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

[a] Graduate School of Engineering, Yokohama National University, Yokohama, 240-8501, Japan

[b] National Research Institute for Metals, Tsukuba, 305-0047, Japan

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Metal Borocarbides as Novel π-Electronic Systems

KAZUYA SUZUKI[a], MASATOSHI KATO[a], RYUTA WATANUKI[a] and TAICHI TERASHIMA[b]

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

Electronic structures and Fermi surfaces of RB_2C_2 (R=La, Ce) were investigated by transport and the de Haas van Alphen (dHvA) oscillation measurements. The transport properties indicate the presence of multi-carriers in RB_2C_2, as suggested by recent band calculation. The angle dependence of the cross sectional area of the Fermi surfaces observed by dHvA oscillation suggests the strong hybridization between the π-electron in the BC layer and the metal 5*d* electron resulting in the presence of three dimensional Fermi surfaces.

Keywords: π-electronic system; borocarbides; rare earth metal; electronic properties; de Haas van Alphen effect

INTRODUCTION

Rare earth metal-boron-carbon ternary systems are known to have various types of low dimensional boron-carbon network structure[1-5]. Among these borocarbides, RB_2C_2 has a layered structure that consists of the 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]. Recently, it has been revealed by us through neutron diffraction that the eight-membered ring is formed of the alternation of individual B and C atoms[6] as suggested by a band calculation[7]. The band calculation indicates the presence of π-electronic bands in the BC network as in graphite. In spite of the simple crystal structure of RB_2C_2 only a few physical property measurements have been made so far on

this type of compounds[8,9]. In order to elucidate the electronic structure of the RB_2C_2, we prepared single crystals of LaB_2C_2 and CeB_2C_2, and measured the transport properties and the de Haas van Alphen effect.

EXPERIMENTAL

Single crystals of LaB_2C_2 and CeB_2C_2 were prepared by the Czochralski method using a tetra-arc furnace. The quality of the crystals was examined by X-ray Laue photographs using imaging plate. The temperature dependence of the resistivity and thermoelectric power was measured for the single crystals between 1.3 K and 300 K. 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 LaB_2C_2 by canti-lever and modulation methods, where the magnetic field was applied up to 17.8 T at the temperature as low as 30 mK.

RESULTS AND DISCUSSION

Figure 1 is 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 LaB_2C_2 is 20 μΩcm and the residual resistivity ratio (RRR=$\rho(rt)/\rho(4.2K)$) reaches ~25. The temperature dependence of the resistivity follows a power law T^2 in the whole temperature range. The T^2 dependence of the resistivity is well known in graphite and its intercalation compounds and that originates mainly due to the significant low-dimensional acoustic phonon scattering in electron-phonon scattering process. In RB_2C_2, the two-dimensional acoustic phonon can be exited in the B-C network. The thermoelectric power of LaB_2C_2 is positive at

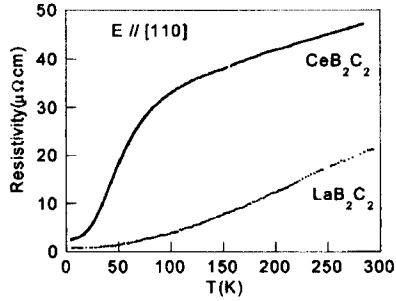

FIGURE 1 Temperature dependence of the in-plane electrical resistivity of LaB_2C_2 and CeB_2C_2

room temperature, and the temperature dependence shows a convex curvature as shown in Fig. 2. The thermoelectric power of metallic system is described by electron diffusion in the Boltzmann equation as,

$$S = \frac{\pi^2 k_B^2}{3e}\left[\frac{\partial \ln \sigma}{\partial \varepsilon}\right] = \frac{\pi^2 k_B^2}{3e}\left[\frac{D(\varepsilon)}{n} + \frac{\partial \ln \mu}{\partial \varepsilon}\right] \quad (1)$$

Where k_B is the Boltzmann constant, e the charge of electron, σ the electrical conductivity, $D(\varepsilon)$ the density of states of the carrier at energy ε, n the carrier density and μ the carrier mobility. When the carrier scattering is dominated by acoustic phonons as in usual metals, the thermoelectric power shows linear temperature dependence. Deviation from the linear temperature dependence of S as seen in Fig. 2 indicates the coexistence of both hole and electron carriers with significantly different effective masses. The Hall coefficient also has a positive value of R_H = 4.1x10^{-4} cm^3/C, corresponding to the carrier density of 1.5x10^{22}/cm^3 by assuming the free electron model. These results indicate the dominant conduction carrier is hole-like, and the density is 1.0 holes per formula unit.

The transport properties of CeB_2C_2 are significantly different from those of LaB_2C_2 because of the presence of magnetic Ce atoms. CeB_2C_2 has a room temperature resistivity of 48 μΩcm and RRR value of ~25. The temperature dependence of the resistivity shows a broad hump around 120 K. After subtracting the resistivity of LaB_2C_2, the remaining resistivity can be considered to originate from the scattering by localized magnetic moments. As reported by Sakai *et al.*[8], the enhanced resistivity is due to the resonating scattering of the carriers by localized 4*f* electron associating with the momentum transfer from

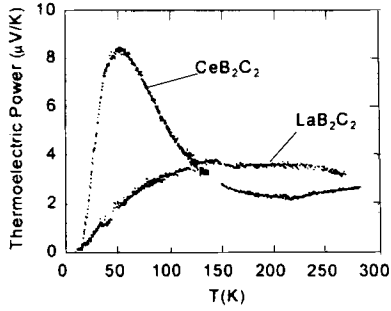

FIGURE 2 Temperature dependence of the thermoelectric power of LaB_2C_2 and CeB_2C_2

the ground state to the exited states of the Ce 4*f* magnetic states[11]. The resistivity associated with the resonating scattering nearly saturates at around the temperature that corresponds to the energy difference *E* of the 4*f* states of Ce. The thermoelectric power of CeB_2C_2 is nearly the same to that of LaB_2C_2 at room temperature, while it steeply increases at lower temperatures to have a peak at around T_{max} = 50 K as shown in Fig. 2. In the presence of the resonating scattering, the second term in the parenthesis in Eq. (1) has significant contribution to *S* since the scattering reduces the carrier mobility. The obtained result is close to the temperature where $d\rho/dT$ has a maximum as one can imagine from Fig. 2.

The magnetization of LaB_2C_2 was measured by the dHvA effect. The dHvA signal of LaB_2C_2 measured at 50 mK is shown in Fig. 3(a). This figure indicates two apparent oscillations, a high-frequency oscillation superposed onto a lower-frequency one. Fast Fourier transformation spectrum (Fig.3(b)) gives frequencies of these two oscillations, F_α = 700 T and F_β = 4574 T, respectively.

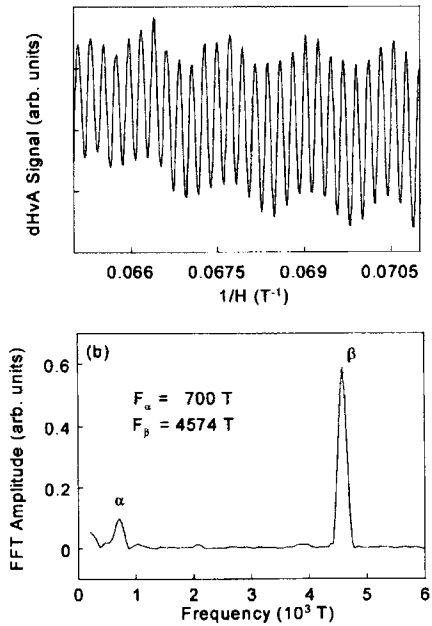

FIGURE 3 (a) de Haas van Alphen signal vs. inverse magnetic field applied in the direction $\theta = 3°$ measured at 50 mK. (b) The FFT spectrum of the oscillation.

These oscillations depend on the direction of applied magnetic field. The angle dependence of the frequency of the oscillations (orbit α and β) has minima at θ = 0° (H // [110]), and with increasing the polar angle they disappear at θ ~50°. A new oscillation (orbit γ) appears at θ > 70°, and the frequency (>4000 T) increases with the angle. The oscillation disappears in a very narrow angle region close to θ = 90° (H // [001]). From the minima of F_α and F_β, we obtain the cross sectional area of the Fermi surfaces of LaB_2C_2 of 6.80×10^{14} cm^{-2} and 4.36×10^{15} cm^{-2} corresponding to 3.6 % and 23 % of the sectional area of the first Briulloin zone normal to the [100] direction.

If LaB_2C_2 has a two-dimensional cylindrical Fermi surface in the π–electronic band expected in the BC network, the oscillation frequency has a minimum at θ = 90°, and the angle dependence of the frequency obeys a $1/\cos\theta$ low. In contrast, the obtained result suggests a maximum of F_γ in this direction. This means that the Fermi surfaces in LaB_2C_2 are three-dimensional and the contribution from the R atom is significant for the electronic structure, namely, direct metal-metal bonding and strong hybridization between 5*d* electron in metals and the π-electrons exist.

A structural study of the B-C network performed by single crystal X-ray diffraction for LaB_2C_2[12] suggests that the eight-membered ring consists of the alternates of the pairs of B-B and C-C, while the tight binding band calculation[7] for the $(B_2C_2)^{2-}$ system indicates that the electronic state is much stable for the eight-membered ring with the alternates of individual B and C atoms. Recent our neutron diffraction study[6] revealed that RB_2C_2 crystallizes in a tetragonal form *P*4/*mbm* with the lattice parameters of a = 5.40 Å and c = 3.86 Å. The eight-membered ring consists of the alternate of the B and C atoms and the four-membered ring is distorted from square that was assumed for the tight binding band calculation. The band calculation shows that the two-dimensional BC network becomes insulating in the case of the ionic charge $(B_2C_2)^{2-}$, which is iso-electronic to graphite. It is known that R ions tend to have a trivalent state R^{3+}, thus, as in graphite intercalation compounds, the electron transfer from R atoms can create conduction carriers on the π-electronic band of the BC layer. The systematic band calculations for the R-B-C system[11] including the contribution of R atoms suggest that the contribution of the metal atom R is significant. Very recently, a band calculation by the Full Linearized Augmented Plane Wave (FLAPW) method was made by Shirai[12] using the lattice

parameters and atomic positions determined by neutron diffraction. The band calculation suggests that there are two energy dispersion curves at which the Fermi energy intersects. These two dispersion curves are similar to the conduction π-bands of the BC network[7], however, the bands shows the strong dispersion along the c^* direction. a modulation method to detect magnetic oscillation. The observed peak positions of the oscillation are proportional to the inverse magnetic field H^{-1}, indicating the oscillation due to

The calculation indicates the conduction carriers of about 0.3 holes and 0.3 electrons in the lower and higher conduction bands, respectively. On the other hand, the experimental results suggest the presence of major hole carriers and minor electron carriers. Since the carrier density can be calculated in the two-carrier model by $1/n_{obs} = 1/n_{hole} - 1/n_{electron}$ using $n_{obs} = 1.0$ holes/formula, the hole carrier density is considered to be about 40% larger than electron carriers in case of $n_{electron} \sim 0.3$.

The electronic structure of RB_2C_2 is not formed of simple two-dimensional π-electronic band. Since detailed experiments on dHvA effect and band calculation are now in progress, we can show the contribution of the π-electron on the conduction more clearly in near future.

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