Thermal transport properties in the normal state of CaAl$_{x}$Si$_{2-x}$ superconductors

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A R T I C L E   I N F O

Abstract

Normal state electrical and thermal properties, including electrical resistivity ($\rho$), Seebeck coefficient ($S$), and thermal conductivity ($\kappa$) of the CaAl$_{0.9-1.2}$Si$_{2} \text{-} x$ system were investigated. It is found that the electrical resistivity and Seebeck coefficient exhibit a typical metallic character throughout the temperature range investigated, and the metallicity of this series is enhanced with increase in Al/Si ratio. On the other hand, the thermal conductivity shows a weak temperature variation at low temperatures, whereas $\kappa$ follows a $T^2$-dependence for $T > 150$ K. Analysis of the electronic thermal resistivity based on Klemen’s model reveals that the scattering of electrons from the defects and static imperfections becomes dominant as the temperature approaches $T_c$. These results are discussed in the light of simultaneous existence of various crystal structures and development of ultra-soft phonon mode recently observed in the CaAlSi system.

1. Introduction

After the discovery of superconductivity in the layered compound MgB$_2$ with a high superconducting transition temperature, $T_c \sim 39$ K [1–3], many isostructural systems such as CaAlSi and SrAlSi were explored for microscopic understanding of superconducting mechanisms [4–6]. Although, both MgB$_2$ and CaAlSi crystallize in the same AlB$_2$-type (C23) crystal structure and exhibit a conventional BCS-type superconductivity in the strong-coupling limit, their superconducting mechanisms are quite different [7,8]. In MgB$_2$, holes instead of electrons in the $\sigma$-bands of the boron layer couple strongly to the in-plane boron bond-stretching phonon modes, while the average electron–phonon coupling over the full Fermi surface is moderate. On the other hand, in CaAlSi, superconductivity is driven by structural instability leading to the presence of ultra-soft phonon mode, resulting from out-of-plane Al/Si vibrations, which couples strongly with electrons [7,8]. Recently, not only ternary silicides but also germanides and even stanides were found to exhibit superconductivity, albeit at lower temperatures [9]. Among these ternary intermetallic compounds, CaAlSi has attracted considerable interests since it has the highest superconducting transition temperature $T_c \sim 7.8$ K. Other unusual physical properties such as an unusual ultra-soft phonon mode (with $\omega \sim 7$ meV), several stacking variants in its crystal structure were also observed in CaAlSi. Coexistence of several isomeric structures of CaAlSi, not very surprising for materials near a structural instability, has intriguing effects on both the normal state and superconducting properties. Recent NMR measurements revealed the coexistence of AlB$_2$ and BaPtSb-type structures in CaAlSi [10]. Many theoretical [7,8] and experimental studies [4–6,9,10] have been performed to understand the properties of CaAlSi. However, the thermal transport properties are relatively less studied. In particular, thermal conductivity $\kappa$ is a property, which exhibits non-zero values in both the normal and superconducting states. The temperature dependence of $\kappa$ allows us to study the most important interactions present in a superconductor. For examples, the magnitude of $\kappa$ reflects the strength of the electronic interactions with the phonons. Moreover, scattering of these particles by static imperfections like impurities, defects, or grain boundaries are reflected.

Recent studies of the lattice dynamics in CaAlSi [11], by inelastic X-ray scattering, showed the presence of a strong anharmonic soft-phonon mode at room temperature, along the $\Gamma$–$A$–$L$ symmetry direction, which softens drastically as the temperature is reduced down to 10 K (near the superconducting transition temperature, $T_c$). Thus, the lattice part of thermal conductivity, which usually dominates in metallic systems such as CaAlSi, is expected to get modified due to the presence of the soft-phonon mode. In order to study and ascertain the effect of soft-phonon mode on the thermal conductivity near the proximity of $T_c$, we performed high-resolution thermal conductivity and Seebeck coefficient along with dc electrical resistivity measurements on CaAl$_{0.9-1.2}$Si$_2 \text{-} x$, with $x = 0.9–1.2$. Temperature dependencies of Seebeck coefficient, $S(T)$, and electrical resistivity, $\rho(T)$, exhibit a typical metallic behavior, being consistent with theoretical calculations. However, the value of thermal conductivity $\kappa(T)$ for the CaAl$_{0.9-1.2}$Si$_2$ system is relatively low as compared with typical metallic compounds. In addition,
k(T) exhibits a weak temperature dependence (\(k(T) \propto T^{1/2}\)) in the low temperature range, whereas a strong temperature dependence (\(k(T) \propto T^2\)) is found for \(T > 150\,\text{K}\). Such a result indicates that the scattering of electrons from the defects and static imperfections become dominant as the temperature approaches \(T_c\). These findings are connected to the presence of several variants of crystal structures and the development of ultra-soft phonon mode in CaAlSi [11].

2. Experimental techniques

The polycrystalline ingots of CaAl\(_x\)Si\(_{2-x}\) with \(x = 0.9\)–1.2 alloys were prepared by an arc melting high-purity elements of aluminum, calcium, and silicon under inert argon atmosphere several times to improve homogeneity. A portion of as-prepared ingot was annealed in a vacuum-sealed quartz tube at 800 °C for 7 days. The Bragg peaks of powder samples prepared from as-prepared and annealed ingots could be indexed according to the AlB\(_2\)-type structure, with two weak peaks of minor CaAl\(_2\)Si\(_2\) phase. The presence of CaAl\(_2\)Si\(_2\) phase is reported in the literature and found to have no effect on the physical properties discussed here [4]. Electrical resistivity measurements were performed using a standard four-point contact method. Seebeck coefficient and thermal conductivity measurements were simultaneously carried out, by a direct heat pulse technique, in a helium closed cycle refrigerator over the temperature range of 8–300 K. The temperature gradient of less than 1 K was maintained and measurements were performed under a slow warming rate of about 20 K/h in good vacuum. Further experimental details are reported elsewhere [12].

3. Results and discussion

3.1. Electrical transport

Fig. 1 shows the temperature-dependent electrical resistivity of CaAl\(_x\)Si\(_{2-x}\) with \(x = 0.9\), 1.0, 1.1, and 1.2 over the temperature range of 9 K < \(T\) < 300 K. It is clear that the electrical resistivity increases almost linearly with temperature above the superconducting transition temperature \(T_c\) for all compositions except for \(x = 1.2\), where it follows a \(T^2\)-law, as displayed in the inset (a) of Fig. 1. The \(T^2\) behavior is usually observed in pure metals at low temperature due to electron–electron interactions. The temperature coefficient of resistivity (TCR) is positive for all the alloys, indicating a metallic nature in the CaAl\(_x\)Si\(_{2-x}\) system, which is consistent with theoretical calculations [7,8]. However, the observed TCR changes drastically when the Al concentration decreases down to \(x = 0.9\), possibly due to a change in the electronic structure by varying \(x\) (i.e. the change in Al/Si ratio). It is noted that, in contrast with very sharp superconducting transitions in the \(x = 1.0\) and 1.1 compounds, a very broad, two step superconducting transition, from \(p(T)\) data of CaAl\(_{0.9}\)Si\(_{1.1}\) \((x = 0.9)\), was reported, which was tentatively attributed to the formation of chemical miscibility region leading to a non-uniform distribution of Al and Si atoms in the honeycomb planes [6]. As shown in the inset (b) of Fig. 1, residual resistivity ratio (RRR), free from sample dimension errors, increases in general with Al concentration. Thus, the metallic characteristic in the CaAl\(_x\)Si\(_{2-x}\) alloys appears to be enhanced with increase in Al concentration or increase in Al/Si ratio. The RRR of about 2.5–3 is in agreement with the reported values of polycrystalline samples [4]. The large residual resistivity values (on the order of a few milliohms) and small RRR are possibly due to a large amount of disorder present in the samples owing to the simultaneous coexistence of AlB\(_2\)-type and BaPSb-type structures (P6\(_3\)m2) [10]. It is important to note that Al/Si atoms in the AlB\(_2\)-type structure (P6\(_3\)/mmm) are randomly arranged on the hexagonal layer without any particular site preference (2d-site in the Wyckoff position).

3.2. Thermal conductivity

The temperature-dependent thermal conductivity \(k(T)\) for CaAl\(_x\)Si\(_{2-x}\) alloys was displayed in Fig. 2. For all studied samples, the entire feature of \(k(T)\) is very similar to that of a typical metal where scattering from static imperfections prohibits a pronounced maximum at low temperatures. However, the values of \(k(T)\) at room temperature are lower than that of ordinary metals. A highest value of \(k(T = 300\,\text{K})\) (\(\approx 54\,\text{mW/cm K}\)) is observed for the stoichiometric CaAlSi but this quantity reduces as varying the Al/Si ratio, presumably due to an increased compositional disorder. In general, the total thermal conductivity for ordinary metals or semimetals is expressed as a sum of electronic and lattice terms. The electronic contribution of heat transport can be estimated by the Wiedemann–Franz law: \(k_e = \sigma T L_0\), where \(\rho\) is the dc electric resistivity and \(L_0 = 2.45 \times 10^{-8} \,\text{W} \,\Omega/\text{K}^2\) is the Lorentz’s number. The lattice thermal conductivity, \(k_l\), is then obtained by subtracting electronic thermal conductivity from the measured total thermal conductivity. On this basis, we found that \(k_l\) is about an order of magnitude lower than that of \(k_e\) in these alloys, which shows that the thermal conductivity of CaAl\(_x\)Si\(_{2-x}\) is mainly due to lattice phonons rather than the charge carriers. This is in sharp contrast with MgB\(_2\) where the magnitudes of \(k_e\) and \(k_l\) are comparable [3,13]. At very low temperatures, \(k_l\) is expected to follow \(T^4\)-law, as it is directly
proximity of superconducting transition regime to this

Near 40 K, the value of $k_T$ would modify the phonon spectrum and thus modify the phonon scattering from the charge carriers. For $T > 150$ K, $\kappa(T)$ is roughly proportional to $T^2$, which is usually attributed to the scattering of phonons from the charge carriers.

According to Klemens’ model [14] in non-magnetic metals, the temperature-dependent electronic thermal conductivity, $W_e$ (reciprocal of $\kappa_e$) can be expressed as $W_e = \frac{1}{k_e} = \alpha + T^2$, where the first and second terms account for interactions of conduction electrons with static imperfections and thermally excited phonons, respectively. The analysis based on this model for CaAlSi (see inset (a) in Fig. 2) yields $\alpha = 35$ cm mW$^{-1}$ K$^{-1}$ and $\beta = 2.6 \times 10^{-6}$ cm mW$^{-1}$ K$^{-1}$. It is evident that the scattering of electrons from static imperfections in these alloys becomes dominant as the temperature approaches $T_c$. While similar behavior was observed in MgB$_2$, the values of $\alpha$ and $\beta$ in CaAlSi are an order of magnitude larger than those of MgB$_2$ ($\alpha = 0.55$ cm mW$^{-1}$ K$^2$ and $\beta = 2.8 \times 10^{-6}$ cm mW$^{-1}$ K$^{-1}$) [3]. Near 40 K, the value of $W_e$ in CaAlSi ($\approx 0.8$ cm K/mW) is an order of magnitude higher than that of MgB$_2$ (0.015 cm K/mW) [3]. Such a large contribution from static imperfections and defects could be attributed to the simultaneous existence of disordered AlB$_2$-type and ordered BaPtSb-type phases in a real sample [10].

### 3.3. Seebeck coefficient

The temperature dependence of Seebeck coefficient for the CaAl$_{2-x}$Si$_{2-x}$ alloys with $x=0.9, 1.0, 1.1, and 1.2$ over the temperature range from 10 to 300 K is illustrated in Fig. 3. The negative sign of $S(T)$ over the measured temperature range indicates that the predominant charge carriers are electrons in the CaAl$_{2-x}$Si$_{2-x}$ alloys. The largest room temperature value of $S$ close to $-7.6$ $\mu$V/K is observed for $x=1.0$, which reduces with the varying Al/Si ratio. The reduction in $S$ is generally attributed to an increase in the Fermi energy, as we will discuss below. A small shoulder-like feature observed in $S(T)$ data around 30 K is presumably due to the phonon-drag contribution, a feature commonly seen at low temperatures in clean metallic samples as a result of dragging of charge carriers from inhomogeneous phonon distribution. For metals, the Seebeck coefficient is expected to be linear in temperature through the classical formula $S = (\frac{\pi^2 k_F^2}{2e \epsilon_F}) T$, assuming a one-band model with an energy-independent relaxation time. Here, $\epsilon_F$ is the Fermi energy. However, the measured $S(T)$ curves for CaAl$_{2-x}$Si$_{2-x}$ alloys exhibit a small upward concave curvature with increase in temperature. To account for this behavior and to separate the linear diffusive contribution from total $S(T)$, we have analyzed the $S(T)$ data with an empirical power law, $S(T) = AT^B$. The first term represents the electronic diffusive contribution whereas the second term sets an upper bound to the contribution from electron–phonon normal processes [15]. The linear portion of $S(T)$ vs $T^B$ plots shown in the inset of Fig. 3 exhibits the temperature range over which the proposed formula is valid. From the relation $A = (\frac{\pi^2 k_F^2}{2e \epsilon_F})$, we extracted the Fermi energy $\epsilon_F = 0.95$ eV for $x=1.0$ and 1.78 eV for $x=1.2$. Such a result is presumably due to an enhancement of the metallic behavior in the CaAl$_{2-x}$Si$_{2-x}$ alloys as increase in the Al/Si ratio, being consistent with the $\rho(T)$ data.

Fig. 2. The temperature-dependent thermal conductivity for CaAl$_{2-x}$Si$_{2-x}$ alloys ($x=0.9–1.2$). Inset (a) shows the electronic thermal resistivity, $W_e$, as function temperature for $x=1$. Solid line is fit according Klemens model with equation $W_e = \frac{\alpha}{T} + \beta T^2$ and inset (b) displays a $k$ vs. $T^{1/2}$ plot at low temperatures. Solid lines are fits to the experimental data.

Fig. 3. The temperature-dependent Seebeck coefficient curves for CaAl$_{2-x}$Si$_{2-x}$ alloys over the temperature range 9 K $< T < 300$. Inset: a linear relation in the $S(T)$ vs $T^B$ plot indicates that the $S(T)$ data roughly follow an empirical power law $S(T) = AT^B$. 

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4. Conclusions

In summary, the positive temperature coefficient of resistivity for all studied samples infers the metallic behavior of CaAl$_x$Si$_{2-x}$ alloys. The measured Seebeck coefficient, for all samples, is negative over the entire measured temperature range, suggesting that the predominant charge carriers are electrons in the CaAl$_x$Si$_{2-x}$ system. Analyses of $S(T)$ and $\rho(T)$ data indicate that the increase in the Al/Si ratio, which increases the number of conduction electrons has an effect to enhance the metallic characteristic of CaAl$_x$Si$_{2-x}$. An estimate from the Wiedemann–Franz law demonstrates that the observed thermal conductivity in the CaAl$_x$Si$_{2-x}$ series is mainly associated with the lattice phonons rather than the charge carriers. In addition, we found a weak temperature dependence as $\kappa(T) \propto T^{1/2}$ at low temperatures, but a strong temperature dependence ($\kappa(T) \propto T^2$) for $T > 150$ K. The low-T behavior in $\kappa$ is presumably attributed to the development of ultra-soft phonon mode, which is recently observed in inelastic X-ray diffraction measurements.

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References