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Lattice parameters and thermal expansion of superconducting boron-doped diamonds

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Using two different high-pressure techniques, we have prepared boron-doped diamonds with atomic concentration of the dopant ranging from 0.04% to 4% (from 7×10^{19} to 7×10^{21} atom/cm^3) and studied the lattice constants and thermal expansion of the diamonds in the temperature range from 90 to 300 K. Both sets of samples demonstrate the same increasing concentration dependence of the lattice parameter with maximum shift of the lattice constant about 0.011 Å. We have established an abnormally high thermal expansion of the heavily boron-doped superconducting diamonds with respect to the undoped ones and a nearly linear correlation between lattice constant and critical temperature of the superconducting transition.

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The record high atomic density of diamond (1.76×10^{23} atom/cm^3) accounts for its record elastic and mechanical properties but at the same time limits the possibilities for doping it. Only nitrogen and boron atoms can be incorporated into the diamond lattice fairly easily. A typical amount of doping of diamond with boron is $10^{17}-10^{20}$ atom/cm^3; however, a number of publications report that the values of 10^{21} atom/cm^3 have been attained.[1–4] At a relatively low concentration, boron atoms seem to substitute for carbon atoms in the diamond lattice. At high concentrations $n_B > 10^{20}$ atom/cm^3, the mechanism of the incorporation of boron into the diamond lattice cannot be considered unambiguously established.[1–7] Boron doping gives rise to semiconducting properties of diamond, until, at a critical concentration of $n_B \approx 2\times10^{20}$ atom/cm^3 the doping results in a metallic-type conductivity in diamond at moderate temperatures.[2,8,9] It has been discovered recently that a further increase in boron concentration to $n_B > 10^{21}$ atom/cm^3 produces superconductivity in diamond.[10] Here, the boron concentration gives the upper limit of the carrier (hole) concentration. The bulk nature of the superconductivity,[11] sufficiently high values of the critical temperature ($T_C \approx 7$ K) and critical field ($H_{cr} \approx 15$ T), and its unique mechanical and thermal properties allow us to consider superconducting diamond as one of the primary materials for electronics of the future.

The study of the nature of superconductivity and of the properties of heavily doped diamonds is at the initial stage yet (see Ref. 11 and references therein), although the latest research on the dynamics of the boron-doped diamond lattice by Raman spectroscopy[3,5,12–14] and inelastic x-ray scattering,[15] as well as the study of the T_c dependence of the doping level,[16] indicate some advances in the experimental study of superconducting diamond. In this respect, data on the boron concentration dependence of the lattice parameter and on the thermal expansion are essential for further insight into the mechanism of the incorporation of boron atoms and the nature of superconductivity in heavily doped diamonds. In particular, the concentration dependence of the lattice parameter can throw light on the mechanism of the penetration of boron into the diamond lattice, while the data on thermal expansion are useful for examining lattice dynamics. The complexity of such studies lies, first, in the difficulty of determining independently the B concentration, and, second, in the low magnitude of the effects measured. For undoped diamond, the lattice parameter is $a=3.5666\pm0.0001$ Å at $T=4.2$ K and $a=3.5669\pm0.0001$ Å at $T=300$ K.[17] The low thermal expansion of diamond is in accordance with its high Debye temperature $\theta_D=1860$ K and high value of bulk modulus $B=443$ GPa. Measurements of the lattice parameter of boron-doped diamond at room temperature[1–4,6,10,11] have shown slightly different values, which is, among other factors, due to the great uncertainty of the boron concentration measurements. Generally, on the basis of published data, one can draw the conclusion of a small ($\approx$0.1%) increase in the lattice parameter for heavily doped diamonds ($n_B \sim 10^{21}$). To our knowledge, only one attempt has been made to examine the thermal expansion of boron-doped diamond with $n_B \sim 10^{19}$ atom/cm^3.[17] According to Ref. 17, for diamond with the above doping level, as well as for undoped diamond, the lattice parameter in the temperature range $4.2 < T < 300$ K increases proportionally to T^4, which is consistent with the Debye model.

In the current paper we present a high-accuracy study of the lattice parameters and thermal expansion of boron-doped diamonds with B concentrations in the range from 7×10^{19} to 7×10^{21} atom/cm^3 (from 0.04 to 4 at. %). In this study our primary attention is focused on heavily doped diamonds with superconducting properties. The obtained data suggest the existence of two different modes of incorporation of boron into diamond, substitutional at low doping levels and for heavily doped diamonds more complex with possible aggregation of boron atoms. One of the principal results of the work is that for heavily doped diamonds we have found very high thermal expansion coefficients, exceeding those for pure diamond by several or dozens of times, depending on

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temperature. We have also determined the correlation between the lattice parameter and superconducting temperature.

Heavily doped diamond samples were produced by two totally different procedures. The first one involved the decomposition of boron-containing hydrocarbons at $P \approx 8$ GPa and $T \approx 2000$ K.[1,18] The resultant product was a powder of single-crystal diamonds with the crystal size of 20–100 μm. Another procedure consisted in the production of large ($\sim 1-3$ mm) doped diamond polycrystals by synthesis from graphite in the presence of B_4C or B at pressure $P \approx 8-9$ GPa and temperature $T \approx 2500-2800$ K.[10,11] After synthesis, diamond crystals were boiled in perchloric acid ($HClO_4$) and etched in hydrofluoric acid to remove graphite and accompanying substances. Diamond samples treated in acids contained less than 0.2 wt. % of metallic impurities. Diamonds with the B concentration $n_B > 2 \times 10^{21}$ atom/cm^3, obtained by both procedures, were superconducting with T_c from 1.5 to 6 K. For the x-ray diffraction study, the samples were pounded between hard-alloy anvils to the particle size of $5-10$ μm.

An independent determination of the B concentration in diamonds is a rather difficult experimental problem. Earlier, different authors have employed various methods, such as secondary ion mass spectroscopy, NMR, etc.[1,10,16] In this work, the relative quantity of boron and carbon in the samples was determined by spectroscopy of the nuclear reactions with deuterons on the electrostatic accelerator of PNPI (Gatchina).[19] The carbon and boron concentrations were determined through the nuclear reactions $^{12}C(d,p)^{13}C$ and $^{10}B(d,\alpha_0)^{88}Be$, respectively. The powder to be studied was pressed into a polished indium plate, and the layer of the sample under examination was 10 μm. This technique allows the determination of the boron concentration in diamond with a high precision up to 3–5 %. Some samples from the first experimental set contained the impurity B_4C that significantly increased the B concentration uncertainty, since the concentration of B_4C was estimated from x-ray diffraction data.

The diamond lattice parameters were measured at the SPring-8 synchrotron radiation facility at the BL02B2 powder diffraction beamline using the Image Plate (BAS-MS2040 by Fujifilm) registration technique in the Debye-Scherrer camera. The powder to be examined was placed in a thin-walled capillary made from quartz glass with internal diameter of $0.1-0.3$ mm. The CeO_2 powder was used as a standard for measuring the radiation wave length. Powder diffraction data have been collected up to scattering vector 21 Å^{-1} using x-ray radiation with wavelength ≈ 0.345 Å, but for accurate determination of the lattice parameter we used the data up to 18.5 Å^{-1}, including 27 diamond reflections (Fig. 1). We did not observe any forbidden reflections of the diamond lattice, like (200). A special fitting procedure was applied to eliminate possible uncertainty in the zero-scattering angle (the beam center) positioning during software analysis of the Image Plate data. The energy resolution of the BL02B2 beamline, $\Delta E/E = 2 \times 10^{-4}$, and the observed variation of the lattice parameter determined from individual reflections (probably due to defects, stresses, etc.) provided an accuracy of determination of the diamond lattice parameter in the range from 1.5×10^{-4} to 3×10^{-4} Å. Thermal expansion of the samples was studied by measuring the lattice parameter in the temperature range $90-300$ K using a low-temperature N_2 gas flow system.

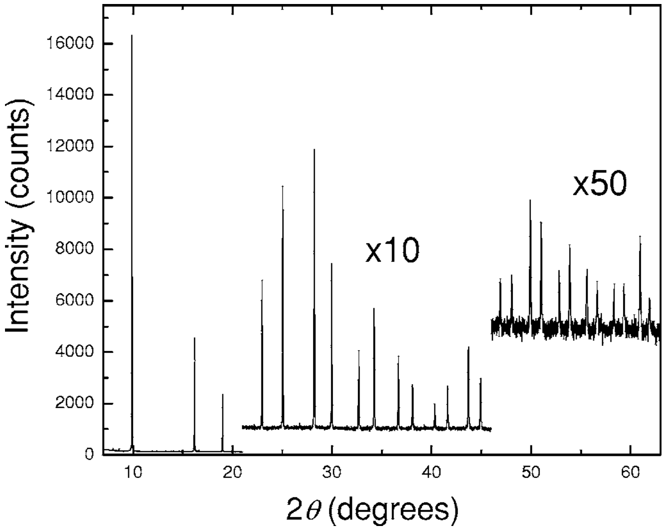

FIG. 1. The x-ray diffraction pattern from the boron-doped diamond showing the typical noise level and interval of scattering angle 2θ. Saturation limit of the Image Plate in the current scanning mode is 40 000 counts per pixel.

The obtained concentration dependence of the diamond lattice parameter $a(x)$ is presented in Fig. 2. Both sets of boron-doped diamonds prepared by totally different methods

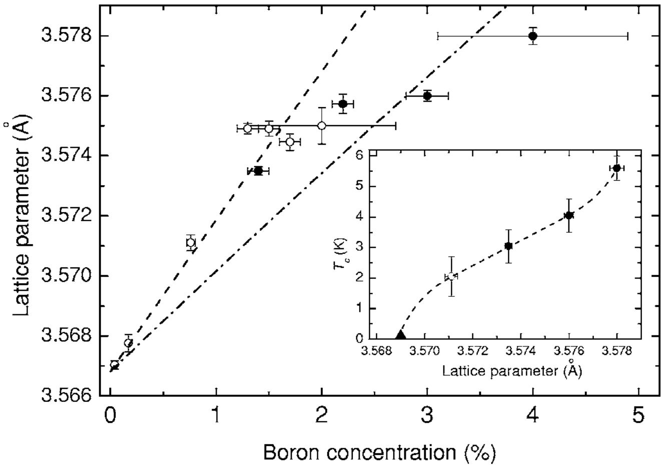

FIG. 2. Diamond lattice parameter vs boron concentration dependence. Dashed line corresponds to the substitutional model, i.e, the Vegard law for covalent radii of C and B. Dashed and dash-dotted lines corresponds to the linear dependence for average atomic volume (see the text). Inset shows the dependence of the superconducting transition temperature on the lattice parameter. In both plots open circles correspond to samples obtained by the decomposition of boron-containing hydrocarbons, and solid circles to samples obtained by synthesis from graphite in the presence of B_4C or B. Triangle point in the inset corresponds to the appearance of superconductivity, and it is estimated from the data of Ref. 16 and the current $a(x)$ dependence. Dashed line is a guide for the eyes.

demonstrate the same dependence, having an overlapping interval of concentrations. The samples of the first set consisted of well-shaped diamond single crystals with homogeneous distribution of boron atoms. For the samples of the second set, some of the boron atoms at a B concentration above 2% formed B_4C impurities at the diamond grain boundaries. One can see a near-linear increase of the lattice parameter with the B concentration at the initial doping range up to ≈1.5 at. % and a change of slope of the dependence at higher B concentrations. For the maximum B concentration ($\approx 7\times 10^{21}$ atom/cm^3), the shift of the lattice parameter is about 0.3% (or 0.011 Å). Two simple models of introducing boron atoms into the diamond lattice can be considered with respect to $a(x)$ dependence. The first one (the substitution model) is based on the linear Vegards law for the lattice parameter, taking into account the covalent radii of B and C, 0.88 and 0.77 Å,[20] respectively. The second model refers to the interstitial boron or boron aggregates and considers in the first approximation a linear dependence for average atomic volume, taking into account the atomic volumes of B and C, 7.28 and 5.67 Å^3/atom,[20] respectively. The experimental data (Fig. 2) clearly show that the initial part of $a(x)$ dependence follows the substitution model, giving evidence of a simple substitution of single carbon atoms by boron in the diamond lattice up to ≈1.5 at. % of B. This is in accordance with the very high energy of formation of isolated B interstitials in diamond.[7] On the other hand, the bend of the $a(x)$ dependence (Fig. 2) at high concentrations may be associated with the appearance of boron aggregates, such as interacting substitutional B pairs and multiboron B_n ($n=1-4$) complexes with vacancies or interstitials.[7] Particularly, interaction of substitutional B pairs is energetically favorable.[7] Raman spectroscopy[13,14] also provides evidence for the existence of interacting boron pairs in heavily doped diamond.

The dependence of the superconducting temperature on the lattice parameter $T_c(a)$ (Fig. 2) demonstrates a linear dependence for lattice parameters between 3.571 and 3.576 Å (i.e., for the B concentrations between ≈0.8% and ≈3%) and a deviation to higher T_c for $a\approx 3.578$ Å. It should be noted that the nonlinear increase of T_c at the maximum B concentration (see inset in Fig. 2) exceeds the measurement uncertainty. Here, the vertical bars in the inset of Fig. 2 do not mean uncertainty of T_c, but show the width of the superconducting transition. Taking into account that, according to Ref. 16, the critical B concentration for the appearance of superconductivity is about $(5-7)\times 10^{20}$ atom/cm^3, one can estimate from our $a(x)$ data the critical lattice parameter for superconductivity as ≈3.569 Å, which implies a nonlinear drop of T_c to the zero value on the extrapolation of the $T_c(a)$ dependence in Fig. 2 to the left side. The samples prepared by the different techniques demonstrate the same $T_c(a)$ dependence, similarly to the situation observed for $a(x)$ dependence. This is an argument in favor of a universal mechanism of B doping during high-pressure and high-temperature synthesis.

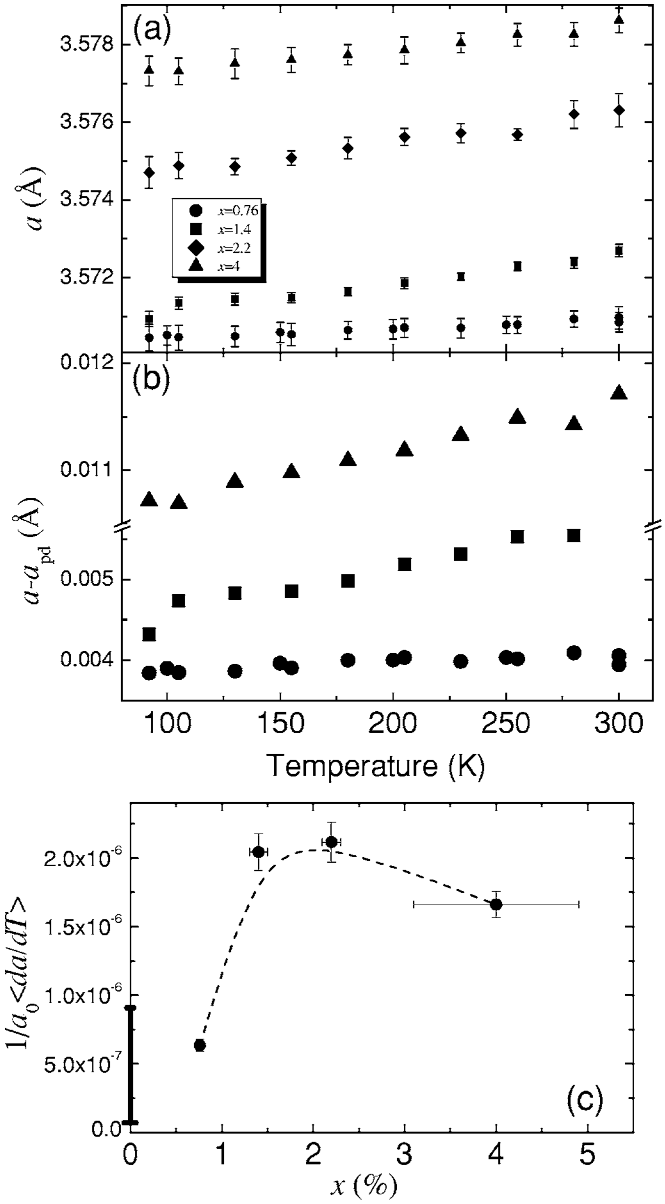

FIG. 3. The temperature dependence of lattice parameter for four different concentrations of boron doping (a); the same dependence after subtraction of the lattice parameter of pure diamond $a_{pd}(T)$ from Ref. 17 (b); and concentration dependence of relative thermal expansion coefficient in linear approximation (c), where a_0 is obtained from linear extrapolation to zero temperature. The symbol notations in (a) and (b) are the same. The vertical bar in (c) corresponds to the interval of variation of the thermal expansion coefficient of pure diamond (for the temperature range from 100 to 300 K). Dashed line in (c) is a guide for the eyes.

The temperature dependences of the lattice parameters for boron-doped diamonds with concentrations between 0.76 and 4 at. % are shown in Fig. 3(a). All dependences follow an almost linear law in the experimental temperature interval 90–300 K, taking into account the uncertainties of the experimental data. This means that they do not follow the T^4 law observed for undoped or weakly doped diamonds.[17] Moreover, for B concentrations 1.4, 2.2, and 4 at. % the contribution of the thermal expansion of pure diamond[17] is negligible with respect to the contribution of B-related and B-influenced phonon modes [see Figs. 3(a) and 3(b)], whereas for $x=0.76$ the thermal expansion of boron-doped diamond becomes comparable with that for pure diamond near room temperature. The effective thermal linear expansion coefficient for heavily doped diamonds is much higher than that for undoped diamond [Fig. 3(c)], and at the initial boron concentration it increases sharply with x, then reaches a maximum near 2%, and decreases at higher x.

It is clear that the additional high thermal expansion of the heavily boron-doped diamonds [Fig. 3(b)] should be associated with the appearance of boron substitutional atoms and boron aggregates. A nearly constant thermal expansion coefficient for our experimental temperature interval is indicative of a low effective Debye temperature ($\sim 10^2$ K) for the B-influenced part of the phonon spectrum and, consequently, of the appearance of soft phonon modes related to the B incorporation. Earlier, the possibility of a noticeable contribution to the thermal expansion of low-frequency optical modes was pointed to in Ref. 16. The Raman data[3,5,12–14] and nonelastic x-ray scattering data,[14] as well as theoretical analysis[21] are also indicative of the softening of the optical phonon modes.

The increase of the number of substitutional B atoms with x (Fig. 2) clearly correlates with the increase of the thermal expansion coefficients [Fig. 3(c)], while the saturation and decrease of the thermal expansion coefficient can be associated with the aggregation of B pairs or other B clusters, when the appearance of B-B bonds toughens the B-influenced phonon modes. We stress that the decrease of the thermal expansion coefficient is actual, that is, it cannot be attributed to the inaccuracy of measurements. The effect of softening and subsequent toughening of the B-influenced part of the phonon spectrum with the increase of x can become pronounced if we normalize the B-dependent contribution to the thermal expansion by the B concentration. In this respect, the decrease of the critical temperature of the superconducting transition with pressure[10] testifies to the toughening of soft phonon modes which might be recognized as responsible for the mechanism of superconductivity.

Summarizing, the present detailed study of the lattice parameter of boron-doped diamonds for different B doping concentrations at different temperatures shows, first, that the incorporation of boron into diamond has a universal two-stage behavior, at least for the high-pressure techniques of incorporation. Second, our study shows an abnormally high thermal expansion of heavily boron-doped diamonds, which can be related to the softening of the phonon spectrum due to the formation of the soft regions located near boron atoms. In turn, the concentration dependence of the thermal expansion coefficient suggests two different modes of B incorporation, substitutional at low doping levels and aggregation-type at higher concentrations of the B dopant. The mechanism of superconductivity of heavily boron-doped diamond can be clarified by further theoretical and experimental study of lattice dynamics for different types of boron aggregation in diamond. Particularly, such a study may involve measurements of boron-doped diamond compressibility and shifts of Raman modes under pressure.

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