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Superconductivity in ternary silicide NaAlSi with layered diamond-like structure

S. Kuroiwa *, H. Kawashima, H. Kinoshita, H. Okabe, J. Akimitsu

Department of Physics and Mathematics, Aoyama-Gakuin University, Sagamihara, Kanagawa 229-8558, Japan

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Abstract

We have succeeded in synthesizing a new member of ternary silicide NaAlSi with a superconducting transition temperature $T_{c-onset} = 7$ K by high pressure technique. The crystal structure of NaAlSi is the layered diamond-like structure with a space group of $P4/nmm$ (no. 129, $Z = 3$) and without inversion symmetry. The superconducting properties in NaAlSi have been investigated by means of DC and AC magnetic susceptibility measurements. These magnetic responses indicate that NaAlSi belongs to a conventional type-II superconductor with a Ginzbrug–Landau parameter $\kappa = 13.8$. From the band structure calculations, we found that the hole band of Si p- and electron Al s-orbitals play an important role for the superconductivity in this system.

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Keywords: Ternary silicide; Superconductivity; Type-II superconductor; NaAlSi

1. Introduction

The relationship between the geometric arrangements of Si atoms in the series of silicide and their physical properties has been attracting much interest. In binary silicide compounds with two-dimensional Si network formed by sp^2 hybridized orbital, $ThSi_2$ [1], USi_2 [2] and several rare-earth metal disilicides crystallize to a AlB_2-type crystal structure common to MgB_2. In particular, calcium disilicide $CaSi_2$ takes AlB_2-like structure above high pressure of 16 GPa, and it becomes superconductor with relatively high $T_c = 14$ K [3].

Moreover, ternary silicide compounds M_1M_2Si (M_1: Ca, Sr, Ba and M_2: Al, Ga), which also have the AlB_2-like crystal structure with the honeycomb layer formed by M_2 and Si atoms, were reported to be a superconductor [4–6]. Interestingly, we reported that T_c and many other transport properties in CaAlSi depend on the superstructured periodicity originated from flat and/or distorted AlSi-layer corresponding to the sp^2- and sp^3-hybridized orbital, respectively [7]. This means that Si bonding network plays an important key for superconducting characteristics in CaAlSi. Therefore, we concentrated our interest to investigate the relationship between the superconducting properties and the two- or three-dimensional electronic state composed by Si-network. A search for an additional Si-based superconducting material may lead to the understanding for character of the Si bonding in different atomic arrangements.

In this paper, we report on the discovery of the new superconducting phase in ternary sodium silicide NaAlSi which crystallizes to an anti-PbFCl-type structure with diamond-like AlSi-network corresponding to the sp^3-hybridization. We also present the results of low temperature physical properties of NaAlSi obtained by means of DC and AC magnetic susceptibility measurements. Moreover,

* Corresponding author. Tel.: +81 42 759 6545; fax: +81 42 759 6287.
E-mail address: kuro@phys.aoyama.ac.jp (S. Kuroiwa).

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the electronic band structure of NaAlSi has been investigated using the full-potential linearized augmented plane wave (LAPW) method to discuss the superconducting mechanism in this system.

2. Experimental and calculation details

As a starting material, the mixture of Na (99.9%), Al (99.99%) and Si (99.999%) with a nominal composition of NaAlSi in a dry box under Ar atmosphere was placed into a BN cell. A polycrystalline sample of NaAlSi was synthesized at 1300–1400 °C for 30 min under a high pressure of 5.5 GPa using cubic-anvil-type equipment. It was quenched to room temperature within a few second. All subsequent sample manipulations were performed in a dry He atmosphere because of the difficulty to stabilize the NaAlSi phase in air.

The crystal structure of obtained polycrystalline sample was examined by the powder X-ray diffraction technique using a conventional X-ray spectrometer with a graphite monochromator (RINT-1100 RIGAKU). The intensity data was collected with Cu Kα radiation over a 2θ range from 5 to 80° at a 0.02° step width. The DC magnetic susceptibility and magnetization were obtained by a superconducting quantum interference device (SQUID) magnetometer (MPMSR2 Quantum Design Co., Ltd.). The AC magnetic susceptibility was measured in static fields by an AC drive coil set that provides an alternating excitation fields using PPMS (Quantum Design Co., Ltd.). All of the AC susceptibility data were obtained at a frequency of 877 Hz with an excitation field of 0.43 Oe parallel to the static fields.

Calculations of the electronic structure were performed on the full-potential LAPW method as implemented in the WIEN2K program package [8] within the local density approximation (LDA). The valence electrons were applied to a scalar-relativistic approximation and the Perdew–Burke–Ernzerhof generalized-gradient approximation (GGA) potential was used for the exchange correlation potential [9]. For the structure parameter, anti-PbFCl-type with $P4/nmm$ symmetry and experimentally determined lattice constants (see below) were applied and internal coordinates were taken from the structure data reported by Westerhaus and Schuster [10]. The LAPW sphere radii of NaAlSi were set to 2.50 a.u. for Na, 2.50 a.u. for Al and 2.47 a.u. for Si. The cut-off parameter RK_{max} was chosen as 8.0, where R is the radius of the Na sphere and K_{max} is the magnitude of the largest reciprocal lattice vector. Self-consistency was imposed on k-point meshes of 144 points ($16 \times 16 \times 8$, we used approximately 2300 special k-points) in the irreducible wedge of the Brillouin zone.

3. Experimental results

Fig. 1 shows the powder X-ray diffraction pattern for NaAlSi at room temperature. The diffraction signal from the NaAlSi phase was observed as a main contribution

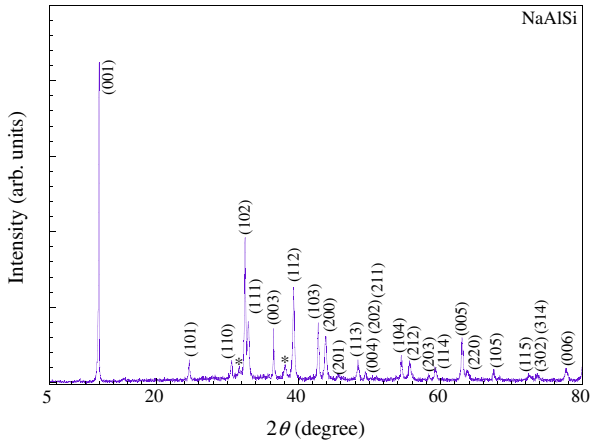

Fig. 1. Powder X-ray diffraction patterns for NaAlSi at room temperature. The unindexed peaks denoted by asterisk symbols are ascribed to an unknown impurity phases.

besides that from a small amount of unknown impurity phases denoted by asterisks symbols. The NaAlSi phase can be indexed as a tetragonal unit cell with the space group $P4/nmm$ (no. 129, $Z = 3$) and crystallized to an anti-PbFCl-type, which is common to those in the first report for NaAlSi by Westerhaus and Schuster [10]. The lattice constants were determined to be $a = 4.119$ Å and $c = 7.362$ Å. As shown in Fig. 2, the crystal structure of NaAlSi seems to be a layered diamond-like structure formed by the sp^3-hybridized layers of Al/Si bonding and an intercalated Na atoms between them. Interestingly, this crystal structure exhibits a breaking of spatial inversion symmetry along the c-axis, as in $CePt_3Si$ [11]. Meanwhile, we also point out that another ternary alkaline-metal silicide LiAlSi has the cubic diamond structure with $F\bar{4}3m$ symmetry and strong covalent sp^3-hybridized state in the Al/Si bonding, indicating that the band structure in LiAlSi is very similar to that of pure Si with diamond structure [12,13].

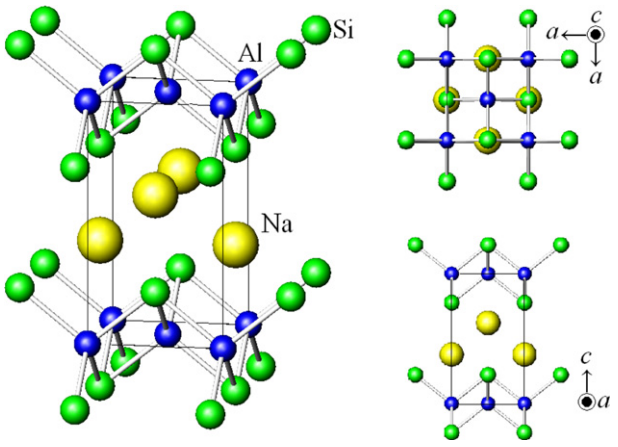

Fig. 2. Crystal structure of NaAlSi with the space group of $P4/nmm$, crystallizing to an anti-PbFCl-type. The black line shows a tetragonal unit cell.