Superconductivity of Ternary Silicide with the AlB_2-Type Structure $Sr(Ga_{0.37}, Si_{0.63})_2$

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(Received 27 February 2001; published 27 July 2001)

A ternary silicide $Sr(Ga_{0.37}, Si_{0.63})_2$ was synthesized by a floating zone method. Electron diffraction and powder x-ray diffraction measurements indicate that the silicide has the AlB_2-type structure with the lattice constants of $a = 4.1427(6)$ Å and $c = 4.7998(9)$ Å, where Si and Ga atoms are arranged in a chemically disordered honeycomb lattice and Sr atoms are inercalated between them. The silicide is isostructural with the high-temperature superconductor MgB_2 reported recently. Electrical resistivity and dc magnetization measurements revealed that it is a type-II superconductor with onset temperature of 3.5 K.

DOI: 10.1103/PhysRevLett.87.077003 PACS numbers: 74.10.+v, 61.66.Fn, 74.70.Dd

Recently, high-temperature superconductivity at 39 K has been reported in an intermetallic compound MgB_2 [1]. Since MgB_2 has the AlB_2-type structure, the intermetallic compounds with the structure have attracted attention as candidates for new superconductors. The discovery and study of new superconductors with the AlB_2-type structure in systems other than the Mg-B system are relevant to our understanding of the origin of high-temperature superconductivity in MgB_2. Silicides, as well as borides, also contain compounds with the AlB_2-type structure or a structure related to it. In binary silicides, $ThSi_2$ [2], USi_2 [3], and several rare-earth metal disilicides [4,5] are known to have the AlB_2-type structure. One of these, β-$ThSi_2$, is known to be a superconductor with a critical temperature T_c of 2.41 K [6]. A high-pressure phase of $CaSi_2$ that appears above 16 GPa has an AlB_2-like structure, where Si atoms form slightly corrugated honeycomb layers and Ca atoms are intercalated between them [7]. It is a superconductor with T_c of 14 K [8], while an ambient-pressure phase is not [9]. The high-pressure phase exits only at high pressures, and it cannot be quenched under ambient conditions.

Here we report the synthesis of a new ternary silicide with the AlB_2-type structure in the Sr-Ga-Si system and demonstrate that the compound becomes superconducting. The compound was characterized by the electron microprobe, electron diffraction, and powder x-ray diffraction methods. Electrical resistivity and dc magnetization measurements showed that the compound is a superconductor.

Samples were prepared as follows: first, an ingot was prepared by Ar arc melting of a 1:1 molar mixture of $SrSi_2$ and Ga. Secondary electron microscope observation indicated that the ingot consists of two phases: an Si clathrate $Sr_8Ga_xSi_{46-x}$ [10] and $Sr(Ga_xSi_{1-x})_2$. Samples that consist of the single $Sr(Ga_xSi_{1-x})_2$ phase were prepared from the ingot by the floating zone (FZ) method with infrared heating. Crystal growth was carried out at 2 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 15 rpm in opposite directions. The details of the FZ furnace and the procedure are described elsewhere [11,12]. The resultant ingots have parts that consist of the single $Sr(Ga_xSi_{1-x})_2$ phase. These single-phase parts were cut for use in the following measurements.

The chemical composition of the single-phase part was determined by an electron probe microanalyzer to be Sr 32.9 at. %, Ga 24.8 at. %, and Si 42.3 at. %; thus its chemical formula can be expressed by $Sr(Ga_{0.37}Si_{0.63})_2$.

Figures 1(a)–1(c) show the electron diffraction patterns of the $Sr(Ga_{0.37}Si_{0.63})_2$ phase taken along the [001], the $[\bar{2}10]$, and the [100] zone axes, respectively. These patterns show the $Sr(Ga_{0.37}Si_{0.63})_2$ phase to have a hexagonal unit cell with lattice parameters of $a = 4.1$ and $c = 4.7$ Å, and the reflections are indexed accordingly. We note that there are no systematic absences in the reflections. Figures 1(d)–1(f) show the convergent-beam electron diffraction (CBED) patterns. Pattern 1(d) was taken along the [001] axis, and patterns 1(e) and 1(f) were taken by tilting the incidence beam slightly from the [001] axis in the *A* and *B* directions indicated in pattern 1(d), to obtain the reflections at the first-order Laue zone.

The CBED patterns confirm the sixfold rotational symmetry axis and two sets of mirror symmetries (total symmetry 6*mm*). These findings strongly suggest that the $Sr(Ga_{0.37}Si_{0.63})_2$ phase has the AlB_2-type structure ($P6/mmm$) [13], where the Ga and Si randomly occupy the *B* (2*d*) site which forms the honeycomb layer, as shown in Fig. 2. It is worth noting that the $EuGe_2$-type ($P\bar{3}m1$) with corrugated hexagonal layer [14] or BaPtSb-type ($P\bar{6}m2$) with chemically ordered honeycomb layer [15] are also considered as possible structures for the present $Sr(Ga_{0.37}Si_{0.63})_2$ phase. However, the CBED patterns [Figs. 2(d)–2(f)] clearly reveal the sixfold rotational symmetry, which is evidently inconsistent with both the $EuGe_2$-type ($P\bar{3}m1$) and BaPtSb-type ($P\bar{6}m2$).

Figure 3 shows the powder x-ray diffraction pattern and the calculated one for the $Sr(Ga_{0.37}Si_{0.63})_2$ phase with the

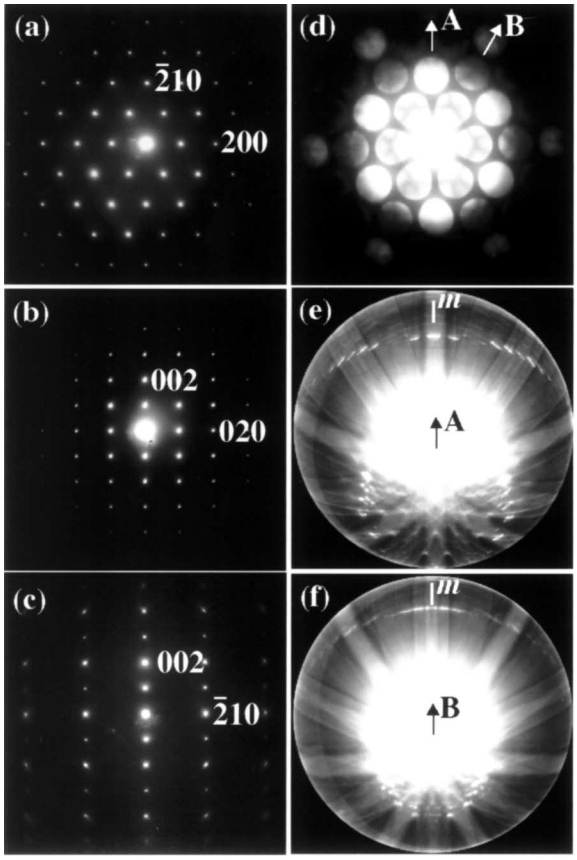

FIG. 1. Electron diffraction patterns taken with the incidence of (a)–(c) parallel beam and (d)–(f) convergent beam along the zone axes. Patterns (a)–(d) reveal the reflections at zero-order Laue zone. Pattern (d) was taken at [001] incidence, and patterns (e) and (f) were taken by tilting the incidence slightly from the [001] axis in the A and B directions indicated in pattern (d), to obtain the reflections at the first-order Laue zone. The symbol "m" shows a mirror plane.

AlB_2-type structure. For the calculation, we assumed the compound $Sr(Ga_{0.37}, Si_{0.63})_2$ to be isostructural with the AlB_2-type, in which the B ($2d$) site is chemically disordered with occupation probabilities of 0.37 for Ga and 0.63 for Si. It is clear that the observed intensities were reproduced well by the assumed structure, confirming the validity of the AlB_2-type structure. The lattice parameters were calculated to be $a = 4.1427(6)$ and $c = 4.7998(9)$ Å from the x-ray patterns. On this basis, we conclude that the $Sr(Ga_{0.37}Si_{0.63})_2$ phase has the AlB_2-type structure, represented as $Sr(Ga_{0.37}, Si_{0.63})_2$, which is hereafter denoted as $Sr(Ga, Si)_2$ for simplification.

Figure 4 shows the electrical resistivity of $Sr(Ga, Si)_2$ as a function of temperature. The resistivity decreases gradually with decreasing temperature down to 3.6 K, which suggests that $Sr(Ga, Si)_2$ is a metal. The resistivity starts to decrease sharply at 3.6 K and becomes negligibly small at 3.4 K, as shown in the inset of Fig. 3. The 10%–90% transition width is smaller than 0.2 K. These results suggest a superconducting transition at 3.5 K.

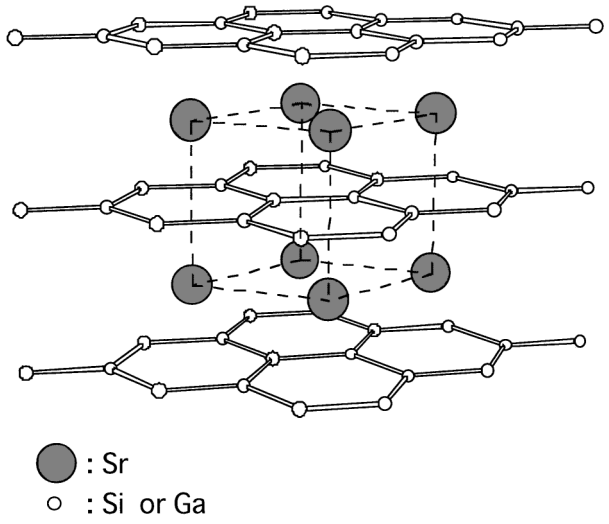

FIG. 2. Crystal structure of $Sr(Ga_{0.37}, Si_{0.63})_2$. The broken lines represent a unit cell. The large spheres correspond to Sr atoms and the small ones to Ga and Si atoms.

Figure 5 shows the dc magnetization at 22.4 Oe as a function of temperature. The triangles and circles show data obtained in zero field cooling (ZFC) and in field cooling (FC), respectively. In FC, a Meissner effect (flux exclusion) can be seen below 3.4 K, which confirms the presence of a superconducting phase below 3.4 K, as indicated by the resistivity measurements. The magnetic shielding fraction in ZFC and the flux exclusion in FC at 1.9 K are calculated to be about 80% and 8% of the theoretical value of the perfect diamagnetism ($1/4\pi$), respectively [16]. This indicates that the superconductivity

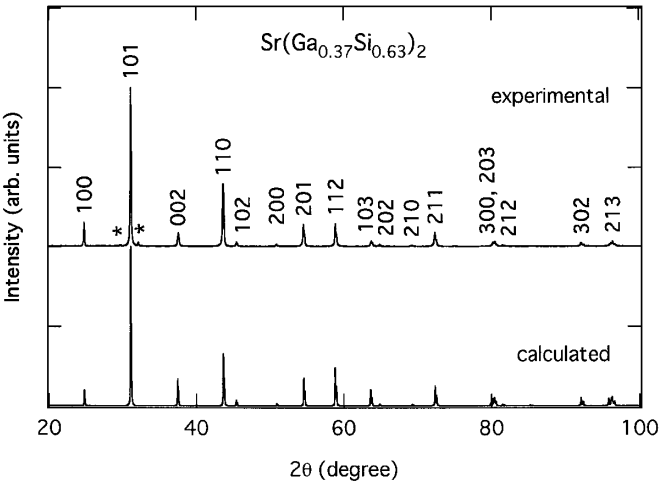

FIG. 3. Powder x-ray diffraction pattern of $Sr(Ga_{0.37}, Si_{0.63})_2$. The asterisks represent the reflections from an inclusion, Si clathrate $Sr_8Ga_xSi_{46-x}$. The lower one was calculated assuming that it has the AlB_2-type structure (space group $P6/mmm$) with the observed lattice constants $a = 4.1427(6)$ Å and $c = 4.7998(9)$ Å, where Sr atoms occupy the $1a$ site and Si and Ga atoms occupy the $2d$ site randomly.

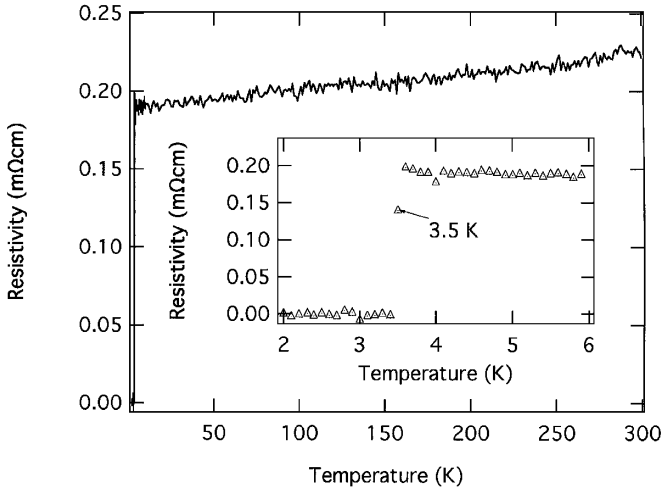

FIG. 4. Electrical resistivity of $Sr(Ga_{0.37}, Si_{0.63})_2$ as a function of temperature.

is a bulk effect. The inset of Fig. 5 shows the dc magnetization at 1.9 K as a function of a magnetic field. It shows that $Sr(Ga, Si)_2$ is a type-II superconductor with a lower critical field (H_{c1}) of about 20 Oe and an upper critical field (H_{c2}) of about 10 000 Oe at 1.9 K. Thus, $Sr(Ga, Si)_2$ turns out to be a type-II superconductor, whose T_c is higher than that of the known superconducting silicide with the AlB_2-type structure β-$ThSi_2$ (2.41 K) [6].

Since the electronic structure of $Sr(Ga, Si)_2$ has never been calculated, we will discuss it based on that of $CaSi_2$ with the AlB_2-type structure calculated by Kusakabe *et al.* [17]. The calculation on the AlB_2-type $CaSi_2$ indicates that (i) the lowest three bands are essentially derived from Si σ orbitals, whose dispersion is similar to that of graphite, (ii) above them, there are bands that arise from the mixing of Si p states with Ca $3d$ states, and (iii) the Fermi level is in the mixed states of Si p with Ca d states. The valence electron density of $Sr(Ga, Si)_2$ is estimated to be about 13% lower than that of the AlB_2-type $CaSi_2$. Consequently, the Fermi energy of $Sr(Ga, Si)_2$ is estimated to be roughly 9% less than that of the AlB_2-type $CaSi_2$, because the Fermi energy is proportional to the $2/3$ power of the valence electron density. In this case, the Fermi energy of $Sr(Ga, Si)_2$ is expected to move downward relative to the lowest band but to be still in the mixed states of Sr $4d$ states and p states of Si and Ga. Therefore, the electronic structure near the Fermi level is attributed to the mixed states of Sr $4d$ states with p states of Si and Ga, which play an important role in the superconductivity.

In summary, ternary silicide $Sr(Ga, Si)_2$ was synthesized by the FZ method. It has the AlB_2-type structure in which Si and Ga atoms form chemically disordered honeycomb layers. Electrical resistivity and dc magnetization measurements reveal that it is a type-II superconductor with onset temperature of 3.5 K. Ternary silicides including alkaline-earth metals have not been exhaustively explored yet, and no phase diagram exists for the Sr-Ga-Si system. Therefore, it may be interesting to prepare other ternary silicides by varying the honeycomb lattice composition and the choice of alkaline-earth element in the search for superconductors with the AlB_2-type structure. This work could stimulate the study of superconductors with the AlB_2-type structure in all the systems, and it could be helpful for understanding the origin of high-temperature superconductivity in MgB_2

The authors thank A. P. Tsai and J. Q. Guo of NRIM for allowing us to use an arc furnace, T. Hirano for allowing us to use an FZ furnace, and I. Nakatani and H. Mamiya of NRIM for allowing us to use Physical Properties Measurement System (Quantum Design). The authors also thank T. Mochiku of NRIM for useful discussions on the analysis of powder x-ray diffraction patterns, and Y. Tateyama of NRIM for useful discussions on the electronic structure of $Sr(Ga, Si)_2$.

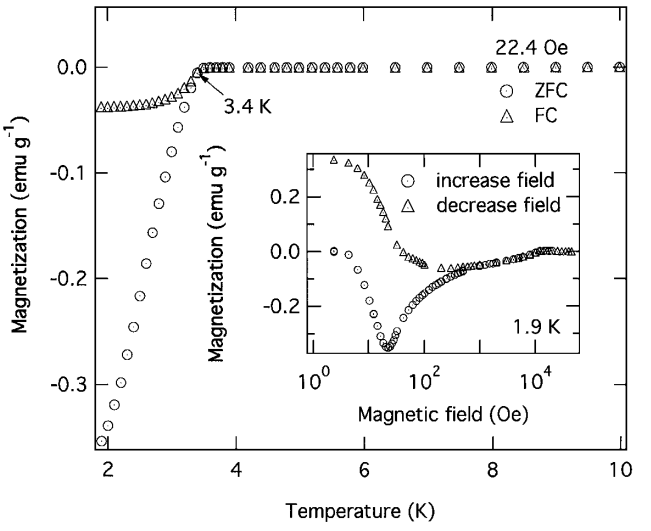

FIG. 5. Magnetization of $Sr(Ga_{0.37}, Si_{0.63})_2$ at 22.4 Oe as a function of temperature. The inset shows magnetization of $Sr(Ga_{0.37}, Si_{0.63})_2$ at 1.9 K as a function of magnetic field.

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