

## Superconductivity in the Silicon Clathrate Compound $(\text{Na,Ba})_x\text{Si}_{46}$

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(Received 8 August 1994)

A new silicon clathrate compound containing barium,  $(\text{Na,Ba})_x\text{Si}_{46}$ , becomes a type-II superconductor with a critical temperature ( $T_c$ ) of about 4 K. In the compound, the silicon atoms are bonded tetrahedrally with about the same bond distances as in ordinary cubic diamond Si, but form 12- and 14-hedral cages which are linked by shared faces. The metal atoms are located in the center of the polyhedra. This is the first superconductor consisting of a Si  $sp^3$  covalent network.

PACS numbers: 74.10.+v, 61.66.Fn, 74.70.Ad

Silicon and carbon are often discussed in comparison with each other in terms of the same group-IV elements. As for elemental carbon, there are two allotropes, diamond and graphite, and recently fullerene has been added as a new member [1]; only the diamond type structure is known for elemental silicon. The recent discovery of relatively high temperature ( $T_c$ ) superconductivity in alkali-metal-doped fullerene [2] is reminiscent of silicon clathrate compounds  $M_x\text{Si}_{46}$  and  $M_x\text{Si}_{136}$  ( $M$  = alkali metal), in which 12-, 14-, and/or 16-hedral large silicon polyhedra (Fig. 1) are linked by shared faces, and the alkali metal atoms are placed, or doped, in the center of the polyhedra from the beginning [3–7]. It has been suggested that the mechanism for the superconductivity in the fullerenes is the conventional phonon-mediated Bardeen-Cooper-Schrieffer (BCS) mechanism, and that the high Debye frequency of the fullerene spheres has the advantage for yielding a high  $T_c$  [8]. Since the three-dimensional framework of the silicon clathrate compounds is composed of rigid  $sp^3$  hybrid Si-Si bonds as in elemental Si, and supposedly provides high Debye frequency, a similar high  $T_c$  is expected for the silicon clathrate compounds. Roy, Sim, and Caplin [7] measured the electric conductivity and magnetic susceptibility on a mixed phase sample of  $\text{Na}_8\text{Si}_{46}$  and  $\text{Na}_x\text{Si}_{136}$ ; however, no superconductivity was detected down to 2 K. We have recently succeeded in encapsulating barium metal atoms in the silicon clathrate structure [9], and in this study we observe superconductivity in the new silicon clathrate compound as shown below.

The sample was prepared according to the method described elsewhere [9]. The procedures were slightly modified in order to avoid magnetic contamination as follows: Two kinds of Zintl phases, NaSi and  $\text{BaSi}_2$ , were first prepared, and the 2:1 molar mixture was placed in a tantalum tube, which was in turn vacuum sealed in a stainless steel tube, and heated at 873 K for several days to obtain a mixed metal silicide with a composition of  $\text{Na}_2\text{BaSi}_4$ . The silicide was heated under a vacuum of about  $10^{-2}$  Pa at 773 K for 8–10 h in a tantalum tube. During this treatment, a part of the Na metal was removed by evaporation, and a mixture of  $M_x\text{Si}_{46}$  type clathrate

phase and  $\text{BaSi}_2$  was obtained. The  $\text{BaSi}_2$  was removed by dissolving with dripping water on a Teflon filter. The resulting residue consisted of a cubic phase of  $M_x\text{Si}_{46}$  type structure with a unit cell dimension of  $a = 1.026$  nm together with a trace amount of  $\text{BaSi}_2$ . The chemical composition was determined to be  $\text{Na}_{2.9}\text{Ba}_{4.5}\text{Si}_{46}$  by atomic absorption. No contamination of the sample with tantalum and tantalum silicides was confirmed by powder x-ray diffractometry (XRD) and x-ray photoelectron spectroscopy (XPS). The x-ray Rietveld analysis revealed that the Ba atoms occupied the center of the larger 14-hedral cages and Na atoms mainly in the 12-hedral cages as shown in Fig. 2.

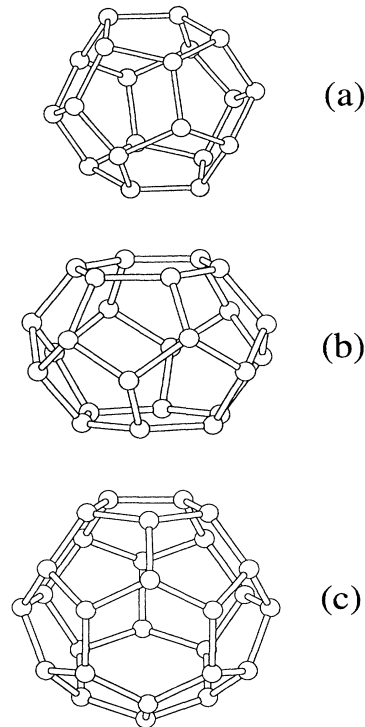


FIG. 1. Polyhedra found in silicon clathrate compounds: (a) 12-hedral, (b) 14-hedral, and (c) 16-hedral silicon cages.

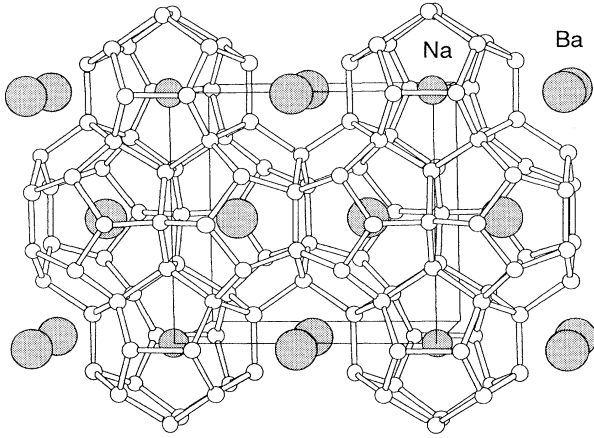


FIG. 2. Schematic illustration of the crystal structure of  $(\text{Na,Ba})_x\text{Si}_{46}$ . Ba atoms (large circles) occupy the center of the large tetrakaidecahedral cages and Na atoms (small circles) mainly the center of smaller dodecahedral cages.

Figure 3 shows the resistivity of the clathrate sample measured using a four-probe method. The polycrystalline sample was pelletized under a pressure of about 600 MPa and platinum thin lead wires were connected with conducting silver paste. The temperature was measured using a calibrated ruthenium oxide thin film resistance thermometer. The rapid drop of the resistivity due to the superconducting phase transition was clearly observed at about 3.5 K. The onset temperature of the decrease was 4.0 K, and the 10%–90% transition width was about 0.4 K. The zero resistance was attained at about 2.5 K. The rather wide transition range may suggest a nonuniformity in the

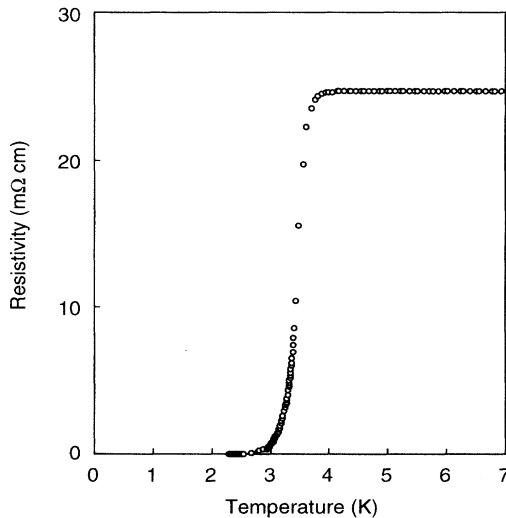


FIG. 3. Temperature dependence of resistivity of the pelletized polycrystalline sample of  $(\text{Na,Ba})_x\text{Si}_{46}$  near the critical temperature.

composition of the sample. The resistivity above  $T_c$  was almost constant at 30 mΩ cm up to room temperature, which is of similar order to those of  $\text{Na}_8\text{Si}_{46}$  and  $\text{K}_7\text{Si}_{46}$  reported by Cros *et al.* [4].

Figure 4 shows the temperature dependence of the magnetization of the sample measured in a magnetic field of 12.1 Oe using a SQUID magnetometer (Quantum Design). The values measured after cooling in zero magnetic field are shown by open circles, and those measured in the course of cooling under the magnetic field are plotted by solid circles. A large magnetic shielding of about 10% of the value expected for perfect diamagnetism was observed at 2 K. The onset temperature was about 4 K, in good agreement with the temperature obtained by the resistivity measurement. The remarkable hysteresis observed between the two types of cooling modes is characteristic for the type-II superconductor. The  $M$ - $H$  curve measured at 2 K also showed the type-II behavior with  $H_{c1}$  of about 200 Oe.

The structure of the clathrate compound with an ideal composition of  $\text{Na}_2\text{BaSi}_{46}$  can be regarded as that consisting of 12-hedral  $\text{Si}_{20}$  silicon clusters containing a Na atom ( $\text{Na@Si}_{20}$ , where @ denotes metalendohedral clusters) with a body-centered arrangement in a cubic unit cell, where the cluster at the center is twisted by  $90^\circ$  to those of the corners. The clusters are connected with each other by forming a hexagonal silicon ring with two additional silicon atoms between each two clusters. As a result, Ba-containing 14-hedral  $\text{Si}_{24}$  clusters are formed, which share faces with the  $\text{Na@Si}_{20}$  clusters. Recently Saito [10] has calculated the band structure on the basis of this arrangement of clusters using density-functional analysis and revealed that Ba states show strong hybridization with  $\text{Si}_{46}$  states, giving very high density of states at the Fermi level. This would be important for the superconductivity observed in  $\text{Na}_x\text{Ba}_y\text{Si}_{46}$ .

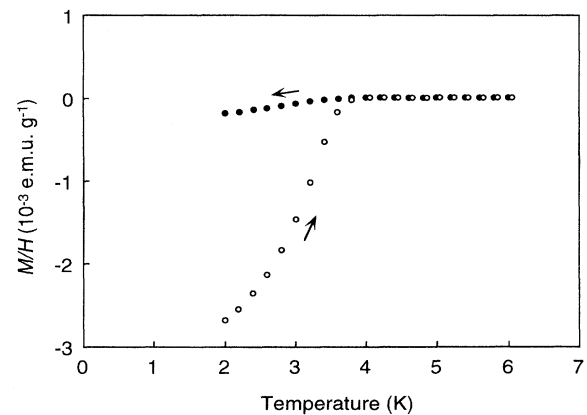


FIG. 4. Temperature dependence of the magnetization of  $(\text{Na,Ba})_x\text{Si}_{46}$  measured in a magnetic field of 12.1 Oe. Open circles indicate the magnetization measured after cooling in zero field and solid circles indicate the data in the course of cooling in the field.

Most rare earth metal disilicides adopt the  $\alpha$ -ThSi<sub>2</sub> type structure, in which planar three-coordinated silicon groups are connected with each other by twisting alternatively by 90° so as to form a tetragonal three-dimensional open network, and the metal atoms are placed in the interstices with 12 Si neighbors [11]. Some of this type of disilicides become superconductors, for instance, LaSi<sub>2</sub> and CaSi<sub>2</sub> (high pressure form) at 2.5 and 1.37 K [12–14], respectively. The concentration of metal atoms doped per Si is much higher in the  $\alpha$ -ThSi<sub>2</sub> type superconductors than that in the silicon clathrate compound. Moreover, in the  $\alpha$ -ThSi<sub>2</sub> type compounds, each Si atom is bonded with three Si atoms in a plane with  $sp^2$  bond character.

It is well known that the cubic diamond (CD) phase of elemental Si is transformed into a metallic phase with the  $\beta$ -Sn structure under high pressure [15]. The  $\beta$ -Sn phase undergoes a series of further structural phase transitions with pressure [16]. Although superconductivity in the  $\beta$ -Sn phase and some of the condensed phases has been reported [15–18], it should be noted that the Si atoms in the clathrate compound are tetrahedrally bonded with about the same bond distances as in the CD phase. The clathrate compound studied here is the first superconductor consisting of an  $sp^3$  covalent network. It should also be emphasized that the metal atoms in the silicon clathrate compounds are doped within the silicon cages rather than outside as in the case of fullerene doping. Consequently, the clathrates are very stable in air and even in acid solutions except hydrofluoric acid. This is also a favorable feature of the silicon clathrate compounds. It will be interesting to prepare a variety of silicon clathrate compounds with different kinds of metal atoms with the hope of developing high  $T_c$  superconductors.

The authors thank Professors T. Fujita and Y. Maeno for the use of the SQUID magnetometer. They also would like to express their thanks to Professor S. Saito for the discussion on the electronic structure of the clathrate compound. This work was supported partly by

the Grant-in-aid for Scientific Research on Priority Area of the Ministry Education, Science, and Culture of Japan.

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