Superconducting and normal state properties of heavily hole-doped diamond synthesized at high pressure

V.A. Sidorov\textsuperscript{a},*, E.A. Ekimov\textsuperscript{a}, A.V. Rakhmanina\textsuperscript{a}, S.M. Stishov\textsuperscript{a}, E.D. Bauer\textsuperscript{b}, J.D. Thompson\textsuperscript{b}

\textsuperscript{a}Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Moscow Region, Russian Federation
\textsuperscript{b}Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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Abstract

Diamonds, synthesized at high pressures and high temperatures in the presence of boron, are heavily hole-doped by incorporation of boron into the diamond lattice. These diamonds become superconducting below \( T_c = 2–9 \) K. Synthesis in the systems B-C and B\(_4\)C-C at \( P = 9 \) GPa and \( T = 2500–2800 \) K result in formation of polycrystalline carbonado-like material, whereas synthesis from B-C-H gives small single crystals and intergrowth plates. Dense superconducting bodies can be prepared by compacting these single crystal particles at \( P = 8 \) GPa and \( T = 1800 \) K. Specific heat and resistivity measurements in magnetic fields prove the bulk nature of superconductivity in all pressure-synthesized samples and provide a consistent set of materials parameters that favor a conventional weak-coupling electron–phonon interpretation of the superconducting mechanism at high hole doping. Schottky barrier tunneling conductance spectra, obtained with contacts fabricated at the surface of these hole-doped diamonds, indicate the appearance of superconducting gap below \( T_c \).

Keywords: Diamond; Boron; Superconductivity; Pressure; Specific heat; Tunneling

1. Introduction

Superconductivity has been recently discovered in B-doped diamond synthesized at high temperature and pressure [1] and in B-doped polycrystalline diamond films deposited by microwave plasma-assisted chemical vapor deposition (MPCVD) [2]. Boron-doped single-crystalline diamond layers produced by MPCVD [3] and chemical transport reaction [4] methods also exhibit superconductivity. These findings show that superconductivity is a universal property of heavily boron-doped diamond. Although the preparation of boron-doped diamond in the form of wafers or thin films by CVD methods is more suitable for applications, for instance, in electronic devices, the high-pressure and high-temperature synthesis technology is most efficient for synthesizing bulk diamond samples necessary for investigations. Some properties of superconducting B-doped diamonds prepared at high pressure from mixtures of B\(_4\)C-graphite and B-graphite were published earlier [1,5]. The synthesis of single-crystalline diamond at high pressure and temperature in the non-metallic B-C-H system was reported previously [6]. Here, we report the observation of superconductivity in these diamonds, compare their properties with properties of diamonds synthesized in B\(_4\)C-graphite and B-graphite systems, and present a new data on the specific heat in high magnetic fields, tunneling spectroscopy, resistivity and magnetic susceptibility of the normal state.

2. Experiment

The details of sample preparation in B\(_4\)C-graphite and B-graphite systems with the use of high-pressure technique were published in previous papers [1,5,7]. Single-crystalline B-doped diamonds were obtained by the method of thermal decomposition at high pressure of homogeneous mixtures of naphthalene C\(_{10}\)H\(_8\) and orthocarborane C\(_2\)B\(_{10}\)H\(_{12}\) [6], which were put in a graphite crucible at the
center of a high-pressure synthesis cell. After the synthesis, diamond crystals were boiled for a long time in perchloric acid (HClO₄). Most of the reaction products were small crystals (10–40 μm), but a few thin intergrowth plates, composed of 20-μm crystals, also were found. These crystals were big enough for Hall effect and resistivity measurements. AC susceptibility measurements were made on microcrystalline powder samples. The total amount of boron in the initial mixture was 10 at.%. The diamonds obtained were characterized by X-ray diffraction and micro-Raman spectroscopy. Values of lattice parameter (a = 3.5748 ± 0.0003 Å) and the position of a zone-center phonon line (1300 cm⁻¹) indicate a B-doping level comparable to that of superconducting diamond samples [1,4,5]. These diamonds, prepared at high pressure in the B-C-H system, are indeed superconducting. Sintering of microcrystalline powder at P = 8 GPa and T = 1800 K results in the formation of dense compacts with uniform microstructure. Powder from this process retains superconducting properties and dense compacts are also superconducting, which is confirmed by resistivity, AC susceptibility and specific heat measurements. It is worth mentioning here that attempts to prepare superconducting diamond by sintering undoped diamond powder with boron at P = 8–9 GPa and T = 2500–2700 K have failed. Boron is easily incorporated in the diamond lattice in the process of lattice formation and stays in the formed lattice with further P, T treatment, but it is difficult to introduce B after the diamond lattice has formed.

Measurements of resistivity were made by a standard four-probe technique using an LR700 resistance bridge. Pt electrodes 25 μm in diameter were attached to the sample by silver epoxy. AC susceptibility was measured by a lock-in technique with the use of coils, calibrated by superconducting transitions in samples of Pb and In which had the shape and size similar to diamond samples. Magnetic susceptibility was measured with a commercial magnetometer (Quantum Design MPMS). Specific heat at temperatures down to 0.45 K and high fields was measured in a commercial relaxation calorimeter (Quantum Design PPMS with ⁴He insert).

Tunneling measurements usually require complicated equipment to prepare a thin tunneling barrier (vacuum furnaces, atomic beam technique, scanning tunneling microscopy (STM), etc.). We have found that silver epoxy or silver paint contacts, attached at the surface of diamond to measure electrical resistivity, have relatively high electrical resistance 30–50 Ω between any two contacts. Four-probe measurements using the same contacts give typical sample resistances of a few mΩ. High contact resistance is due to a Schottky barrier that always exists at the surface of diamond [8]. Current is governed by tunneling of holes through this Schottky barrier, and this offers the possibility to find a signature of the superconducting energy gap of diamond in the conductance spectra of the contacts. We used a standard phase sensitive detection technique where a small AC excitation voltage at a frequency of 157 Hz was superimposed on a DC bias voltage. A signal from a first harmonic, proportional to contact conductance, was measured by a SR830 lock-in amplifier. Because bias voltage is always applied to two contacts connected in series, the bias voltage acting on a single contact is actually half of the total bias, assuming contacts to be identical. Surprisingly, these very simple contacts and measuring technique give the possibility to find the superconducting gap of diamond and its temperature dependence. Because there is no vacuum gap involved in the measurement, this technique can be adapted to high-pressure experiments and to other superconductors.

In the following, we report properties of three representative samples prepared from B-graphite (sample EEA18) and B₄C-graphite near the eutectic melting line (sample EEA16) as well as of an intergrowth plate prepared from B-C-H (sample AR3).

3. Results and discussion

Specific heat measurements C(T) on sample EEA18 have proved the bulk nature of superconductivity in diamond [4,5]. A characteristic feature of this sample is a presence of two separate superconducting transitions at ~2.3 and at ~4 K, as well as a component of charge carriers that do not support superconductivity. The latter contribute to the specific heat and produce a C/T value that does not extrapolates to zero at T = 0. The origin of this bimodal superconductivity is probably related with the difference in ability to absorb boron by different growth sectors in the process of diamond synthesis. This leads to different Tc’s (the highest for <111> sector).

All diamond samples prepared from B-graphite exhibit two transitions at 2.3 and 4 K. Specific heat measurements on a dense compact of microcrystalline powder, synthesized from B-C-H, show a broad peak-like anomaly in the range 1.5–3 K in the same temperature range where the superconducting transition in this sample is observed by resistivity and AC susceptibility measurements. Application of a magnetic field to sample EEA18 changes its specific heat in two ways. As expected, a high magnetic field suppresses specific heat anomalies related to superconducting transitions and shifts them to lower temperatures. At the same time, a low temperature upturn of the specific heat is developed below 1 K on increasing field strength. This low-temperature contribution to the specific heat changes with temperature as A/T², and the value of A is roughly proportional to magnetic field as it should be if this response is due to a nuclear Schottky anomaly. The upturn interferes with the peak due to superconductivity and masks it at the highest fields. Our belief is that the nuclear Schottky anomaly comes from ¹⁸B or some other impurities in the sample. But we cannot make more certain conclusions at the moment. After subtracting this field-dependent low-temperature upturn and phonon contribution, we can plot the temperature dependences of the electronic specific heat at different fields (Fig. 1).
Field-induced shifts of the two superconducting specific heat anomalies determine the upper critical field \( H_{c2}(T) \) dependences for sample EEA18 (insert in Fig. 1). An average slope \( dH_{c2}/dT \approx -1.4 \text{T/K} \) is very close to that obtained for this sample by resistivity measurements in magnetic fields [5]. These observations unambiguously prove the bulk nature of superconductivity in B-doped diamond.

It is interesting to compare electrical properties of samples EEA18 and AR3, which were synthesized by different routes. Both exhibit superconducting transitions, with the onset temperatures different by a factor of 1.5 (Fig. 2a). Hall effect measurements show that the concentration of holes in sample EEA18 is 1.5 times higher than in sample AR3 in the whole temperature range of the normal state. This perfect correlation is in line with other observations [2,3] that the superconducting transition temperature is directly related to the number of charge carriers (holes) and boron concentration in a diamond sample. The temperature dependence of resistivity of AR3 diamond in the normal state is very similar to that found in polycrystalline diamonds prepared in B4C-graphite and B-graphite systems [1,5]. It has a metallic behavior near room temperature, passes through a minimum near \( T_{\text{min}} \approx 220 \text{K} \) and increases slightly between \( T_c \) and \( T_{\text{min}} \). The number of charge carriers decreases slightly with decreasing temperature in accordance with this weak semiconducting behavior (Fig. 2b).

Measurements of specific heat, Hall effect, resistivity and upper critical field on sample EEA18 were published earlier [5] and provide arguments in favor of a phonon-mediated BCS-like mechanism of superconductivity in diamond, at least for a high level of boron doping. Observation of the superconducting energy gap \( \Delta \) and measurement of its value and temperature dependence are very important for reliable identification of the mechanism of superconductivity. Tunneling conductance spectra, obtained with silver paint contacts, fabricated at the surface of sample EEA16, are depicted in Fig. 3. A dip in conductance with a width \( 2\Delta \) is clearly visible in these spectra at \( T<T_c \), which was found to be 5.1 K for this sample by resistivity measurements (insert in Fig. 4). The dip disappears at \( T>T_c \), indicating the presence of superconducting energy gap in this sample below \( T_c \). We observed similar behavior for other pressure-synthesized samples. A superconducting energy gap was observed in diamond by means of STM in pressure-synthesized samples by Troyanovsky et al. [9] and in single-crystalline CVD films by Sacepe et al. [10]. The latter authors were able to observe a triangular Abrikosov vortex lattice and to find a precise temperature dependence of the energy gap in the superconducting state of B-doped diamond. They concluded that their B-doped CVD diamond \( (T_c = 1.85 \text{K}) \) is well described by s-wave BCS superconductivity with \( \Delta(0)/k_B T_c = 1.74 \), characteristic of weak coupling. This picture of diamond superconductivity was developed in a number of theoretical papers [11–14] and is now finding increasing experimental support. The temperature dependence of the energy gap of superconducting EEA16 diamond is shown in Fig. 4. It is
well fitted by a weak coupling BCS dependence with $\Delta(0)/k_BT_c = 1.74$. This observation indicates that a BCS-type mechanism of superconductivity in diamond is valid in a wide range of $T_c$'s (hole doping) 2–5 K and for samples prepared in different ways.

Most of experimental observations existing now indicate the BCS-like, optical phonon-assisted mechanism of superconducting pairing in B-doped diamond. But the first model of superconductivity in this material, proposed by Baskaran [15,16], was based on a resonating valence bond mechanism in which superconductivity is developed via strong electronic correlations in an impurity band. Though this model has no strong experimental support, it does predict that normal state properties of superconducting B-doped diamond may be anomalous. The semiconducting behavior of the normal state resistivity of heavily B-doped diamond is itself anomalous. All samples—indeed of their method of preparation and $T_c$—have a negative $\rho/dT$ just above $T_c$. Attempts to fit this temperature dependence by an activation law $\rho \propto \exp(E_a/k_BT)$ or variable range hopping dependence $\rho \propto \exp[(T_0/T)^{1/4}]$ fail or give physically unrealistic values of $E_a$ and $T_0$ and represent data only in a limited temperature range. At the same time, it is well established that B-doping leads to a metal–insulator transition (MIT) and superconducting diamond samples are indeed metallic near room temperature. The low temperature electrical conductivity of doped semiconductors very close to a MIT is usually described by the equation $\sigma(T) = \sigma(0) + BT^x$, where $B = \text{const}$, $x = 1/3$ or $1/2$, and $\sigma(0)$ is the extrapolated electrical conductivity at zero temperature. $\sigma(0)$ is finite on the metallic side of MIT and equals zero on the insulating side [17,18]. This equation usually holds at low temperatures and close to a MIT, but it well fits the temperature dependence of resistivity of sample EEA18 over a surprisingly wide temperature range from 4.8 K (just above $T_c$) to 125 K (Fig. 5). This sample has $\sigma(0) = 370 \Omega^{-1}\text{cm}^{-1}$ and is well on the metallic side of the MIT. Other samples prepared at high pressure from B$_4$C-graphite and B-C-H also exhibit similar behavior in wide temperature intervals. The magnetic susceptibility of sample EEA18 in the range 4.5–360 K is shown in Fig. 6. This B-doped diamond is slightly paramagnetic, in contrast to undoped diamond, which is diamagnetic with a temperature-independent $\chi = -4.5 \times 10^{-7} \text{emu/g}$ [19]. The paramagnetic susceptibility of EEA18 can be well described by the equation $\chi(T) = \chi_0 + aT^{0.034}$ in a wide temperature range 4.8–125 K (Fig. 6)—the same range where anomalous conductivity is observed. At present, we cannot explain the observed dependences of susceptibility and resistivity of the normal state of superconducting B-doped diamond. Measurements on more uniform and well-characterized samples are needed.
4. Conclusion

Specific heat measurements in high magnetic fields on superconducting B-doped diamonds prove unambiguously the bulk nature of superconductivity in this material. Tunneling measurements on pressure-synthesized samples are consistent with a BCS-like phonon-assisted mechanism for superconductivity in diamond. Anomalous electric and magnetic properties of the normal state may indicate the importance of electronic correlations in hole-doped diamond and require further analysis.

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