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Superconductivity in heavily boron-doped silicon carbide

Markus Kriener¹, Takahiro Muranaka², Junya Kato², Zhi-An Ren², Jun Akimitsu² and Yoshiteru Maeno¹

¹ Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan
² Department of Physics and Mathematics, Aoyama-Gakuin University, Sagamihara, Kanagawa 229-8558, Japan

E-mail: mkriener@scphys.kyoto-u.ac.jp

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Abstract
The discoveries of superconductivity in heavily boron-doped diamond in 2004 and silicon in 2006 have renewed the interest in the superconducting state of semiconductors. Charge-carrier doping of wide-gap semiconductors leads to a metallic phase from which upon further doping superconductivity can emerge. Recently, we discovered superconductivity in a closely related system: heavily boron-doped silicon carbide. The sample used for that study consisted of cubic and hexagonal SiC phase fractions and hence this led to the question which of them participated in the superconductivity. Here we studied a hexagonal SiC sample, free from cubic SiC phase by means of x-ray diffraction, resistivity, and ac susceptibility.

Keywords: boron-doped SiC, hexagonal and cubic SiC, type-I superconductor

(3Some figures in this article are in colour only in the electronic version)

1. Introduction

The possibility to achieve a superconducting phase in wide-band-gap semiconductors was suggested in 1964 by Cohen in Ge and GeSi [1]. Right after the prediction, several semiconductor-based compounds were indeed found to be superconducting at rather low temperatures and high doping concentrations. In the last decade, superconductivity was found in doped silicon clathrates [2–4] crystallizing in a covalent tetrahedral sp³ network with a bond length similar to that in diamond. In 2004, type-II superconductivity was found in highly boron-doped diamond (C : B) [5], the cubic carbon modification with a large band gap. The boron (hole) concentration of the sample was reported to be about \( n = 1.8 \times 10^{21} \text{cm}^{-3} \) with a critical superconducting transition temperature \( T_c \approx 4.5 \text{ K} \) and an upper critical field strength \( H_{c2} \approx 4.2 \text{ T} \). At higher doping concentrations \( n = 8.4 \times 10^{21} \text{cm}^{-3} \), \( T_c \) was found to increase to about 11.4 K and \( H_{c2} \) to about 8.7 T [6, 7]. In 2006, type-II superconductivity was discovered in its next-period neighbor in the periodic system cubic silicon (Si : B) at boron concentrations of about 8.4 \( \times 10^{21} \text{cm}^{-3} \) [8]. However, the critical temperature is only 0.4 K and the upper critical field 0.4 T³.

In 2007, we found superconductivity in the stoichiometric composition of carbon and silicon: heavily boron-doped silicon carbide (SiC : B) [9]. One interesting difference between these three superconducting systems is the well-known polytypism in SiC meaning that SiC exhibits various ground states of slightly different energy. More than 200 such structural modifications are reported [10]. There is only one cubic ‘C’ modification labeled as 3C-SiC (zincblende = diamond structure with two different elements) or \( \beta \)-SiC. All other observed unit cells are either hexagonal ‘H’ (wurtzite or wurtzite related) or rhombohedral ‘R’, labeled as mH-SiC or a-SiC and mR-SiC, respectively. The variable \( m \) indicates the number of carbon and silicon bilayers which are needed to form the unit cell. The most important hexagonal modifications are 2H-SiC, which is
the only pure hexagonal polytype, and 4H- and 6H-SiC, which consist of cubic and hexagonal bonds. The two relevant modifications for this paper are 3C- and 6H-SiC shown in figure 1. For a more comprehensive introduction to SiC see [11] and references therein. We note here that all SiC polytypes break inversion symmetry which is known to give rise to quite unconventional superconducting scenarios, e.g. in heavy-fermion compounds, in contrast to the inversion-symmetry conserving systems C: B and Si : B. However, we do not believe that any exotic superconducting scenario applies to SiC : B because of the comparably light elements carbon and silicon.

2. Superconducting properties of SiC : B

In the discovery paper [9], we used a multiphase polycrystalline boron-doped SiC sample which contained three different phase fractions: 3C-SiC, 6H-SiC, and unreacted Si. The charge-carrier concentration of this particular sample was estimated to 1.91 x 10^{21} holes cm^{-3} [9]. The critical temperature, at which we observe a sharp transition in resistivity and ac susceptibility, is ∼1.45 K. The critical field strength amounts to \( H_c \approx 115 \text{ Oe} \), much lower than those of the two parent compounds C: B and Si : B. A big surprise was the finding that SiC : B is a type-I superconductor as indicated by a clear hysteresis between data (resistivity and ac susceptibility) measured upon cooling from above \( T_c \) to the lowest accessible temperature and a subsequent warming run in different applied external DC magnetic fields. This is in clear contrast to the reported type-II behaviour of C : B and Si : B [5, 7, 8] (see footnote 3). Another surprise is the low residual resistivity \( \rho_0 = 60 \mu \Omega \text{ cm} \) at \( T_c \), which is unexpected for an impure semiconductor-based system, i. e., for a multi phase polycrystalline sample. Above \( T_c \), the system features a metallic-like temperature dependence with a positive slope of \( d\rho/dT \) in the whole temperature range up to room temperature and a residual resistivity ratio \( \text{RRR} = \rho(300 \text{ K})/\rho_0 \) of about 10. These observations are again in contrast, especially to C : B, which exhibits a more or less temperature independent resistivity with \( \rho_0 \approx 2500 \mu \Omega \text{ cm} \) and \( \text{RRR} \approx 1 \). In a subsequent specific-heat study [11], using the same sample, we found a very small normal-state Sommerfeld parameter \( \gamma_v \approx 0.29 \text{ mJ mol}^{-1} \text{ K}^{-1} \). Moreover, we could clearly demonstrate that SiC : B is a bulk superconductor, as indicated by a specific-heat jump at about 1.45 K coinciding with the critical temperature \( T_c \) estimated from resistivity and ac susceptibility data. The jump in the specific heat is rather broad reflecting the multiphase polycrystalline character of the sample used. In addition, there is a third remarkable surprise. The electronic specific heat \( c_{el}/T \) exhibits a strictly linear temperature dependence below its jump down to the lowest so-far accessed temperature \( \sim 0.35 \text{ K} \) and extrapolates almost identical to 0 for \( T \rightarrow 0 \). The jump height is estimated to \( \Delta c_{el}/\gamma_v T_c \approx 1 \), which is only 2/3 of the expectation in the Bardeen–Cooper–Schrieffer theory (BCS) of a weak-coupling superconductor and is close to the value theoretically expected for a superconducting gap with nodes [13, 14]. However, a strictly linear temperature dependence is only expected well below \( T_c \), where the superconducting gap is nearly temperature independent. When approaching \( T_c \), the specific heat should deviate from \( c_{el}/T \propto T \) due to the reduction of the gap magnitude. We note here that the assumption of a BCS-like scenario with a residual contribution to the specific heat \( \gamma_{res} \), e.g., due to non-superconducting parts of the sample, yields a reasonable description of the data, too, with \( \gamma_{res} \approx 0.14 \text{ mJ mol}^{-1} \text{ K}^{-1} \), see [11]. The jump height in this scenario is 1.48, almost matching the BCS expectation of 1.43. In the description of the specific heat, assuming a linear \( c_{el}/T \), no residual contribution is needed. A respective fit to the data yields \( \gamma_{res} \approx 0 \text{ mJ mol}^{-1} \text{ K}^{-1} \), as suggested by the almost perfect extrapolation of the data down to 0 for \( T \rightarrow 0 \). These results for \( \gamma_{res} \) for the two approaches imply a superconducting volume fraction of about 100% for the nodal gap scenario and about 50% for the BCS-like scenario.

In [15], we reported that the hexagonal phase fraction is superconducting and exhibits a similar linear temperature dependence of the electronic specific heat \( c_{el}/T \) in the superconducting state and also a reduced jump height. In this paper, we focus on this particular sample referred to as 6H-SiC in more detail and discuss the \( H-T \) phase diagram derived from ac susceptibility data. We give an evaluation of the Ginzburg–Landau parameter and compare these results with those obtained for the aforementioned ‘mixed’ sample used in [9] and [11] referred to as 3C/6H-SiC.

3. Experiment

The details of the sample preparation of sample 3C/6H-SiC are given in [9], sample 6H-SiC was synthesized in a similar way. The charge-carrier concentration of this sample is \( 0.25 \times 10^{21} \text{ holes cm}^{-3} \) as estimated from a Hall effect measurement. The electrical resistivity was measured by a conventional four-probe technique using a commercial system.
Figure 2. (a) Powder x-ray diffraction patterns of boron-doped 6H-SiC. Three phases, 6H-SiC, 15R-SiC, and silicon, are identified. There is no indication for a cubic SiC modification in this sample. The respective data for 3C/6H-SiC : B from [9] is shown in panel (b), for comparison.

4 The phase fractions were estimated from the relative x-ray spectra peak intensities.

4H-SiC:B
\[ \rho (6H-SiC:B) \]
\[ \rho (3C/6H-SiC:B) \]

Figure 3. Resistivity vs. temperature of 6H-SiC : B (blue symbols) (a) up to room temperature and (b) around \( T_c \). The sample used exhibits a metallic-like temperature dependence in the whole examined temperature range above \( T_c \). At \( T_c \), we detect a sharp drop to zero resistance. The respective data for 3C/6H-SiC : B from [9] are shown for comparison (red symbols), too. Please note that the resistivity data of 3C/6H-SiC : B is multiplied by 10. The dotted line marks the transition; see text.

Figure 4. Temperature dependence of the ac susceptibility \( \chi_{ac} \) of 6H-SiC. In (a) the real part \( \chi' \) and in (b) the imaginary part \( \chi'' \) are shown. The respective data for 3C/6H-SiC : B from [9] is shown in panels (c) and (d), for comparison. The dotted line in panels (a) and (c) signals the zero-field transition temperature. The arrows in panels (a) and (c) denote the temperature sweep direction; see text.

4A metallic-like behaviour, i.e., \( d\rho /dT > 0 \), in the whole examined temperature range above \( T_c \). However, a linear temperature dependence is observed only in a very small temperature range 60–120 K. The slope decreases at higher temperatures. Below approximately 1.5 K, a clear drop to zero-resistance with a transition width of about 25 mK is found indicating the onset of a superconducting phase. The residual resistivity is \( \rho_0 \approx 1.2 \text{ m} \Omega \text{ cm} \) and the residual resistivity ratio estimates to RRR \( \approx 4.7 \).

Figure 4 summarizes the results of our ac susceptibility measurements on sample 6H-SiC : B. The data for sample 3C/6H-SiC : B from [9] are included for comparison. In panels (a) and (c) the real parts and in (b) and (d) the imaginary parts of \( \chi'' = \chi''' + i \chi'''' \) are shown. The measurements were performed upon cooling and warming at constant \( H_{dc} \) as well as upon sweeping \( H_{dc} \) up and down at constant temperature. The temperature dependence of the in-field susceptibility data was taken as follows: The external dc magnetic field was set above \( T_c \). Then the

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temperature was reduced down to approx. 300 mK and subsequently increased above $T_c$. Figure 4 shows the results of temperature sweeps (solid lines: cooling run, dashed lines: warming run) for $H_{dc} = 0, 20, 40$ and 60 Oe. In zero field, a single sharp transition with a $T_c$ of about 1.5 K is observed in good agreement with the resistivity data. In finite magnetic fields (‘in-field’), a hysteresis between cooling and subsequent warming run appears as can be clearly seen in both $\chi'$ and $\chi''$ (figures 4(a) and (b)). The arrows in panel (a) denote the temperature sweep direction for $H_{dc} = 60$ Oe. This in-field first-order phase transition is known as supercooling effect and is an indication of a type-I superconductor with a Ginzburg–Landau parameter $\kappa_{GL} \lesssim 0.417$ [16–18]. We observed a similar hysteresis in field-dependent data measured at constant temperature, too. In case of a supercooled type-I superconductor, the observed critical field upon warming gives the thermodynamical critical field $H_c(T)$. The Ginzburg–Landau parameter is discussed in more detail in the next section.

From these data, we derived the $H$–$T$ phase diagram of 6H-SiC:B shown in figure 5(a). The phase diagram of 3C/6H-SiC:B from [9] is shown in panel (b) for comparison. The critical temperature was estimated from the shielding-fraction data ($\chi'$). Here we define $T_c$ as the temperature at which the absolute value of $\chi'$ decreased by 1% of the total difference in the signal between the normal and the superconducting state. This procedure was applied to the data obtained upon decreasing and increasing temperature. The resulting two lines are the lower superconducting field phase line $H_{sc}(T)$ and the higher lying critical field phase line $H_c(T)$. The black dashed lines are fits to the data applying the empirical formula $H_c(T) = H_c(0)[1 - (T/T_c(0))^\alpha]$ yielding for $T \rightarrow 0$ a supercooling field of $H_{sc}(0) = (90 \pm 5)$ Oe with $\alpha = 1.3$, which can be identified as the upper limit of the intrinsic supercooling limit. The thermodynamical critical field was estimated to $H_c(0) = (110 \pm 5)$ Oe, again with $\alpha = 1.3$.

5. Discussion

Next, we briefly compare the newly presented with the previously published data [9], which is included to the figures 2–5, and, together with the results of respective specific-heat studies in [11, 15], discuss the superconducting parameters.

The comparison of the resistivity data in figure 3 reveals that 6H-SiC:B ($\rho_0 = 1200 \mu\Omega$ cm) is the much dirtier crystal, as indicated by the different RRR values of 5 (6H-SiC:B) and 10 (3C/6H-SiC:B). Please note, that the data of 3C/6H-SiC:B ($\rho_0 = 60 \mu\Omega$ cm) is multiplied by a factor of 10 in figure 3. Obviously, the transition width is smaller for the cleaner 3C/6H-SiC:B sample ($\sim 15$ mK compared to $\sim 25$ mK). Surprisingly, the difference in the charge-carrier concentration does not affect the onset temperature of superconductivity which is $\sim 1.5$ K for both samples, see the dashed line in figure 3.

As seen in figure 4, both samples exhibit a clear supercooling behaviour, which is usually observed in clean systems like type-I elemental superconductors. In both compounds, the shielding signal is strong and robust, and the shielding fraction is almost field independent, although the hysteresis is more pronounced in 3C/6H-SiC:B as seen in the $H$–$T$ phase diagrams (figure 5). The thermodynamical critical field strength $H_c \approx 110–115$ Oe is almost identical, too. The additional features at the low-temperature side of $\chi''$ are likely due to superconducting grains with a slightly lower critical temperature. Remembering the comparably higher purity of sample 3C/6H-SiC:B, it is surprising that these features are much less pronounced in 6H-SiC:B. Assuming that both phase fractions in 3C/6H-SiC:B are superconducting, which will be discussed next, one might speculate that the cubic phase fraction has a lower $T_c$ leading to these features. However, this conclusion is in contradiction with the observation of only one single sharp transition in the $\chi'$ data of that sample.

At the time of writing [9], we were not sure which of the two SiC phase fractions (3C or 6H) is responsible for the superconductivity in this system. The comparison of figures 2(a) and (b) clearly demonstrates that there is no indication for a cubic phase fraction in sample 6H-SiC:B and hence the hexagonal modification of SiC:B is a bulk superconductor. Very recent data on 3C-SiC:B implies that also the cubic modification participates in the superconductivity [19]. The unreacted silicon in our samples is likely to be an insulating phase fraction with no electronic and almost no phononic contributions to the specific heat at low temperatures. Therefore, a residual contribution caused by this phase fraction cannot easily explain the values for $\gamma_{res}$ found in the specific-heat analysis assuming a BCS-like scenario given in [11, 15], as mentioned in the Introduction. However, a possible inhomogeneous distribution of boron doping can be responsible for parts of the sample remaining normal-conducting 3C- and/or 6H-SiC leading to a residual contribution.

Together with the analysis of the specific-heat data, we are able to estimate the superconducting parameters for 6H-SiC:B as described in detail for 3C/6H-SiC:B in [11]. The parameters for both systems are summarized in table 1. Here, the Ginzburg–Landau parameter is derived from the experimental values of the charge-carrier concentration $n$, the critical temperature $T_c$, and the Sommerfeld parameter of the normal-state specific heat $\gamma_0$. Using the values given in table 1 yields $\kappa_{GL} = 7$. This is much higher than the value

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Figure 5. (a) $H$–$T$ phase diagram of 6H-SiC:B. The dashed lines are fits to the data; see text. The respective data for 3C/6H-SiC:B from [9] is shown in panel (b), for comparison. The lower phase lines $H_{sc}$ correspond to the 'supercooling' effect; see text.
suggested by the observation of a supercooling effect $\kappa_{GL} \lesssim 0.417$ and the finding for $3C/6H$-SiC : B, i.e. $\kappa_{GL} = 0.35$. The values of $T_c$ and $\gamma_s$ are similar for both samples, but the charge-carrier concentration of 6H-SiC : B is about one order of magnitude smaller than that of 3C/6H-SiC : B, and indeed, this is the crucial parameter. The Ginzburg–Landau parameter is defined as $\kappa_{GL} = \lambda/\xi$, compare the discussion in [11]. The penetration depth depends on the charge-carrier concentration as $\lambda \propto 1/n^{2/3}$, the coherence length as $\xi \propto n^{1/3}$ and hence $\kappa_{GL} \propto 1/n^{4/3}$. Using a charge-carrier concentration of about $2 \times 10^{23}$ cm$^{-3}$ yields a Ginzburg–Landau parameter of the right order of magnitude. Therefore the determination of $n$ needs further clarification.

6. Summary

In summary, we present a study of mainly hexagonal boron-doped 6H-SiC, without any indication of a cubic 3C phase fraction, by means of x-ray diffraction, resistivity, and ac-susceptibility measurements. We compare these results with those obtained for a sample containing noteworthy fractions of both, the 3C- and the 6H-SiC modification. Both samples are bulk type-I superconductors as suggested by the $H$–$T$ phase diagrams, i.e. the finding of a pronounced supercooling indicated by an in-field first-order phase transition and recent specific-heat studies, revealing a clear jump at $T_c$. The sample consisting of both SiC phase fractions contained a one order of magnitude higher charge-carrier concentration and exhibited a lower residual resistivity. The Ginzburg–Landau parameter for the hexagonal SiC sample is much higher than expected for a type-I superconductor with a strong supercooling effect. This could be due to an erroneous determination of the charge-carrier concentration and needs further clarification. Taking all data together, we have strong indications that boron-doped cubic as well as hexagonal SiC are bulk superconductors.

Acknowledgments

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References


Table 1. Normal-state (left) and superconducting state properties (right) of 6H-SiC : B (this work) and 3C/6H-SiC (taken from [11]). The parameters $\ell$, $\xi(0)$, and $\lambda(0)$ are the mean-free path and the superconducting penetration depth and coherence length.

<table>
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<th>6H-SiC : B</th>
<th>3C/6H-SiC : B</th>
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<td>$n$ (cm$^{-3}$)</td>
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