Isotopic composition dependences of lattice constant and thermal expansion of $\beta$-rhombohedral boron

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Abstract. Boron isotope substitution in boron-containing crystalline structures is important because many properties of these materials are structure sensitive. In the present work, we studied the unit cell expansion at the fixed temperature and temperature dependence of thermal expansion for the $\beta$-rhombohedral modification of boron, when $^{11}\text{B}$ is replaced by $^{10}\text{B}$ isotope. Theoretical analysis of experimental results associates the observed changes in structures of the $\beta$-rhombohedral boron samples of various isotope compositions with isotope effects rather than with technologically concomitant impurities.

1. Introduction

Boron, together with boron-rich alloys and compounds, forms the class of materials suitable for fabrication of devices and products, which can be used in extreme conditions of high temperatures, chemically aggressive environments, strong electric fields, irradiation, etc. Since in the Nature boron can be found in form of two stable isotopes $^{10}\text{B}$ and $^{11}\text{B}$ with masses differing by ~10 %, the physical properties of boron modifications and boron-rich solids are expected to be significantly affected by their isotopic compositions.

Indeed, there is a number of boron isotopic effects: fluctuations of the equilibrium positions of atoms and of the electron-phonon coupling constant can lead to the intrinsic electron localization in semiconducting boron characterized by the narrow electron bands [1]; changes in the isotopic composition shift the phonon frequencies in boron carbide [2]; the heat flow increases in isotopically pure $\beta$-rhombohedral boron crystals, because of decrease in the phonon scattering [3]; replacement of one of the boron isotope by another changes the critical temperature of the high-temperature superconductor magnesium diboride [4], as well as melting temperature [5] and melting enthalpy [6] of pure boron itself.

As it is known, variations in isotopic composition affect main characteristics of the crystalline semiconductors not only by the renormalization of the phonon spectrum, but also through the changes in lattice parameters [7-9]. The purpose of present work is experimental and theoretical estimation of the isotopic effect on the structure of $\beta$-rhombohedral boron ($\beta$-B).
2. Experimental details
Macrocrystalline $\beta$-B samples were produced by floating-zone refining of the $^{10}$B (enrichment 97.2 %, purity 98.5 %) and $^{11}$B (enrichment 99.8 %, purity 98.3 %) isotopically modified powders’ mixed at certain compositions. With the purpose of relaxation of the strains arisen in the production process, elimination of pores, and healing of microdefects in crystals, before testing samples were exposed to annealing in argon atmosphere at temperatures up to $\sim 1300$ K for 10 h. Contents of main metallic impurities in zone-refined specimens are following: Al – about 0.001, Ca – 0.004 ± 0.008, Cu – 0.001 ± 0.003, Fe – less than 0.001, Mg – 0.001 ± 0.003, Mn – less than 0.001, and Ni – 0.001 ± 0.002 wt %. Besides, they contained 0.010 ± 0.014 wt % Si. As for the carbon C, the major impurity in $\beta$-B, its content in initial powders was $\sim$ 1 wt %, while that in refined samples was less than 0.06 wt %. All these $\beta$-B specimens were produced using the same initial material (high-pure boron powders) in the same technological conditions; measurements were also performed using the same equipment and methods.

X-ray diffraction patterns were recorded at room temperature using automatic X-ray diffractometer HZG – 4A. Software allowed scanning of the most reliable maxima for the purpose of measuring the $\beta$-B unit cell parameters. Continuous diffractograms from the rotating samples were obtained using the nickel-filtered radiation, anode voltage 20 ÷ 30 kV, anode current 15 ÷ 20 mA, counting rate $10^3$ pps, time constant 3 s$^{-1}$, plotter sensitivity 100 mV/cm$^2$. Averaged errors of measurements of the hexagonal unit cell parameters $a_{hex}$ and $c_{hex}$ were 0.0007 and 0.0009 Å, respectively. This translates into averaged error of 0.0005 Å for the unit rhombohedron edge $a$ values, which are calculated from $a_{hex}$ and $c_{hex}$.

X-ray structural analysis of the investigated samples reveals the general trend of growth of the unit rhombohedron edge $a$ in dependence on the $^{10}$B isotope content $x$ in the range 0.2 – 97.2 %. The results are presented in table 1 and figure 1.

Table 1. Lattice constant values of $\beta$-rhombohedral boron samples with various isotopic compositions at room temperature.

| No | $^{10}$B content, % | Lattice parameter $a$, Å |
|----|---------------------|------------------------|
| 1  | 0.2                 | 10.1233                |
| 2  | 1.8                 | 10.1279                |
| 3  | 10.0                | 10.1335                |
| 4  | 19.0                | 10.1366                |
| 5  | 60.0                | 10.1436                |
| 6  | 87.8                | 10.1543                |
| 7  | 97.2                | 10.1560                |
Figure 1. $\beta$-rhombohedral boron lattice constant in dependence on $^{10}\text{B}$ isotope content; black squares – experimental values, solid line – trend theoretically expected from the quasi-classical B–B interatomic potential.

High-temperature thermal expansion $\Delta = \Delta l/l$ of the $\beta$-B specimens with sizes of $3 \times 3 \times (10 \div 12) \text{mm}^3$ has been investigated in the temperature range 400 – 1100 K using vacuum quartz dilatometer equipped with inductive sensor. Heating rate was 3 K/ min. Errors of relative elongation and temperature measurements were 3 % and 0.5 K, respectively. The elongations temperature-curves for samples with relatively low and relatively high composition of $^{10}\text{B}$ isotope are shown in figures 2 and 3.
Figure 2. Thermal expansion of β-rhombohedral boron crystals containing 0.8 (1) and 10 % $^{10}$B (2); circles – experimental points, crosses – data calculated from the experimental results using universal theoretical relation.
Figure 3. Thermal expansion of $\beta$-rhombohedral boron crystals containing 60 (1) and 97 $\%$ $^{10}$B (2); circles – experimental points, crosses – data calculated from the experimental results using universal theoretical relation.
3. Results and discussion

Isotopic composition effect on the crystalline structure built up from the light atoms theoretically can be considered using some first-principles approaches [10-12] or special semi-empirical pair interatomic potentials (for instance, parameterized in form of Mie–Lennard–Jones [13,14]). However, such calculations for semiconductors with simple crystalline structures are practically impossible in case of β-B structure with 105 regular atomic sites in the unit cell. Therefore, our analysis will be carried out within the frames of the diatomic model of a crystal [15].

In this model, the pair B–B interatomic interaction potential energy $U$ can be written as

$$U(a) = U(a_o) + c(a-a_o)^2 - g(a-a_o)^3,$$

where $a$ is the interatomic distance; $a_o$ is its equilibrium value corresponding to the potential energy minimum $U(a_o)$; $c > 0$ and $g$ are the constants at harmonic and anharmonic terms, respectively.

Constant $g$ is positive or negative depending on the sign of thermal expansion coefficient. There are boron-rich solids (some rare-earth-metal dodecaborides) with negative thermal expansion coefficient in certain temperature ranges [16]. This fact is considered as a consequence of nearly non-interacting free oscillations of the metal ions in cavities of a simple cubic lattice formed by $\text{B}_{12}$ cage units. However, β-B structure has only covalent bonds (some deficit of the bonding electrons characteristic for ideal structure in real β-B crystals is exactly compensated by the point defects stabilizing the structure [17]). Then, it is not surprising that thermal expansion coefficient for all crystalline modifications of boron is positive [18-21]. This is why a boron crystal can be modelled by the assembly of diatomic bonds with $g > 0$.

According to the model, the averaged relative change in equilibrium interatomic distance $\Delta a_o / a_o$ caused by anharmonic correction to the harmonic potential equals to

$$\frac{\Delta a_o}{a_o} = \frac{3g \overline{E}}{4a_o c^2} = \frac{3g}{4a_o c^2} \left( \frac{h\omega}{2} + \frac{h\omega}{\exp(h\omega/kT) - 1} \right).$$

Here $\overline{E}$ is the averaged energy of relative interatomic vibrations in diatomic system within the harmonic approximation. It was demonstrated [22] that same simple relation can be obtained using rigorous statistical method, while macroscopic theory of thermal expansion based on corresponding diatomic model allows to estimate [23] thermal expansion coefficient values for number of crystalline substances. The diatomic model is successfully used in calculations of the anharmonicity effects in solids [24].

In general, the averaged energy of relative interatomic vibrations in diatomic system within the harmonic approximation is a sum of two terms. One of them, $h\omega / 2$, is temperature independent and related to the zero-point vibrations with cyclic frequency $\omega$, while another is temperature dependent and related to the thermal excitations. If the lattice temperature $T$ is low, $h\omega/kT >> 1$, the main contribution in $\overline{E}$ is zero-point vibrations and thus it can be approximated as $\overline{E} \approx h\omega / 2$. At high temperatures, $h\omega/kT << 1$, the vibration energy of atoms is mainly determined by the crystal temperature, $\overline{E} \approx kT$, and not by their masses. This results in no isotopic composition influence on the interatomic distances mediated by the thermally excited phonons. Thus, at any temperature (for example, at room temperature), isotopic composition influence on the lattice parameter is quantum effect exclusively related to the zero-point vibrations and, consequently, in the formula (2) one can substitute $\overline{E}$ for $h\omega / 2$ even in the high-temperature range.

Let us firstly consider the case when the masses of all constituent atoms have one and same value and denote reduced mass of any atomic pair by $\mu$. In this case $\omega = \sqrt{2c / \mu}$ and

$$\frac{\Delta a_o}{a_o} = \frac{3hg}{4a_o c \sqrt{2c \mu}}.$$


The right part of the above formula would describe anharmonic relative changes in any structure parameter of a crystal if the crystal contains only chemically identical atoms with equal masses. It is convenient to analyze the isotopic composition effect on the structure parameters by considering elemental boron crystal with a random distribution of two isotopes in its otherwise perfect lattice.

Namely, aiming to separate isotopic contribution, we suppose that crystal consists of two isotopes with masses $M_1$ and $M_2$ at $M_1 < M_2$ and with relative concentrations $x$ and $1-x$ randomly distributed in the lattice sites ($0 \leq x \leq 1$). There exist three types of diatomic pairs with reduced masses of $M_1/2$, $M_2/2$, $1/(1/M_1 + 1/M_2)$, and probabilities of $x^2$, $(1-x)^2$, $2x(1-x)$, respectively. Then, generalized equation (3) leads to

$$\frac{\Delta a_o(x)}{a_0} = \frac{3gh}{4a_0c\sqrt{C}} \left( x^2 + \left(\frac{1}{M_1} + \frac{1}{M_2}\right) + x(1-x)\sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \right) . \quad (4)$$

Here term $\frac{3gh}{4a_0c\sqrt{C}}M_2$ expresses the relative change in the structural parameter of monoisotopic crystal (built up only from atoms of the heavier isotope) caused by the thermal effect. As for the isotopic effect, it is expressed by the reminder

$$\delta(x) = \frac{3ghx}{4a_0c\sqrt{C}} \left( \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} - \frac{2}{\sqrt{M_2}} \right) - x \left( \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} - \frac{1}{\sqrt{M_1}} - \frac{1}{\sqrt{M_2}} \right) . \quad (5)$$

In general case, function $\delta = \delta(x)$ exhibits the maximum at the concentration of

$$x_{\text{max}} = \frac{\sqrt{2(1 + M_1/M_2)} - 2}{2(\sqrt{2(1 + M_2/M_1)} - \sqrt{M_1/M_2} - 1)} . \quad (6)$$

However, condition $M_1 < M_2$ yields inequality $x_{\text{max}} > 1$ contradicting to the restriction $0 \leq x \leq 1$.

Equation (5) determines a relative change in a structural parameter value arisen as a result of substitution of the $x$ part atoms of isotope with mass $M_2$ by the atoms of isotope with mass $M_1$. Note that both coefficients of the linear form in parenthesis are positive, and first coefficient exceeds second one if $M_1 < M_2$; besides, $g > 0$. Consequently, substituting the heavier isotopes by the lighter ones one can expect the quadric (in respect to concentration) expansion of crystal structure parameters: $\delta(x) > 0$. However, for most chemical elements, including boron, $M_1 \approx M_2$ (only exception is hydrogen) and the linear form in parenthesis is almost constant. It means that function $\delta = \delta(x)$ is nearly linear:

$$\delta(x) \approx \delta_{\text{max}} x , \quad (7)$$

where

$$\delta_{\text{max}} = \frac{3gh}{4a_0c\sqrt{C}} \left( \frac{1}{\sqrt{M_1}} - \frac{1}{\sqrt{M_2}} \right) . \quad (8)$$

denotes maximal expansion when all heavier isotopes are substituted by the lighter ones ($x = 1$).

The numerical estimations of isotopic composition effect on the boron crystal structure parameters given below are based on B–B interatomic interaction potential function obtained previously [25,26] within the quasi-classical approach. Corresponding dependence of the binding energy $E_{\text{Binding}} = E_{\text{Binding}}(a)$ of this diatomic system from the interatomic distance $a$ is presented in figure 4.
Figure 4. Boron–boron binding energy in dependence on interatomic distance.

Note that a parameter of the corresponding potential curve like the core charge of $Z^* \approx 3.151$, which is near the boron atom valence of 3, already was with success applied [6] to interpret isotopic composition effect on boron melting characteristics. This curve leads to equilibrium values of interatomic distance and binding energy of $a_0 = 3.37 \text{ au}$ and $E_{\text{binding}}(a_0) = 0.103 \text{ au}$. If the atomic mass of boron is taken as the mass weighted according to its natural isotopic composition, the relative vibration frequency $\omega$ in B–B diatomic system is $\omega = 4.80 \cdot 10^{-3} \text{ au}$. These quasi-classical values deviate by only by few percents from experimental bond lengths in the main structural unit of boron and boron-rich compounds – icosahedron with boron atoms at vertexes $- 3.40 \text{ au}$ [27], dissociation energy $0.099 \text{ au}$ [28], and oscillatory quantum $4.79 \cdot 10^{-3} \text{ au}$ [29] of diboron molecule B$_2$, respectively. Thus, the quasi-classical B–B interaction potential curve together with equation (5) seems to be useful for estimation of the isotopic composition effect on the boron lattice parameters.

Trend analysis of the quasi-classical potential curve in the vicinity of equilibrium point yields the factors at harmonic and anharmonic terms: $c = 0.12 \text{ au}$ and $g = 4.0 \text{ au}$. Taking into account masses of isotopes $^{10}\text{B}$ and $^{11}\text{B}$ ($M_1 = 10.01$ and $M_2 = 11.01$, respectively) we get the constant standing in equation (8) for the relative change in structure parameter under the boron atoms isotopic replacement in the lattice sites: $\delta_{\text{max}} = 0.0042$. Thereby, the maximal isotopic effect (it occurs at $x = 1$ meaning that $^{11}\text{B}$ is completely substituted by $^{10}\text{B}$) is estimated as 0.42%.

A line described by the approximated equation (7) (i.e. with slope of $\sim 0.0042$) is shown in figure 1 together with the experimental points. It is evident that the theory explains general trend of the lattice constant growth with lighter isotope concentration. The sign and order of magnitude are in agreement with the theoretical estimation based on quasi-classical B–B interatomic potential, from which follows the approximately linear concentration-dependence of the boron-rich crystal lattice constant.

The temperature dependence of thermal expansion $\alpha = \alpha(T)$ has been analyzed based on the Zhernov’s universal relation between the thermal expansion coefficient for two crystals with different averaged masses of constituent atoms $M'$ and $M^*$ [8]:

$$\alpha'(T) = \alpha^*(T \sqrt{M'/M^*}).$$

In case of two isotopes, the averaged mass $M$ is determined as
\[
M = xM_1 + (1-x)M_2.
\]
It is easy to modify equation (9) for elongation \( \Delta \):
\[
\Delta'(T) = \sqrt{M'/M} \Delta'(T\sqrt{M'/M'}).
\]

Figures 2 and 3, together with experimental data, show points calculated from the elongation-temperature curves using universal relation (11). There is a good agreement between observed and calculated points. Thus, in temperature range 400 \(-\) 1100 K, the experimental curves of thermal expansion of the \( \beta \)-B samples with various isotope compositions with satisfactory accuracy follow the required universal relations [8].

Note that figures 2 and 3 represent data of thermal expansion for \( \beta \)-B samples with relatively low (0.8 and 10 %) and relatively high (60 and 97 %) contents of \(^{10}\)B isotope, respectively. A curve is made up from the experimental points for one (labelled) isotopic composition and theoretical points evaluated for this composition from the experimental ones for another (counterpart) isotopic composition using universal relation between two temperature-curves of the samples with different isotopic compositions. On the one hand, errors in elongation measurements are about 3 %. It is evident that relative difference between curves obtained for \( \beta \)-B samples with different isotopic composition should be less than maximal relative difference between masses of two boron stable isotopes \( \sim \) 10 %. Therefore, if the points shown in figures 2 and 3 are combined, the difference between curves will be barely distinguishable. In spite of this, one may believe that these experimental curves demonstrate universal theoretical relation valid for isotopic effect.

The isotopic changes in \( \beta \)-B lattice parameter measured at room temperature (figure 1) are larger in \(^{10}\)B enriched crystals, in agreement with quantum correlation formula (8) determining isotopic effect at any fixed temperature. However, the same order does not to work for the thermal elongation temperature-curves presented in figures 2 and 3. The explanation may be related with the losses of linearity: according to general formula (2), at sufficiently high temperatures, \( \hbar \omega/kT << 1 \), averaged relative elongation of a crystal is a linear function of temperature almost independent from its isotopic composition, whereas at relatively lower temperatures it should reveal slight, but complicated temperature and averaged isotopic mass dependencies.

Regardless of the fact that \( \beta \)-B specimens with different isotopic composition have different impurity contents too, a satisfactory agreement obtained between experiment and theory shows that detected changes in \( \beta \)-rhombohedral micro- and macro-structural parameters to a greater extent are of isotopic origin.

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