Thermal Expansion of Diamond at Low Temperatures

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Temperature variation of a lattice parameter of a synthetic diamond crystal (type IIa) was measured using high-energy-resolution x-ray Bragg diffraction in backscattering. A 2 order of magnitude improvement in the measurement accuracy allowed us to directly probe the linear thermal expansion coefficient at temperatures below 100 K. The lowest value measured was $2 \times 10^{-9}\ \mathrm{K}^{-1}$. It was found that the coefficient deviates from the expected Debye law (T^3) while no negative thermal expansion was observed. The anomalous behavior might be attributed to tunneling states due to low concentration impurities.

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Negative thermal expansion is a well-established phenomenon for Si, Ge, and some other semiconductors with diamond structure at temperatures $\lesssim 100$ K. The possibility of negative thermal expansion for C (diamond) was suggestive from early theoretical works [1,2] due to its structural identity with Si. More recent theoretical studies predict that in contrast to Si, the effect does not exist for diamond, since the transverse-acoustic-mode Grüneisen parameters are predicted to be positive [3–5]. Thus far, these theoretical predictions have not been confirmed experimentally.

A vast literature is dedicated to physical properties of diamond due to its ever-increasing technological importance. However, none of these contain reliable data on thermal expansion of diamond at low temperatures. Among many high-tech applications of diamond, cryogenic applications are expected to play a special role in x-ray optics for fourth-generation synchrotron sources. For example, it was recognized recently that diamond is indispensable for the realization of an x-ray free-electron laser oscillator (XFELO) [6,7], a future hard x-ray source of highest average and peak brightness. Stable diamond x-ray cavities for the XFELO would be feasible if the thermal expansion coefficient is $\lesssim 10^{-8}\ \mathrm{K}^{-1}$.

For many decades, the experiment has been challenging because the available measurement accuracy ($\approx 10^{-7}\ \mathrm{K}^{-1}$) [8–13] was apparently larger than the values of the linear thermal expansion coefficient of diamond in the low-temperature range. In this Letter, we demonstrate a 1.2×10^{-8} relative accuracy in determination of lattice parameters with x rays. The accuracy was obtained using diffraction in backscattering of extremely highly monochromatic x-rays from a selected, nearly perfect region of a diamond crystal. It allows us to achieve an accuracy of $\approx 10^{-9}\ \mathrm{K}^{-1}$ in determining the linear thermal expansion coefficient of diamond at low temperatures. We report a solution to the critical problem described above and an unexpected anomalous effect for which we propose an explanation. The new data on thermal expansion coefficient of diamond are consistent with previous studies at temperatures above 100 K. Below this temperature, the thermal expansion coefficient is predicted to be a monotonous function of temperature [3–5]. In contrast, it is found that in the temperature range of 10–50 K, the thermal expansion coefficient exhibits an anomalous increase of at least an order of magnitude relative to the expected Debye law (T^3).

High-energy-resolution Bragg diffraction in a backscattering configuration has been previously used to measure lattice parameters and x-ray wavelengths with high accuracy [14–18]. The Bragg's law in backscattering is

$$\lambda(1 + w) = 2d(1 - \Theta^2/2), \tag{1}$$

where λ is the wavelength of radiation reflected backwards from a set of parallel atomic planes with interplanar distance d. In this equation, Θ is a small angular deviation from normal incidence to the reflecting planes, and w is the refraction correction, which is to a good approximation a small invariant magnitude for a given set of atomic reflecting planes [19]. In the backscattering configuration, the influence of the angular variations $\delta\Theta$ on λ is minimized due to the Θ^2 dependence. If $\Theta \leq \sqrt{2\epsilon}$, where ϵ is the required relative uncertainty of measurements, a direct relation between the radiation wavelength and the interplanar distance can be established: $\lambda(1 + w) = 2d$.

However, any Bragg reflection and the incident radiation both have finite spectral widths. Only the central wavelength of the reflected x rays satisfies Eq. (1). The precision in measuring the interplanar distance is determined by several factors: the intrinsic spectral width ΔE of the chosen Bragg reflection, the bandwidth of the incident x-rays ΔE_X, and the statistics with which the reflection is measured in the experiment.

The experiment was performed at the undulator beam line XOR 30-ID at the Advanced Photon Source at Argonne National Laboratory. A high-order reflection C (995) with spectral bandwidth of $\Delta E = 2.76$ meV was chosen for the experiment. The Bragg energy of exact backscattering for this reflection ($E_H = hc/2d = 23.765$ keV) is within an energy range of a six-bounce high-resolution monochromator (HRM) operated at the beam line. The HRM provides monochromatic x-ray beam with a bandwidth of $\Delta E_X \simeq 1$ meV in the energy range 23.7–29.7 keV [20]. The relative spectral resolution of this instrument is thus $\Delta E_X/E \simeq 4 \times 10^{-8}$, where $E = hc/\lambda$ is the photon energy. The precision for measurement of a relative change in the central energy (or central wavelength) of a single diffraction peak is expected to be much better due to good counting statistics.

The experimental setup is shown in Fig. 1. The x-ray beam passes through the HRM and is incident on the diamond crystal placed $\simeq$10 m downstream. The intensity of the beam reflected from the C (995) planes is measured using an avalanche photodiode (APD) placed next to the HRM. The choice of the large distance permits a small angular offset $\Theta = 1.3 \times 10^{-4}$ from normal incidence, which yields a negligible angular correction in Eq. (1) ($\Theta^2/2 = 8.5 \times 10^{-9}$). The asymmetry angle between the reciprocal vector of the C (995) reflection and the normal to the (111) crystal surface is $\eta = 13.82°$. The ion chamber (IC) facilitates search of the back reflection.

Monochromatization of x rays in the HRM is obtained using properties of Bragg reflections from two crystals in the dispersive configuration. A relative change of the central wavelength of the monochromatized beam is given by

$$\frac{\delta\lambda}{\lambda} = \frac{\delta\psi_{12}}{\tan\theta_1 + \tan\theta_2}, \tag{2}$$

where ψ_{12} is an angle between reciprocal vectors $\boldsymbol{H}_1$ and $\boldsymbol{H}_2$ of the Bragg reflections of the two crystals, and θ_1 and θ_2 are glancing angles of incidence to the first and the second crystal, respectively (see, e.g., [19] for details).

The angle ψ_{12} is varied with an increment as small as 25 nrad [20]. Equation (2) is used to draw a correspondence between the angular scale of the monochromator and the energy of the monochromatized x rays. A high quality synthetic diamond single crystal was chosen for the experiment (Sumitomo, type IIa). Diamond crystals of this type are almost devoid of impurities. The concentration of nitrogen as a major impurity is $\lesssim$1 ppm. The crystal was a platelet of (111) orientation with dimensions $\simeq 8 \times 4$ mm and a thickness of $\simeq$0.4 mm.

Preliminary measurements of reflectivity and the energy width ΔE were conducted at room temperature for different positions of the x-ray beam on the sample [21]. A region of the crystal ($\approx 0.7 \times 0.7$ mm) was selected exhibiting a narrow and symmetric reflectivity curve. The curve measured in this region is shown in Fig. 2 along with a theoretical curve calculated using a dynamical theory of x-ray diffraction for a diamond crystal of 0.4 mm thickness and an incident x-ray beam with a bandwidth of 1 meV. The full width at half maximum (FWHM) of the experimental curve (2.9 meV) closely matches the theoretical result. Variation of the FWHM of the reflectivity curve with temperature did not exceed 20%. These observations indicate that the probed region was of a very high quality and strain-free in the course of all the measurements.

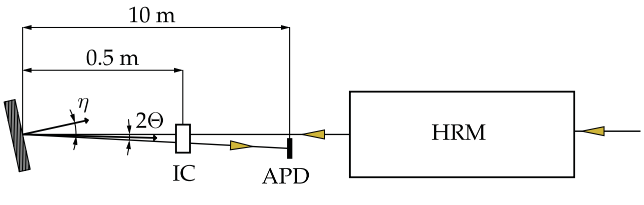

FIG. 1 (color). Experimental setup (see text for details).

In the first step, the absolute value of the diamond lattice parameter was evaluated ($a = d\sqrt{n^2 + k^2 + l^2}$, where n, k, l are the Miller indices of the C(995) reflection). The (12 12 12) Bragg back-reflection from Si was used as a reference. The obtained value for the lattice parameter was $a = 3.56712(2)$ Å at 298 K, which is in agreement with the result of Holloway *et al.* (3.56714(5) Å) [22] and that of Yamanaka *et al.* (3.56711(5) Å) [23] for diamond crystals with natural isotopic abundance.

In the second step, measurements of the relative change in the lattice parameter were performed as a function of temperature. Two independent experiments were conducted within a two-month interval. In the first experiment, the range of temperatures studied was 45–300 K. In the second experiment, the temperature range was from 6 to 300 K. The same region of the crystal was probed in both experiments. To obtain data for each point the temperature of the cryostat was lowered and allowed to equilibrate. The energy region of the Bragg reflection was searched by monitoring a signal from the ion chamber while scanning the energy of the HRM. When found, the reflected beam was aligned on the APD detector assuring the same value of the angular offset Θ with an accuracy $\delta\Theta \approx 3.5 \times 10^{-5}$. This produces a negligible uncertainty in the wavelength $\delta\lambda/\lambda \approx \Theta\delta\Theta \approx 4.6 \times 10^{-9}$.

Starting from the room temperature value, reported above, the lattice parameter $a(T)$ was subsequently determined for all temperature points using Eqs. (1) and (2), The resulting temperature dependence can be approximated with a sixth-order polynomial

$$a(T) = \sum_0^6 a_n T^n. \tag{3}$$

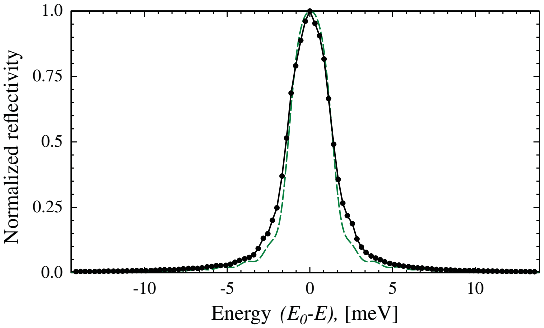

FIG. 2 (color). Reflectivity of diamond from the (995) atomic planes. Filled circles, solid line: experimental dependence. Dashed line: calculations using dynamical theory of x-ray diffraction.

TABLE I. Coefficients of the polynomial approximation to the temperature dependent lattice parameter.

a_0	3.56682 Å	a_4	1.11×10^{-16} Å K^{-4}
a_1	2.50×10^{-8} Å K^{-1}	a_5	1.92×10^{-16} Å K^{-5}
a_2	-5.19×10^{-10} Å K^{-2}	a_6	-3.46×10^{-19} Å K^{-6}
a_3	4.96×10^{-12} Å K^{-3}		

The coefficients a_n are given in Table I. The data and the approximation (3) are shown in Fig. 3 where the temperature-independent value a_0 was subtracted and used for normalization.

The major instrumental source of errors in the conducted experiment is a limited reproducibility in mechanical motion of the ψ_{12} angular stage of the HRM. The statistical uncertainty was estimated from a maximum observed mismatch between different statistical characteristics for the angular position (e.g., position of the maximum vs the peak center of gravity) while a peak position as determined from a Gaussian fit was chosen to obtain the experimental points. The mismatch did not exceed $\Delta\psi_{12} = 0.1$ μrad, which yields $\delta a/a = 1.2 \times 10^{-8}$. The size of the error bars in Fig. 3 is twice this number, which reflects the subsequent calculation of the lattice parameter (i.e., the use of the value at the previous temperature to calculate a new value at a current temperature).

The linear thermal expansion coefficient, calculated as $\alpha(T) = (da(T)/dT)/a_0$ from the polynomial (3), is shown in Fig. 4. This curve approximates well the data of the two independent experiments obtained by point-by-point calculation. The error bars are those described above, normalized by the temperature interval ΔT between the experimental points and combined with uncertainty in the sample temperature $[\alpha(T)\delta T/T]$.

Temperature variation of the lattice parameter approximated with $[a(T) - a_0]/a_0 = 1.085 \times 10^{-14} T^4$ is plotted in Fig. 3 for comparison. The temperature derivative of the curve

$$\alpha(T) = 4.34 \times 10^{-14} T^3 \tag{4}$$

is plotted in Fig. 4 and is the behavior of the thermal expansion coefficient expected from the Debye model, as will be discussed further. The experimental data are in good agreement with Eq. (4) in the temperature range 50–300 K. However, a deviation by more than 1 order of magnitude is observed at $T < 50$ K in Fig. 4 relative to the expected curve.

In a commonly used Grüneisen theory, the linear expansion coefficient of an isotropic crystalline solid is given by

$$\alpha(T) = \frac{C_v^{\mathrm{lat}}(T)\gamma(T)}{3BV}, \tag{5}$$

where V is the specific volume, B is the bulk modulus, $C_v^{\mathrm{lat}}(T)$ is the heat capacity, and $\gamma(T)$ is the mean Grüneisen parameter

$$\gamma(T) = \frac{\sum_{q,j} \gamma_j(q) C_j(q,T)}{\sum_{q,j} C_j(q,T)}, \qquad \gamma_j(q) = -\frac{\partial \ln \omega_j(q)}{\partial \ln V}. \tag{6}$$

Here, $\gamma_j(q)$ are Grüneisen parameters of phonon modes with frequencies $\omega_j(q)$, and $C_j(q,T)$ are individual contributions of the modes to the heat capacity. At temperatures $T \ll \Theta_D$ (Θ_D is the Debye temperature), only acoustic phonon modes with wave vectors $q \ll 2\pi/a$ are excited. Since $\Theta_D \approx 2000$ K for diamond is quite large, $C_v^{\mathrm{lat}}(T) \sim T^3$ according to the low-temperature approximation of the Debye model. Theoretical studies [3,4] predict that $\gamma_j(q)$ of the acoustic modes take only positive values and are weak functions of q. Thus, $\gamma(T)$ is approximately a constant at the low temperatures, and the thermal expansion coefficient of a diamond crystal should have the same T^3 temperature dependence as $C_v^{\mathrm{lat}}(T)$, according to

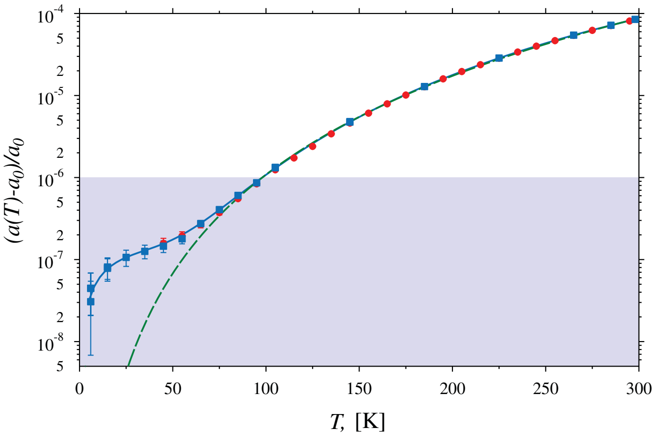

FIG. 3 (color). Relative change in the diamond lattice parameter with temperature. Circles: experiment 1; squares: experiment 2. Solid line is the sixth-order polynomial approximation. Dashed line is the approximation with T^4. The shaded area represents a region previously inaccessible due to the limited measurement accuracy.

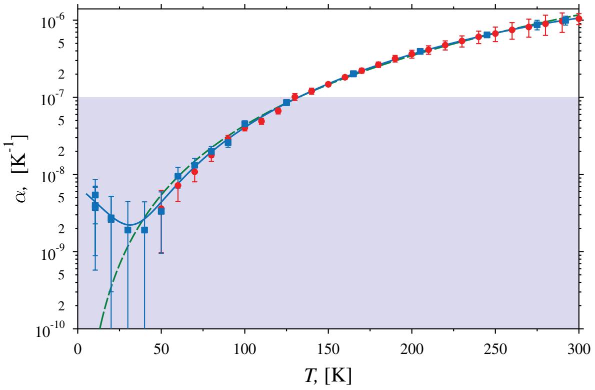

FIG. 4 (color). Linear thermal expansion coefficient of diamond: obtained by point-by-point determination from experiment 1 (circles) and from experiment 2 (squares), calculated from the polynomial approximation (3) (solid line) and the Debye model approximation (4) (dashed line). The shaded area represents a region previously inaccessible due to the limited measurement accuracy.

Eq. (5). Hence, the observed anomaly can not be related to the weak temperature dependence of the mean Grüneisen parameter.

The anomalous increase might be attributed to the presence of tunneling states due to low-concentration impurities and vacancies in diamond. For example, it was observed that NaCl containing OH^- at concentrations of a few ppm exhibits a substantial increase in thermal expansion coefficient at low temperatures as a result of tunnel splitting [24]. A simple model to account for the tunneling states includes additive contributions to the thermal expansion coefficient (5):

$$\alpha(T) = \frac{C_v^{\mathrm{lat}}(T)\gamma(T)}{3BV} + \frac{C_v^i(T)\gamma^i(T)}{3BV}, \tag{7}$$

where $C_v^i(T)$ is the impurity contribution to heat capacity. Here, $\gamma^i(T) = -d\ln\Delta/d\ln V$, with Δ being the tunnel-splitting parameter. Assuming that $C_v^{\mathrm{lat}}(T)$ and $C_v^i(T)$ are of the same order of magnitude, $\gamma^i(T)$ must be at least an order of magnitude greater than $\gamma(T) \simeq 1$ of diamond to agree with the experimental data.

Although, a nearly perfect crystal region was chosen in our experiment, virtually any diamond sample contains impurities and/or vacancies. X-ray-induced luminescence of the diamond in the visible range was observed in our experiment. Only optically active defect centers can be responsible for this effect. These same defect centers may have tunneling states with the tunnel-splitting parameter being a strong function of the crystal volume.

In summary, we have demonstrated a very high accuracy in measuring relative change in lattice parameters and applied this technique to solve a long-standing problem in solid state physics. Thermal expansion of diamond has been directly probed at low temperatures ($\lesssim$100 K). A 2 order of magnitude improvement in the accuracy reveals the extremely small value of the linear thermal expansion coefficient: $\alpha(T) \simeq 2 \times 10^{-9}\ \mathrm{K}^{-1}$ at 30–40 K. This new knowledge is of major importance for basic science and for applications, such as diamond cavities and monochromators in x-ray optics at fourth-generation synchrotron sources [6,7,25]. No negative thermal expansion has been observed. However, an anomalous increase was found with decrease in temperature. The effect could be attributed to the influence of defects in diamond. The magnitude of the anomalous increase compared to thermal expansion of diamond as a Debye solid is likely due to the presence of tunneling states at the defect sites. We note that direct experimental evidence is required to further validate the proposed explanation. Further studies on a variety of diamond crystals are in progress.

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