Effect of Isotopic Constitution of Diamond on Its Elastic Constants: ^{13}C Diamond, the Hardest Known Material

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Elastic moduli of ^{13}C diamond, deduced from the Brillouin shifts experienced by inelastically scattered monochromatic radiation, are ~0.5% higher than the corresponding values for natural diamond. This suggests ^{13}C diamond is harder than natural diamond. A simple model incorporating the zero-point motion and the anharmonicity of the interatomic forces is proposed; it explains quantitatively the increase in the elastic moduli, the decrease in the lattice parameter, and a correction to the Raman frequency beyond its $M^{-1/2}$ dependence (where M is the average atomic mass) observed for ^{13}C diamond with respect to their values for natural diamond.

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The isotopic constitution of matter can lead to pronounced manifestations in the behavior of its condensed phases. A spectacular example is the large difference in the molar volumes of liquid and solid ^{4}He and ^{3}He, on the one hand, and their departures from the values expected for the theoretical close packed arrangements based on the known atomic radii, on the other hand; they are a consequence of the *zero-point motion of the constituent atoms* [1]. Such isotope related effects, though generally expected, are accessible to observation in materials composed of heavy atoms only through high precision measurements, e.g., the x-ray determination of the difference in the lattice parameters of natural and isotopically enriched Ge [2]. In this context, the case of diamond is particularly attractive for discovering isotopic effects in view of the relatively small mass of carbon. The natural abundance of the stable isotopes of carbon, 98.9% ^{12}C and 1.1% ^{13}C, results in even the most perfect single crystals of diamond having an unavoidably small isotopic disorder [3]. However, single crystals of diamonds of any desired ^{12}C:^{13}C ratio can now be grown, thanks to recent developments in diamond synthesis [4–6]. One thus has available single crystals of diamond of any isotopic constitution, ranging from purely ^{12}C to exclusively ^{13}C. Several fundamental studies have addressed the consequences of the isotopic constitution of diamond, e.g., thermal conductivity [7], Raman spectrum [8], lattice parameter [9], vibrational, vibronic, and defect-associated local modes [10], and indirect gap [11]. In this Letter we report the first determination of the elastic moduli of ^{13}C single crystal diamond deduced from the Brillouin shifts experienced by inelastically scattered monochromatic radiation from longitudinal acoustic phonons propagating along ⟨100⟩ and ⟨111⟩. The elastic moduli thus deduced taking due account of the change in density and refractive index are ~0.5% higher than the corresponding values for natural diamond. *Thus ^{13}C diamond is the hardest terrestrial material known.* We present also the results of a simple theoretical model which yields the quantum corrections to the elastic moduli, to the lattice parameter, and to the frequency of the zone center optical phonon; the model demonstrates that the corrections are traced to the *zero-point motion taking into account the anharmonicity characterizing the interatomic potential.*

The specimen of ^{13}C diamond investigated was synthesized by first growing it in the polycrystalline form using the low-pressure chemical vapor deposition (CVD) technique [6]. This CVD diamond was then used as feedstock to grow an isotopically "pure" ^{13}C diamond gemstone by the high-pressure, high-temperature gradient process [5]. The resulting 0.9 carat gemstone is pyramidal in shape, with four {111} faces and a (001) base and contains 99% ^{13}C. We shall refer to this specimen as "^{13}C diamond" in the following. Several natural diamonds were also studied in the course of the present work. A single moded Ar$^+$ laser provided the monochromatic radiation ($\lambda_L = 5145$ Å) and the scattered radiation was spectrally analyzed with a high contrast, piezoelectrically scanned, multipassed tandem Fabry-Pérot interferometer [12]. The interferometer could be used in the tandem mode with the primary pair of plates multipassed 5 times and the secondary pair 4 times, or in the nontandem mode with the primary pair in the 5-times-passed mode bypassing the secondary pair. Brillouin spectra were recorded employing the backscattering geometry. The high precision in the measurements was obtained by following the procedure outlined in [13]. It

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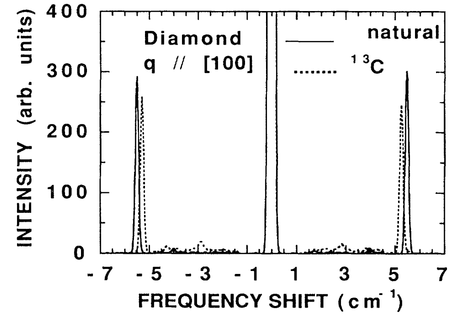

FIG. 1. Brillouin spectra of natural and isotopically pure ^{13}C diamond. The spectra were recorded in the backscattering geometry for 5145 Å radiation incident along [100] and the backscattered light analyzed with a (5+4) tandem Fabry-Pérot interferometer. The phonon wave vector **q** is along [100].

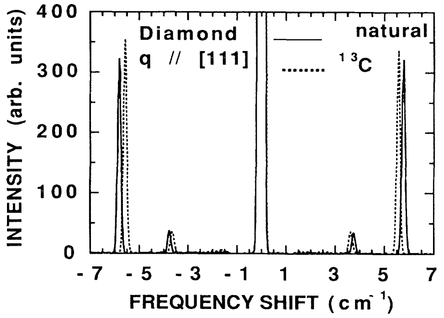

FIG. 2. Brillouin spectra of natural and isotopically pure ^{13}C diamond. The spectra were recorded in the backscattering geometry for 5145 Å radiation incident along [111] and the backscattered light analyzed with a (5+4) tandem Fabry-Pérot interferometer. The phonon wave vector **q** is along [111].

involved the use of the interferometer without its tandem feature in which the free spectral range (FSR) was set at a value for which the Brillouin components are separated from the parent laser line by as many as 8 full orders and a fraction of the FSR. The procedure also involved the measurement of the Brillouin shift as a function of propagation direction close to the desired direction, thereby eliminating any errors due to sample misorientation. In Figs. 1 and 2 we display the Brillouin spectra for ^{13}C and natural diamond for backscattering with $\mathbf{q} \parallel [100]$ and $\mathbf{q} \parallel [111]$, respectively, where **q** is the phonon wave vector. For the convenience of display, these were recorded with the interferometer in the tandem mode using (5+4) multipasses.

From the Brillouin shifts ($\Delta\omega$) recorded in backscattering we deduce the sound velocities (v_s) of the relevant acoustic phonons from $\Delta\omega = \pm 2\omega_L n(v_s/c)$. Here ω_L is the frequency of the incident light (rad/s); c, the velocity of light in vacuum; n, the refractive index for ω_L; v_s, the velocity of sound $=\sqrt{X/\rho}$, where ρ is the density, and X equals c_{11} and $(c_{11}+2c_{12}+4c_{44})/3$ for longitudinal acoustic phonons with $\mathbf{q} \parallel [100]$ and [111], respectively. We have taken into account the change in ρ and n resulting from the change of isotopic composition including the effect of 1.1% ^{13}C in natural diamond; these can be deduced from the change in a, the lattice parameter [9], viz., $a(^{13}\mathrm{C}) = 3.56662$ Å and $a(^{12}\mathrm{C}) = 3.56715$ Å and the elasto-optic constant $(p_{11}+2p_{12})/3$ [13]. It yields $\rho(^{13}\mathrm{C})/\rho = 1.08226$ and $n(^{13}\mathrm{C})/n = 1.000082$, where ρ and n, referring to natural diamond, are 3.512 g/cm^3 and 2.4293 ($\lambda_L = 5145$ Å), respectively. For $\mathbf{q} \parallel [100]$ we measured the Brillouin shifts for three natural diamond specimens. The results, summarized in Table I, show that the elastic moduli of ^{13}C are ~0.5% larger than those of natural diamond. We note here that Anthony and Banholzer reported values for c_{11} deduced from an ultrasonic measurement (Table II in Ref. [5] and Table I in Ref. [14]). While the c_{11} for ^{13}C was found to be higher than that for natural diamond, we feel the observed difference is too large. The ultrasonic technique requires large samples for high precision; measurements of Brillouin shifts with high resolution with a Fabry-Pérot interferometer enable the values of elastic moduli to be determined with high precision and a small sample size is not a limitation [13].

In order to understand the effect of isotopic composition on the elastic moduli (as well as on a, the lattice parameter, and ω_0, the frequency of the zone center optical phonon) one must consider not only the *increase in the kinetic energy* of a light atom arising from the spatial confinement as required by the uncertainty principle but also the *anharmonicity* of the interatomic forces. In fact, in the absence of anharmonicity, there would be no change in the lattice parameter with isotopic mass, contrary to the experimental observation [9].

A simple Einstein model provides a qualitative, and even a quantitative, explanation for the isotopic effects in the elastic moduli and the zone center optical phonon. The anharmonicity appears in the Taylor expansion of $V(u)$, the potential energy of an atom as a function of its displacement u in a given direction with respect to its equilibrium position, viz., $V(u) = ku^2/2 - ru^3/6 + \cdots$, where k and r are positive constants.

Because of the zero-point motion of the atoms, the expansion of $V(u)$ is not appropriate for the determination of the frequencies of vibration, i.e., the Born–von Karman procedure fails here as it does in a more spectacular fashion in solid helium. We describe the quantum range of values of u with a wave function of the form $\psi(u)$

TABLE I. Elastic moduli of diamond (10^{11} dyn/cm^2).

X	**q**	^{13}C	Natural diamond
c_{11}	[100]	108.33 ± 0.05	107.88 ± 0.04
			107.90 ± 0.05
			107.96 ± 0.05
$\frac{1}{3}(c_{11}+2c_{12}+4c_{44})$	[111]	121.87 ± 0.05	121.27 ± 0.05

$=(\alpha/\sqrt{\pi})^{1/2}\exp[-\alpha^2(u-\delta)^2/2]$, where α and δ are parameters to be determined by minimizing the total energy. After minimizing with respect to α, the total energy is

$$E=\frac{\hbar}{2}\left[\frac{k}{M}\right]^{1/2}+\frac{1}{2}K\left[\delta-\frac{\hbar r}{4K(kM)^{1/2}}\right]^2 -\frac{\hbar^2 r^2}{32KkM}+\cdots, \tag{1}$$

where M is the mass of the atom and

$$K=k-(\hbar r^2/8k)(kM)^{-1/2}. \tag{2}$$

From Eqs. (1) and (2) one can deduce [15] that the lattice constant a is given by

$$a=a_B+(\hbar r/4k)(kM)^{-1/2}, \tag{3}$$

where a_B is the value in the absence of zero-point motion. From Eqs. (1) and (2) we obtain the frequency ω_0 of the triply degenerate zone center optical phonon, i.e., of the F_{2g} Raman mode [16],

$$\begin{aligned}\omega_0&=(K/M)^{1/2}\\ &=(k/M)^{1/2}[1-(\hbar r^2/8k^2)(kM)^{-1/2}]^{1/2}.\end{aligned} \tag{4}$$

The microscopic origin of the elastic moduli is, of course, the renormalized force constants of which only K appears in our model. A generalized model will also be characterized by a similar renormalization. Cerdeira and Cardona [17] identify the elastic modulus c_{44} with $k/8a$ which, when renormalized, becomes

$$c_{44}\cong(k/8a)[1-(\hbar r^2/8k^2)(kM)^{-1/2}]. \tag{5}$$

In order to compare the experimental results for the changes in the properties of ^{13}C diamond with respect to those of natural diamond with the predictions of the model we need only the single parameter r; we deduce it to be 3.2×10^{15} ergs/cm^3 from the experimental value of $\Delta a/a=1.5\times10^{-4}$, measured by Holloway *et al.* [9], in conjunction with Eq. (3). Using this value of r we obtain $\Delta c_{44}/c_{44}\sim0.7\%$, in reasonable agreement with the $\Delta X/X$ in Table I. We expect that all three independent elastic moduli experience comparable fractional changes associated with the change in the isotopic mass. Using the experimental value 1332.3 cm^{-1} for ω_0 of natural diamond, Eq. (4) yields $\omega_0(^{13}\text{C})=1285.0$ cm^{-1}. The experimental value for $\omega_0(^{13}\text{C})$ is 1284.8 cm^{-1} [18]. Had the quantum correction in Eq. (4) been ignored, the entire decrease of ω_0 from its value for natural diamond being solely due to $M^{-1/2}$ in the prefactor, $\omega_0(^{13}\text{C})$ would have been 1281.0 cm^{-1}.

The value of the anharmonic constant r used above is in satisfactory agreement with that deduced from the coefficient of linear thermal expansion (α_T). For making this comparison we used the expression based on the model used in this work, viz.,

$$\alpha_T=\frac{2rk_B}{\sqrt{3}ak^2}\left[\frac{x}{2\sinh(x/2)}\right]^2, \tag{6}$$

where $x=\hbar(k/M)^{1/2}(k_BT)^{-1}$. The experimental values for α_T have been reported by Krishnan [19]. The value of r (6×10^{15} ergs/cm^3) obtained from such a comparison at 300 K is somewhat larger than that used above; however, since Eq. (6) is based on an Einstein model, the calculated α_T for a given r is underestimated.

The present work shows that the elastic moduli of ^{13}C diamond are larger than those for natural diamond. Wooster [20] has presented an empirical relationship between hardness (H) and c_{11} where H is in Moh's scale, viz., $c_{11}\propto H^{7/4}$, thus making ^{13}C diamond the hardest known terrestrial material. We also cite the remark by Holloway *et al.* [9] that the atomic density of ^{13}C diamond at 1.7632×10^{23} cm^{-3} makes it the material with the "largest atomic density of any known solid." The increase in the elastic moduli, the decrease in the lattice parameter, and the correction to the Raman frequency beyond the $M^{-1/2}$ decrease observed for ^{13}C diamond with respect to their values for natural diamond are truly quantum effects, all originating in the zero-point motion and described by the single anharmonicity parameter r. It is of interest to recall that the quantum theory of solids was initiated in Einstein's theory of specific heats in which diamond also provided the crucial evidence [21].

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