Sp³-network superconductors made from IVth-group elements

Takeshi Rachi,*, Ryotaro Kumashiro, Hiroshi Fukuoka, Shoji Yamanaka, Katsumi Tanigaki

Department of Physics, Graduate School of Science, Tohoku University and CREST-JST, 6-3 Aoba Aramaki Aoba-ku, Sendai, Miyagi 980-8578, Japan

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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Abstract

Discussions are made among the polyhedral superconductors made from IVth-group elements (C, Si and Ge). Important superconducting physical parameters of Ba₈Si₄₆ are deduced from magnetic measurements and are compared to those of K₃C₆₀. Using the lower and the upper critical fields of 78 and 5.5 × 10⁴ Oe determined by magnetization measurements, the penetration depth λ = 270 nm and the coherence length ζ = 7.7 nm are estimated for Ba₈Si₄₆. The high density of states at the Fermi level is the most important parameter to give rise to a relatively high Tc in Ba₈Si₄₆, while the high phonon frequency is essential for K₃C₆₀. In contrast, the experimental facts found in IV₁₀₀ where IV = Si and Ge imply that the rattling phonons in the open cage potentials seem to control the superconducting transition temperature.

Keywords: Superconductivity; Fullerenes and related materials; Phonons

1. Introduction

Continuing to the discovery of the high Tc cuprates in 1986 [1], a variety of superconductors have been found ranging from organic [2], cluster [3–5] to inorganic [6–8] solids. In the series of the cluster-based superconductors found in 1990s, C₆₀ and Si₄₆ materials, as schematically shown in Fig. 1, are the most typical carbon and silicon superconducting materials with relatively high Tcs. The mechanism of these superconductors has been elucidated to be associated with the phonon-mediated Bardeen–Cooper–Schrieffer (BCS) formalism [9,10]. In this paper, we compare the BCS superconducting physical parameters between C₆₀ and Si₄₆ superconductors. Many important physical parameters for Ba₈Si₄₆, the most standard superconductor having the silicon framework [11], will be deduced from the magnetization measurements and discussed by emphasizing the similarities and the differences for the both systems of Si₄₆ and C₆₀. In addition, the superconductivity newly found in another Si-network cluster solid of Si₁₀₀ will be demonstrated and compared to that of the isostructural Ge-network one. In the latter material, the possible superconductivity associated with the rattling phonons showing time- and space-dependent motions, confined in the potentials created by polyhedral open cage structure will be demonstrated.

2. Experimental

Ba₈Si₄₆ was synthesized using Ba ingot and Si powder under high pressure of 3 GPa by resistive heating at 800°C according to the previous report [11]. The sample of 10 mg was covered by a sheet of plastic food wraps and inserted to a straw to be fixed in the middle position for measurements. Physical parameters were magnetically deduced from the magnetic properties measured using an MPMS7 (quantum design) apparatus according to the standard procedures.

3. Results and discussion

3.1. Physical parameters in Ba₈Si₄₆

The important parameters in superconductivity can be deduced both from the magnetic moments as a function of
temperature \((T)\) under various magnetic fields and those as a function of magnetic field \((H)\) at various temperatures below \(T_c\).

Fig. 2 displays the magnetic moments as a function of temperature from above the \(T_c\) down to 2 K for various magnetic fields from 10 to \(5.5 \times 10^4\) Oe. As clearly seen, the onset \(T_c\) suppressed from 8.0 K under 10 Oe to 3.1 K under \(5.0 \times 10^4\) Oe. The plots were made using the combination of the obtained \(T_c\) as a function of magnetic field and this is shown in Fig. 2(b). By applying the Werthamer–Helfand–Hohenberg (WHH) formula, \(H_{c2}(0) = 0.69[\delta H_{c2}/\delta T]_{T_c} T_c\), the upper critical field \(H_{c2}(0)\) was deduced to be \(5.5 \times 10^4\) Oe as an extrapolation point to \(T = 0\) K. This can be compared to \(H_{c2}(0) = 49 \times 10^4\) Oe reported for \(K_3C_{60}\) [12]. When the obtained \(H_{c2}(0)\) is employed to the equation of \(H_{c2}(0) = \Phi_0/[2\pi \xi^2]\), where \(\Phi_0 = 2.07 \times 10^{-15}\) Wb and \(\xi\) denote the fluxoid quantum and the coherence length of paired electrons, respectively, \(\xi\) can be estimated to be 7.7 nm.

In order to obtain the lower critical field \(H_{c1}\), the magnetic moments have been measured as a function of magnetic field under various temperatures as shown in Fig. 3. In each plot, the \(H_{c1}\) was estimated from the departure away from a linear behavior. These \(H_{c1}\) values were then plotted as a function of \(T\) as displayed in Fig. 3(b). The value of \(H_{c1}(0)\) was obtained to be 78 Oe from the extrapolated end point as \(T \to 0\) K according to the equation \(H_{c1}(T) = H_{c1}(0)[1 - (T/T_c)^2]\). This value is slightly lower than that of 132 Oe reported for \(K_3C_{60}\) [12].

Using the equation \(H_{c1}(0) = [\Phi_0/(4\pi \xi^2)] \ln(\lambda/\xi)\) together with \(\xi \approx 7.7\) nm, the penetration depth \(\lambda\) can be estimated to be 270 nm. Using the two values of \(\lambda\) and \(\xi\) estimated from \(H_{c1}(0)\) and \(H_{c2}(0)\) in the present study, \(\kappa = \lambda/\xi\) can be evaluated to be 35. This value is larger than \(1/5\) and thus indicates that \(Ba_8Si_{46}\) is classified as a type II superconductor. The physical parameters of \(Ba_8Si_{46}\) and \(K_3C_{60}\) described earlier are listed in Table 1. The common feature between \(Ba_8Si_{46}\) and \(K_3C_{60}\) is the coherence length spreading over a few cluster units. The differentiated features are the possible phonons associated with the electron paring and the density of states at the Fermi level, where high-frequency phonons are the predominant factor giving \(T_c\) in \(K_3C_{60}\) and the high density of states is important in \(Ba_8Si_{46}\).

The resistivity of \(Ba_8Si_{46}\) is reported to be \(2.5 \times 10^{-3}\) Ohm cm for its pelletized bulk sample [11]. Applying a three-dimensional free electron system to \(Ba_8Si_{46}\) for the estimation of resistivity \(\rho = m_e/(ne^2\tau)\), here \(m_e\) is the mass of an electron, \(n\) is the carrier concentration, and \(\tau\) is the relaxation time, \(\tau = 9.77 \times 10^{-17}\) s can be deduced. In this calculation, \(n = 1.45 \times 10^{22}\) cm\(^{-3}\) calculated from the cubic lattice constant of 1.0328 nm was used. Combining this value to the mean free path \(\ell = v_F\tau\), where \(v_F = (h/m_e)(3\pi^2n)^{1/3}\) denotes the Fermi velocity and can be estimated to be \(8.74 \times 10^7\) cm s\(^{-1}\), \(\ell\) can roughly be estimated to be 0.1 nm. Although the validity of this estimation may not be sufficient, this indicates that the mean free path is in the order of the unit length of the polyhedral \(Si_{20}\) and that the superconductivity in \(Ba_8Si_{46}\) is categorized to be in the dirty limit of \(\ell \ll \xi\).

Referring to the physical parameters obtained in the present studies together with those reported for \(K_3C_{60}\), we will compare the features between the two cluster superconductors of \(Ba_8Si_{46}\) and \(K_3C_{60}\). The most important parameters would be phonon frequencies \(\omega\) and \(N_E\). \(K_3C_{60}\) has high \(\omega\) and relatively high \(N_E\) [13], while \(Ba_8Si_{46}\) possesses medium \(\omega\) and extremely high \(N_E\) [9,14]. These features can account for the relatively high \(T_{c}\)'s of 19.3 and 8.07 K in these cluster superconductors.

### 3.2. Superconductivity in \(Si_{100}\) and \(Ge_{100}\) networks: rattling phonons in the open cage potentials

We will demonstrate another clathrate, so-called type III, where \(IV_{20}\) cages are arranged helically as shown in Fig. 4. In this structure remarkable rattling motions are expected due to the existence of the large spaces in the open cage structure. Fig. 5 shows electric resistivities of \(Ba_{24}IV_{100}\) (\(IV = Si\) and \(Ge\)) materials under pressure [15]. Resistivity changes drastically around 200 K under normal
pressure in the case of Ba$_{24}$Ge$_{100}$ (Ref. [16]). In contrast, such phase transitions were not observed for Ba$_{24}$Si$_{100}$. Furthermore, the critical temperature $T_c$ of superconducting state rises interestingly by applying pressure for Ba$_{24}$Ge$_{100}$ (Ref. [17]), while the same influence decreases the $T_c$ for Ba$_{24}$Si$_{100}$. Since the framework structure made from the IV$_{20}$ polyhedral arrangement is the same between Si$_{100}$ and Ge$_{100}$ in the Bravais lattice, it is most likely that the differences observed in Ba$_{24}$Si$_{100}$ and Ba$_{24}$Ge$_{100}$ are associated with the Ba-rattling motions residing inside the hollow cage in the lattice.

There are three kinds of Ba atoms in Ba$_{24}$IV$_{100}$ (IV = Si and Ge) from the crystallographical viewpoint as is seen in Fig. 4. In order to see the differences in the rattling motion of Ba between Ba$_{24}$Si$_{100}$ and Ba$_{24}$Ge$_{100}$, an MEM (maximum entropy method) refinement has been performed. Fig. 6 showed the density maps of these three kinds of Ba atoms at 100 K [15]. Immediately we can recognize that the Ba(3) accommodated in the open cage structure rattles in a very anisotropic fashion, while Ba(1) and Ba(2) atoms do isotropically in the case of the Ge$_{100}$ network. When similar analyses were adopted to the Si$_{100}$ network.
network, such anisotropic electron distributions were not observed even at 100 K. The Ba(3) atoms showing large thermal vibrations at high temperatures will eventually move to a specific trapping site and the electron density map will statically become very anisotropic. The reason that such motion was not observed, even in the Ba(3) position in the case of Ba$_2$Si$_{100}$, is not apparent at the present stage. It is, however, conceivable that the hybridization of Ba 5d and 6s orbitals and the 3d orbitals of the Ge-polyhedra may play an important role in controlling such rattling motion other than a larger space in the Ge$_{100}$ network than that in Si$_{100}$ one.

4. Conclusion

Magnetic properties as a function of both temperature and magnetic field were measured in order to determine the lower and the upper critical fields, $H_{c1}$ and $H_{c2}$, for Ba$_8$Si$_{46}$. From these values, a various important superconducting parameters were deduced. The comparison of

![Graph showing magnetic field dependences of the magnetic moments for Ba$_8$Si$_{46}$ at various temperatures.](image)
these parameters to those of K₃C₆₀ indicate that the most prominent feature for giving a relatively high \( T_c \) in Si₄₆ superconductor family is the high density of states at the Fermi level, being in good agreement with the photoelectron spectroscopy data. As for the new superconductor families, Ba₂₂₄IV₁₀₀'s (IV = Si and Ge) were demonstrated.

The both superconductors showed a remarkably large differences in the physical parameters although the whole framework is crystallographically the same as each other. A possible contribution of the rattling phonons was described. It is interesting to see in the future whether the \( T_c \) can further be increased in these polyhedral network compounds by optimizing the electron–phonon coupling parameters in the framework of the BCS mechanism.

### Table 1

|                  | K₃C₆₀     | Ba₂₂₄Si₄₆ |
|------------------|-----------|-----------|
| \( T_c \) (K)    | 19.3 \(^a\) | 8.07      |
| \( H_{c1} \) (Oe) | 132 \(^a\) | 78        |
| \( H_{c2} \) (>10⁴ Oe) | 49 \(^a\) | 5.5       |
| \( \xi \) (nm)   | 2.6 \(^a\) | 7.7       |
| \( \lambda \) (nm) | 240 \(^a\) | 270      |
| \( \kappa = \lambda/\xi \) | 92 \(^a\) | 35       |
| \( \langle \omega \rangle_{ph} \) (K) | 1400 \(^b\) | 300 \(^c\) |
| \( N(E_F) \) (states eV⁻¹(C₆₀, Si₄₆)⁻¹) | 14 \(^b\) | 31 \(^c\) |

\(^a\)Ref. [12].  
\(^b\)Ref. [13].  
\(^c\)Ref. [9].

Fig. 4. Structure of type III clathrate (left). There are three kinds of Ba atoms in this structure. Ba(1), Ba(2) and Ba(3) are accommodated in closed IV₂₀ dodecahedra, pseudo-cubic and open cage, respectively (right).

Fig. 5. Resistivity of Ba₂₂₄Ge₁₀₀ and Ba₂₂₄Si₁₀₀ under several pressures.

Fig. 6. The equi-charge-density surfaces of Ba₂₂₄Ge₁₀₀ and Ba₂₂₄Si₁₀₀ obtained by MEM analyses for high-resolution X-ray data at 100 K.
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