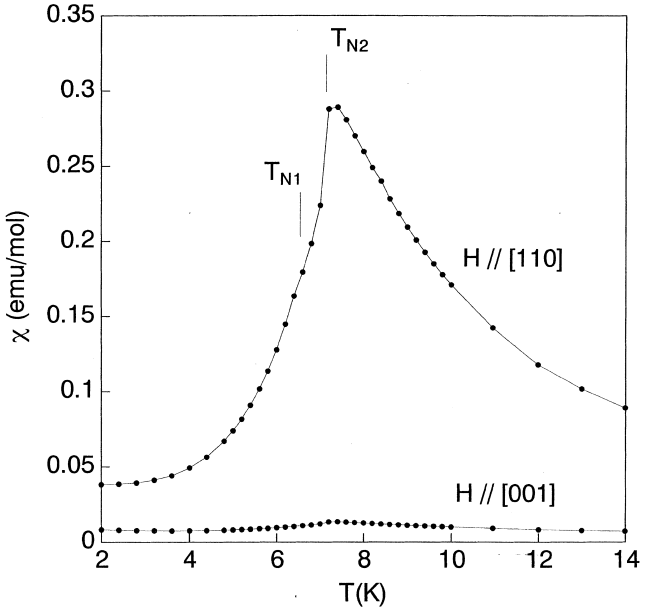

Fig. 1. Temperature dependence of the magnetic susceptibility of CeB_2C_2 measured at $H=0.1$ T.

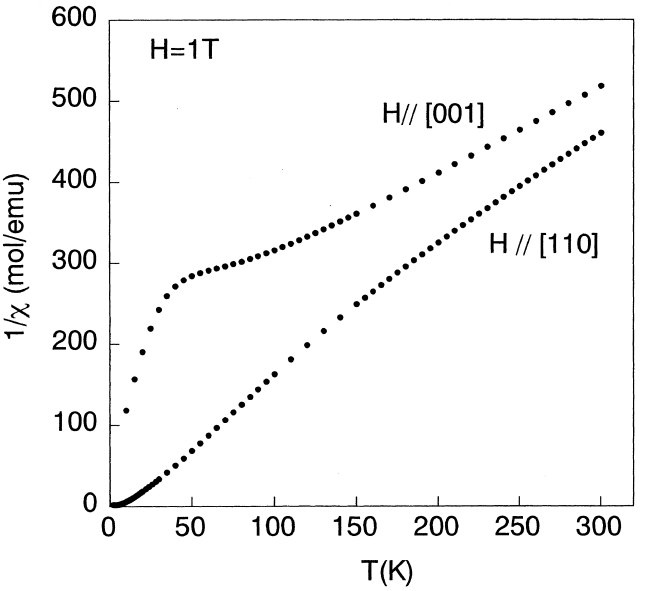

Fig. 3. Temperature dependence of the inverse susceptibility of CeB_2C_2 measured at $H=1.0$ T.

metamagnetic transition at the critical magnetic field of 0.9 T, and nearly saturates to 0.95 μ_B/Ce. On the other hand, the magnetization with H // c-axis is only 0.06 μ_B/Ce at $H=5$ T. It is noted that the magnetic behavior is nearly the same when the direction of the applying magnetic field is rotated within the layer. Fig. 3 shows the inverse magnetic susceptibility of CeB_2C_2. By applying the Curie–Weiss law above 200 K, the effective magnetic moments were estimated at 2.44 μ_B for H // [110] and 2.74 μ_B for H // c-axis, respectively. These values are significantly deviated from that of free Ce^{3+} ion, 2.54 μ_B. By an analysis of the crystal field splitting fit to the temperature dependence of the inverse susceptibility, we roughly obtained the energy differences between the ground state and the first exited state E_1 ~80 K and the second exited state E_2 ~300 K, respectively. The 4f states are similar to the Γ_7 and Γ_8 states for the Ce 4f states in the cubic symmetry, where the Γ_8 ground state split by a tetragonal distortion in CeB_2C_2 with the ground state $J_z=\pm 1/2$. However, the average susceptibility at room temperature is much smaller than that expected by this fitting it is necessary to consider the presence of the Kondo effect. The heat capacity measured by an AC method is shown in Fig. 4. The heat capacity shows a λ-like anomaly at 7.1 K and a small hump at 6.4 K, as reported previously [11]. By applying magnetic field, both anomalies in the heat capacity shifts to lower temperature side. This fact suggests that these anomalies are successive magnetic transitions from one to another antiferromagnetic state.

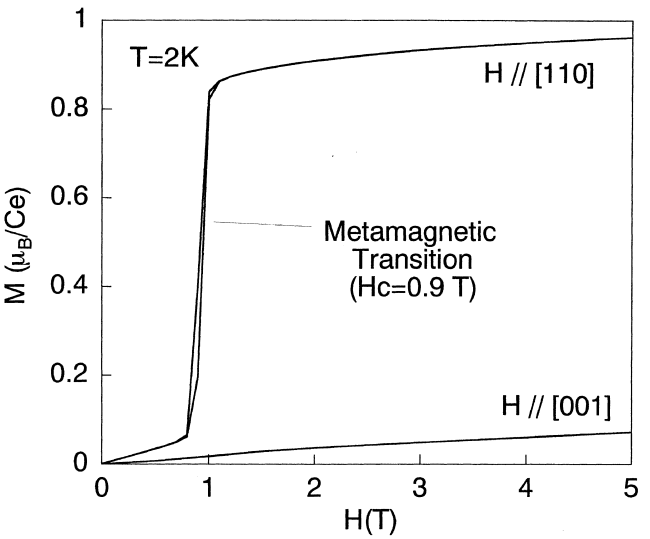

Fig. 2. The magnetization curves of CeB_2C_2.

Fig. 5 shows the temperature dependence of the resistivity in the [110] direction of the single crystals of LaB_2C_2 and CeB_2C_2. The room temperature resistivity of CeB_2C_2 is 48 μΩcm and the residual resistivity ratio of ~25. The temperature dependence of the resistivity shows a broad hump around 100 K. After subtracting the resistivity of LaB_2C_2, the remaining resistivity can be considered to originate from the scattering by localized magnetic moments. The enhanced resistivity can be well fitted to the spin-disorder resistivity ρ_{sd} by assuming the crystal field splitting obtained by the analysis for the susceptibility data, as the same treatment of the calculation of ρ_{sd} [12]. It

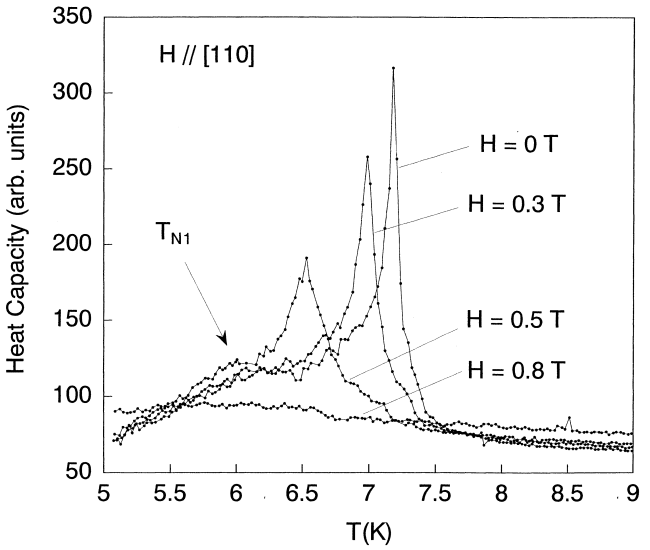

Fig. 4. Heat capacity under magnetic field of CeB_2C_2 applying magnetic field parallel to the [110] direction. A sharp peak at 7.1 K at zero field rapidly shifts to lower temperature by applying magnetic field, almost vanishing at $H=0.8$ T due to metamagnetic transition. The shoulder peak at 6.4 K at zero field (denoted as T_{N1}) slightly shifts to lower temperature with increasing magnetic field.

should be noted that the $-\ln T$ dependence. of the resistivity that is typical for the Kondo compounds was not found in the resistivity of CeB_2C_2 in the whole temperature measured.

The quantum oscillation of the magnetization of LaB_2C_2 and CeB_2C_2 at low temperature and high magnetic field was measured by a modulation method. The observed peak positions of the oscillation are proportional to the inverse magnetic field H^{-1}, indicating the oscillation due to the dHvA effect. Fig. 6 shows the angle dependence of the oscillation frequency of the dHvA signal between [110] and [100] direction. More than ten branches of the oscillation were observed in this angle region. A strong oscillation with the frequency of ~3000 T (branch β) was observed in the [110] direction, and with increasing the angle from this direction, this oscillation splits to form two branches β_1, and β_2. The branch, $\beta_1$has a maximum in the [100] direction with the frequency of 5470 T, while the branch β_2 has a minimum with the frequency of 2510 T. Among these many branches, α, β and γ indicated in Fig. 6 are considered to originate from the electron Fermi surfaces with the comparison of a preliminary band calculation [13].

The cyclotron masses for the branches α, β_1, β_2 and γ with H // [100] were estimated by the temperature dependence of the oscillation amplitude. The cyclotron mass of the branch β_2 with the frequency of 5470 T reaches 9.3 m_0, where m_0 is the mass of free electron. The enhancement of the cyclotron mass in CeB_2C_2 is undoubtly due to the Kondo effect, similar to those of typical Ce intermetallic compounds that exhibit magnetic transition such as $CeIn_3$ or $CeAl_3$. These compounds have rather low Kondo temperatures and the RKKY interaction overcome the Kondo effect to form a magnetic transition at low temperatures. As in Fig. 5, the $-\ln T$ dependence of the resistivity was not observed for CeB_2C_2 whole temperature measured, it is considered that the Kondo temperature

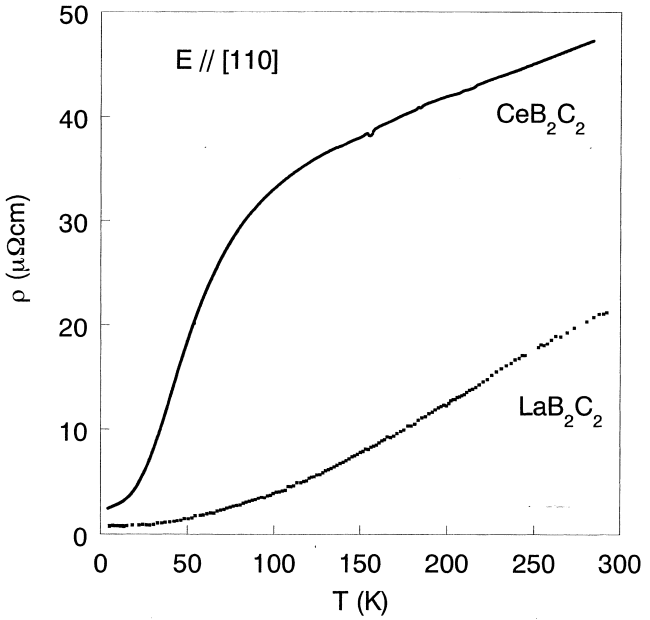

Fig. 5. Temperature dependence of the resistivity of LaB_2C_2 and CeB_2C_2. Note that a logarithmic increase of the resistivity with temperature does not appear.

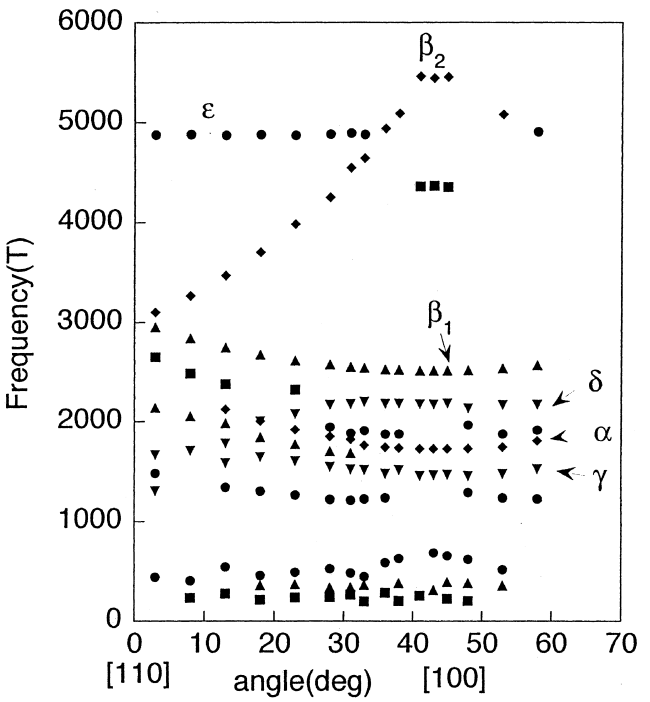

Fig. 6. Angle dependence of the oscillation frequency of the dHvA signal of CeB_2C_2. Branches α, β_1, β_2 and γ originates from corresponding electron Fermi surfaces.

of CeB_2C_2 is even lower than these intermetallics. The present results of the dHvA measurements are preliminary. It is necessary to make clear the difference of the angle dependence of the oscillations in the La and Ce compounds and to make more quantitative analysis and comparison between the calculated and observed Fermi surfaces.

Acknowledgements

This work is supported partly by the Grant-in-Aid for Scientific Research No.11124219 from the Ministry of Education, Science, Sports and Culture, Japan.

References

[1] P.K. Smith, P.W. Gilles, J. Inorg. Nucl. Chem. 29 (1967) 375.
[2] J. Bauer, O. Bars, Acta Crystallogr. B 36 (1980) 1540.
[3] J. Bauer, D. Ansel, F. Bonhomme, Ph. Gosselin, J. Less-Common Met. 87 (1982) 45.
[4] J. Bauer, H. Nowotony, Monatsh. Chem. 102 (1971) 1129.
[5] F. Wiitkar, J.-F. Halet, J.-Y. Sallard, P. Rogl, J. Bauer, Inorg. Chem. 104 (1993) 377.
[6] T. Onimaru, H. Onodera, K. Ohoyama, H. Yamauchi, Y. Yamaguchi, J. Phys. Soc. Jpn. 68 (1999) 2287.
[7] J. van Duijn, K. Suzuki, J.P. Attfield, Angew. Chem. 112 (2000) 373.
[8] J.K. Burdett, E. Canadell, T. Hughbanks, J. Am. Chem. Soc. 108 (1986) 3971.
[9] T. Sakai, G. Adachi, J. Shiokawa, Solid State Commun. 40 (1981) 445.
[10] T. Sakai, G. Adachi, J. Shiokawa, J. Less-Common Met. 84 (1982) 107.
[11] K. Hirota, M. Ishikawa, Physica B. 186–188 (1983) 478.
[12] V.U.S. Rao, W.E. Wallace, Phys. Rev. B 2 (1970) 4613.
[13] M. Shirai, private communication.