Superconductivity in Carbide Compounds

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Abstract

The discovery of superconductivity in MgB₂ and B-doped diamond has stimulated the search for new superconducting materials in similar systems containing light elements. In the framework of BCS theory, high frequency phonons induced in a network of light elements can yield a higher superconducting transition temperature (Tc). It shows that light element superconductors provide one of the most promising paths to a room-temperature superconductor taking account of the relationship electronic state and bonding state.

Keywords: Superconductivity; Phonons; Sesqui-carbides

Introduction

The discovery of superconductivity in MgB₂ [1] and B-doped diamond [2] has stimulated the search for new superconducting materials in similar systems containing light elements. In the framework of BCS theory [3], high frequency phonons induced in a network of light elements can yield a higher superconducting transition temperature (Tc). These discoveries turned our attention towards new combinations of intermetallic compounds, and we discovered new superconductors in carbide systems, Y₂C₃ [4] and B-doped SiC [5]. In this paper, we review these superconductors.

Superconductivity in Y₂C₃

Sesqui-carbides (R₂C₃; R=Y, La, Lu) such as Pu₂C₃, which crystallize as bcc structures without an inversion center, are reported to exhibit superconductivity at relatively high temperatures for intermetallic compounds, with Tc’s that depend on their carbon content [6-10]. The crystal structure of Y₂C₃ is shown in Figure 1. In this structure, Y atoms are aligned along the <111> direction and C atoms form C-C dimers.

In particular, Th substituted sesquicarbides of yttrium and lanthanum, (R₃Th)C₃, have attracted attention because their Tc’s are close to those of niobium-based A15-type superconductors. These materials showed superconductivity with a variable Tc, having a maximum at 17 K. So, we attempted to synthesize the sesquicarbide material under higher temperature and pressure conditions. With a high temperature and pressure synthesis at 1473–1873 K and 4–5.5 GPa, using cubic-anvil-type equipment, we found that Y₂C₃ had a maximum Tc of 18 K, as shown in Figure 2.

From a theoretical point of view, the band structure of Y₂C₃ shows that the hybridization of C-C dimer antibonding and the Y-4d characterstics are dominant at the Fermi level [11,12]. The electronic structure of Y₂C₃ with C dimers suggests that the electronic structure could have substantial C-C antibonding character near the Fermi level [12]. It has been reported that low-frequency metal atom vibrations have the largest electron-phonon coupling in Y₂C₃, while the contribution of high-frequency C-C stretching vibrations is comparatively small [13].

However, the mechanism of superconductivity in Y₂C₃ has not been well understood because of the difficulty involved in synthesizing stable, single-phase Y₂C₃, in air. We established a technique for synthesizing high-purity samples, and prepared samples having various Tc’s to investigate the mechanism of the variation of Tc in this system [14,15]. As shown in Figure 3, the magnetic susceptibility of Y₂C₃ decreased significantly at each Tc and the superconducting volume fraction of each Tc sample at lowest temperature in susceptibility measurements (1.8 K) was estimated to be approximately 40% in the field cooling process. The magnetization vs. magnetic field (M-H) curves exhibit typical type-II superconducting behavior.

The electronic specific heat (Cₑ) of each sample (11K material, 13K material, and 15K material) is shown in Figure 4. The total specific heat (C) is expressed by following formula;

\[ C = C_d + C_{ph} = γT + βT^3 + δT^5 \]  

(1)

The Cₑ is obtained by subtracting the lattice part of the specific heat (Cₙ) from the total specific heat (C), which is measured at zero field and 1T, respectively. In this case, an applied field cannot completely suppress superconductivity, and γT in the Cₑ term provides a minor contribution. So we used the normal-state entropy formula;

\[ S_n = γT + \frac{1}{3} βT^3 + \frac{1}{5} δT^5 \]  

(2)

For determination of γ and Θₑ (derived from β = N(12/5)n*(0)Θₑ (γ, α, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β, γ, β,  

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Received June 13, 2016; Accepted July 15, 2016; Published July 22, 2016

Citation: Muranaka T, Akimitsu J (2016) Superconductivity in Carbide Compounds. Chem Sci J 7: 3. doi: 10.4172/2150-3494.1000135
Therefore we focus on the relationship between $\gamma$ and $T_c$. The $T_c$ of $Y_2C_3$ increases as $\gamma$ increases. The $\gamma$ value is given by $\gamma = \pi^2 k_B^2 D(\epsilon_F) / 3$, where $D(\epsilon_F)$ is the density of states at the Fermi level. In BCS theory, $T_c$ is given by $\Delta T_c = 1.1 \Theta_D \exp(-1/\gamma) D(\epsilon_F)$, so it is considered that $T_c$ in $Y_2C_3$ increases as $D(\epsilon_F)$ increases. However, the $\gamma$ value of $Y_2C_3$ is not very high in comparison with that of Nb3Sn, where $\gamma=13 \text{ mJ/molK}^2$ [17]. So, we concluded that its high Debye temperature makes $T_c$ relatively high despite its small Sommerfeld coefficient.

Nakane et al. looked for the causes of different $T_c$'s in $Y_2C_3$, structural properties, using neutron powder diffraction [19]. As they reported, high-$T_c$ (15K) and low-$T_c$ (11K) phases involved a small difference in C-C dimer distance, $1.298(4)$ Å for 15K phase and $1.290(4)$ Å for 11K phase, while the lattice parameter was constant for all samples. Thus a change in C-C dimer distance may induce a change of the electronic state of the C-C dimer, resulting in an altered $T_c$ in $Y_2C_3$.

Considering some other superconducting materials without an inversion center, CePt3Si and Li2Pt3B, their superconducting states are interesting because of the admixture of spin-singlet and spin-triplet superconducting states that is induced by spin-orbit coupling [20,21]. Because $Y_2C_3$ does not have an inversion center in its crystal structure, the determination of the order parameter and the details of the superconducting gap structure are worth some attention.

In a $^{13}$C-NMR study of $Y_2C_3$ with a $T_c=15.7$ K at $H=0$ T, a clear decrease in $^{13}$C Knight Shift and an increase in the full width at half maximum (FWHM) of $^{13}$C-NMR spectra are observed below $T_c$, as shown in Figure 7 [22]. It is suggested that the decrease of Knight Shift is due to a reduction of spin susceptibility associated with an onset of spin-singlet superconductivity in $Y_2C_3$, with the increase of FWHM possibly being due to an inhomogeneous distribution of vortex lattices.

Table 1 lists the superconducting parameters of three phases of $Y_2C_3$, with various $T_c$'s, $Y_2C_3$ has a higher than Nb3Sn ($T_c=18K$, $\Theta_D=230K$) [17], being comparable to that of YNi$_2$B$_2$C ($T_c=14K$, $\Theta_D=533K$) [18]. From relatively high $\Theta_D$, it is considered that the light element, Carbon, plays an important role in the superconductivity in $Y_2C_3$, and yields relatively high $T_c$. But $T_c$ in $Y_2C_3$ is not related to $\Theta_D$ as tabulated in Table 1.

Table 1: A summary of superconducting parameters of $Y_2C_3$.

| $T_c$ [K] | $\gamma$ [mJ/molK$^2$] | $\Theta_D$ [K] | $\mu_0 B_{c2}(0)$ [T] | $2\Delta_0/k_B T_c$ | $\xi$ [Å] |
|----------|----------------------|----------------|-----------------------|----------------------|----------|
| 11.6     | 4.7                  | 540            | 22.7                  | 3.6                  | 38       |
| 13.9     | 6.0                  | 530            | 24.7                  | 3.9                  | 36       |
| 15.2     | 6.3                  | 530            | 26.8                  | 4.1                  | 35       |

Figure 6. The plots show a linear temperature dependence with the gradients $dH/dT$, and $\mu_0 H_{c2}(0)$ estimated to be about 22.7 T, 24.7 T, and 26.8 T, respectively, for the 11K, 13K, and 15K materials, from the relationship for type-II superconductors in the dirty limit:

$$\mu_0 H_{c2}(0) = 0.69 \times (dH/dT) \times T_c$$ (3)

and the coherence lengths, $\xi$, were determined to be 38, 36, and 35 Å, respectively, for the 11K, 13K, and 15K materials from following formula:

$$\mu_0 H_{c2}(0) - \phi_0 / \pi \xi^2$$ (4)

Table 1 shows an expanded view near the $T_c$ region.
Figure 4: Temperature dependence of $C_p$ for (a) 11K, (b) 13K, and (c) 15K materials. The dashed lines show exponential curves.

Figure 5: Temperature dependence of specific heat at various magnetic fields for (a) 11K, (b) 13K, and (c) 15K materials.
The temperature dependence of $1/T$ exponential term and seems to have small kink at around 5K. 

Figure 6: Upper critical fields, $H_c(0)$, of $Y_2C_3$, determined by midpoint of jump of specific heat in magnetic fields. The solid lines are guides for the eye.

Figure 7: Temperature dependences of (a) $^{13}C$ Knight shift and (b) FWHM of $^{13}C$-NMR spectrum in $Y_2C_3$ with $T_c=12.2$ K at $H=9.85$ T. The inset shows the NMR spectra at several temperatures.

Figure 8 shows the Arrhenius plot of $(T_c/T)/(T_c/T_{max})$ vs. $T_c/T$, with $T_c=12.2$ K at $H=9.85$ T to help analyzing the details of the superconducting gap structure. The temperature dependence of $(T_c/T)/(T_c/T_{max})$ does not obey a simple power-law behavior such as $T^k$ dependence. It seems that a large full gap opens in the high-temperature region are dominated by the presence of a small full gap. The large and small superconducting gaps, $2\Delta/k_BT_c$, are estimated to be about 5 ($T=5$ K~$T_c$) and 2 ($T<5$ K), respectively. This behavior supporting multigap superconductivity in $Y_2C_3$ is not due to an extrinsic factor such as inhomogeneity of the samples, because $1/T$ is uniquely determined by the simple exponential curve of nuclear magnetization as shown in the inset of Figure 9.

This multigap behavior in $Y_2C_3$ is also detected by μSR measurements [23,24]. In the μSR study, muon spin relaxation rates of $La_2C_3$ and $Y_2C_3$ are reported. The crystal structure of $La_2C_3$ is a Pu$_2$C$_3$-type structure and its $T_c$’s are reported to be 6–13 K in different samples [9,25,26]. Therefore, an electronic structure similar to $Y_2C_3$’s is expected for $La_2C_3$, making $La_2C_3$ a good candidate for comparative study with $Y_2C_3$. The specific heat measurement of $La_2C_3$ is reported to suggest single-gap superconductivity [27].

Figure 10 shows the temperature dependence of the muon spin relaxation rate for $La_2C_3$ and $Y_2C_3$. It is noted that plots of $La_2C_3$ reveal a deviation from single-gap BCS-type superconducting behavior, though in the case of $Y_2C_3$ no strong anomaly is observed in the muon spin relaxation. However, the temperature dependence below ~6 K ($T/T_c<0.4$) cannot be explained by a single-gap BCS picture. These temperature dependences can be understood from the double-gap structure in each compound by considering the Fermi surface of $Y_2C_3$ (three hole bands and one electron band) obtained by first-principles calculation [28].

Two superconducting gaps in $Y_2C_3$ and $La_2C_3$ can be realized by the differences in the density of states and Fermi velocities between hole and electron bands, so the temperature dependence of muon spin relaxation in each compound is affected by them. Taking the inter-band
In the penetration depth, $\lambda(H)$, both compounds are described in the regime of strong electron-phonon coupling and $\lambda(T)$ shows $T$-linear dependence at $T< T^*$, indicating the existence of a superconducting gap with line nodes, and the $\mu_s H_s(T)$ presents a weak upturn at low temperature with a rather high value of about 29, which exceeds the weak-coupling Pauli limit [31]. In $^{139}$La and $^{13}$C NMR of La$_2$C$_3$, $^{139}$La and $^{13}$C NMR shifts in the superconducting state do not differ from the normal state, and the $^{139}$La spin-lattice relaxation rate is strongly enhanced below $T_s$ [32]. These unconventional results can be attributed to the absence of inversion symmetry, which allows the possible mixture of spin-singlet and spin-triplet Cooper pairs in both compounds.

**Superconductivity in Boron-Doped SiC**

The superconductivity of doped semiconductors such as B-doped diamond in bulk [2] and films [33,34], and in B-doped Si [35] has stimulated renewed interest in the low-carrier-density superconductivity of doped semiconductors. In the case of B-doped diamond, experimental and theoretical research has sought to clarify whether its metallic nature arises from the holes at the top of the diamond valence band or from the boron impurity band formed above the valence band [36-47]. In particular, a higher-$T_c$ is suggested, where bonds transform into bands by carrier-doping to a semiconductor [48-50].

In terms of structural features and physical properties, we focused on SiC, which has many stable polytypes including cubic zinc-blende, hexagonal and rhombohedral polytypes. As shown in Figure 11, in the cubic zinc-blende structure, labeled as 3C-SiC or β-SiC, Si and C occupy ordered sites in a diamond framework, and in hexagonal polytypes, nH-SiC, and rhombohedral polytypes, nR-SiC, generally referred to as α-SiC, nSiC bilayers consisting of C and Si layers are stacked in a primitive unit cell.

Undoped SiC is a wide-band-gap semiconductor with a band gap of 2–3 eV depending on the crystal modification [51], and N, P, B, Al, etc. are lightly doped as donors or acceptors by ion implantation or thermal diffusion. When the dopant-induced carrier concentration increases, an insulator-to-metal transition occurs in semiconductors, and superconductivity has been induced in some semiconductors.

From the superconducting parameters of Y$_2$C$_3$ and La$_2$C$_3$, which are deduced from μSR measurements, the superconductivities in both compounds are described in the regime of strong electron-phonon coupling and s-wave symmetry, which is basically in good agreement with previous reports. However, in recent reports, the possibility of a nontrivial superconducting state in both compounds is pointed out. In the penetration depth, $\lambda(T)$, and the upper critical field, $\mu_s H_a(T)$, of Y$_2$C$_3$, using a tunnel-diode-based resonant oscillation technique, $\lambda(T)$ shows $T$-linear dependence at $T< T^*$, indicating the existence of a superconducting gap with line nodes, and the $\mu_s H_a(T)$ presents a weak upturn at low temperature with a rather high value of about 29, which exceeds the weak-coupling Pauli limit [31].

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In this situation, we succeeded in inducing type-I superconductivity in p-type boron-doped 3C-SiC with a carrier concentration of 1.06-1.91 \times 10^{21} \text{ cm}^{-3} \ [5], and after this report we confirmed a superconducting transition in B-doped 6H-SiC at a similar carrier concentration [59]. The question arises whether SiC exhibits superconductivity with different dopant elements. In fact, p-type Al-doped 4H-SiC with an Al concentration of \( 8.7 \times 10^{20} \text{ cm}^{-3} \) showed metallic behaviors and a slight drop around 7 K in the temperature-dependence of sheet resistance [60]. We note that this drop may indicate the onset of a superconducting transition, but a superconducting transition has not been confirmed. However, we did induce type-II superconductivity in p-type Al-doped 3C-SiC with a carrier concentration of 3.86-7.06 \times 10^{20} \text{ cm}^{-3} \ [59].

From typical PXRD patterns of B-doped 3C-SiC and 6H-SiC, the main phases in each sample were indexed as cubic zinc-blende 3C-SiC, and hexagonal 6H-SiC phases, respectively, as shown in Figure 12.

The refined lattice parameter of the major 3C-SiC phase increased after sintering, though only by \( \sim 0.1\% \), from 4.3575(3)\text{Å} to 4.3618(4) \text{Å}, and the refined lattice parameter, \( c \), of the major 6H-SiC phase also increased after sintering by \( \sim 0.2\% \), from 15.06 \text{Å} to 15.09 \text{Å}. However, the refined lattice parameter, \( a \), of 6H-SiC (in commercial 3.064 \text{Å}) did not change (within experimental accuracy). Because the atomic sizes of boron and carbon are comparable, but both are much smaller than silicon, the small changes in the lattice parameters suggest that boron substitutes at the carbon site in these samples. By means of the Hall effect at room temperature, the hole concentrations, \( n \), were estimated to be \( \sim 1.91 \times 10^{21} \text{ cm}^{-3} \) for B-doped 3C-SiC and \( \sim 2.53 \times 10^{20} \text{ cm}^{-3} \) for B-doped 6H-SiC. The samples had much higher doping levels than those in previous reports [61-64]. The presence of liquid silicon in the sintering process may have helped boron diffusion and enhanced boron-substitution efficiency.

As shown in Figure 13, the magnetic susceptibility of B-doped 3C-SiC and 6H-SiC under a magnetic field of 1 Oe (zero field cooling process) significantly decreases at \( \sim 1.4 \) K, suggesting the occurrence of superconductivity with a superconducting volume fraction over 100% by the shielding effect.

Figure 14 shows magnetization vs. magnetic field (\( M-H \)) curves of B-doped 3C-SiC and 6H-SiC. These curves reveal type-I superconducting behavior. In both compounds, the onset field of magnetization shows a hysteresis about 30 Oe wide at the lowest temperature. Hysteresis during increasing and decreasing fields suggests that a 1st order transition under a finite magnetic field is occurring in both compounds, supporting type-I superconductivity. From the \( M-H \) curves, the critical field, \( H_c \), is estimated to be about 100 Oe.

As shown in Figure 15, the electrical resistivity in B-doped 3C-SiC:B and 6H-SiC reveals metallic conductivity, reflecting the high carrier-doping level with residual resistivity ratios, RRR (\( \rho_{300K}/\rho_{0} \)), of 11.4 and 4.7, respectively. B-doped 3C-SiC exhibits a much smaller resistivity, almost \( T \)-linear, but B-doped 6H-SiC exhibits a broad feature at around 150 K suggesting the weak localization of carriers or a contribution from non-metallic grain boundaries. The inset of Figure 15 shows an expanded view of the low-temperature data. The resistivities exhibit sharp drops at 1.5 K (B-doped 3C-SiC) and 1.4 K (B-doped 6H-SiC), corresponding to the \( T_c \)’s observed from the susceptibility.

To determine the phase diagram in the magnetic field-temperature (\( H-T \)) plane for both samples, the resistivities were measured by varying the temperature at different magnetic fields (\( T \)-scan shown in Figure 16), and varying the magnetic fields at different temperatures (\( H \)-scan shown in Figure 17). In the \( T \)-scan, only one transition was observed at \( T_c \) at zero field, while a large super cooling effect was observed in both SiC samples in finite fields. In the \( H \)-scan, hysteresis was also observed under 130 Oe in B-doped 3C-SiC and 100 Oe in B-doped 6H-SiC. The (i) in-field hysteresis, (ii) absence of hysteresis in a zero field, and (iii) very small value of the critical field, give strong evidence for type-I superconductivity in both SiC polytypes.

The \( H-T \) phase diagram determined from the resistivity data (\( T \)-scan and \( H \)-scan) is shown in Figure 18. Applying the conventional
The formula \( H_c(T) = H_c(0)(1-\frac{T}{T_c})^\alpha \) yields \( \kappa \approx 0.32 \) for B-doped 3C-SiC and 125 \( \pm 5 \) Oe with \( \alpha \approx 1.6 \) for B-doped 6H-SiC in the warming plots. The same procedure applied to the cooling plots yields \( \alpha \approx 1.6 \) in both SiC polytypes. This transition is identified as the upper limit of the intrinsic supercooling limit. The corresponding transition fields are denoted as \( H_c(0) \) (the subscript “sc” stands for supercooling) with an estimated \( H_c(0) = 102 \pm 6 \) Oe for B-doped 3C-SiC and 94 \( \pm 3 \) Oe for B-doped 6H-SiC, respectively.

Applying the Ginzburg-Landau (GL) theory of type-I superconductivity to these data, one can estimate an upper limit of the GL parameter \( \kappa \) from the difference of the critical fields obtained by a field-cooling run and a subsequent warming run [65,66]:

\[
\kappa(0) \leq \kappa_{GL}(0) = \frac{1.695}{2} \sqrt{H_c(0)}.
\]

This formula yields \( \kappa \sim 0.32 \) for B-doped 3C-SiC and 0.31 for B-doped 6H-SiC, in agreement with the analysis of the Hall effect and the specific heat data [67,68]. This supports the type-I nature of superconductivity in B-doped SiC. Note that the value of \( \kappa \) is below 0.41, which is required in a model based on supercooling [66,69,70].

Table 3 lists basic normal-state parameters: Fermi wave number \( k_F \), effective mass \( m^* \), Fermi velocity \( v_F \), mean free path \( l \), as well as superconducting state parameters: penetration depth \( \lambda \), coherence length \( \xi \) and Ginzburg-Landau parameter \( \kappa_{GL} \), deduced from \( T \)-scan and \( H \)-scan in resistivity, Hall effect, and specific heat [67,68].

For comparison, the previously reported parameters for B-doped diamond (C:B) and B-doped Si (Si:B) are added. The coherence lengths of B-doped 3C-SiC and 6H-SiC are compared with B-doped diamond and B-doped Si. Type-I superconductivity in B-doped SiC originates in these long coherence lengths.

However, it is not clear why SiC:B reveals type-I superconductivity in spite of the dirty limit \((l << \xi)\). From SEM images of B-doped SiC samples (not shown in this paper), the maximum crystal grain size is about 5 \( \mu \)m, and in higher B-content samples (higher starting ratio), the crystal grain size tends to grow much larger. Crystal grain size growth is enhanced by adding Si and B during the synthesis process.

However, \( T_c \) in superconducting B-doped SiC samples does not change with the B-nominal composition. It is considered that the growth is enhanced by adding Si and B during the synthesis process.

Table 3: Parameters in normal and superconducting states of B-doped 3C-SiC, B-doped 6H-SiC [5,59,67,68], B-doped diamond [2,36] and B-doped Si [35].
Figure 16: Temperature dependence of resistivity under magnetic fields (T-scan) in (a) B-doped 3C-SiC (3C-SiC:B) and (b) B-doped 6H-SiC (6H-SiC:B).

Figure 17: Magnetic field dependence of resistivity (H-scan) in (a) B-doped 3C-SiC (3C-SiC:B) and (b) B-doped 6H-SiC (6H-SiC:B).

Figure 18: H-T phase diagram for (a) B-doped 3C-SiC (3C-SiC:B) and (b) B-doped 6H-SiC (6H-SiC:B), determined from the onset of superconductivity in T-scan and H-scan of resistivity.
B-doping level in B-doped SiC has already reached the limiting level (a certain constant B/C ratio) in a solid state reaction. As a result, Tc does not change. Moreover, the mean free path l in B-doped SiC samples is reduced by grain boundary effects or un-reacted starting powder. Thus the mean free path l in B-doped SiC can be extended up to the high limit (l >> ξ) in a high quality sample.

Conclusion

We have reviewed superconductivity in carbide compounds, whose Tc’s are unfortunately limited to the 10K–20K range. During the process in the developments of these superconductors, we focused on the high frequency phonon which was induced by light element. The maximum Tc in sesqui-carbides and wide band-gap semiconductors are 18K and 11K, respectively, at this stage. So, other routes have to be sought for development of new high-Tc superconductor. Recently, much attention has been paid to the new superconductor H3S (Tc ~ 200K) under ultra-high pressure (200 ~ GPa), which can be described by the BCS theory [71]. This probably shows that light element superconductors provide one of the most promising paths to a room-temperature superconductor taking account of the relationship between electronic state and bonding state.

Acknowledgements

This work is supported by Grant-in-Aid from Ministry of Education, Culture, Sports, Science and Technology (MEXT) under No. 2500053, 26247057, and by JSPS KAKENHI Grant Number 15H05886 and partially by the Program for Advancing Strategic International Networks to Accelerate the Circulation of Talented Researchers from Japan Society for the Promotion of Science.

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