Superconductivity and physical properties of $\text{Ba}_{24}\text{Si}_{100}$ determined from electric transport, specific-heat capacity, and magnetic susceptibility measurements


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Both $\text{Ba}_{24}\text{Si}_{100}$ and $\text{Ba}_{24}\text{Ge}_{100}$ with crystallographically identical structure are found to be superconducting at 1.4 and 0.27 K, respectively. Physical properties of this superconductor $\text{Ba}_{24}\text{Si}_{100}$ are studied by electric transport, specific heat capacity, and magnetic susceptibility measurements. The density of states at the Fermi level $N_{\text{F}}=0.148$ states eV$^{-1}$ (Si atom)$^{-1}$ and a distinct jump of $C_p$ at the superconducting transition temperature $\Delta C_p=0.272$ J K$^{-1}$ mol$^{-1}$ are obtained. An exponential fit of $C_p$ below the superconducting states gives an energy gap $2\Delta=0.423$ meV and shows that this is a superconductor having $s$-wave character or isotropic energy gap. On the basis of our experimental data other important physical parameters are also derived.

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I. INTRODUCTION

Among a variety of clathrates so far reported,1 the three types as shown in Fig. 1 have intensively been studied. The superconducting silicon network solid was discovered for Na$_2$Ba$_6$Si$_{46}$ by Yamanaka’s group in 1995,2 where Na and Ba atoms are accommodated as endohedral elements inside the silicon polyhedra of Si$_{20}$ and Si$_{24}$ in the type I clathrates. Subsequently, a binary system Ba$_8$Si$_{46}$ was successfully synthesized by the same group using high pressure syntheses.3

In the present paper, we have shown that the both silicon and germanium clathrates of $\text{Ba}_{24}IV_{100}$ ($IV=$Si and Ge) with

FIG. 1. (Color online) Three types of clathrates classified from type I to III. The type I consists of $IV_{20}$ dodecahedra and $IV_{24}$ tetrakaidecahedra and the type II consists of $IV_{20}$ and $IV_{28}$ hexakaidecahedra. The type III contains closed $IV_{20}$ with helical geometry, pseudocubic cases and open cages. The three kinds of cages are also shown using a ball and stick model.
identical crystal structure are superconductors. Because this a situation that superconductivity occurs both in the Si and Ge polyhedral network solids with crystallographically identical structure after the discovery of superconductivity for these families in 1995, the direct comparison on the fundamental physical parameters between these two superconductors shall give many important insights into the mechanism of superconductivity.9–11

We will exemplify that many physical properties are very much differentiated between Si and Ge polyhedral network solids even if their crystal structures are identical. Especially, it will be highlighted that \( T_c \) changes toward a reverse direction between Ba24Si100 and Ba24Ge100 upon high pressure. We will discuss the physical properties using the experimental data obtained from specific heat capacity \( C_p \) and magnetic susceptibility \( \chi \) measurements. The evolution of \( C_p \) and \( \chi \) as a function of temperature unambiguously shows that the system can be featured by a large electron-phonon coupling parameter.

II. EXPERIMENT

Ba24Si100 was synthesized under high pressure according to the previous method.\(^8\) It is noted that to improve the quality, precise control of both temperature and pressure was needed. Otherwise, superconducting Ba8Si46 and BaSi2 were also produced as contaminants. To obtain x-ray powder diffraction data of good counting statistics with high angular resolution, measurements were carried out at the SPring-8 BL02B2 beam line.\(^12\) For specific heat capacity measurements PPMS (Quantum Design), with a 3He dilution cryogenator and a heat capacity cell, was used. The ingot Ba24Si100 sample weighted by 2.7 mg was put on a platform with four straight wires to measure \( C_p \). In order to figure out the rattling motion, the same measurements were repeated three times at low temperatures below 20 K. Magnetic susceptibilities were measured by a superconducting quantum interference device (SQUID) (Quantum Design MPMS7) system. Ba24Si100 generally of 7.0 mg was wrapped by a thin plastic film for measurements. Magnetic susceptibilities of the conduction electrons were obtained by subtracting the magnetic moment values measured under 4 T from those under 6 T with a correction of the temperature dependent Curie term.

III. RESULTS AND DISCUSSION

A. Electric transport

The four-probe transport measurement using a \(^3\)He cryostat system showed that Ba24Si100 enters into a superconducting state at 1.4 K as shown in Fig. 2. No electronic phase transitions were observed until the superconductivity occurs, being different from that of Ba24Ge100 where a large resistivity upturn is reported at 200 K.\(^13\) The resistivity at room temperature reduces to one fifth with decreasing temperature. It is very important to emphasize that superconductivity occurs both in Si and Ge networks with the identical crystal structure, like diamond Si and Ge, and this is such an example.

We have employed ac susceptibility experiments on this sample in order to confirm whether the observed superconductivity is bulk superconductivity as shown in the inset of Fig. 2. The volume of Ba24Si100 was estimated to be 1.44 mm\(^3\) using the lattice parameter of 0.73 mm\(^3\) and Sn (0.49 mm\(^3\)) as internal standards indicates that Ba24Si100 is a real bulk superconductor.

It is reported that the \( T_c \) observed in Ba24Ge100 at ~270 mK was eventually elevated until 3.8 K by applying pressure of 2.7 GPa,\(^6\) which is generally very unusual in the conventional superconductors. Therefore, we have repeated the experiments. As shown in Fig. 3 (right), the \( T_c \) actually rises to 3.2 K under 1.5 GPa. We have also examined how the \( T_c \) of Ba24Si100 changes upon pressure until 1.15 GPa and found that, in contrast to the situation encountered for Ba24Ge100, the \( T_c \) decreases a little as shown in Fig. 3 (left). No structural change has been confirmed in Ba24Si100 by x-ray diffraction studies under high pressure up to 3 GPa and this is also consistent with the recent high pressure Raman studies.\(^14\)

The temperature dependence of the resistivity was not perfectly linear, and small deformation was observed. Since the lattice parameter of the network does not significantly change, such deformation will not be due to the change in the polyhedral framework. The rattling motion of Ba atoms inside the cluster cages may be related to this phenomenon. Actually, as reported in the crystallographically identical Ba24Ge100 with a larger accommodation space inside the cluster cage, resistivity drastically changes at 200 K from...
a high metallic state to a low metallic one. It should be noted that the resistivity at 300 K of Ba$_{24}$Si$_{100}$ is 50 m$\Omega$ cm and this is larger by 50 times than 1 m$\Omega$ cm of Ba$_{24}$Ge$_{100}$ at 300 K.

### B. Magnetic susceptibilities

The magnetic susceptibility of Ba$_{24}$Si$_{100}$, measured under high magnetic fields using SQUID, was nearly temperature independent and indicates Pauli magnetism. The isolated spin number giving the Curie term appearing at low temperatures was estimated to be 0.063 spins/mol for Ba$_{24}$Si$_{100}$ in the present case, per lattice and was apparently ascribed to the defects in the crystal. The temperature evolutions of the magnetic susceptibilities after the correction of Curie terms are shown in Fig. 4. The temperature-independent value $\chi_{\text{const}}$ was $-1.54 \pm 0.12 \times 10^{-3}$ emu mol$^{-1}$ considering the scattering error of the present data. In the same figure, $\chi_{\text{const}}$ of Ba$_{24}$Ge$_{100}$ is also displayed at low temperatures and high temperatures straddling the electronic phase transition at 200 K. For extracting the intrinsic Pauli magnetic terms from these data, core diamagnetic susceptibilities were calculated using the values in the literature: $-24 \times 10^{-6}$ for Ba$^{2+}$, $-3.1 \times 10^{-6}$ for Si, and $-7.7 \times 10^{-6}$ emu mol$^{-1}$ for Ge, giving $\chi_{\text{core}}$ values of $-0.888 \times 10^{-3}$ for Ba$_{24}$Si$_{100}$ and $-1.35 \times 10^{-3}$ emu mol$^{-1}$ for Ba$_{24}$Ge$_{100}$.

Although the concept of diamagnetic susceptibilities produced from the ring current $\chi_{\text{ring}}$ in the polyhedral cluster solids has not fully been established, such corrections are known to be needed. Using the modified Pauling’s formula for handling the Larmor diamagnetic susceptibility, $\chi_{\text{ring}} = \frac{[Z \cdot N_A \cdot (e^2/12mc^2)]^2}{4 \pi^2}$ emu mol$^{-1}$, $\chi_{\text{ring}}$ is evaluated to be $-3.28 \times 10^{-3}$ for Ba$_{24}$Si$_{100}$ and $-3.59 \times 10^{-3}$ emu mol$^{-1}$ for Ba$_{24}$Ge$_{100}$. In the formula, $Z$ denotes the number of electrons involved in the cyclic ring current formation, $N_A$ is Avogadro’s number, $e$ is the Coulomb charge of an electron, $m$ is the mass of an electron, and $c$ is the speed of light. We used the number of elements constructing polyhedral $IV_{20}$ in the Bravais lattice as $Z$. These corrections gave the $\chi_{\text{Pauli}}$ values to be $2.63 \times 10^{-3}$ for Ba$_{24}$Si$_{100}$ as well as $2.79 \times 10^{-3}$ for high-$T$ and $2.10 \times 10^{-3}$ emu mol$^{-1}$ for low-$T$ phases of Ba$_{24}$Ge$_{100}$.

Another method of estimation for $\chi_{\text{Pauli}}$ has been made. Knowing that the ratio of $N_{E_F}$ values in high-$T$ phase to that in low-$T$ phase of Ba$_{24}$Ge$_{100}$ achieved from soft x-ray photoelectron spectroscopy (XPS), the $\chi_{\text{Pauli}}$ values can be directly extracted. We have studied the electronic states in the vicinity at the Fermi level using XPS at a high energy radiation facility. As shown in Fig. 5, the density of states at the Fermi level $N_{E_F}$ of Ba$_{24}$Ge$_{100}$ measured at 300 K reduced at 20 K to a very low value. The change in $N_{E_F}$ observed at 20 K is due to the electronic phase transition, being consistent with the idea of the rattling motion of the endohedral Ba atoms. These situations are consistent with maximum entropy method (MEM) analyses described later in the present paper.

By optimizing the value of $\chi_{\text{dia}}$ as an off-set parameter so that the $N_{E_F}$ observed by XPS can be explained, the...
The equi-charge-density surfaces of Ba$_{24}$Si$_{100}$ and Ba$_{24}$Ge$_{100}$ obtained by MEM analyses for high resolution x-ray data at 80 K.

\[ \psi_{Pauli}^{2} = \psi_{con}^{2} \frac{\chi_{dia}}{\chi_{ring}} \]

This method gives more reliable experimental diamagnetic susceptibility \( \chi_{dia} \) of Ba$_{24}$Ge$_{100}$ to be \(-3.11 \times 10^{-3} \) emu mol$^{-1}$. When the value of Ba$_{24}$Ge$_{100}$ is scaled to that of Ba$_{24}$Si$_{100}$ using the ratio in \( \chi_{ring} \) described earlier, \( \chi_{dia} \) of Ba$_{24}$Si$_{100}$ is estimated to be \(-2.50 \times 10^{-3} \) emu mol$^{-1}$. As a result, the \( \psi_{Pauli} \) values can be obtained to be \(9.59 \times 10^{-6} \) emu (Si mol)$^{-1}$ for Ba$_{24}$Si$_{100}$, \(9.65 \times 10^{-6} \) emu (Ge mol)$^{-1}$ for the high-$T$ phase, and \(2.75 \times 10^{-6} \) emu (Ge mol)$^{-1}$ for the low-$T$ phase of Ba$_{24}$Ge$_{100}$. From the relationship \( \psi_{Pauli}^{2} = 2\mu_{B}^{2}N_{F}E_{F} \frac{D}{k_{B}T} \)

the \( N_{F}E_{F} \) values are determined to be 0.148 states eV$^{-1}$ (Si atom)$^{-1}$ for Ba$_{24}$Si$_{100}$, 0.149 states eV$^{-1}$ (Ge atom)$^{-1}$ for the high-$T$ phase, and 0.0427 states eV$^{-1}$ (Ge atom)$^{-1}$ for the low-$T$ phase of Ba$_{24}$Ge$_{100}$.

There are three kinds of Ba atoms in Ba$_{24}$JV$_{100}$ (JV=Si and Ge) from the crystallographic viewpoint as is seen in Fig. 1. In order to see the differences in the rattling motion of Ba between Ba$_{24}$Si$_{100}$ and Ba$_{24}$Ge$_{100}$, a MEM/Rietveld method has been performed. The MEM analysis was carried out with a program ENIGMA. Figure 6 showed the equi-charge-density surfaces of these three kinds of Ba atoms at 80 K. 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, such anisotropic electronic distributions were not observed even at 80 K. The Ba(3) atoms showing large thermal vibrations at high temperatures will eventually move to a specific trapping site and the equi-charge-density surface will statically become very anisotropic. The reason that such motion was not observed, even in the Ba(3) position in the case of Ba$_{24}$Si$_{100}$, is not apparent at the present stage. It is, however, conceivable that the hybridization of Ba 5$d$ and 6$s$ orbitals and the 3$d$ orbitals of the Ge polyhedra may play an important role in controlling such a rattling motion other than a larger space in the Ge$_{100}$ network than that in Si$_{100}$ one.

\[ C_{p}(T) = \frac{\Delta C_{p}}{2T_{c}} \frac{T_{c}}{T} \]

where \( \Delta C_{p} \) is the specific heat capacity jump at \( T_{c} \) and \( T \) is the temperature.

### C. Specific heat capacity

Specific heat capacity \( C_{p} \) of Ba$_{24}$Si$_{100}$ is shown in Fig. 7. The specific heat jump at \( T_{c} \)=1.4 K corresponds to the superconducting phase transition observed in electric transport. The evolution of \( C_{p} \) as a function of temperature under the superconducting state can be fitted well using an exponential function of \( C_{p}(T) = \exp[-\Delta/k_{B}T] \) better than \( T^{2} \) function as shown in Fig. 7. This indicates that the superconductivity can be categorized as a $s$-wave superconductor or a superconductor having an isotropic energy gap. The superconducting energy gap can be estimated to be \( \Delta = 0.423 \) meV. It is noted here that the \( C_{p} \) data below 8 K scatters to a small extent. Considering the fact that \( C_{p} \) greatly changes at 200 K in Ba$_{24}$Ge$_{100}$ due to the influences of the Ba rattling in the open cage structure, this phenomenon will be most likely due to the rattled Ba atoms. Although we do not have any exact explanations on this unconventional feature, this was gradually suppressed while the temperature scans were repeated. Therefore, nevertheless of the \( C_{p} \) fluctuations, the Sommerfeld parameter \( \gamma \) was able to be estimated as \( 0.182 \) J K$^{-2}$ mol$^{-1}$. From the \( C_{p} \) by applying a standard method of the \( C_{p}/T \) vs \( T^{2} \) relationship. When \( \Delta C_{p}/T_{c} = 1.43 \) derived in the weak coupling BCS regime is applied, the \( \gamma \) value was determined to be 0.136 J K$^{-2}$ mol$^{-1}$ as another estimation of \( \gamma \). These \( \gamma \) values in turn give \( N_{F}E_{F} \) to be 0.386 and 0.288 states eV$^{-1}$ (Si atom)$^{-1}$, respectively.

Owing to the rattling phonons existing at low temperatures, Debye \( \Theta_{D} \) and Einstein \( \Theta_{E} \) terms may not be obtained with good accuracy directly from the experimental data. Therefore, the \( \Theta_{D} \) value was empirically estimated using the \( \Theta_{D} \) and \( \Theta_{E} \) values of Ba$_{24}$Ge$_{100}$. For this purpose, the following equation can be applied:

\[ \Theta_{D}(Ba_{24}Si_{100}) \sim \left[ a_{D}(Ba_{24}Ge_{100})/a_{D}(Ba_{24}Si_{100}) \right] \times \Theta_{D}(Ba_{24}Ge_{100}) \]

where \( \nu \) is the sound velocity. Because the Ba rattling occurs
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The Raman spectra measured for Ba$_2$Si$_{100}$ and Ba$_2$Ge$_{100}$ at 300 K. For comparison, the spectra of BaSi$_2$, Si, and Ge in the diamond type are displayed. The arrows indicate the corresponding shifts between Si and Ge as described in the text.

at a relatively high temperature of 200 K, hence, it will give little influence on the analyses. From this equation, $\Theta_p$ = 411 K was estimated for Ba$_2$Si$_{100}$ when $v$ (diamond Si) = 5.88 $\times$ 10$^3$ m s$^{-1}$, $v$ (diamond Ge) = 3.55 $\times$ 10$^3$ m s$^{-1}$ and $\Theta_D$ = 240 K for Ba$_2$Ge$_{100}$ (Ref. 13) were used. The Einstein $\Theta_E$ term was also been empirically scaled by the lattice parameters $a_0$ between Ba$_2$Si$_{100}$ and Ba$_2$Ge$_{100}$. The correlation between $\Theta_E$ values and lattice parameters can be seen for skutterudite and pyrochlore compounds. The $\Theta_E$ values of 44 and 104 K for Ba$_2$Ge$_{100}$ were employed, which were extrapolated to be 0.24 T. This leads to a Ginzburg-Landau coherence length $\xi$ = 372 Å using $\xi$ = $\Theta_p / D = 10^{-4}$ emu mol$^{-1}$ and $\gamma_{Pauli}$ = 2$\mu_B^2$ / ($341)$ m$^{-1}$ (38$^3$)$^1/2$. The mean free path $\ell$ of conduction electrons can be estimated to be 0.67 Å using $\ell = \mu_F / ($ne$^2$)$^1/2$. Here the resistivity $\rho$ = 10 mΩ cm and Fermi velocity $v_F = $hk$_F / m$ of 4.92 $\times$ 10$^7$ cm s$^{-1}$ were employed, and $k_F$ for the carrier concentration was estimated by the Seebeck coefficient. This concludes that Ba$_2$Si$_{100}$ is a superconductor classified as a dirty limit of $\xi < \ell$.

D. Superconducting parameters of Ba$_2$Si$_{100}$

In the concept of the Zintl phase$^{20}$ for (Ba$_{2+}$)$_{12}$(3b$_{14}$)$^{1/3}$(4b$^0$)$^{6}$(16e$^-$)$^{13}$ 16 electrons per Bravais lattice will be considered. Using the lattice constant of 1.407 nm for Ba$_2$Si$_{100}$, the electron carrier concentration is 5.75 $\times$ 10$^{21}$ cm$^{-3}$. This is roughly consistent with the carrier concentration $n$ of 2.60 $\times$ 10$^{21}$ cm$^{-3}$ obtained by measurements of the Seebeck coefficient. Applying a three-dimensional electron model to Ba$_2$Si$_{100}$ supposing the carrier concentration $n$ of 2.60 $\times$ 10$^{21}$ cm$^{-3}$, Fermi wave number $k_F$ of 4.25 $\times$ 10$^{-3}$ cm$^{-1}$ is obtained. Using the equations of $\gamma_{Pauli} = 2\mu_B^2 / (341)$ m$^{-1}$ (38$^3$)$^1/2$, $\gamma_{Pauli}$ and $\gamma_{exp}$ can be estimated to be 5.09 $\times$ 10$^{-4}$ emu mol$^{-1}$ and 0.371 J K$^{-2}$ mol$^{-1}$. Although the Ba rattling influences on the specific heat capacity as is pointed out earlier, it is indeed meaningful to have a large enhancement in the experimental $\gamma$ value ranging from 0.136 to 0.182 K$^{-2}$ mol$^{-1}$. Actually, the Wilson factor $R_W = (\pi^2 / 3) \mu_B^2 / (\gamma_{Pauli} / \gamma)$, calculated from the experimental $\gamma_{exp}$ and $\gamma_{Pauli}$, is from 0.38 to 0.51 and significantly small. This fact indicates that the system is controlled greatly by electron-phonon interactions rather than electron-electron ones. 

In order to explain the $T_c$ of 1.4 K using the McMillan equation, $T_c = (\Theta_p / 1.45) \exp(-[1.04(1 + \lambda)] / [\lambda - \mu^*)(1 + 0.62\lambda)])$, $\lambda = 0.399$ is needed for $\Theta_D = 411$ K if one can suppose $\mu^* = 0.1$ (the general value of $\mu^*$ ranges from 0.1 to 0.2). Here $\lambda = N_F^F / V$, V is the electron-phonon coupling parameter, and $\mu^*$ is the electron-electron repulsive screening parameter to the Cooper pairing attractive force. If this is the case, a large electron-phonon coupling strength must be constrained in this system considering that the $N_F^F$ is small.

From the evolution of specific heat as a function of magnetic field, $[\partial H_c / \partial T]$ can be estimated as a linear plot of $H_c$ vs $T_c$. Using the WHH equation of 0.69 $\times [\partial H_c / \partial T]_{T = T_c}$, the upper critical field of $H_c$ ($T = 0$) was extrapolated to be 0.24 T. This leads to a Ginzburg-Landau coherence length $\xi$ = 372 Å using $\xi = (\Theta_p / [2\pi^2 (\Theta_p/T_c(T_c = 0))]^{1/2}$. The mean free path $\ell$ of conduction electrons can be estimated to be 0.67 Å using $\ell = \mu_F / ($ne$^2$)$^1/2$. Here the resistivity $\rho$ = 10 mΩ cm and Fermi velocity $v_F = $hk$_F / m$ of 4.92 $\times$ 10$^7$ cm s$^{-1}$ were employed, and $k_F$ for the carrier concentration was estimated by the Seebeck coefficient. This concludes that Ba$_2$Si$_{100}$ is a superconductor classified as a dirty limit of $\xi < \ell$.

IV. CONCLUSION

Ba$_2$Si$_{100}$ was reported to superconduct like Ba$_2$Ge$_{100}$. Physical parameters were obtained for the Ba$_2$Si$_{100}$ superconductor from resistivity, specific heat capacity, and ac and dc magnetic susceptibility measurements. The physical parameters derived by these experiments implied that this system can be featured by the extremely strong electron-phonon coupling strength and is a superconductor in the dirty limit. The endohedral Ba atom rattling motion seems to be closely associated with this strong e-ph coupling parameter from the experimental viewpoint and this may open a route for searching exotic materials in the future.
Note Added in Proof. Recently, the superconductivity of Ba$_{24}$Si$_{100}$ was also confirmed\textsuperscript{21}.

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