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Electrical Properties of Single-Crystalline $CaAl_2Si_2$

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Electrical resistivity and Hall coefficient measurements of single-crystalline $CaAl_2Si_2$ revealed that $CaAl_2Si_2$ is a metal in which both electrons and holes contribute to the transport properties; its dominant carriers are holes at temperature below 150 K but electrons above that temperature.

Binary Ca−Si and ternary Ca−Al−Si systems have compounds with characteristic layered structures, which can be related to a crystalline form of elementary Si, the diamond-type structure. In the diamond-type structure, chair-type corrugated hexagonal layers stack along the [111] direction, as shown in Figure 1a.[1] The binary Ca−Si system has six kinds of compounds.[2] One of the compounds, $CaSi_2$, has the $CaSi_2$-type structure (space group: $R\bar{3}m$ (No. 166), $a = 3.86$ Å, $c = 30.6$ Å, $Z = 6$), in which hexagonal Ca layers stack alternatively with chair-type corrugated hexagonal Si layers along the [001] direction,[3] as shown in Figure 1b. This structure can be made up by intercalating Ca layers to the diamond-type Si and changing its stacking sequence. When some Si atoms are replaced with Al atoms, the corrugated hexagonal layers transform into flat honeycomb layers. Figure 1c shows a crystalline form of $Ca(Al_x,Si_{1-x})_2$ ($0.225 \le x \le 0.675$), the AlB_2-type structure (space group: $P6/mmm$ (No. 191), $a = 4.1905(5)$ Å, $c = 4.3992(8)$ Å for $x = 0.5$, $Z = 1$), in which Ca hexagonal layers stack alternatively with Al−Si honeycomb layers.[4,5] The ternary Ca−Al−Si system has another compound with a layered structure, $CaAl_2Si_2$. $CaAl_2Si_2$ has the La_2O_3-type structure (space group: $P\bar{3}m1$ (No. 164), $a = 4.130$ Å, $c = 7.145$ Å, $Z = 1$), where Si and Al atoms are arranged in the chemically ordered double-corrugated hexagonal layers and Ca atoms are intercalated between them,[4] as shown in Figure 1d. For the characteristic forms of the Al−Si layers, the bonding nature and stability of the layers in $CaAl_2Si_2$ and those in the related compounds have been examined by calculations.[6−9] The physical properties of these compounds have been studied experimentally. $CaSi_2$ is a semimetal.[10−13] Recently, $Ca(Al_{0.5}, Si_{0.5})_2$, $Ca(Al_x, Si_{1-x})_2$ for $x = 0.5$, which is isostructural to a superconducting material MgB_2 with a transition temperature for superconductivity T_C of 39 K,[14] was reported to be a superconducting material with a T_C of 7.8 K.[5,15] On the other hand, the physical properties of $CaAl_2Si_2$ have not been studied.

In this paper, we report the electrical resistivity and Hall coefficient of single-crystalline $CaAl_2Si_2$ at temperatures ranging from 2 to 300 K. The transport measurements revealed that $CaAl_2Si_2$ is a metal whose dominant carriers are holes at temperatures below 150 K while they are electrons above 150 K.

Single crystals were grown by the floating (FZ) method. The details of the FZ furnace are described elsewhere.[16] The feed rods were prepared by the Ar-arc melting of a mixture of $CaSi_2$ and Al. Crystal growth was carried out at a growth rate of 10 mm/h in a flowing Ar atmosphere with a flow rate of 2000 cm^3/min. During the growth, the seed and feed rods were rotated at 13 rpm in opposite directions to reduce the asymmetry of the temperature distribution and induce forced convection in the molten zone. The grown material had a cylindrical shape with a diameter of about 10 mm and a length of about 60 mm. The surface has a metallic luster. Observation by scanning electron microscope showed that the grown crystal was a single phase.

Chemical compositions determined by inductively coupled plasma mass-spectroscopy are 19.7 at. % Ca, 39.3 at. % Al,

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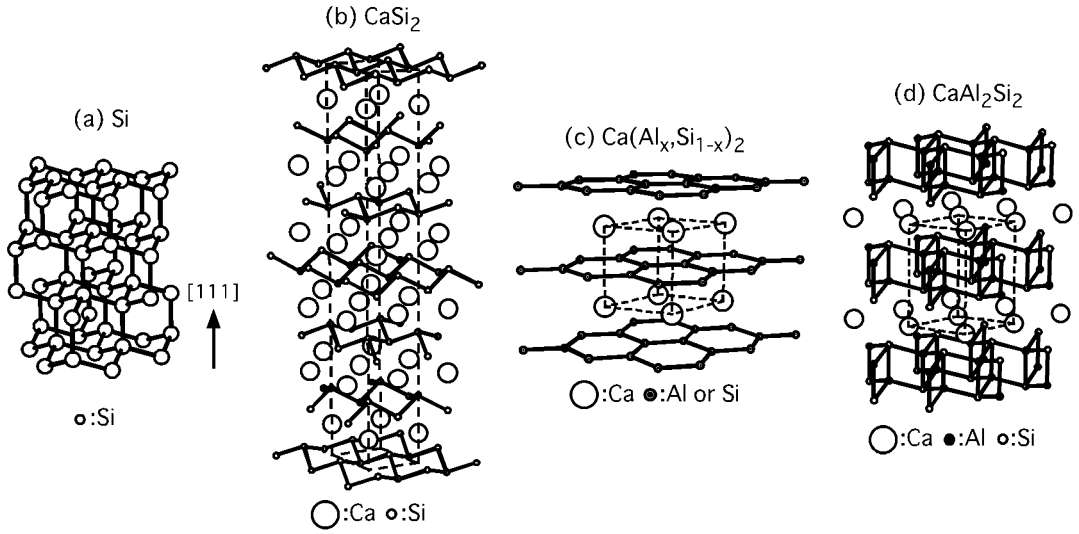

Figure 1. Crystal structures of (a) Si, (b) $CaSi_2$, (c) $Ca(Al_x,Si_{1-x})_2$ ($0.225 \leq x \leq 0.675$), and (d) $CaAl_2Si_2$.

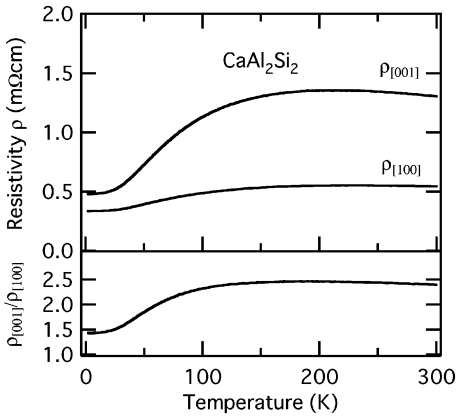

Figure 2. Electrical resistivity along the [100] direction ($\rho_{[100]}$) and that along the [001] direction ($\rho_{[001]}$) as a function of temperature. The lower panel shows the anisotropy ratio of the electrical resistivity $\rho_{[001]}/\rho_{[100]}$ as a function of temperature.

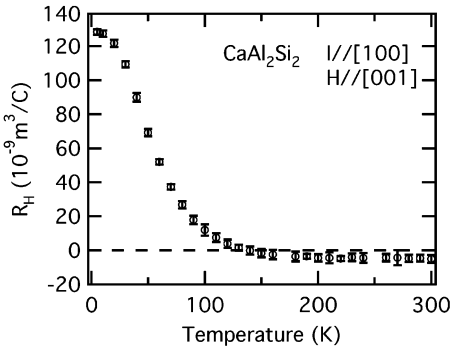

Figure 3. Hall coefficient R_H as a function of temperature. The current direction is the [100] direction, and the direction of the applied magnetic field is the [001] direction.

and 41.0 at. % Si, which is consistent with an ideal chemical compositions of $CaAl_2Si_2$. An analysis of the powder X-ray diffraction pattern showed that $CaAl_2Si_2$ has a hexagonal unit cell with lattice constants of $a = 4.1410(3)$ Å and $c = 7.1329(7)$ Å, which is consistent with the previous report ($a = 4.130(10)$ Å and $c = 7.145(15)$ Å).[4] X-ray back Laue photographs of the grown crystal indicated that the grown crystal is a good-quality single crystal.

The top part of Figure 2 shows the electrical resistivity of $CaAl_2Si_2$ along the [100] direction ($\rho_{[100]}$) and that along the [001] direction ($\rho_{[001]}$) as a function of the temperature. Electrical resistivity was measured by means of the standard four-probe method. The resistivity of $CaAl_2Si_2$, which has a finite value at 2 K, increases with increasing temperature, and saturates around 200 K. The resistivity $\rho_{[001]}$ is larger than $\rho_{[100]}$ throughout the temperature range. The bottom part of Figure 2 shows the anisotropy ratio of the resistivity $\rho_{[001]}/\rho_{[100]}$, which increases from 1.4 to 2.5 with increasing temperature.

Figure 3 shows the Hall coefficient R_H as a function of the temperature. The Hall coefficient was measured by means of the standard four-probe method. The current direction is the [100] direction, and the direction of applied magnetic field is the [001] direction. The Hall coefficient R_H was evaluated from the antisymmetric part of transverse resistivity ρ_{xy} measured at a magnetic field of -1 T and $+1$ T, $R_H = [\rho_{xy}(+1T) - \rho_{xy}(-1T)]/2$, to exclude the longitudinal contribution due to a possible misalignment of the Hall contacts. The value of R_H, which is $+130 \times 10^{-9}$ m^3/C at 5 K, decreases with increasing temperature and reaches -5.1×10^{-9} m^3/C at 300 K through zero at about 150 K. The sign reversal in R_H is observed also in $CaSi_2$, a semimetal in which both electrons and holes contribute to the transport properties, although the sign of R_H in $CaSi_2$ changes from negative to positive with increasing temperature.[13] In the framework of a two-band model in which the electrons and holes contribute to the transport properties, the electrical conductivity σ (the inverse of electrical resistivity ρ) and R_H can be written as follows:

$$\frac{1}{\rho} = \sigma = n_e e\mu_e + n_h e\mu_h \tag{1}$$

$$R_H = \frac{n_h\mu_h^2 - n_e\mu_e^2}{e(n_h\mu_h + n_e\mu_e)^2} = \frac{n_h - n_e b^2}{e(n_h + n_e b)^2} \tag{2}$$

$$b = \mu_e/\mu_h \tag{3}$$

Table 1. Tranport Parameters of $CaSi_2$, $Ca(Al_{0.5},Si_{0.5})_2$, and $CaAl_2Si_2$

	$\rho_{4.2K}$ ($\mu\Omega$ cm)	ρ_{273K} ($\mu\Omega$ cm)	$\rho_{273K}/\rho_{4.2K}$	$\rho_{\|c}/\rho_{\|ab}$ at 273 K	R_H (10^{-10} m^3/C)	type of dominant carriers	remarks
$CaSi_2$	10.1[a]	33.2[a]	3.29[a]	1.4[b]	−13 at 10 K[a] +3 at 280 K[a]	electrons[a] holes[a]	semimetal
[100][c]	19.5[b]	63[b]	3.2[b]				
[001][c]	25.5[b]	56[b]	2.2[b]				
$Ca(Al_{0.5},Si_{0.5})_2$				12[d]	−7.3 at 290 K[e]	electrons[e]	superconductor with a T_C of 7.8 K
$\|ab$	17[e]	78.5[e]	4.62[e]				
$\|c$	539[d]	949[d]	1.76[d]				
$CaAl_2Si_2$				2.4	+1300 at 5 K −51 at 300 K	holes electrons	
[100]	335	548	1.64				
[001]	479	1327	2.77				

[a] Reference 13. [b] Reference 12. [c] The rhombohedral lattice is used in ref 12. The lattice is transformed into the hexagonal lattice here. [d] Reference 18. [e] Reference 15.

where e, n_i, and μ_i (i = e or h) are an elemental charge, the carrier density of electrons or holes, and the mobility of electrons or holes, respectively.[17] The positive value of R_H means that $n_h\mu_h^2$ is larger than $n_e\mu_e^2$, suggesting that the dominant carriers are holes. On the other hand, the negative value of R_H means that $n_e\mu_e^2$ is larger than $n_h\mu_h^2$, suggesting that dominant carriers are electrons. Therefore, the observed temperature dependence of R_H in $CaAl_2Si_2$ suggests that both electrons and holes contribute to the transport properties, and that the dominant carriers are holes at the temperatures below 150 K but electrons at the temperatures above 150 K.

The transport parameters of $CaSi_2$, $Ca(Al_{0.5}, Si_{0.5})_2$, and $CaAl_2Si_2$ are listed in Table 1.[12,13,15,18] Both ρ and R_H of $CaAl_2Si_2$ are one order larger than those of $CaSi_2$ and $Ca(Al_{0.5}, Si_{0.5})_2$, suggesting that the number of carriers in $CaAl_2Si_2$ is less than those in $CaSi_2$ and $Ca(Al_{0.5}, Si_{0.5})_2$. The anisotropy ratio of $CaAl_2Si_2$ is the same order as that of $CaSi_2$. $CaAl_2Si_2$ is a metal in which both electrons and holes contribute to the transport properties, as is $CaSi_2$.

The electrical resistivity in most elemental metals can be described by Bloch−Grüneisen theory or Wilson's modification of it:

$$\rho = \rho_0 + A(T/\theta_D)^n \int_0^{\theta_D/T} \frac{z^n\,dz}{(e^z - 1)(1 - e^{-z})}, \qquad (4)$$

where ρ_0, θ_D, and A are the residual resistivity, the Debye temperature, and a constant, respectively. The constant n is equal to 3 when the "s−d electron−phonon" scattering dominates the resistivity, and the constant n is equal to 5 when the "s−s electron−phonon" scattering dominates.[17,19−21] At temperatures from 2 to 40 K, the resistivity of $CaAl_2Si_2$ is fitted well with eq 4 with $n = 3$. Above that temperature, the resistivity further increases with temperature, but it saturates around 200 K, which is in contrast to temperature dependence described by eq 4, according to which the resistivity just keeps increasing with temperature. In these theories, the main effect of the temperature is on the relaxation time, which in turn affects mobility; however, it has no effect on the number of carriers. The temperature dependence of R_H in $CaAl_2Si_2$ shows that the sign of the numarator of eq 2 ($n_h - n_e b^2$) changes from negative to positive with increasing temperature, which suggests the possibility that n_e and/or b^2 become larger with increasing temperature. When n_i changes with the temperature, the temperature dependence of ρ does not obey eq 4. This may be the reason that the temperature dependence of ρ in $CaAl_2Si_2$ is different from that in typical elemental metals.

The band structure of $CaAl_2Si_2$ has not been calculated yet although that of ionized double-hexagonal corrugated Al−Si layers, the $Al_2Si_2^{2-}$ layers, has been calculated.[7] The band calculations of $CaSi_2$ and $Ca(Al_{0.5}, Si_{0.5})_2$ showed that Ca d states locate around E_F and play an important role for transport properties.[10,22] Also in $CaAl_2Si_2$, the states originating from Ca are expected to locate around E_F and to affect the transport properties, as do those of $CaSi_2$ and $Ca(Al_{0.5}, Si_{0.5})_2$.

In summary, the electrical resistivity and Hall coefficient measurements of single-crystalline $CaAl_2Si_2$ revealed that $CaAl_2Si_2$ is a metal in which both electrons and holes contribute to the transport properties; the dominant carriers are holes at temperature below 150 K but electrons above that temperature.

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