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## Thermal expansion of a boron-doped diamond single crystal at low temperatures

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**Abstract.** The lattice parameter of a single-crystal boron-doped synthetic diamond has been measured in the range 4.2–300 K by x-ray diffraction (Bond method), with precision  $\pm 2.0 \times 10^{-6}$ . Over the whole range the results are consistent with  $a = 3.566\,662 + 4.25 \times 10^{-14} T^4$  Å, where  $T$  is the absolute temperature. The dilation due to doping indicates a boron concentration of about 100 ppm. The increase of thermal expansion over that of an undoped synthetic diamond is found to be unexpectedly large (10–15%), giving an apparent dilation on doping that is markedly temperature dependent.

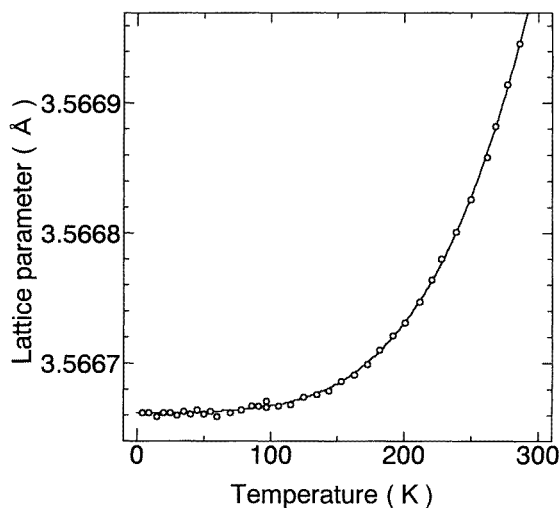
### 1. Introduction

Diamond is the simplest case of a purely covalent solid and consists of light carbon atoms held together by strong forces. In this crystal the number density of atoms is extremely high. It is the tight bonding in diamond that leads to the closeness of the atoms and to the low compressibility. The low thermal expansion is due (apart from the low compressibility) not so much to small anharmonicity as to the balance between positive and negative anharmonic effects (some modes have positive Grüneisen parameters  $\gamma$ , some negative), and also—above about 120 K—to the high Debye temperature  $\Theta_D$ . Nitrogen and boron are the only elements that significantly affect the electrical conductivity of diamond. Diamond containing boron impurity atoms is a p-type semiconductor.

Because the thermal expansion coefficient  $\alpha$  of diamond is very small and a specimen used for measurement is small, the thermal expansivities have often been measured by x-ray determinations of the change in lattice parameter of a crystal. Haruna *et al* [1] measured the lattice parameter of a synthetic diamond single crystal in the temperature range 4.2–320 K by the x-ray diffraction method. In this paper we report on low-temperature thermal expansion of a synthetic boron-doped diamond single crystal. Our results allow the determination of the thermal expansion coefficient at low temperatures. Furthermore, we have investigated the effect of the boron impurity on the thermal expansion. The paper is organized as follows. The experimental procedures are described in section 2. Results of the experiments are presented in section 3. In section 4 we show the temperature dependence of the thermal expansion coefficient and investigate the effect of the boron impurity on the thermal properties of this material.

## 2. Experimental procedures

The synthetic diamond crystal used in our experiment was purchased from Sumitomo Denko. The specimen is diamond doped with boron and is coloured black. Its shape is thin square plates with dimensions  $3.0 \times 3.0 \times 0.3 \text{ mm}^3$ . Its surfaces are orientated parallel to the (100) plane. In the measurements of the thermal expansion of lattice parameter, the x-ray Bond method [2] was used, with which absolute determination of the lattice parameter is possible. For the x-ray source, a fine-focus Fe target is used with a collimator of 0.2 mm in width attached to make the x-ray beam thinner. In this method, two scintillation counters are placed at symmetrical positions with respect to the incident x-ray beam, and only the single-crystal specimen is rotated during a measurement. By this method, any possible error that arises in a conventional diffraction from the rotating mechanism of the counter can be avoided. Furthermore, to improve the accuracy the highest possible diffraction line of the (400)-reflection is used. For this plane  $2\theta = 160.01^\circ$ . The wavelength of the  $K\beta$  line is taken as  $1.75653 \text{ \AA}$ . Before each measurement, the tilt angle of the specimen was carefully adjusted and the relative accuracy of  $1 \times 10^{-6}$  was maintained in determining the lattice parameter. The temperature was varied in the range 4.2–300 K. To make possible low-temperature measurements, a glass cryostat specially designed for the Bond method was used. The temperature of the specimen during the measurement was controlled within an accuracy of 0.1 K by using an automatic temperature controller. Hence, the relative accuracy of  $\pm 2 \times 10^{-6}$  was finally attained in determining the temperature variation of the lattice parameter.



**Figure 1.** Temperature dependence of lattice parameter  $a$ . Open circles represent the experimental data of the lattice parameter. Full line represents the fifth polynomial.

## 3. Experimental results

In figure 1 we show the temperature dependence of the lattice parameter in the temperature range 4.2–300 K. The values are corrected for refraction, absorption and Lorentz factors. In this diamond a distinct minimum in the plot of the lattice parameter over a wide temperature

range is not observed. This situation is consistent with the case of the synthetic non-doped diamond [1]. In the figure the solid line traces reasonable values of the lattice parameters that are fitted to the fifth-order polynomial

$$a = \sum_{n=0}^5 a_n T^n. \quad (3.1)$$

These coefficients, determined by the method of least squares, are as follows,

$$\begin{aligned} a_0 &= 3.566\ 66 \\ a_1 &= -3.05 \times 10^{-8} \\ a_2 &= 1.22 \times 10^{-9} \\ a_3 &= -1.18 \times 10^{-11} \\ a_4 &= 8.64 \times 10^{-14} \\ a_5 &= -5.68 \times 10^{-17}. \end{aligned} \quad (3.2)$$

In thermal equilibrium a crystal minimizes its free energy  $F$ , which consists of its internal energy  $U$ , the temperature  $T$  and the entropy  $S$

$$F = U - TS. \quad (3.3)$$

Because the lattice vibrations are anharmonic, their frequencies  $\omega$  depend on the volume  $V$  of the crystal, obeying

$$\frac{d\omega}{dV} = -\frac{\gamma\omega}{V}. \quad (3.4)$$

A crystal changes its volume from  $V_0$  to  $V$  and, hence, its elastic energy increases by  $V_0(B/2)((V - V_0)/V_0)^2$ . The factor  $B$  is the bulk modulus and  $\kappa = 1/B$  is the compressibility. Though the free energy increases by the elastic energy, the crystal expansion lowers the vibrational frequencies, that is the free energy of the crystal. Equilibrium is reached when the decreasing vibrational energy is balanced by the increasing elastic energy. We have used the Debye approximation to estimate the volume change. The volume change [3, 4] becomes

$$V - V_0 = \frac{9}{8}\kappa N_0 \gamma k_B \Theta_D + \frac{9\pi^4}{15}\kappa N_0 \gamma k_B \frac{T^4}{\Theta_D^3} \quad (3.5)$$

where  $N_0$  is the number of constituting atoms and  $k_B$  the Boltzmann constant. The low-temperature thermal expansion becomes

$$\frac{\Delta a}{a_0} \equiv \frac{\Delta V}{3V_0} = \frac{3\pi^4 N_0 \kappa k_B}{15 V_0 \Theta_D^3} \gamma T^4. \quad (3.6)$$

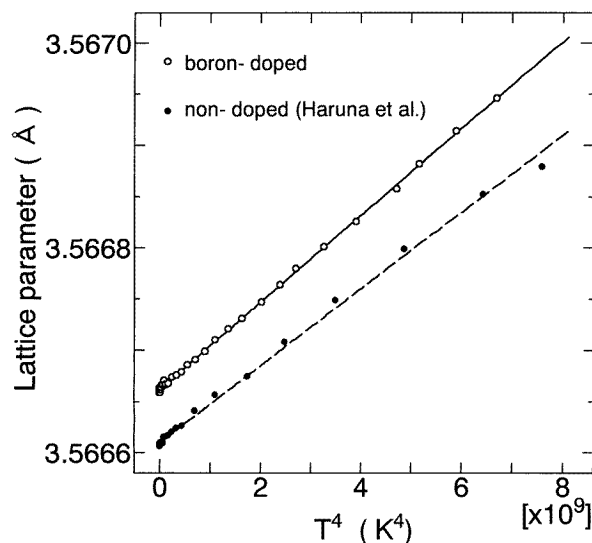
At sufficiently low temperature, the thermal dilation due to vibrational anharmonicity is proportional to  $T^4$ . In figure 2 we have plotted the relative thermal expansion of the lattice parameter against  $T^4$ . As shown in the figure the  $T^4$ -law is valid for our diamond specimen within the measuring temperature range. For a Debye solid in which the phonon spectrum approximates to the Debye assumption it is necessary to go down to about  $\Theta_D/50$  to match this  $T^4$ -law. As  $\Theta_D$  of diamond is about 2000 K,  $\Theta_D/50$  is nearly equal to 40 K. The thermal expansion of diamond behaves in quite a normal way, being represented quite well by the simple Debye theory, within the measuring temperature range. In figure 2 we also show the temperature dependence of the lattice parameters of the synthetic non-doped

diamond, which was measured by Haruna *et al* [1]. The thermal expansion curves can be expressed as

$$a = 3.566662 + 4.25 \times 10^{-14} T^4 \quad \text{for boron-doped diamond} \quad (3.7)$$

$$a = 3.566610 + 3.73 \times 10^{-14} T^4 \quad \text{for non-doped diamond} \quad (3.8)$$

respectively. The lattice parameter of the boron-doped diamond is larger than that of the non-doped diamond over the whole temperature region. We assume that the difference at  $T = 0$  K arises from the lattice mismatch between boron atomic radius and carbon atomic radius.



**Figure 2.**  $T^4$ -plots of the lattice parameter  $a$ . Full line represents the result for boron-doped diamond. Dashed line represents the result for non-doped diamond.

In the boron-doped diamond these solutes occupy substitutional positions in the diamond lattice. The atomic radius of the boron atom is  $0.88 \text{ \AA}$ . On the other hand, the atomic radius of the carbon atom is  $0.77 \text{ \AA}$  [5]. The volume dilation  $\delta V$  due to the substitutional boron impurity atom is thus estimated to be

$$\frac{\delta V}{V} = \frac{(0.88)^3 - (0.77)^3}{(0.77)^3} = 0.49. \quad (3.9)$$

Then the lattice expansion  $\delta a = a(\text{boron doped}) - a(\text{non-doped})$  is due to the volume dilation  $\delta V$  and  $\delta a/a(\text{non-doped})$  can be expressed as follows

$$\frac{\delta a}{a(\text{non-doped})} = \frac{1}{3} \left( \frac{\delta V}{V_0} \right) c(B) = 0.16c(B) \quad (3.10)$$

where  $c(B)$  is the fractional atomic concentration of boron in the crystal. We must notice that the volume dilation caused by the substitutional boron changes appreciably with temperature. At  $T = 0$  K, from (3.7) and (3.8) the lattice relative dilation due to the doping is  $\delta a/a(\text{non-doped}) = (3.566662 - 3.566610)/3.566610 = 1.46 \times 10^{-5}$ . Hence, we may estimate the boron concentration to be  $c(B) = 100$  ppm by comparing this relative dilation with (3.10).

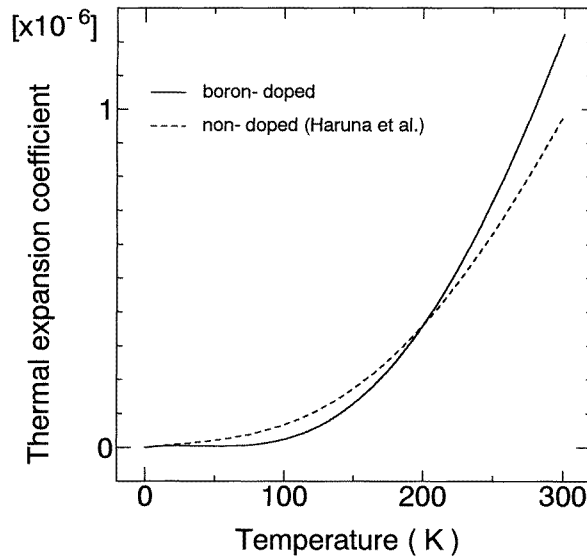
When the mass of a crystal is 1 mol, (3.6) can be written with Avogadro number  $N_A$  as

$$\frac{\Delta a}{a_0} \equiv \frac{\Delta V}{3V_0} = \frac{3\pi^4 N_A \kappa k_B}{15V_0 \Theta_D^3} \gamma T^4 = \frac{3\pi^4 R \kappa}{15V_0 \Theta_D^3} \gamma T^4 \quad (3.11)$$

where  $R = N_A k_B$  is the gas constant. We use  $B = 4.42 \times 10^{11} \text{ N m}^{-2}$  for the bulk modulus of diamond [6]. The Debye temperature is  $\Theta_D = 2246 \text{ K}$  [6], the density  $\rho = 3514 \text{ kg m}^{-3}$  [7] and the Gruneisen parameter  $\gamma = 1$  [7]. We obtain the following expression:

$$\Delta a/a_0 = 0.95 \times 10^{-14} T^4. \quad (3.12)$$

From (3.8) we obtain  $\Delta a/a_0 = (3.73 \times 10^{-14}/3.566610)T^4 = 1.05 \times 10^{-14} T^4$ . This expression is nearly equal to (3.12). From (3.7) we have  $\Delta a/a_0 = 1.19 \times 10^{-14} T^4$ . The dopant boron increases the thermal expansion. The force constant for substitutional impurity boron–host carbon atoms might be weaker than that for host carbon–host carbon atoms. As a result dopant boron atoms reduce the Debye temperature and the bulk modulus of the crystal, respectively, and hence are expected to increase the thermal expansion.



**Figure 3.** The temperature dependence of the thermal expansion coefficient. Full line represents the result of the boron-doped diamond. Dashed line represents the result of the non-doped diamond.

#### 4. Thermal expansion coefficient

The thermal expansion coefficient is calculated from the observed lattice parameter values. The linear thermal expansion coefficient is defined by

$$\alpha = \frac{da}{a_{(He)} dT} \quad (4.1)$$

where  $a_{(He)}$  is the lattice parameter at He temperature.

In figure 3, smoothed curves for the temperature dependence of  $\alpha$  for both boron-doped and non-doped diamonds are shown. From figures 2 and 3, we find that the boron-doped diamond tends to possess larger thermal expansion coefficient compared to the non-doped diamond at high temperature region. At lower temperatures, any difference between them is within experimental scatter. At 300 K the ratio of  $\alpha(\text{boron-doped})/\alpha(\text{non-doped})$  is about 1.15. Litzman [8] has calculated the thermal expansion coefficient of the linear chain with isolated defects. According to his results, if force constant for the impurity-host atom  $f'$  is weaker than that for host-host atom  $f$ , the thermal expansion coefficient of a doped crystal becomes larger. His expression in the high temperature region is as follows:

$$\alpha_{\text{impure}} = \alpha_{\text{pure}} \left( 1 + 4c(B) \frac{f - f'}{f} \right). \quad (4.2)$$

In the above expression the changes of the third order coupling constants of a crystal due to the dopant are neglected. In our specimen the boron concentration is estimated to be about  $c(B) = 100$  ppm and furthermore, the ratio of  $\alpha(\text{boron-doped})/\alpha(\text{non-doped})$  is about 1.15. Hence, Litzman's model might not be applied to our experimental results. But, it is certain that boron dopants weaken the bulk modulus of diamond and increases the thermal expansion. Furthermore, a relatively large change in thermal expansion for a small amount of impurity could possibly indicate contributions from extra fairly low optical frequency mode centred on imperfections with high  $\gamma$  values. This explanation may be accepted qualitatively. But quantitative explanations await further work.

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