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Heat capacity of bulk boron doped single crystal HPHT diamonds in the temperature range from 2 to 400 K

Heat capacity C_p of boron-doped single crystal diamonds grown by the temperature gradient method was studied. Boron content was about $< 10^{16}$, $\sim 10^{18}$ and $\sim 10^{20}$ cm^{-3}. Heat capacity data for all tested crystals match well within the measurement accuracy (1 %) in the temperature range of 150–400 K and obey the Debye law. At low temperatures heat capacity follows linear law possibly due to metallic inclusions in diamond bulk. Using this data the amount of metal can be calculated for each sample.

Keywords: *synthetic diamond, boron-doped diamond, superconductivity, heat capacity, cryogenic temperatures.*

INTRODUCTION

Boron doped diamonds are rare in nature. They exhibit all extreme properties of diamond crystal and have semiconducting properties due to boron related acceptor states at 0.37 eV above the valence band. Bulk boron doped single crystal diamonds could be used simultaneously as electric and thermal conductive substrates for wide variety of electronic devices. This requires detailed experimental analysis of their electrical and thermal properties. We reported the electrical transport properties [1] and thermal conductivity [2] of bulk synthetic crystals grown by the temperature gradient method under high pressure and high temperature (HPHT) in TISNCM. For thermal transport analysis heat capacity data are required.

It is known that heavily boron-doped polycrystalline diamonds grown by HPHT method possess heat capacity anomaly at transition to superconducting state [3, 4]. Recently we reported the superconducting transition on the as grown surface of our bulk heavily boron-doped single crystal diamonds grown by HPHT [5]. The heat capacity data at low temperatures for these diamonds could also possibly clarify the origin of superconductivity.

EXPERIMENTAL PROCEDURE

In this work we studied heat capacity C_p of boron-doped single crystal diamonds. Type II*b* diamond crystals were grown by the temperature gradient method under high-

pressure of 5.5 GPa and high temperature 1440 °C in toroid-type high-pressure apparatus. Fe–Al–C alloy (91:5:4 by wt %) was used as the solvent metal. Al was added to solvent as nitrogen getter. High purity (99.9995 %) graphite was used as carbon source. Different amount of amorphous boron powder was added to the carbon source to grow diamonds with different doping level. We studied three single crystals from 100 to 200 mg (0.5–1.0 ct.) weight (Fig. 1). Boron content was about $<10^{16}$, 10^{18}, 10^{20} cm^{-3}. It was confirmed by SIMS measurements in the bulk of the crystals. Boron concentration differs for different growth sectors of diamond crystal [6]. Thus average boron content for each crystal was used.
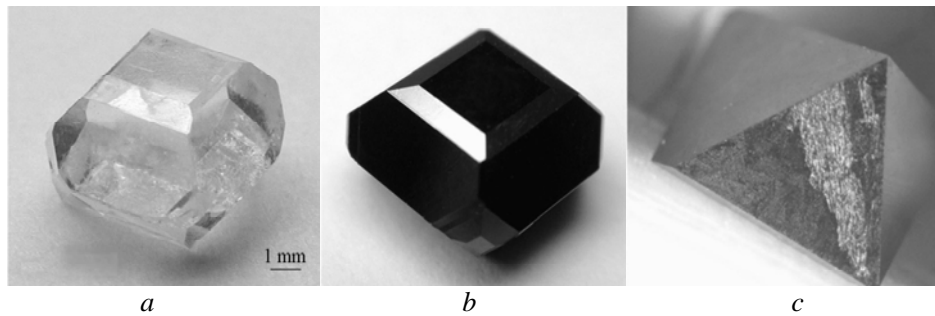

Fig. 1. Photos of diamond single crystals grown temperature gradient technique under HPHT with different boron content: $< 10^{16}$ (*a*), $\sim 10^{18}$ (*b*), $\sim 10^{20}$ (*c*) cm^{-3}.

Heat capacity measurements were carried out using Quantum Design PPMS by the relaxation method (two τ-model) in the temperature range from 400 to 2 K. The system (Fig. 2) exhibits an overall accuracy better than 1 % in the temperature range from 100 to 300 K, while at lower temperatures the accuracy diminishes [7].
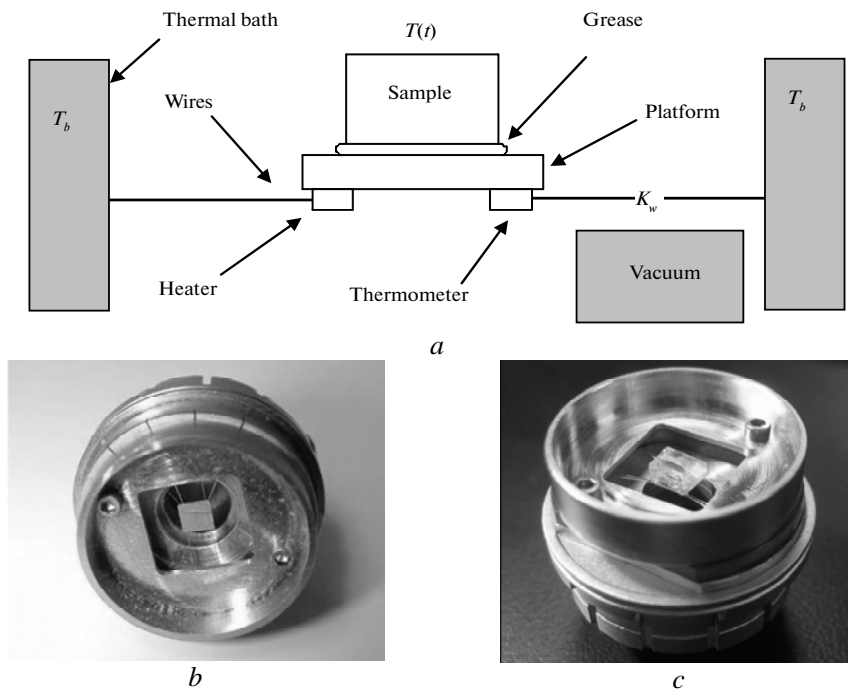

Fig. 2. Experimental equipment for heat capacity measurement: schematic view of sample platform (agenda) (*a*), sample holder with agenda photo (*b*), agenda with low-doped diamond (*c*).

RESULTS AND DISCUSSION

The heat capacity data for all tested crystals match well within the measurement accuracy (1 %) in the temperature range of 150–400 K (Fig. 3). In this temperature range C_p follows $\sim T^3$ law with small deviations due to peculiarities in diamond phonon density of states.
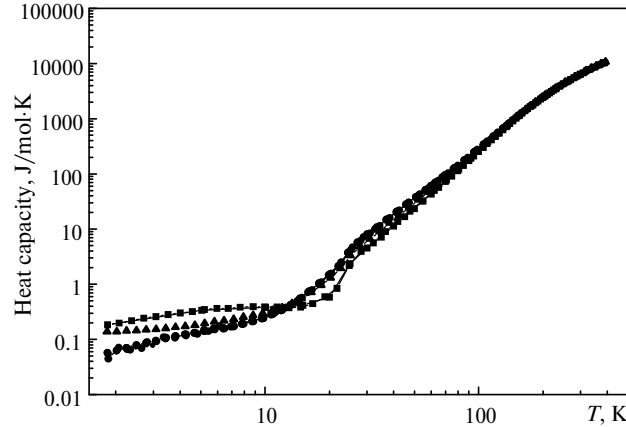

Fig. 3. Heat capacity of boron-doped diamonds with different boron contents are indicated by: $\sim 10^{20}$ (square), $\sim 10^{18}$ (triangles), $< 10^{16}$ (circles) cm^{-3}.

It should be noted that in the temperature range of 10–40 K the heat capacity of sample is very small with respect to the agenda (the measurement platform). It means that sample heat capacity adds only a little part (about 10 %) to overall measured heat capacity. Thus the error of heat capacity measurement of the sample in this temperature range is more than 1 %.

We compared our results with literature data from [8] (Fig. 4). There are deviations of our data from Cardona's ones (about 5 %) in C_p/T^3 vs T plot in the mid-temperature region. This could be due to possible metal inclusions in diamond). There was no clear difference between samples with different doping level. It means that boron doping does not affect much on diamond phonon spectra and its Debye temperature.
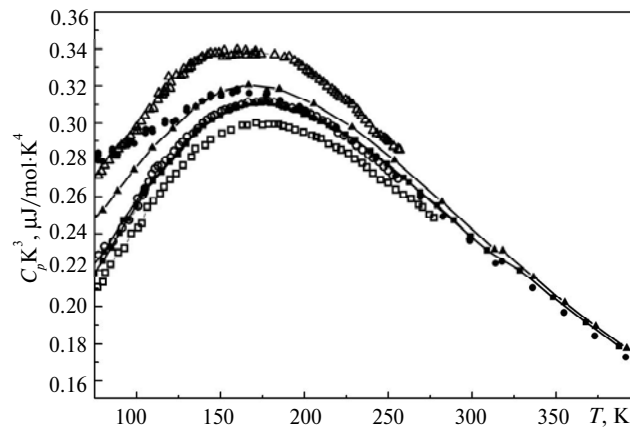

Fig. 4. C_p/T^3 vs T plot, boron contents are indicated by: 10^{20} (square), 10^{18} (triangles), $< 10^{16}$ (circles); data from [8] – ^{12}C (empty squares), ^{12}C/^{13}C 50:50 (empty circles), ^{13}C (empty triangles).

Our experimental data also coincide with the molecular-dynamics simulations based on first-principles local density-functional scheme [9] for pure diamond in terms of peak position when plotted in C_p/T^3 versus T coordinates (Fig. 5). It is noted in [9] that the isotope effect of ^{13}C on heat capacity of diamond is very small and hard to detect. In our case graphite with natural isotopic content (only 1 % of ^{13}C) was used as carbon source for diamond synthesis. But the obtained C_p data is close to pure ^{13}C diamond. It is possible that either calculations underestimate heat capacity of diamond or the real mass of our crystals is less than measured due to metallic inclusions in their bulk.
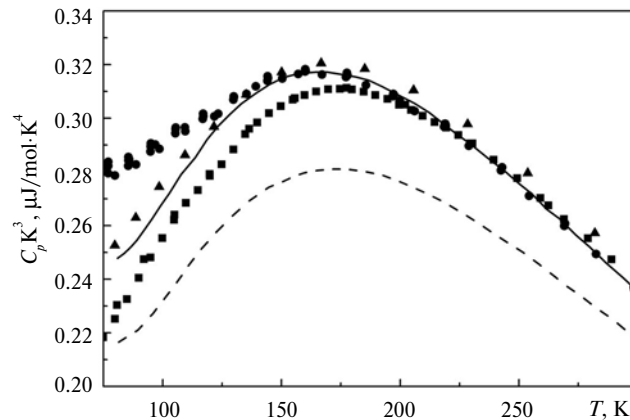

Fig 5. C_p/T^3 vs T plot, comparison with first-principles local density-functional calculations [9]: boron contents are indicated by: 10^{20} (squares), 10^{18} (triangles), $< 10^{16}$ (circles) cm^{-3}; calculations from [9] for [13]C (solid line), for [12]C (dash line).

Fig. 6 displays the C_p data in low temperature region < 100 K. C_p deviates from Debye model and follows $\sim \alpha T$ law. Each sample has its own α. One might connect this feature with the metallic-like behaviour of a phase which was found on the surface of the heavily boron-doped diamonds [5,10]. However in that case the metallic-like heat capacity behaviour should be closely related to boron content. The fact that even low doped diamond sample has metallic heat capacity behaviour at low temperature indicates that the reason for such a behaviour is not boron doping, but most likely takes place due to metallic inclusions.

An absence of a characteristic superconductivity transition peak in heat capacity which was observed on polycrystalline superconducting diamonds [4] agrees with the conclusion about surface superconductivity in single crystals evaluated on the basis of studies of structure of the samples, electrical and magnetic measurements [5].

During growth of bulk HPHT crystal the solvent metal ambient could be captured into crystal. We attribute metallic C_p law to metal inclusions with electronic heat capacity linear dependence. Heat capacity of the diamond crystal growth media was also measured. Fig. 6 compares the growth media heat capacity with diamond C_p. One could see that at low T the heat capacity of diamonds could be attributed to 1.5–4.0 weight % of the growth media inclusions. Inclusions cause the overestimation of the diamond weight. This error could explain why our C_p data exceeds the literature data [8] (see Fig. 4).

The heat capacity measurements at low $T < 10$ K could be used as non-destructive quantitative method for metal inclusions control in non-transparent II*b*

HPHT diamonds, along with magnetization measurements. One could also notice that metal inclusions content increases with boron concentration.
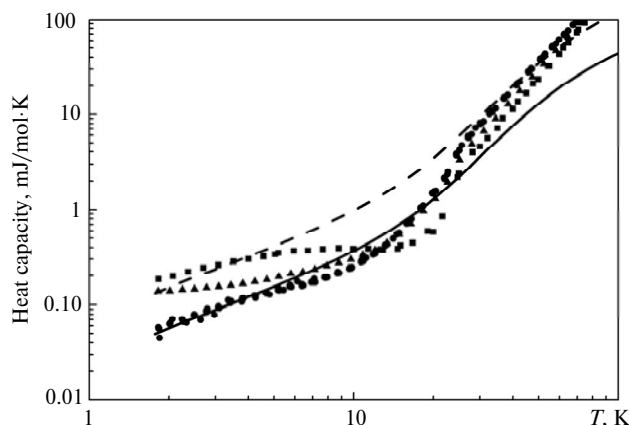

Fig. 6. Heat capacity of diamonds with different boron content (low temperature region): 10^{20} (squares), 10^{18} (triangles), $< 10^{16}$ (circles) cm^{-3}; lines show possible C_p addition caused by metallic-like inclusions of growth ambient: growth mixture $C_p \times 1.5$ % (solid line) and $C_p \times 4$ % (dash line).

CONCLUSIONS

Heat capacity of three bulk boron-doped diamond crystals with different boron content up to 10^{20} cm^{-3} was investigated in a wide temperature range of 2–400 K. We did not find substantial effect of boron content in diamond crystal on heat capacity versus temperature dependencies.

We attribute metallic-like C_p law at low temperatures to metal inclusions in a diamond bulk. After special calibration the heat capacity measurements at $T < 10$ K may be used as non-destructive quantitative method for metal inclusions control in non-transparent IIb HPHT diamonds, as well as magnetization measurements.

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Досліджено теплоємність C_p легованих бором монокристалічних алмазів, вирощених методом температурного градієнта. Вміст бору був $< 10^{16}$, $\sim 10^{18}$ і $\sim 10^{20}$ см$^{-3}$. Дані по теплоємності для всіх досліджених кристалів добре узгоджуються в межах точності вимірювань (1 %) в інтервалі температур 150–400 К і підпорядковуються закону Дебая. При низьких температурах теплоємність змінюється за лінійним законом, можливо, через наявність металевих включень в алмазі. Використовуючи ці дані, кількість металу може бути обчислена для кожного зразка.

Ключові слова: синтетичний алмаз, легований бором алмаз, надпровідність, теплоємність, кріогенні температури.

Исследована теплоемкость C_p легированных бором монокристаллических алмазов, выращенных методом температурного градиента. Содержание бора было $< 10^{16}$, $\sim 10^{18}$ и $\sim 10^{20}$ см$^{-3}$. Данные по теплоемкости для всех исследованных кристаллов хорошо согласуются в пределах точности измерений (1 %) в интервале температур 150–400 К и подчиняются закону Дебая. При низких температурах теплоемкость

изменяется по линейному закону, возможно, из-за присутствия металлических включений в алмазе. Полученные данные позволяют рассчитать долю металлических включений в каждом из образцов.

Ключевые слова: *синтетический алмаз, легированный бором алмаз, сверхпроводимость, теплоемкость, криогенные температуры.*

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