

**High-pressure synthesis and superconductivity of LaGe<sub>5</sub> containing a tunnel germanium network**

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Superconducting LaGe<sub>5</sub> was synthesized by the reaction of La and Ge mixtures under a pressure of 5 GPa at 1200 °C. It crystallized in the orthorhombic space group *Immm* (No. 71) with  $a=4.0290(6)$ ,  $b=6.307(1)$ , and  $c=9.978(2)$  Å,  $V=253.54(6)$  Å<sup>3</sup>, and  $Z=2$ . Single-crystal studies revealed that LaGe<sub>5</sub> had a germanium network with tunnels running along the  $a$  axis, where La atoms are located. There are two crystallographically different Ge sites in the structure La[(Ge1)<sub>4</sub>(Ge2)<sub>1</sub>]. The tunnel network is composed of folded  $sp^3$ -Ge1 layers coupled by eight coordinated Ge2 atoms. Electrical resistivity and magnetic-susceptibility measurements showed that the compound was a type-II superconductor with a transition temperature of 7.0 K.

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**I. INTRODUCTION**

A rush of discoveries of copper oxide high-critical temperature ( $T_c$ ) superconductors started after the work of Bednorz and Müller in 1986,<sup>1</sup> and it has been established that the existence of the charge-controlled two-dimensional [CuO<sub>2</sub>] conducting layers is essentially important for the high- $T_c$  superconductivity. We are now in the second rush of discoveries of an increasing number of noncuprate superconductors. Although their  $T_c$ 's are not so high, they include a variety of structures, and interestingly most of them consist of layer-structured conducting skeletons such as [CuO<sub>2</sub>] layers in copper oxide superconductors. Some examples are Sr<sub>2</sub>RuO<sub>4</sub> ( $T_c \sim 1$  K) with [RuO<sub>2</sub>] layers,<sup>2</sup> Y<sub>2</sub>C<sub>2</sub>Br<sub>2</sub> ( $T_c \sim 10$  K) with [Y<sub>2</sub>C<sub>2</sub>] layers,<sup>3</sup> Li<sub>x</sub>KCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> ( $T_c \sim 6$  K) with [NbO<sub>2</sub>] layers,<sup>4</sup> Li<sub>x</sub>ZrNCl ( $T_c = 14$  K) with [ZrN] layers,<sup>5</sup> Li<sub>0.48</sub>(THF)<sub>y</sub>HfNCl ( $T_c = 25.5$  K) with [HfN] layers (THF: tetrahydrofuran),<sup>6</sup> and MgB<sub>2</sub> ( $T_c = 39.7$  K) with [B] layers,<sup>7</sup> and so on. Metal-doped fullerenes such as K<sub>3</sub>C<sub>60</sub> and RbCs<sub>2</sub>C<sub>60</sub> with  $T_c$ 's = 19 and 33 K, respectively,<sup>8,9</sup> are also superconductors with cage or porous structures, where the delocalization of the conducting electrons is restricted on the surface of polyhedra of fullerenes. A concept of superconductivity in porously delocalized chemical bonding topology was proposed by King<sup>10,11</sup> on the basis of graph theory-derived methods; superconductivity is favored when the electron mobility is restricted to fewer than three dimensions such that in as layers and cagelike geometries. Note that most of the more recent superconductors are characterized by this concept.

Among the more recent superconductors, there are a number of intermetallic compounds containing porous covalent networks composed of the elements near the so-called Zintl border, the vertical line on the Periodic Table between Groups 13 and 14. The above-mentioned MgB<sub>2</sub> with two-dimensional [ $sp^2$ -B] layers is the most fascinating example;<sup>7</sup> it established a record of a  $T_c$  of 39.7 K for alloys since Nb<sub>3</sub>Ge with  $T_c = 23.2$  K was studied 28 years ago.<sup>12</sup> Zintl phases exhibit a rich diversity of crystal structures, and could be interesting materials to investigate structure and property relationships. Binary silicides with alkaline-earth

and rare-earth metals contain a variety of Si networks and clusters. Those include isolated Zintl anions Si<sub>4</sub><sup>4-</sup> in BaSi<sub>2</sub>,<sup>13</sup> two-dimensional layers in trigonal CaSi<sub>2</sub>,<sup>14,15</sup> and different types of three-dimensional networks in SrSi<sub>2</sub>,<sup>13</sup> LaSi<sub>2</sub>,<sup>15-17</sup> and clathrate structures.<sup>18,19</sup> The type-I silicon clathrates ( $M_x$ Si<sub>46</sub>) consist of the metal-containing Si<sub>20</sub> dodecahedra ( $M @ Si_{20}$ ) and Si<sub>24</sub> tetrakaidecahedra ( $M @ Si_{24}$ ), which are connected by shared faces. This structure is also characterized as a compound having a cagelike covalent skeleton. We have recently succeeded in preparing the Ba-containing silicon clathrate compound (Na, Ba)<sub>x</sub>Si<sub>46</sub>, and found that the compound exhibited superconductivity of  $T_c \sim 4$  K.<sup>20,21</sup> The binary silicon clathrate Ba<sub>8</sub>Si<sub>46</sub> was prepared using high-pressure and high-temperature (HPHT) conditions (3 GPa, 800 °C), which showed superconductivity of  $T_c = 8.0$  K.<sup>22,23</sup> Theoretical studies on the band structures were reported by Saito and Oshiyama<sup>24</sup> and Moriguchi, Munetoh, and Shintani.<sup>25</sup> It is interesting to note that the silicide networks are responsive to a pressure treatment, and superconductors with porous networks have been derived using a HPHT treatment. The superconducting BaSi<sub>2</sub> ( $T_c = 6.8$  K) isotypic with the trigonal layer-structured CaSi<sub>2</sub> is a high-pressure phase.<sup>26</sup> The layer-structured CaSi<sub>2</sub> transforms into another layer structure of the AlB<sub>2</sub> type under a pressure higher than 14 GPa, which shows superconductivity of  $T_c = 14.0$  K under the pressure.<sup>27,28</sup> A clathrate compound Ba<sub>24</sub>Si<sub>100</sub> composed of Ba@Si<sub>20</sub> polyhedra was prepared using a moderate range of pressure of  $\sim 1.5$  GPa at 800 °C.<sup>29</sup>

Studies have been made of synthesis of binary germanide analogs. We prepared the germanium clathrate compound Ba<sub>24</sub>Ge<sub>100</sub> isotypic with Ba<sub>24</sub>Si<sub>100</sub> under an ambient pressure.<sup>30-32</sup> Recently, Grosche *et al.*<sup>33</sup> reported that Ba<sub>24</sub>Ge<sub>100</sub> showed superconductivity of  $T_c = 0.24$  K. The superconductivity was sensitive against pressure, and the  $T_c$  was raised up to 3.8 K by applying a pressure of 2.7 GPa.<sup>33</sup> In this study, an attempt has been made to prepare a Ge-rich compound in the binary system La-Ge in an effort to explore a Ge-based porous skeleton. The presence of La<sub>3</sub>Ge, La<sub>5</sub>Ge<sub>3</sub>, La<sub>4</sub>Ge<sub>3</sub>, La<sub>5</sub>Ge<sub>4</sub>, LaGe, and LaGe<sub>2</sub> is known in this binary system.<sup>34-38</sup> Those were prepared by a simple melting of the constituent mixtures in ambient pressure. We

TABLE I. Crystallographic data and atomic parameters of  $\text{LaGe}_5$ . The space group is  $Immm$  (No. 71), the lattice constants are  $a = 4.0290(6)$ ,  $b = 6.307(1)$ ,  $c = 9.978(2)$  Å;  $V = 253.54(6)$  Å<sup>3</sup>;  $Z = 2$ , and  $R/R_w[I > 3\sigma I] = 0.028/0.036$  for 872 reflections (185 unique peaks).

Atom	$x$	$y$	$z$	$B_{eq}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
La	0	0	0	1.05(3)	0.0131(8)	0.0119(8)	0.0149(9)	0	0	0
Ge1	0.5	0.2994(2)	0.8280(2)	1.30(3)	0.0170(8)	0.0143(7)	0.0183(9)	0	0	0.0008(6)
Ge2	0	0.5	0	1.71(7)	0.029(2)	0.015(1)	0.020(2)	0	0	0

have tried to prepare a Ge-rich phase using HPHT conditions, and found a phase  $\text{LaGe}_5$  with a different framework, which shows superconductivity with a  $T_c$  of 7.0 K. This compound has no counterpart in the La-Si binary system.

## II. EXPERIMENTAL SECTION

Powder samples of  $\text{LaGe}_5$  were synthesized by the following two-step reactions: flakes of lanthanum metal (Furuuchi Chemical 99.9%) and germanium (Mitsuba Pure Chemical 99.999%) were mixed with a stoichiometric composition of La:Ge = 1:5, and the mixture was subjected to reaction in an arc furnace in an Ar atmosphere. The resulting silver metallic product was a mixture of  $\text{LaGe}_2$  of the  $\alpha$ - $\text{ThSi}_2$  structure and unreacted Ge. It was ground in an Ar-filled glove box, and then put into an  $h$ -BN cell (5 mm in inner diameter and 5 mm in depth). The cell was placed in a carbon tube heater, and was put in a pyrophyllite cube as a pressure medium ( $20 \times 20 \times 20$  mm<sup>3</sup>). The cube was pressed at 5 GPa in a multianvil assembly and heated at 1200 °C for 30 min, followed by quenching to room temperature. The pressure was gradually released at room temperature. X-ray powder-diffraction (XRD) patterns were measured using graphite monochromated  $\text{CuK}\alpha$  radiation. The obtained sample was analyzed for magnetic properties by a superconducting quantum interference device magnetometer (Quantum Design MPMS-5) and for electrical resistivity by a dc four-probe method (van der Pauw method).

Single crystals of  $\text{LaGe}_5$  were obtained from the product with a mixed molar ratio of La:Ge = 1:8. The mixture was pressed at 5 GPa and heated to 1200 °C, then the temperature decreased to 900 °C at a cooling rate of 100 °C/h. In this reaction excess germanium acted as a mother liquid for  $\text{LaGe}_5$  single crystals. After quenching the product from 900 °C to room temperature, many single crystals of  $\text{LaGe}_5$  were obtained in the Ge matrix. A single crystal suitable for the x-ray single-crystal structure analysis with dimensions of  $0.15 \times 0.05 \times 0.02$  mm<sup>3</sup> was selected and its intensity data were collected on a Rigaku R-AXIS imaging plate area de-

tektor with graphite monochromated  $\text{MoK}\alpha$  radiation. The structure was solved by direct methods using the CRYSTAL-STRUCTURE crystallographic software package.<sup>39</sup> The crystallographic data and atomic parameters of  $\text{LaGe}_5$  are listed in Tables I and II, respectively. The chemical composition of  $\text{LaGe}_5$  was determined to be La:Ge = 1:4.97 on six single crystals by an electron probe microanalyzer (EPMA) (JEOL JCMA-733II). The composition is in good agreement with the result of the x-ray refinement.

## III. RESULTS AND DISCUSSION

The crystal structure determined for  $\text{LaGe}_5$  is shown in Fig. 1. This is a Ge-rich compound in the La-Ge system. It crystallized in the orthorhombic space group  $Immm$  with lattice constants of  $a = 4.0290(6)$ ,  $b = 6.307(1)$ , and  $c = 9.978(2)$  Å, and  $V = 253.54(6)$  Å<sup>3</sup>. The structure of  $\text{LaGe}_5$  is characterized as a unique germanium network with channels running along the  $a$  axis, where lanthanum atoms are situated. The framework is composed of two types of germanium atoms, Ge1 and Ge2. The Ge1 atoms are tetrahedrally coordinated by three different Ge1 atoms with bond distances of 2.531(3) and 2.621(2) Å  $\times 2$ , forming buckled layers. The buckled layers are composed of six-membered rings of Ge1 atoms in a boat-type conformation. Note that the buckled layer is very similar to that of black phosphorus, although the latter layers are composed of six-membered rings in a chair-type conformation. The bond angles of 104.0° and 100.3° in  $\text{LaGe}_5$  are smaller than the normal tetrahedral angle of 109.47°. In Fig. 2 the structure of the buckled layers of black phosphorus in the chair conformation is shown. Most layer-structured compounds with six-membered rings such as P, As, Bi, Sb,  $\text{CaSi}_2$ , and  $\text{EuGe}_2$  (Ref. 40) adapt the chair conformation. The boat conformation found in  $\text{LaGe}_5$  is very rare.

The Ge2 atoms connect the Ge1 buckled layers to form a three-dimensional framework leaving tunnels. The Ge2 atoms have a quite unique coordination number of 8. The relatively long distance of 2.93 Å between Ge2 and Ge1 atoms is

TABLE II. Selected interatomic distances (Å) and bond angles (°) in  $\text{LaGe}_5$ .

Ge1-Ge1	2.621(2) $\times 2$ ,	2.531(3)	Ge2-Ge1	2.933(1) $\times 8$
Ge1-Ge2	2.933(1) $\times 2$		Ge2-La	3.154(1) $\times 2$
Ge1-La	3.251(1) $\times 8$			
$\angle \text{Ge1-Ge1-Ge1}$	103.75(7),	100.48(11)		
$\angle \text{Ge1-Ge2-Ge1}$	51.11(6),	86.74(5)		

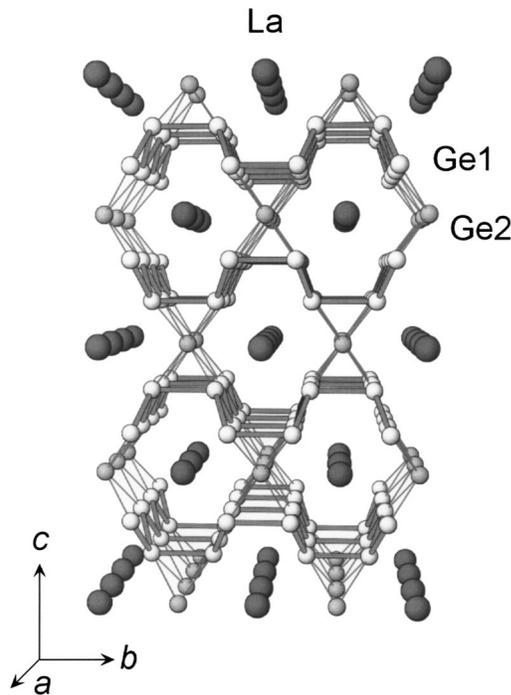


FIG. 1. Schematic illustration of the crystal structure of  $\text{LaGe}_5$  with buckled Ge layers. La atoms (large circles) occupy the center of the tunnels running along the  $a$  axis. Small bright and dark circles represent two types of Ge sites, Ge1 in the buckled layers and Ge2 between the layers, respectively.

due to the large coordination number of Ge2 atoms. Although such a high coordination number for Ge was not found in other germanides, a similar arrangement is found in the body-centered tetragonal structure of the high-pressure phase of Sn.<sup>41</sup> Each La ion is coordinated by ten Ge atoms: eight Ge1 atoms through the lone pairs at a distance of

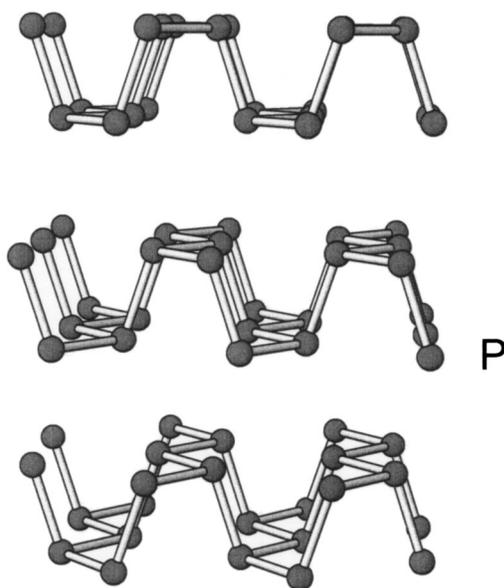


FIG. 2. Schematic illustration of the buckled layers of black phosphorus with six-membered rings in the chair conformation.

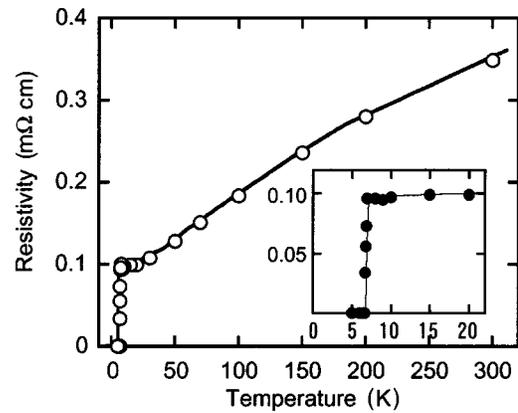


FIG. 3. Temperature dependence of resistivity of  $\text{LaGe}_5$  in a range of 5–300 K. The inset shows the low-temperature data near the critical temperature.

3.251(1) Å and two Ge2 atoms at a distance of 3.154(1) Å, which are comparable with the Ge-La distances of 3.11–3.82 Å found in  $\text{La}_5\text{Ge}_3$  and  $\text{LaGe}_2$ .<sup>35</sup>

The XRD pattern of the powder sample was in good agreement with the pattern obtained from the single crystal, and all the diffraction peaks could be indexed on the basis of the single-crystal data. The physical properties were measured using the powder samples. The temperature dependence of the resistivity of  $\text{LaGe}_5$  was measured and the result is shown in Fig. 3. The compound attained the zero resistivity at 6.9 K. Figure 4 shows the temperature dependence of the magnetic susceptibility of  $\text{LaGe}_5$  measured under a field of 20 Oe. The magnetic susceptibility starts to decrease at 7.0 K and becomes diamagnetic due to the superconducting transition, consistent with the result of the resistivity measurement. The magnetic shielding fraction in the zero-field-cooled measurement at 3 K is calculated to be about 80% of the theoretical value for perfect diamagnetism; this together with the sizable Meissner (field-cooled) effect (30%) indicate that  $\text{LaGe}_5$  is a bulk superconductor. In the La-Ge system,  $\text{LaGe}_2$  with the  $\text{GdSi}_2$  structure (the distorted  $\alpha$ - $\text{ThSi}_2$  structure) has only been known as a superconductor with a  $T_c$  of

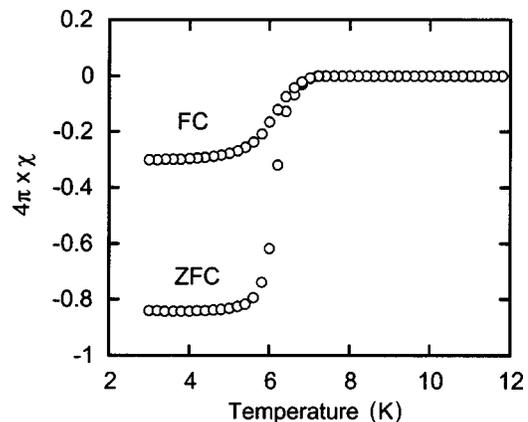


FIG. 4. Temperature dependence of the susceptibility of  $\text{LaGe}_5$  measured in a magnetic field of 20 Oe for zero-field-cooling (ZFC) and field-cooling (FC) modes.

2.65 K.<sup>42,43</sup> LaGe<sub>5</sub> is the second superconductor in this system.

The Ge1 atom in the buckled layer should have a  $sp^3$  configuration, forming three Ge1-Ge1 bonds and a lone electron pair. According to the Zintl-Klemm rule, each Ge1 has a formal charge of Ge<sup>-1</sup> isoelectronic with arsenic, and should fulfill the octet. La atoms should be ionized to provide electrons to the buckled Ge1 layers. However, the electrons are not sufficient to complete the octet. The electronic state of Ge2 is not clear.

We also performed the band calculation for LaGe<sub>5</sub> using the WIEN97 package with a general potential linear augmented plane-wave code.<sup>44</sup> The density-of-states (DOS) diagram around the Fermi level ( $E_F$ ) is given in Fig. 5. It is clear from the DOS diagram that LaGe<sub>5</sub> is metallic. The sharp band at about 2.5-eV above  $E_F$  is attributed to empty  $4f$  orbitals of lanthanum atoms. The band lying across the Fermi level is mainly contributed by the  $4s$  and  $4p$  orbitals of Ge1 atoms. The contribution of Ge2 atoms to the conduction band is small. The La state is weakly hybridized with the conduction band, therefore, in this electronic system, lanthanum plays a role of carrier donor to the germanium network.

#### IV. CONCLUSION

We have described superconductor, LaGe<sub>5</sub>, with  $T_c = 7.0$  K. The compound was synthesized by a reaction under a pressure of 5 GPa at 1200 °C. The compound was found to contain a germanium network composed of buckled  $sp^3$ -Ge1 layers coupled with eight coordinated Ge2 atoms. The band calculation of this compound shows that the bands lying across the Fermi level are mixed states of germanium  $s$  and  $p$  states, and the La atoms contribute mainly as electron donors for the germanium network. It should be noted that LaGe<sub>5</sub> consists of a layered or porous conducting skeleton. The buckled covalent bonded layers resemble those of black phosphorus, but the six-membered rings have the boat conformation rather than the chair one of the normal buckled layers. This is the layer-structured germanium superconducting skeleton. The chemical bonding of the eight coordinated Ge atoms and the contribution to the superconductivity are interesting mysteries that remain to be solved.

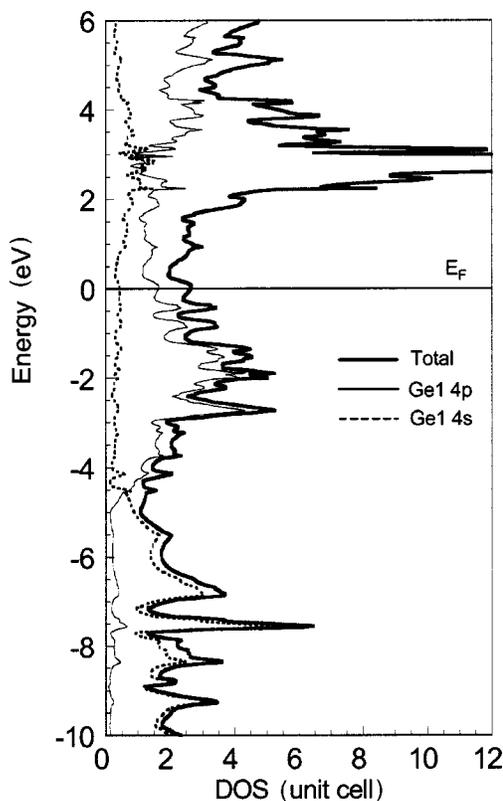


FIG. 5. The DOS for LaGe<sub>5</sub>. The thick line corresponds to the total DOS for LaGe<sub>5</sub>. The dotted and thin solid lines correspond to the  $4s$  and  $4p$  states of Ge1 atoms, respectively. The contributions of La and Ge2 atoms are not shown in the figure for simplification.

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