Electronic Structure of Novel Binary Superconductor SrGe$_2$: A First-Principles Study

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Abstract. Due to the simplicity of its composition, many binary superconductors have been developed so far. Some are practically used like Nb$_2$Ge, and others have high $T_c$ like MgB$_2$ or single layer FeSe. Recently we discovered that tetragonal SrGe$_2$_d shows superconductivity by high pressure synthesis. This compound attracts our attention because it has the highest $T_c$ among AGe$_2$ series ($A$: alkaline-earth or rare-earth element). In this paper we investigated the electronic structure of SrGe$_2$ from first principles. There are several polymorphs of SrGe$_2$, and the obtained density of states at the Fermi level ($=D(E_F)$ per SrGe$_2$) is 1.00, 1.20, 1.12 eV$^{-1}$ for trigonal, hexagonal and tetragonal structure, respectively. $D(E_F)$ of tetragonal SrGe$_2$ is not more than the isostructural and isovalent compound BaGe$_2$, which has lower $T_c$ than SrGe$_2$.

1. Introduction

Now that quantum computers are becoming a reality, the necessity of developing new superconductors is increasing more and more. Among them, binary superconductors are very important in terms of their applications because of their simple composition. For example, Nb$_2$Ge and MgB$_2$ are used as superconducting wires. Moreover, some binary superconductors have very high $T_c$, such as MgB$_2$, monolayer FeSe, and H$_3$S with applying very high pressure.

Recently we have discovered a new binary superconductor SrGe$_2$_d, which has ThSi$_2$-type tetragonal structure[1]. SrGe$_2$ has several polymorphs. It crystalizes into BaSi$_2$-type orthorhombic structure under ambient pressure, and transforms to EuGe$_2$-type trigonal structure under high pressure[2]. This experimental result is also supported by a theoretical study using first-principles calculation[3]. Therefore, our finding of the tetragonal phase of SrGe$_2$ (hereafter called $te$-SrGe$_2$) is rather unexpected. The band structure calculation of this $te$-SrGe$_2$ has not been reported yet. There are several binary superconductors MX$_2$ (M=Ba,Sr,La; X=Si,Ge) which have the same crystal structure as $te$-SrGe$_2$. Interestingly, $te$-SrGe$_2$ has the highest $T_c$ among them.

The crystal structure of $te$-SrGe$_2$ has also a unique feature. Focusing on the network of Ge atoms, it forms the same network as what is called hyper-graphite or 3D-honeycomb lattice. There are intensive studies on hyper-graphite, and there are reported novel electronic structure such as Dirac point and Dirac loop [4-6]. It is interesting whether $te$-SrGe$_2$ has also the similar electronic state.

In this paper, we investigated the electronic structure of SrGe$_2$ by first-principles calculation. We found that the calculated density of states at the Fermi level ($=D(E_F)$) is much larger than that of the...
trigonal phase, and comparable with the AlB$_2$-type hexagonal phase. We also compare the electronic structure of tetragonal BaGe$_2$, SrGe$_2$ and SrSi$_2$ and found that they have pseudo-Dirac points, where three bands are entangled instead of two.

2. Methods
We have calculated the electronic structure of tetragonal BaGe$_2$, SrGe$_2$ and SrSi$_2$ from first-principles. As for SrGe$_2$, we also calculated that for three types of crystal structure: tetragonal, trigonal and hexagonal one. This calculation is based on the density functional theory (DFT) and the full-potential linearized augmented plane wave method (FLAPW), and the exchange-correlation potential is approximated by general gradient approximation (GGA) \[7\]. The whole calculation is implemented by the computer code WIEN2k \[8\]. We used the parameter $R_{\text{max}}=7.0$, and the muffin-tin radii are set as $r(\text{Sr/Ba})=2.5$ a.u. and $r(\text{Ge/Si})=2.19$ a.u. We used the experimentally determined lattice parameters and space group (#141, I4$_1$/amd), and for SrGe$_2$ we optimized the internal parameter $u$ of Ge($0, 1/4, u$) within the above restrictions. We obtained $u=0.2905$, which agrees well with the experimental value for tetragonal BaGe$_2$ ($u_{\text{exp,Ba}}=0.29178$). As for the structure optimization and the self-consistent calculation we used the 1000 k-points mesh in the 1$^\text{st}$ Brillouin zone. After convergence of potential, we performed the DOS calculation using 8000 k-points mesh. Spin-orbit interaction is not included in this calculation.

3. Results and Discussions
First we show the band dispersion of tetragonal BaGe$_2$, SrGe$_2$ and SrSi$_2$ in figure 1. Since they are isovalent, their band structures are very similar. In these band structures, k-point similar to the Dirac point can be seen. That is, $E_F$ is located near the point where the bands are crossed. However, unlike the usual Dirac point, three bands are crossing instead of two. In this case, perturbation such as spin-orbit interaction cannot open gap due to anti-crossing, as shown in figure 2. Therefore, they can neither be topological insulators, nor the point-nodal semimetals, predicted for the hypothetical 3D-honeycomb lattice model \[4-6\]. This kind of band crossing is similar to that in MoP \[9\], which is a topological semimetal and in which curious three-component fermion is observed. However, in MoP it differs in that two of the three bands are strictly degenerated. We speculate that this new type of band crossing in BaGe$_2$, SrGe$_2$ and SrSi$_2$ may emerge novel topological states.

![Figure 1](image_url)

**Figure 1.** Energy dispersion curves of tetragonal BaGe$_2$, SrGe$_2$ and SrSi$_2$. The units of vertical axis are eV. The lower panel shows the close-up view near the pseudo-Dirac point (shown in circle) in SrGe$_2$, and the notation of the k-points.
Next we compare the density of states curves for tetragonal BaGe$_2$, SrGe$_2$ and SrSi$_2$, shown in figure 3. Overall peak structure is very similar since they are isovalent, while for BaGe$_2$ there are large peaks which are composed of Ba5p and Ba5d orbitals at the energy ~ -13eV and 9eV. We can see that Ba/Sr partial DOS is almost zero at $E_F$, and the shape of the Ba/Sr partial DOS is completely different with the Ge/Si partial DOS. This result means that the hybridization between Ba/Sr and Ge/Si is quite small, and these compounds can be regarded as forming the Zintl phase, (Ba/Sr)$_2$(Ge/Si)$_2$. As for the unoccupied states, Ge/Si partial DOS is almost flat: i.e. it hardly depends on energy. This shape of partial DOS may suggest a 2D free electron system. However, these three compounds have 3D-honeycomb network of Ge/Si. And as we show later, the polymorphs with 2D-honeycomb network of Ge also have similar shape of Ge partial DOS for unoccupied states. Therefore, we cannot attribute this characteristic shape of the Ge/Si partial DOS to the 2D free electrons.

![Figure 2. Schematic view of normal Dirac point and pseudo-Dirac point. Small perturbation can open a gap around normal Dirac point, while it cannot open a gap around pseudo-Dirac point.](image)

![Figure 3. Density of states curves of tetragonal BaGe$_2$, SrGe$_2$ and SrSi$_2$. The units of vertical axis are eV$^{-1}$ per unit cell.](image)
Here we consider the material dependence of $T_c$ for tetragonal BaGe$_2$, SrGe$_2$, and SrSi$_2$. In most mechanisms of superconductivity, most important quantity is the DOS at $E_F$ (=$D$). We plot $D$ vs $T_c$ for these three compounds in figure 4, filled circle. Since there are no magnetic atoms, we assume that the mechanism of superconductivity is simple BCS type. In the standard BCS theory $T_c$ is estimated as:

$$T_c = 1.14 \theta_D \exp \left( -\frac{1}{DV} \right)$$

where $V$ is the magnitude of the attracting interaction (usually caused by electron-phonon interaction) and $\theta_D$ is the Debye temperature. We can regard this equation as the fitting curve with two parameters $\theta_D$ and $V$. Then we obtained the fitting curve as the solid line in figure 4. The quality of fitting is not so good for the following reasons. First, $\theta_D$ and $V$ can be varied with compound. Second, randomness can decrease $T_c$ for the real sample. Finally, $D$ can be also changed by off-stoichiometry of the sample. In fact, we found that tetra-SrGe$_2$ has the composition SrGe$_{1.66}$, which means that ~16% of Ge is deficient [1]. Since the Zintl phase-like description Sr$_{2+}$ (Ge$_{1.66}$)$^{2-}$ is valid as shown above, we can estimate the valence of Ge is Ge$^{1.2}$. For stoichiometric sample the valence of Ge is Ge$^{1.0}$. The Ge atom in the Ge-deficient sample has 0.2 excess electrons. This situation can be described by the rigid band model with shifting $E_F$ so as to contain 0.2 excess electrons per Ge. We obtain $D$ for SrGe$_{1.66}$ as $D = 0.91 \mathrm{eV}^{-1}$. Since the amount of Ge/Si deficiency in BaGe$_2$ and SrSi$_2$ is not estimated, we tentatively assume they also have 0.2 excess electrons per Ge/Si. In this way we obtained $D = 0.97$ and 0.77 $\mathrm{eV}^{-1}$ for BaGe$_{1.66}$ and SrSi$_{1.66}$, respectively. We also plot $D$ vs $T_c$ for these three compounds in figure 4, filled triangle.

![Figure 4](image)

**Figure 4.** $D(=\text{DOS at } E_F)$ vs $T_c$ plot for tetragonal BaGe$_2$, SrGe$_2$, and SrSi$_2$. The filled circles are for stoichiometric case, and the filled triangles are for Ge/Si deficient case. We assumed that all of these three compounds have the same amount of Ge/Si deficiency, and treated within the rigid band model with 0.2 excess electrons by shifting $E_F$. Dotted lines and solid lines are the BCS curves for stoichiometric case and Ge/Si deficient case, with fixing the parameters $\theta_D$ and $V$.

Although the quality of fitting is not good, this result is still suggestive. First, when we increase $\theta_D$ by factor 2, only ~15% decrease of $V$ can mostly reproduce the fitting curve. In other words, for realistic $\theta_D$ we can estimate $V$ as 0.2~0.3 eV for these compounds. This means that the electron-phonon coupling constant $\lambda = DV$ is estimated as 0.2~0.35, which indicates that these compounds are in the...
weak-coupling regime. We also note that the $D$ vs $T_c$ plot is almost similar for non-doped and 0.2 electron-doped case. This result may show that our rigid-band approach is essentially good, and Ge/Si deficiency increases $D$ for all these three compounds almost in the same manner.

Next we show the DOS curves for the several polymorphs of SrGe$_2$ in figure 5. Since the local coordination for Ge atom is common between these three polymorphs, i.e. they all have (pseudo) planer coordination of nearest-neighbor Ge atom, these three polymorphs have similar DOS curves. As for the trigonal structure, the buckling of the Ge atom along the $c$-axis splits the peak at $E_F$ and opens a pseudogap. The total energy of the trigonal structure is lower than that of the hexagonal structure. This behavior is explained by the Peierls transition, i.e. the lattice modulation doubles the unit cell, opens a gap and the system gains kinetic energy. The total energy of the tetragonal structure is also higher than that of the trigonal structure, agreeing with the previous calculation[3]. However, it is difficult to transform from tetragonal to trigonal structure due to the steric barrier. As a result, once SrGe$_2$ forms the tetragonal structure, it does not easily transform to the more stable trigonal structure with less $D(E_F)$, and keeps the high $D(E_F)$ which leads to relatively high $T_c$.

![Figure 5. Density of states curves of tetragonal, hexagonal and rhombohedral polymorphs of SrGe$_2$. The units of vertical axis are eV$^{-1}$ per unit cell.](image-url)
We have calculated the band structure of tetragonal SrGe$_2$, BaGe$_2$ and SrSi$_2$ from first-principles. They have Dirac-point-like band structure, but are not topological insulator because three bands are entangled instead of two. BCS analysis suggests that these compounds are in the weak coupling regime. We also calculated the electronic structure for several polymorphs of SrGe$_2$, and the tetragonal phase has rather high $D(E_F)$ which is advantageous for high $T_c$.

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