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Abstract

Superconducting boron-doped diamond samples were synthesized with isotopes of ^{10}B, ^{11}B, ^{13}C and ^{12}C. We claim the presence of a carbon isotope effect on the superconducting transition temperature, which supports the 'diamond-carbon'-related nature of superconductivity and the importance of the electron–phonon interaction as the mechanism of superconductivity in diamond. Isotope substitution permits us to relate almost all bands in the Raman spectra of heavily boron-doped diamond to the vibrations of carbon atoms. The 500 cm^{-1} Raman band shifts with either carbon or boron isotope substitution and may be associated with vibrations of paired or clustered boron. The absence of a superconducting transition (down to 1.6 K) in diamonds synthesized in the Co–C–B system at 1900 K correlates with the small boron concentration deduced from lattice parameters.

1. Introduction

Diamond heavily doped with boron is a promising structural material thanks to its high electrical conductivity, chemical stability and excellent mechanical properties. The discovery of superconductivity in polycrystalline boron-doped diamond (BDD) [1] synthesized at high pressures and high temperatures (HPHT) stimulated studies of the mechanisms of boron incorporation in diamond and of the BDD properties at low temperatures [2–7]. Physical properties and the structure of BDD strongly depend on the method of diamond production. In this context, it is pertinent to compare here some methods for the synthesis of BDD using the HPHT technique. In the initial work [1], polycrystalline BDD was obtained in the boron–carbon (B$_4$C–C) system at pressures 8–9 GPa and temperatures about 2500–2800 K. In this system, B$_4$C reacts with graphite to form the eutectic melt; graphite dissolves in the melt and diamond crystallizes from it [8]. Boron is incorporated into the diamond lattice directly in the course of diamond crystallization. In accordance with current views on phase diagrams of partial solid solutions, the amount of boron incorporated into the diamond lattice during the synthesis must correspond to the boron solubility limit at the synthesis temperature. It was reported in [9] that an increase of pressure for the synthesis of BDD from 8–9 GPa [1] to 20 GPa [9] reduced the cubic lattice parameter of diamond from 3.5755 ± 0.0005 Å [1] to 3.5724–3.5739 Å [9] and decreased the superconducting transition temperatures from 4–2.3 K [1] to 2.3–1.4 K [9]. We believe that this effect is related to a change in the mechanism of the graphite-to-diamond transformation at higher pressure. Graphite directly transforms into diamond at pressures of 12–25 GPa and temperatures exceeding 1900 K [10], and one cannot exclude that the synthesis of BDD in the B$_4$C-graphite system at 20 GPa [9] begins from the direct conversion of graphite to diamond, which finally leads to a BDD formation scenario very different from that in [1]. In [11, 12], the BDD synthesis was carried out using a temperature gradient

method at a pressure of 5.5 GPa and temperatures of about
1700–1800 K. A metallic alloy was used as a crystal growth
medium for the BDD synthesis. It was reported that the
concentration of boron in the crystals did not reach the
critical value 7×10^{20} cm^{-3}, at which a metal-to-insulator
transition takes place in the bulk HPHT single crystals of BDD
synthesized with a metal melt [13] and in single-crystalline
superconducting films grown by chemical vapor deposition
(CVD) [14]. Note that crystals in [13] were cooled down to
2–4 K, probably a little above any possible superconducting
transition. Unfortunately, the conditions for diamond crystal
synthesis were not reported in [13]. Undoubtedly, the problem
of the BDD synthesis in the form of single crystals is rather
difficult because incorporation of boron in diamond strains
the diamond lattice and thus might interfere with the crystal
growth. On the other hand, it is necessary to consider the
effect of kinetic factors on the doping and the effect of the
synthesis temperature on the solubility of boron in diamond.
For example, solubility of boron (substitutional impurity) in
graphite increases from 1% at 2100 K to 2.35% at 2600 K
(temperature of the B$_4$C-graphite eutectic) [15].

Little is known about the properties of the solid solution
of boron in diamond at high boron doping levels. With
increasing boron concentration in diamond, the zone-centre
optical phonon peak in Raman spectra of diamond broadens
and shifts from 1332 cm^{-1} towards lower wavenumbers [16,
17]. Also, new strong bands appear at 1225 and 500 cm^{-1};
the origin of these bands is yet uncertain. The observation of
an isotope effect would be very important for identification of
the vibrational modes as well as for understanding the nature
of superconductivity in BDD. Recent work [7] on isotopic
substitution of ^{12}C by ^{13}C in BDD (C + 7% B) has reported a
large carbon-isotope effect on the superconducting transition
temperature T_c. If this result is correct then it indicates a
diamond-related nature of superconductivity in BDD even
with boron-rich (95% B + C) inclusions [18]. Considering the
sensitivity of the physical properties of BDD to the sample
preparation procedures, it is necessary to reveal the isotope
effect on superconductivity of BDD using another HPHT
route.

The purpose of this work is to study the carbon and boron
isotope effects on vibrational properties and superconducting
transition temperature of heavily boron-doped diamond.
Assuming that Co has no substantial effect on the solubility of
boron in diamond, the effect of temperature during diamond
synthesis on properties of BDD was tested using the Co–B–C
system.

2. Materials and methods

Polycrystalline samples of BDD were synthesized in the
B–C system at pressure of 8–9 GPa and a temperature of
about 2500 K for 6–10 s. Under pressure, an HPHT cell was
heated by passing electric current through a graphite bar
with a piece of boron in the centre of the bar. As soon as
the temperature inside the bar reaches the temperature of
the eutectic melting in the B–C system, diamond formation
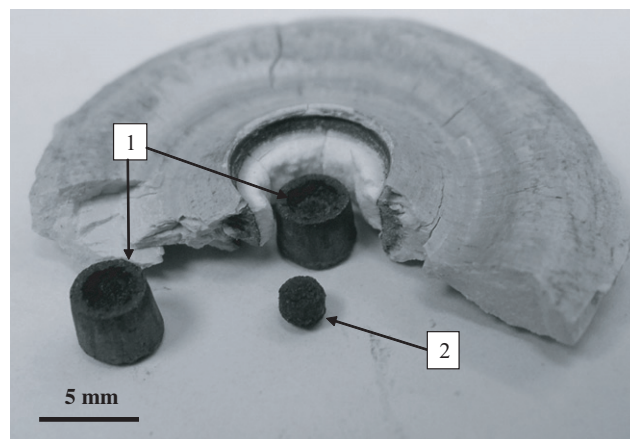takes place at the boron-graphite boundary. In principle, the

Figure 1. Parts of a high pressure cell after experiment: (1) two
parts of a graphite bar (heater), (2) a ball-like sample of BDD
recovered from the hole in the bar.

mechanism of BDD synthesis is similar to that [1] briefly
described above. A polycrystalline aggregate (30–35 mg) of
BDD with grain size up to 10 μm is produced at the boundary
of the graphite bar and the piece of boron (0.8–1.5 mg).
Parts of a high-pressure cell with a sample of BDD are
shown in figure 1. The overall amount of boron in a
sample of BDD (with unreacted boron in the centre of a
sample) was calculated as about 4 at.%. All samples in
the B–C system were produced under the same synthesis
conditions. For the synthesis of BDD from ^{13}C carbon, an
amorphous carbon (^{13}C 99 at.%, Fe 0.001%, Isotec) pellet
with a piece of boron was placed inside a graphite bar.
Samples of BDD were produced from graphite (^{12}C 99%,
C 99.999%) and amorphous carbon (^{13}C) using boron with
the natural isotope composition (^{10}B 20 at.% + ^{11}B 80 at.%,
crystalline, B 99.7%, Aldrich Chem. Co.), ^{10}B (^{10}B 96 at.%,
B 99.9% crystalline, Alfa Aesar) and ^{11}B (^{11}B 96 at.%,
B 99.9%, crystalline, Alfa Aesar). The samples synthesized
from carbon and natural boron are labelled as B-^{13}C and
B-^{12}C. The samples obtained with ^{10}B and ^{11}B are denoted as
^{10}B-^{12}C(^{13}C) and ^{11}B-^{12}C(^{13}C), respectively. Electron probe
microanalysis (INCA ENERGY, JSM-6390LV) did not detect
metallic impurities (<0.2%) in diamond samples synthesized
in the B–C systems. Synthesis of BDD using metallic growth
medium was carried out in two ways: by placing a piece of
the B (15 mass%)–Co alloy in the centre of a graphite bar and
by placing a piece of Co in the centre of the graphite-boron
(10%) mixture. Note that the presence of Co in the diamond
growth system decreases the BDD synthesis temperature to
about 1700–1900 K. After the synthesis, diamond samples
were boiled in HClO$_4$ and a mixture of H$_2$SO$_4$ with
HNO$_3$ acids to remove the growth medium. A LabRam
HR-800 spectrometer with He-Ne and Ar lasers emitting at
632.8 and 488 nm, respectively, were used for micro-Raman
analysis of BDD samples. Laser radiation was focused to
a spot of about 1–2 (objective ×100), 5 (×50) and 10 μm
(×10) in diameter. X-ray diffraction patterns were recorded
with a powder diffractometer STADI MP (Stoe) using
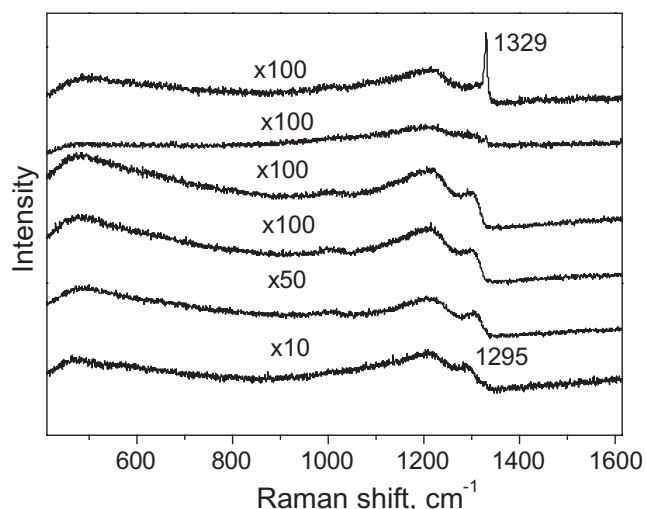monochromatic Cu Kα_1 radiation. Magnetic ac susceptibility

Figure 2. Raman spectra of the B-^{12}C BDD excited at 488 nm using different objectives: ×100, ×50, ×10. Spectra were collected from different parts of the same sample and shifted for presentation purposes. Inhomogeneous incorporation of boron in BDD was revealed when the measuring spot size on the sample surface was decreased from 10 (objective ×10) to 1–2(×100) μm: tiny inclusions of slightly B-doped diamond (one-phonon diamond Raman line at 1329 cm^{-1}) were detected in the polycrystalline heavily boron-doped diamond matrix.

measurements were performed with a home-built coil system and SR830 lock-in amplifier.

3. Results and discussion

3.1. Raman study

Micro-Raman spectroscopy (488 nm excitation) revealed inhomogeneous incorporation of boron in our BDD samples when the measuring spot size on the sample surface was decreased from 10 (objective × 10) to 1–2 μm (×100). Analysis of the spectra in figure 2 suggests that microstructure of our BDD samples can be envisioned as a polycrystalline BDD matrix with tiny inclusions of slightly B-doped diamond. These inclusions can be accidently detected in the samples with the laser spot of 1–2 μm. The formation of slightly doped diamond is believed to be due to the formation of diamond growth sectors which accept less boron [19].

Because the intensities of the bands at 1225 and 500 cm^{-1} in the Raman spectra of our samples increased with excitation wavelength (from 488 to 632.8 nm), we used the 632.8 nm excitation for the investigation of an isotope effect in the Raman scattering spectra. Note that inhomogeneous incorporation of boron in BDD complicates evaluation of an isotope effect in these experiments. We compared Raman spectra from the most heavily boron-doped regions of our samples, assuming that these regions belong to {111} sectors of diamond grains [19]. A signature of the most heavily doped regions is an extreme low-frequency shift of all the BDD Raman bands. Thus, spectra of B-^{13}C and B-^{12}C, ^{11}B-^{12}C and ^{10}B-^{12}C in figures 3 and 4 correspond to such most heavily boron-doped regions which are typical of the polycrystalline BDD matrix. Figures 3 and 4 plot representative spectra for
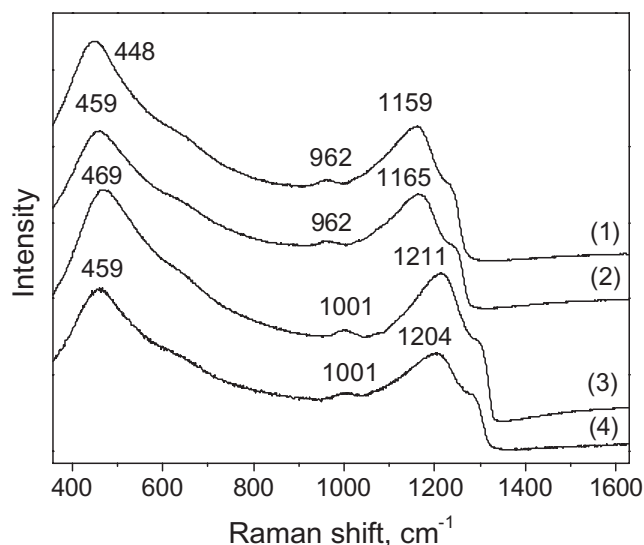

Figure 3. Raman spectra of isotope-enriched BDD excited at 632.8 nm: B-^{13}C (1, 2) and B-^{12}C (3, 4); objective ×100. Each couple of spectra along with wavenumbers (cm^{-1}) of Raman band position demonstrates local variation of Raman spectra characteristic of the samples. Spectra are shifted for presentation purposes.

Figure 4. Raman spectra of isotope-enriched BDD excited at 632.8 nm: ^{11}B-^{12}C (1, 2) and ^{10}B-^{12}C (3, 4); objective ×50. Each couple of spectra along with wavenumbers (cm^{-1}) of Raman band position demonstrates local variation of Raman spectra characteristic of the samples. Spectra are shifted for presentation purposes.
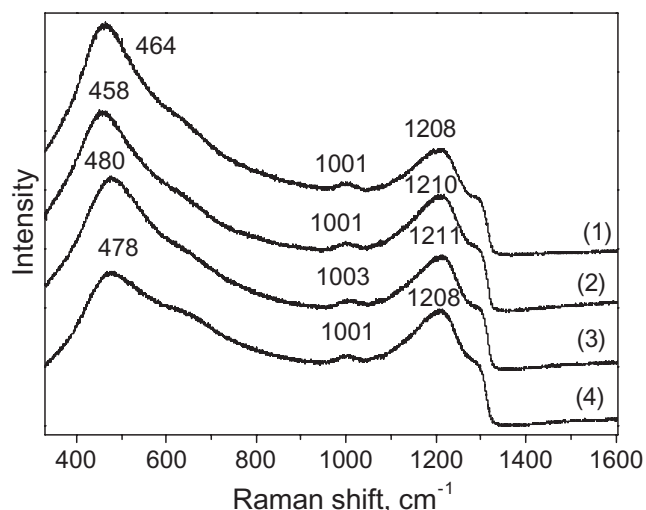
each sample. They show the extreme band positions (largest shift) among numerous measurements on the same sample. Except for the 500 cm^{-1} band, the carbon isotope substitution shifts the Raman bands in the corresponding spectra in good agreement with the relationship $M^{1/2}(^{12}C)\nu(^{12}C) = M^{1/2}(^{13}C)\nu(^{13}C)$, where ν is the corresponding Raman frequency and M is the atomic mass. The situation with the 500 cm^{-1} band is more complicated. An average carbon isotope shift of the 500 cm^{-1} band $\nu(^{12}C)/\nu(^{13}C) \sim 1.02$, is less than 1.04 expected for a carbon-only vibration. The 500 cm^{-1} band in Raman spectra of BDD was previously

Table 1. Lattice parameters of BDD samples used for magnetic ac susceptibility measurements.

Sample	^{12}C-^{10}B	^{12}C-^{11}B	^{13}C-^{10}B	^{13}C-^{11}B	^{12}C	^{12}C-B(Co–B–C)
Lattice parameter (± 0.0001 Å)	3.5749	3.5748	3.5743	3.5744	3.5667	3.569 (± 0.001 Å)

assigned to a local vibrational mode of boron pairs [17, 21]. Consistent with this assignment, the isotope shift $\nu(^{10}\text{B})/\nu(^{11}\text{B}) \sim 1.04$ of the 500 cm^{-1} band was observed by changing the boron isotope in BDD prepared with ^{12}C. The observation of a strong boron isotope shift of the 500 cm^{-1} Raman band along with a less pronounced carbon isotope shift suggests that boron dimers or clustered boron atoms contribute to this band. No changes caused by boron isotopic substitution were detected in the frequencies of other bands in the Raman spectra of BDD. This result suggests that 1225 and 1000 cm^{-1} Raman bands of BDD originate from the phonon density of states of diamond.

3.2. The effect of temperature of the diamond synthesis on properties of BDD

Introduction of Co into the B–C system decreases the BDD synthesis temperature to about 1700–1900 K, at which the eutectic melting takes place in the Co–B–C system. Assuming that Co has no substantial effect on solubility of boron in diamond, the effect of the temperature of the diamond synthesis on properties of BDD was tested using the Co–B–C system. Diamond samples obtained in the Co–C–B growth system at temperatures of about 1700–1900 K did not show a superconducting transition down to 1.6 K. At temperatures ranging from 1.6 to 300 K, all the samples demonstrated semiconducting behaviour of their resistivity. X-ray diffraction patterns of these samples reveal substantially smaller expansion of the diamond lattice compared to BDD synthesized in the B–C system (figure 5, table 1). A Vegard's model, in the case of substitutional incorporation of boron in diamond, estimates boron concentration in the samples produced in the Co–C–B system as $\sim 10^{20}$ cm^{-3}, which is critical for observation of superconductivity in BDD. A decrease in efficiency of boron doping in Co–C–B (~ 1700–1900 K) as compared with doping in the B–C (~ 2500 K) system can be explained in terms of a temperature-dependent solubility of boron in diamond, boron carbide formation and solubility of boron carbide in the Co–C melt.

3.3. Isotope effect on T_c

The observation of an isotope effect on superconductivity of BDD is a very difficult task. The shift of the critical temperature T_c due to isotopic substitution is expected to be small $\sim (12/13)^{0.5} = 0.96$ and can be easily masked by a shift of T_c due to different boron doping level; that is, the doping level of two samples composed of different isotopes should be equal. The inherent inhomogeneity of boron distribution in diamond samples broadens the superconducting transition thereby masking the isotope effects. Doping levels of two samples can be compared via, for example, their Hall
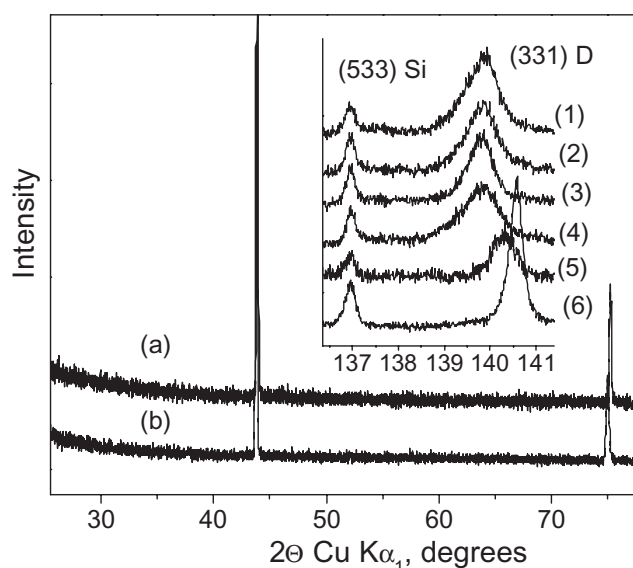

Figure 5. Characteristic x-ray diffraction patterns of diamond samples synthesized in the B–C–Co (a) and B–C (b) systems (after removing a growth medium): non-diamond peaks were not detected. Inset: x-ray diffraction patterns of diamond samples near the (331) diamond (D) reflection: (1) ^{13}C-^{10}B, (2) ^{13}C-^{11}B, (3) ^{12}C-^{11}B, (4) ^{12}C-^{10}B, (5) ^{12}C-B, synthesized in the Co–C–B system, (6) ^{12}C, undoped diamond sample. The (533) peak of a Si standard was used to calculate the lattice parameter of diamond. Si powder was placed on the surface of a small diamond sample. X-ray diffraction patterns are shifted for presentation purposes.

concentrations or lattice parameters. The comparison of the critical temperatures is possible via electrical resistivity or magnetic susceptibility measurements. We used susceptibility measurements to study the isotope effect on T_c, because resistivity measurements on different samples may be affected by different percolation paths in the samples compared. The macroscopic inhomogeneity of BDD sample properties can be reduced by choosing as small a sample as possible. First, we determined lattice parameters of the selected samples using x-ray diffraction, with Si as a standard. And finally, ac susceptibility measurements were made on these samples (having approximately equal masses, ~ 0.5 mg) in the same coil system. Even when synthesizing samples at the same P-T parameters, it is difficult to obtain samples of BDD with exactly the same lattice parameters because of the different initial structures of ^{12}C (graphite) and ^{13}C (amorphous) materials. However, we were able to prepare a series of samples with sufficiently close values of the lattice parameters of ^{12}C and ^{13}C BDD.

The x-ray diffraction patterns near the (331) peak are shown in figure 5 for selected samples of this series. The (533) peak of a Si standard was used to calculate the lattice parameter of diamond (table 1). Si powder was placed on the surface of a small diamond piece. The (331) peak
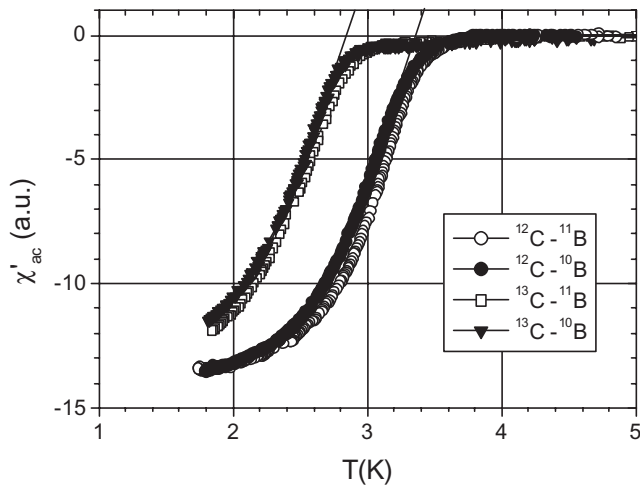
Figure 6. The dispersive part χ' of the magnetic ac susceptibility of four boron-doped diamond samples (1–4 in figure 5).

of BDD samples is broad and slightly asymmetric, which may be related to the presence of grains with different growth directions in these polycrystalline samples. The results of ac susceptibility measurements χ' on these samples are shown in figure 6. All samples of the series exhibit one broad superconducting transition. The transitions in two ^{13}C diamonds are shifted by about 500 mK to lower temperatures compared to two ^{12}C samples. To extract an isotope effect from this shift of T_c, one should take into account the difference in boron doping, which can be calculated from experimentally determined values of the lattice parameters (table 1), and the dependence of T_c on the lattice parameter [22]. We estimated ΔT_c due to a difference in boron doping as 0.25 K for samples ^{12}C-^{10}B and ^{13}C-^{10}B and 0.16 K for samples ^{12}C-^{11}B and ^{13}C-^{11}B. The value of the isotope effect coefficient is $\beta_0 = -d\ln T_c/d\ln M$. The value $\beta_0 = 0.5$ is expected for phonon-mediated superconductivity. After correction of measured T_c for different boron doping, we obtained a large carbon isotope effect (β_{0C}) in our samples. For diamond samples doped with ^{10}B, the value is $\beta_{0C} = 1.1 \pm 0.4$. For diamond samples doped with ^{11}B, the value is $\beta_{0C} = 1.4 \pm 0.4$. Recently Dubrovinskaia *et al* [7] reported a large carbon isotope effect on superconductivity in B-doped diamond. They found a 0.2 K difference in T_c of two samples of ^{12}C and ^{13}C BDD, with $T_c \sim 2.4$ K (zero resistance at 1.4 K), synthesized at 20 GPa. The calculated isotope effect coefficient $\beta_{0C} \sim 1.8$ is even larger than we found for our samples. Experimental values of β_{0C} are well above $\beta_0 = 0.5$, which is expected for 'pure' electron–phonon mechanism of superconductivity. In most superconductors with the electron–phonon mechanism of superconductivity, β_0 deviates to lower values relative to 0.5. This is explained by accounting for the Coulomb repulsion. When the Coulomb pseudopotential μ^* is significant compared to the electron–phonon interaction, the value of β_0 may be reduced below 0.5. In some rare cases, enhanced values of β_0 were observed. One model (Carbotte *et al* [23]) of this β_0 enhancement looks relevant to the case of BDD. This model describes the pair-breaking effect of paramagnetic impurities

(in the manner of Abrikosov–Gor'kov theory) on the isotope effect in superconductivity. The pair-breaking effect in this model is isolated in the sense that all other mechanisms of changing β_0 are ignored and $\beta_0 = 0.5$ without pair-breaking. Pair-breaking is introduced via a parameter τ_p, which is equal to infinity in the absence of pair-breaking (infinite life-time of Cooper pairs) but becomes finite and small in the case of strong pair-breaking. Calculations [23] show that an increase of pair-breaking (decrease of τ_p) results in suppression of T_c and an increase of β_0 well above $\beta_0 = 0.5$. The role of the τ_p parameter for diamond may affect the real life-time of Cooper pairs which is short in BDD due to strong disorder [24]. A high degree of disorder in BDD manifests itself in broad superconducting transitions and a very short mean free path of doped holes. Calculations [24] showed that ordering of boron atoms incorporated into the diamond lattice will substantially enhance the superconducting transition temperature of BDD. In the case of highly disordered boron atoms in BDD with broad transitions, it is natural to expect an enhanced isotope effect in the spirit of the model of Carbotte *et al* [23]. More experimental and theoretical work is needed on the isotope effect in boron-doped diamond.

4. Conclusions

Polycrystalline samples of BDD were synthesized at high pressure (8 GPa) and high temperatures (1700–2500 K) in the Co–C–B and B–C systems. The effects of carbon and boron isotopic substitutions and of the synthesis temperature were studied. We observed a carbon isotope effect on the superconducting transition temperature T_c that supports the importance of the electron–phonon interaction as the mechanism of superconductivity in diamond. Isotopic substitution permits us to relate almost all bands in the Raman spectra of BDD with vibrations of carbon atoms. The 500 cm^{-1} Raman band shifts either with carbon or boron isotope substitution and may be associated with vibrations of paired or clustered boron. The absence of a superconducting transition (down to 1.6 K) in BDD synthesized in the Co–C–B system at 1700–1900 K was explained by the reduced solubility of boron in diamond with decrease in temperature of the BDD synthesis.

Acknowledgments

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