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Note	

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Elastic constant C_{11} of ^{12}C diamond between 10 and 613 K

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We measured the temperature dependence of the elastic constant C_{11} of a ^{12}C diamond monocrystal using picosecond ultrasonics between 10 and 613 K. We found that C_{11} is almost temperature independent below room temperature; the temperature coefficient around 300 K is −6.6 MPa/K. Our results show a significantly higher Einstein temperature than reported values by ~30%, indicating that diamond has a larger zero-point energy, which remains dominant around ambient temperature. We also calculated the temperature dependence of the elastic constants using *ab-initio* methods, resulting in good agreement with measurements. Our study shows that below-ambient-temperature measurements are not sufficient to extract the Debye temperature and the Grüneisen parameter of high-Debye-temperature materials. *Published by AIP Publishing.*
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Diamond is chemically, mechanically, and thermally stable, and it exhibits the highest thermal conductivity,[1] hardness,[2,3] and stiffness.[4] This ultrastable nature allows very small temperature coefficients for the unit-cell dimension[5,6] and elastic constants.[7,8] These properties are essentially represented by the high Debye characteristic temperature Θ_D and the small Grüneisen parameter γ; Θ_D of typical solids is about 100–600 K (Ref. 9) and that of diamond is 2244 K.[8] Θ_D relates to the plateau region of lattice constants and elastic constants at cryogenic temperatures. On the other hand, γ represents the lattice anharmonicity, which relates to the thermal expansion and temperature coefficients of elastic constants at higher temperature. γ typically takes values of 1–3,[10–16] and that of diamond is roughly unity.[8]

To describe the temperature dependence of elastic constants C_{ij} in a wide temperature T range, Einstein-Leibfried-Ludwig-Varshni's (E-L-L-V) equation is well applicable[17]

$$C_{ij}(T) = C_0 - \frac{s}{\exp(\Theta_E/T) - 1}, \tag{1}$$

where C_0 is the elastic constant at 0 K, and s and Θ_E are a parameter governing the lattice anharmonicity and the Einstein temperature, respectively. Θ_E is proportional to Θ_D,[18] and given by $\Theta_E = \hbar\omega_E/k_B$, where $\hbar$, ω_E, and k_B are the Planck constant, the Einstein frequency, and the Boltzmann constant, respectively. The dependence of $[\exp(\Theta_E/T) - 1]^{-1}$ in Eq. (1) is derived from the Planck distribution function, involving the important parameter Θ_E/T, the ratio of vibration energy $\hbar\omega_E$, and thermal energy k_BT. This ratio determines the plateau regions and the contribution of the zero-point vibrational energy at a finite temperature. Therefore, the temperature dependence of elastic constants at cryogenic temperatures allows us to evaluate the contribution of the zero-point vibrational energy. On the other hand, s relates to the temperature coefficients of elastic constants at higher temperature (lattice anharmonicity). For the temperature dependence of bulk modulus, Ledbetter derived a relationship between γ, s, and Θ_E[19]

$$s = \frac{3k_B\gamma(\gamma + 1)\Theta_E}{V_a}. \tag{2}$$

Here, V_a is the atomic volume. Using Eqs. (1) and (2), we can define the mode Grüneisen parameter, γ_{ij}, for each $C_{ij}(T)$. The temperature dependence of elastic constants at low and high temperatures thus provides the intrinsic thermodynamic properties of a material.

The temperature dependence of the elastic constants of diamond still remains unclear due to measurement and synthesis difficulties. Because diamond has very large sound velocities, conventional ultrasonic methods require large specimens, but synthesis of a large and highly pure diamond is difficult. Moreover, the temperature dependence of elastic constants of diamond is so small that we must measure it over a wide temperature range to extract reliable Θ_E and γ_{ij}. For example, the lattice constant changes by only 0.009% between 0 and 300 K.[6] Migliori *et al.* have measured the elastic constants of diamond using resonant ultrasound spectroscopy (RUS) below 330 K, where temperature variation was not sufficient to extract the key parameters. The RUS method also requires simple geometric shapes with accurately determined dimensions for determination of the values of elastic moduli. However, the ultra-high hardness of diamond also limits the dimensional accuracy. Brillouin scattering and picosecond ultrasonics do not require a strict-shape specimen; they need only a flat face. Zouboulis *et al.* measured the elastic constants of diamond between 300 and 1700 K by the Brillouin scattering method.[20] Their room-temperature value of C_{11}, however, varies in 1070–1088 GPa with 0.6% standard deviation (SD), which exceeds the small stiffness change with temperature. For example, it is reported that C_{11} changes by a factor of −0.1% from 10 to 330 K.[8]

In this study, we synthesized a highly pure ^{12}C diamond and measured the elastic constant C_{11} between 10 and 613 K using picosecond ultrasonics. Highly pure ^{12}C diamond allows us to evaluate the intrinsic physical properties of diamond without any kind of impurity. ^{13}C can be regarded as an isotopic impurity, which affects physical properties of diamond. Anthony and coauthors reported that thermal

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[a)] akira.nagakubo@abc.me.es.osaka-u.ac.jp conductivity of ^{12}C diamond was increased by 50% compared to that of natural-isotope-ratio diamond.[21,22] Watanabe *et al*. reported that the band-gap energy of diamond can be controlled by 15.4 meV by changing the ^{13}C ratio between 0% and 100%.[23,24] Although such a significant isotope effect was not reported concerning the lattice parameter,[25–27] it is necessary to use a highly pure ^{12}C diamond to study the intrinsic elastic properties of diamond. ^{13}C has 8.3% higher mass, which affects the phonon frequency and then the Debye and Einstein temperatures. Therefore, the isotopic impurity of ^{13}C should be removed to evaluate the true nature of diamond.

Highly pure ^{12}C diamond was synthesized by a temperature gradient method under high pressure and high temperature.[28,29] The nitrogen and boron concentrations were less than 0.1 ppm (undetectable by optical absorption analysis). The ^{12}C isotope ratio of the diamond was 99.995% (measured by a secondary ion mass spectrometer). Specimen size is about $2.5 \times 2.5 \times 0.6\,\mathrm{mm}^3$, and [100] directions lie in the thickness (0.6-mm) direction. To measure C_{11} using picosecond ultrasonics, we deposited a 10-nm Al thin film on a surface as a transducer by the radio-frequency magnetron sputtering method. Picosecond ultrasonics is one of pump-probe ultrasonics, which uses a femtosecond pulsed laser.[30,31] The repetition rate, wavelength, and bandwidth of our Ti/sapphire pulsed laser are 80 MHz, 800 nm, and 7.0 nm, respectively. A femtosecond pump light pulse is absorbed in the Al film, leading to a transient thermal expansion and a strain pulse. A time-delayed probe light pulse enters the specimen normal to the incident plane and is diffracted backward by the strain pulse. The diffracted light and reflected probe light at the specimen surface interfere with each other. The amplitude and phase of the interfering light periodically change as the strain pulse propagates. This is called Brillouin oscillation, and its frequency f is given by Bragg's diffraction law[32–34]

$$f = \frac{2nv}{\lambda}. \tag{3}$$

Here, n and v are refractive index and longitudinal-wave sound velocity of diamond, respectively, and λ is the wavelength of the probe light. We converted λ from 800 nm into 400 nm by a second harmonic generator, and measured the precise wavelength by a spectrometer.[35] We can then obtain the elastic constant $C_{11} = \rho v^2$, where ρ is the mass density.

We built two vacuum chambers for low-temperature[36] and high-temperature[37] measurements. The specimens were attached to heat exchangers, and both pump and probe lights were normally incident to them through a 20-times objective lens and a glass window. The chamber pressure during measurement was below 4×10^{-3} Pa. We controlled the temperature of the heat exchangers by liquid He and heaters. The temperature fluctuation during a measurement was less than 0.1 K. At each temperature, we measured f at several different points on the surface. The power of the pump and probe light pulses was 30 and 20 mW, respectively.

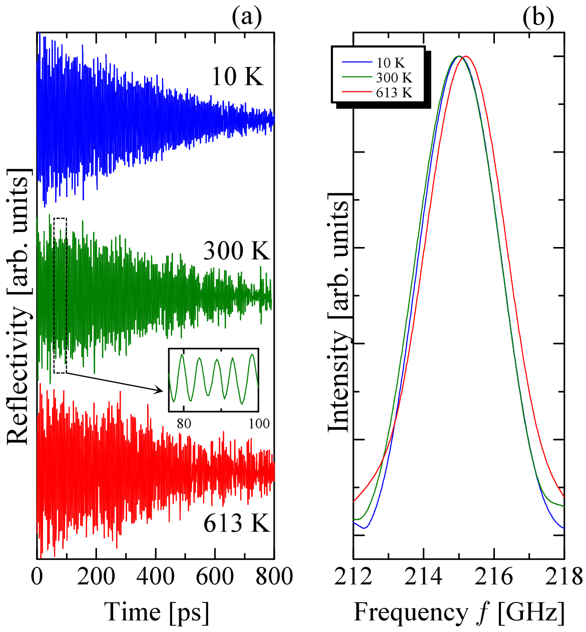

FIG. 1. (a) Observed Brillouin oscillations and (b) corresponding FFT spectra at typical temperatures.

Observed Brillouin oscillations and corresponding fast Fourier transform (FFT) spectra are shown in Fig. 1. First, we determined the ambient-temperature value of C_{11} using the refractive index n and the mass density ρ; we measured n of ^{12}C diamonds by ellipsometry[38] between 370 and 1000 nm. (For example, $n = 2.4522$ at $\lambda = 400.0$ nm.) ρ was calculated from the theoretical mass and volume of the unit cell and considered isotope effects for the mass and volume. We averaged reported values of lattice constants of natural-isotope-ratio diamonds[5,6,39,40] and considered the isotope effect.[27] Then, we obtained $C_{11} = 1086.7 \pm 1.4$ GPa, which is 0.8% higher than reported values. The isotope effect on elastic constants was theoretically estimated and a monotonic increase in elastic constant with increasing ^{13}C was predicted. For a 100% ^{13}C diamond, it is predicted that the bulk modulus B increases by 0.18%.[41] Although there are some controversial experimental results which suggest that elastic constants of ^{13}C diamond are higher or lower than those of ^{12}C diamond,[41–44] none predicts that C_{11} of ^{12}C diamond is higher than that of natural-isotope-ratio diamond by a factor of about 1%. Therefore, the 0.8% increase in the pure ^{12}C diamond disagrees with the theory and measurements. We consider that this is not the isotope effect, but caused by ambiguity in mass density since it is difficult to obtain ρ with 0.1% accuracy.

Next, we consider the temperature dependence of n and ρ. Hu and Hess measured n of nanocrystalline diamond films for $\lambda = 400$ nm between 300 and 800 K.[45] However, they ignored thermal-expansion effects on their analysis. Although they argued that the effects can be neglected, n at 673 K was overestimated by 0.1% without thermal expansion,[46] which cannot be neglected in this study. Then, we used the temperature dependence of n reported by Ruf *et al.*[46] Concerning the temperature dependence of ρ, Reeber and Wang evaluated numerous reports and derived a quasiharmonic-model function, which is available between 0 and 2000 K.[40] This function was used in this work.

Moreover, adiabaticity must be considered because diamond exhibits a high thermal diffusivity and we observed high-frequency ultrasound. A thermal diffusion length for a period $\tau = 1/f$ is represented by $\sqrt{4D\tau}$ while ultrasound propagates $v\tau$. Here, $D = \kappa/\rho C_P$ is thermal diffusivity, where κ and C_P is thermal conductivity and specific heat at constant pressure, respectively. If ultrasound propagates much faster than heat conduction ($4Df/v^2 \ll 1$), we obtain the adiabatic sound velocity. On the other hand, we obtain the isothermal sound velocity when $4Df/v^2 \gg 1$.[47] We calculated the temperature dependence of $4Df/v^2$ using the reported temperature dependence of κ[48] and C_P,[40,49] whereas we considered f and v to be constant because their change ratios will not exceed 0.2% between 10 and 613 K. $4Df/v^2$ monotonically decreases as temperature increases above 30 K, and it is larger than unity below 480 K. Even at 613 K, $4Df/v^2 = 0.6$, indicating that we measured isothermal sound velocity at low temperatures (at 300 K, $4Df/v^2 = 4.3$).

Therefore, we evaluate the difference between the adiabatic elastic constant C_{11}^A and the isothermal elastic constant C_{11}^I. The difference is estimated by $C_{11}^A - C_{11}^I = T(\beta B)^2/C_V$, where β and C_V are volume thermal expansion and specific heat at constant volume, respectively. Below 480 K, the difference is roughly 0.1% at most. For example, C_{11}^A and C_{11}^I agree within 0.03% at 300 K, which is less than measurement inaccuracy and therefore can be neglected. The difference reaches 0.2% at 613 K. However, $4Df/v^2$ falls below unity, indicating that we measured C_{11}^A. The measured values, therefore, can be considered to be C_{11}^A.

TABLE I. For C_{11}, determined fitting parameters C_0, s, and Θ_E in Eq. (1), and obtained mode Grüneisen parameter γ_{11} and temperature coefficient of C_{11} around ambient temperature. Reference data are from McSkimin and Andreatch[7] and Migliori *et al.*[8]

References	C_0 (GPa)	s (GPa)	Θ_E (K)	γ_{11}	dC_{11}/dT (MPa/K)
^{12}C (this work)	1087.3	33.0	1263	1.5	−6.6
Theory (this work)	1051.2	50.0	1439	1.7	−6.7
McSkimin and Andreatch	1080.8	36.3	986	1.8	−16.0
Migliori *et al.*	1079.3	22.0	996	1.3	−9.5

Obtained and reported temperature dependence of C_{11} is shown in Fig. 2. We fitted E-L-L-V equation[17] to them and determined parameters are listed in Table I. Our results show weaker temperature dependence below room temperature, indicating that diamond has a larger zero-point energy than previously estimated. C_{11} at 300 K decreases by a factor of 0.04% from 0 K in our measurements, which is less than a half of previous measurements (−0.08% to −0.13%).[7,8] This finding suggests that physical properties of diamond must be discussed carefully below ambient temperature. The larger zero-point energy is quantitatively represented by Θ_E, which is higher than previous measurements by 30%. We believe that our results are more reliable than previous reports because of the wider-temperature range of our measurements. Migliori *et al.* and McSkimin and Andreatch measured the elastic constants only below room temperature, and it is noted that Migliori *et al.* estimated their inaccuracy as 0.3% for C_{11}.[8] We estimate that our experimental error of C_{11} is less than 0.2%: The measurement precision is determined by SD of $(f\lambda)^2$, which was 0.12% at most. The measurement accuracy of λ was within 0.03%. We measured λ with two different spectrometers, which were corrected using an Hg-Ar calibration source. The measured λ agree with each other to within 0.03%. The accuracies of n and ρ would be on the order of 0.1%; however, their absolute values do not affect the temperature dependence of C_{11}. Although there is uncertainty due to the adiabaticity, it leads to further smaller temperature dependence of C_{11} of diamond. We measured C_{11}^I which is smaller than C_{11}^A, and the difference increases as the temperature increases. Therefore, our measurement results indicate that the adiabatic elastic constants of diamond exhibit much smaller temperature dependence than previously reported.

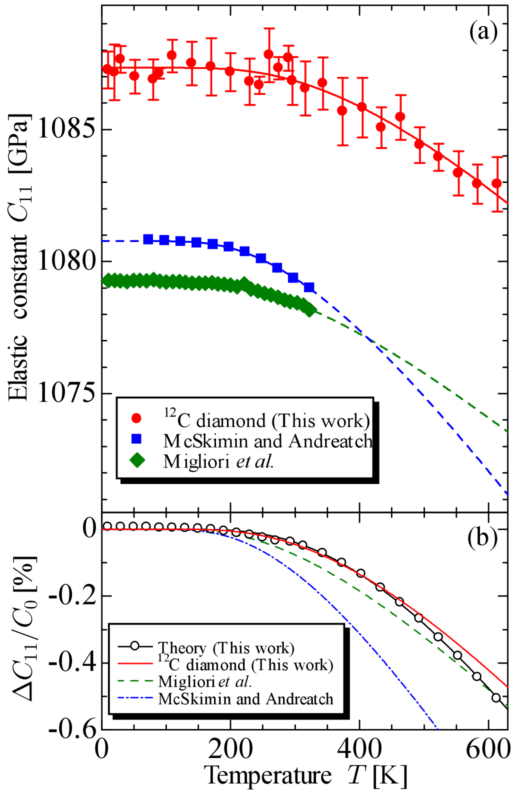

FIG. 2. (a) Measured and reported temperature dependence of C_{11}. Solid lines are Eq. (1) using the parameters in Table I, and dashed lines show extrapolated regions. (b) Relative changes of C_{11} from 0 K. Reference data are from McSkimin and Andreatch[7] and Migliori *et al.*[8]

The anharmonicity of diamond is comparable to previous measurements. The anharmonicity is represented by the mode Grüneisen parameter γ_{11}. Using the obtained parameters and Eq. (2), we obtained $\gamma_{11} = 1.5$, which is comparable to an estimated value of $\gamma_{11} = 1.3$ from Migliori *et al.* as shown in Table I. However, the temperature coefficients of C_{11} of diamond around room temperature are suppressed by the high Θ_E and Θ_D. To discuss the anharmonicity of diamond, our results should be compared to accurate measurements above room temperature.

Our measurement results are supported by *ab-initio* calculation. We calculated the temperature dependence of elastic constants by the Vienna *ab-initio* simulation package (VASP),[50] using generalized gradient approximation (GGA)[51] as the exchange correlation potential. The cutoff energy of plane wave and the k-point mesh are 1300 eV and $10 \times 10 \times 10$, respectively. Calculated lattice constant and elastic constants agree with experimental values within

0.1% and 3%, respectively. To calculate the elastic constants between 10 and 613 K, we changed the initial cell size on the basis of the reported thermal expansion,[40] and applied ±1% strains to the cell. The calculated temperature dependence of C_{11} with fitted E-L-L-V equation is shown in Fig. 2(b), which well agrees with that of the present measurements (^{12}C diamond) between 10 and 400 K. Note that our theoretical calculation fails to reproduce the previous measurements as shown in Fig. 2.

The agreement between the measurements and calculations allows us to estimate the Grüneisen parameter from the calculated temperature dependence of the bulk modulus $B(T)$; from Eqs. (1) and (2), we obtained $\gamma = 1.21$. Moreover, by assuming the Debye model, $B(T)$ at cryogenic temperatures can be expressed by the following T^4 law:[52]

$$B(T) = B_0 - \frac{3\pi^4 k_B \Theta_D \gamma (3\gamma - 1)}{5V_a}\left(\frac{T}{\Theta_D}\right)^4. \tag{4}$$

Because Eq. (4) is only applicable at low temperatures where only long-wavelength phonons are excited, we fitted Eq. (4) for the calculated $B(T)$ below $\Theta_D/10 \approx 220$ K, leading to $\gamma = 1.32$. Note that we obtained $\gamma = 0.81$ using Eq. (4) and calculated $B(T)$ between 0 and 613 K. Migliori *et al*. reported $\gamma = 1.26$ from their measurements and Eq. (4), and $\gamma = 1.10$ from the lattice specific heat ($\gamma = \beta B / C_V$). Our calculation provides us with comparable Grüneisen parameters to experimental values.

In conclusion, we have measured the temperature dependence of C_{11} and evaluated harmonic and anharmonic properties for highly isotopically pure ^{12}C diamond. Our results show smaller temperature dependence below room temperature, which indicates that the zero-point vibrational energy of diamond is still dominant at room temperature, suggesting that the Debye temperature of diamond is higher than previously reported values (∼2200 K). The mode Grüneisen parameter γ_{11} is 1.5, which is comparable to a previous measurement. We also calculated the temperature dependence of the elastic constants by *ab-initio* calculation considering lattice expansion. Calculation results agree well with our measurements. From the calculated temperature dependence of B, we estimated the Grüneisen parameter $\gamma = 1.2$–1.3 using the Debye model and E-L-L-V equation.

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