Comparison of physical properties in BaAlSi and CaAlSi

T. Nakagawa*, M. Tokunaga, T. Tamegai

Department of Applied Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received 16 December 2005; received in revised form 16 March 2006; accepted 31 March 2006
Available online 18 September 2006

Abstract

CaAlSi, with the AlB2-type structure, is a superconductor with relatively high \( T_c \) of 7.7 K and the related compounds, SrAlSi and BaAlSi have the same crystal structure. Despite the fact that the density of states in SrAlSi and BaAlSi is higher than that of CaAlSi, \( T_c \) of SrAlSi is 4.2 K and BaAlSi does not show superconductivity down to 2 K. We synthesize polycrystalline and single crystalline BaAlSi and compare their physical properties with those in CaAlSi. The transport and the specific heat measurements show the higher density of states in BaAlSi, consistent with the band structure calculations. We interpret that the absence of superconductivity in BaAlSi is due to the much weaker electron-phonon coupling constant compared with that in CaAlSi, because of the absence of the soft-phonon mode. In the course of the study, we find a superconductor with a composition close to Ba\(_2\)Al\(_4\)Si\(_3\).

© 2006 NIMS and Elsevier Ltd. All rights reserved.

PACS: 74.70.Ad; 75.20.En

Keywords: CaAlSi; BaAlSi; Soft-phonon mode

1. Introduction

Since the discovery of MgB\(_2\) [1], a lot of superconductors with AlB\(_2\) structure have been developed [2–6]. Among them, CaAlSi is a superconductor with a relatively high superconducting transition temperature \( T_c \) of 7.7 K [7]. Several anomalous properties are reported in CaAlSi, such as the anomalous positive pressure dependence of the transition temperature [8], and the anomalous angular dependence of the upper critical field [9]. Replacements of Ca in CaAlSi by other alkaline earth elements also result in the compounds with AlB\(_2\) structure, such as SrAlSi and BaAlSi [2]. Band structure calculations show that the density of states in BaAlSi and SrAlSi is higher than that of CaAlSi [8]. \( T_c \) depends on the Debye temperature, the electron-phonon coupling constant, and the density of states at the Fermi level. Since it is expected that the Debye temperatures in these compounds are similar, SrAlSi and BaAlSi should also show superconductivity with \( T_c \) comparable to CaAlSi. However, \( T_c \) of SrAlSi is reported to be 4.2 K, lower than that of CaAlSi, and BaAlSi does not even show superconductivity at temperature down to 2 K [2].

In order to clarify the discrepancy between the naive expectation and the actual properties of the materials in AAlSi (A = Ca, Sr, Ba), we have synthesized both polycrystalline and single crystalline BaAlSi and compared their physical properties with CaAlSi.

2. Experiments

Polycrystalline BaAlSi is synthesized by arc-melting in high-purity Ar atmosphere. The synthesized polycrystalline material is unstable in the air and decomposes in a few days. Single crystals of BaAlSi are grown by the floating-zone technique using an image furnace at a growth rate 2 mm/h. Unlike polycrystalline samples, single crystals are stable in the air. The phase purity and the lattice parameter of these materials are determined by using powder X-ray diffractometer. Electrical resistivity is measured by the conventional four-probe method in a temperature range between 0.4 and 300 K. Hall coefficient is measured by applying magnetic field range from −50 to 50 kOe and in a temperature range between 2 and 300 K. Hall resistance is
not linear as a function of magnetic field due to the contamination of magnetoresistance. After separating the Hall resistance and magnetoresistance components, we obtain the temperature dependence of the Hall coefficient. The electronic specific coefficient and the Debye temperature are estimated by measuring the specific heat using the relaxation method.

3. Results and discussion

Figs. 1(a) and (b) show the temperature dependence of resistivity in polycrystalline BaAlSi before and after annealing at 700 °C for 24 h. Samples before annealing shows the onset of superconductivity at 2 K (Fig. 1(a)). However, when the current is increased up to 3 mA, the resistive transition is completely suppressed. This may suggest that the superconductivity comes from the impurity phase. In order to suppress possible impurities, we anneal the samples in vacuum at 700 °C for 1 week. We obtain two kinds of samples with different \( T_c \)'s at 0.5 K (sample #1) and 2 K (sample #2) (Fig. 1(b)). According to the chemical analysis by Electron Probe Micro-Analysis (EPMA), the sample before annealing contains BaAlSi and an unknown phase with the composition close to Ba\(_2\)Al\(_4\)Si\(_3\). After annealing, sample #1 consists of rather uniform BaAlSi, although the composition is slightly different from 1:1:1. On the other hand, BaAlSi and Ba\(_2\)Al\(_4\)Si\(_3\) still coexist in sample #2. These facts may suggest that the superconductivity at 2 and 0.5 K originates from Ba\(_2\)Al\(_4\)Si\(_3\) and slightly off-stoichiometric BaAlSi, respectively.

Figs. 2(a) and (b) show the powder X-ray diffraction pattern of polycrystalline and single crystalline BaAlSi before annealing, respectively. Diffraction peaks of the single crystal do not contain impurity phase and they are much shaper than those of the polycrystal. No structural changes occur by annealing at 600 and 700 °C for 24 h. From the results, it is confirmed that BaAlSi single crystal is formed in the AlB\(_2\) structure, same as MgB\(_2\) and CaAlSi, and the lattice constants are \( a = 4.292 \text{ Å}, \quad c = 5.154 \text{ Å} \), almost the same as those of polycrystalline samples [5].
While CaAlSi has the superlattice in the (0,0,l)- and (1,0,l)-zone due to the periodic displacements of Al and Si along the c-axis [9], BaAlSi has no superlattice in all zones.

Fig. 3 shows the temperature dependence of the resistivity in BaAlSi single crystals. The in-plane resistivity, \(\rho_{ab}\), at room temperature and at 2 K is 60, 20\(\mu\Omega\)cm, respectively. The out-of-plane resistivity, \(\rho_c\), at room temperature and at 2 K is 171, 51\(\mu\Omega\)cm, respectively. Residual resistivity ratio (RRR) in BaAlSi is approximately 3.0. The resistivity of BaAlSi is lower than that of CaAlSi for both directions in all temperature range [11], consistent with the larger density of states at the Fermi level in BaAlSi [10]. However, BaAlSi single crystal, which is more close to the stoichiometry compared with polycrystalline samples does not show superconductivity at least down to 0.4 K as shown in the inset of Fig. 3.

Fig. 4 shows the temperature dependence of the Hall coefficient \(R_H\) in BaAlSi with magnetic field parallel to the c-axis and current perpendicular to it. \(R_H\) in BaAlSi is negative at all temperature from 2 to 300 K, suggesting that the main carriers are electrons, and it is almost temperature independent. \(R_H\) is related to the carrier density \(n\) by \(R_H = 1/ne\), where \(e\) is the elementary charge. In BaAlSi, the carrier density is estimated as \(2.1 \times 10^{22} \text{ cm}^{-3}\), which is larger than that in CaAlSi, \(8.4 \times 10^{21} \text{ cm}^{-3}\) [12]. This again agrees with the band-structure calculations [10] and the resistivity measurements mentioned above.

Generally, the specific heat is expressed by the sum of the contributions from the electrons and the lattice. By plotting \(C/T\) versus \(T^2\) as shown in Fig. 5, the electronic specific heat coefficient \(\gamma\) and Debye temperature \(\Theta\) are estimated from the intercept and the slope. \(\gamma\) and Debye temperature in CaAlSi is 4.5 mJ/mol/K\(^2\), 225 K, respectively [9]. On the other hand, in BaAlSi, \(\gamma\) is 7.0 mJ/mol/K\(^2\), and Debye temperature is 217 K. The larger \(\gamma\) in BaAlSi is consistent with the band-structure calculation even after considering the renormalization by electron–phonon coupling [10,13]. The lower Debye temperature in BaAlSi is reasonable, since Ca is lighter than Ba. The relation between the electronic specific heat coefficient \(\gamma\), the density of states at the Fermi level \(D(\varepsilon_F)\) and the electron–phonon coupling constant \(\lambda\) is described as \(\gamma = 1/3\pi^2k_B^2D(\varepsilon_F)(1 + \lambda)\). Employing this relation and the density of states at the Fermi level from the band-structure calculations, the electron–phonon coupling constant \(\lambda\) in BaAlSi and CaAlSi is estimated as 0.13 and 0.70, respectively. The weaker coupling constant in BaAlSi is the origin of the absence of superconductivity.
Why is the coupling constant in BaAlSi so low? The relation between the coupling constant $\lambda$ and the phonon frequency $\omega$ is described as $\lambda \propto 1/\omega^2$. For example, in the case of MgB$_2$, the strong coupling of the soft phonon of B and the $\sigma$ band of B gives rise to the appearance of superconductivity with relatively high $T_c$ [14]. In the case of CaAlSi, $T_c$ is also high due to the presence of the soft-phonon mode [15]. The anomalous increase of $T_c$ under pressure in CaAlSi [8] is explained by the further softening of the phonon mode under pressure [15]. So, it is suggested that the soft-phonon mode plays an important role in this class of materials to raise $T_c$. The absence of such a soft-phonon mode in BaAlSi results in the weak electron–phonon coupling and the absence of superconductivity above 0.4 K.

Finally, we have tried to synthesize Ba$_2$Al$_4$Si$_3$ polycrystalline samples by arc-melting. X-ray diffraction pattern shows that BaAlSi is the main phase and some peaks from impurities are observed. The magnetization measurement shows the onset of superconductivity at 2.1 K with the shielding fraction about 15% at 2.0 K. The resistivity measurement also shows the onset of superconductivity at 2 K. However, the superconductivity is again current dependent. The annealing at 700 °C for 3 days does not affect its structure and the superconducting properties. So, we conclude that superconductivity exists close to Ba$_2$Al$_4$Si$_3$ composition. However, we need to seek for different technique other than the simple arc melting to have single-phased Ba$_2$Al$_4$Si$_3$ samples.

4. Summary

We have synthesized polycrystalline and single crystalline BaAlSi and compared their properties with CaAlSi single crystal. BaAlSi is found to have anisotropic resistivity similar to CaAlSi. The transport and the specific heat measurements confirmed the higher density of states in BaAlSi compared with that in CaAlSi, consistent with the band structure calculation. However, BaAlSi single crystal does not show superconductivity down to 0.4 K in contrast to $T_c \approx 8$ K in CaAlSi. This discrepancy is explained by the absence of the soft-phonon mode in BaAlSi as seen in CaAlSi and MgB$_2$. We find superconductivity in the Ba–Al–Si system with the composition close to 2:4:3.

Acknowledgements

This work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology.

References

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature 410 (2001) 63.
[2] M. Imai, K. Nishida, T. Kimura, H. Kitazawa, H. Abe, H. Kitô, K. Yoshii, Physica C 382 (2002) 361.
[3] H. Kitô, Y. Takano, K. Togano, Physica C 377 (2002) 185.
[4] A. Yamamoto, C. Takao, T. Masui, M. Izumi, S. Tajima, Physica C 383 (2002) 197.
[5] M. Imai, E. Abe, J. Ye, K. Nishida, T. Kimura, K. Honma, H. Abe, H. Kitazawa, Phys. Rev. Lett. 87 (2001) 077003.
[6] M. Imai, K. Nishida, T. Kimura, H. Abe, Physica C 383 (2002) 191.
[7] M. Imai, K. Nishida, T. Kimura, H. Abe, Appl. Phys. Lett. 80 (2002) 1019.
[8] B. Lorenz, J. Cmaidalka, R.L. Meng, C.W. Chu, Phys. Rev. B 68 (2003) 014512.
[9] T. Tamegai, K. Uozato, S. Kasahara, T. Nakagawa, M. Tokunaga, Physica C 426 (2005) 208.
[10] I.R. Shein, N.I. Medvedeva, A.L. Ivanovskii, J. Phys.: Condens. Mater. 15 (2003) L541.
[11] T. Tamegai, K. Uozato, A.K. Ghosh, M. Tokunaga, Int. J. Mod. Phys. B 19 (2005) 369.
[12] M. Imai, E.S. Sadki, H. Abe, K. Nishida, T. Kimura, T. Sato, K. Hirata, H. Kitazawa, Phys. Rev. B 68 (2003) 064512.
[13] G.Q. Huang, L.F. Chen, M. Liu, D.Y. Xing, Phys. Rev. B 69 (2004) 064509.
[14] A.Q.R. Baron, H. Uchiyama, Y. Tanaka, S. Tsutsui, D. Ishikawa, S. Lee, R. Heid, K.-P. Bohanen, S. Tajima, T. Ishikawa, Phys. Rev. Lett. 92 (2004) 197004.
[15] G.Q. Huang, L.F. Chen, M. Liu, D.Y. Xing, Phys. Rev. B 71 (2005) 172506.