Quantum effects in diamond isotopes at high pressures

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An influence of quantum effects on the equation of states and phase transitions in compressed matter is of primary interest in the physics of giant planets and in astrophysics. To gain some insight into the problem we carried out precision Raman studies of diamond isotopes ^{12}C, ^{13}C, and their mixture $^{12.5}$C in the pressure range up to 73 GPa using helium as a hydrostatic pressure-transmitting medium. The ratio of Raman frequencies of ^{12}C and ^{13}C diamonds, which differs from the classical value (1.0408), was found to slightly, but nonmonotonically, change up to 60 GPa. One can propose that the quantum effects in diamonds initially are enhanced on compression to ∼30 GPa and then decrease up to the maximum experimentally measured pressure. This behavior probably unveils hidden features of covalent interaction in crystals. Examination of the isotopically mixed $^{12.5}$C diamond shows that the effective mass determining the Raman frequency varies under compression from 12.38 a.u. at ambient pressure to 12.33 a.u. at pressure of 73 GPa.

According to the Heisenberg uncertainty principle, the ground-state energy of any condensed matter system includes a dynamic part, called the "zero-point" energy. The "zero-point" energy contributes significantly to the properties of systems of low mass particles [1,2]. A result of this contribution is that the helium isotopes ^{3}He and ^{4}He do not crystallize down to the zero temperature at low pressures. The "zero-point" energy considerably influences processes occurring in the "cold" stars and giant planets. By definition, this energy increases as a material is compressed, but its impact on material properties depends on the form of the total energy [1]. Generally, it is hard to observe directly the quantum effects in condensed matter, but fortunately, nature provided us with isotopes, whose mass-dependent properties can be studied.

The isotope effects manifest themselves rather clearly in diamond, as carbon has a small atomic mass and a large relative difference among the masses of its different isotopes (^{12}C, ^{13}C, ^{14}C). Moreover, because of its extremely high Debye temperature (2200 K), diamond is in a "quantum" regime even at room temperatures. The high perfection and the simple structure of diamond crystals facilitate precision measurements of its various physical properties. Investigations of the lattice parameters, the Raman frequency, and elastic characteristics of different diamond isotopes at both ambient and high pressures were measured in Refs. [1,3–7]. Nevertheless, the question on a role of quantum effects in diamond under pressure remains open.

At ambient pressure ^{12}C diamond volume exceeds that of ^{13}C diamond by 0.05–0.07% due to the quantum effects [1,8,9]. From the data on elastic characteristics measured by Brillouin scattering it was estimated by the authors or Ref. [4] that the bulk modulus of ^{13}C diamond is larger by 0.5% than that for ^{12}C diamond. However according to later estimates [6] the bulk modulus ^{13}C diamond is only by 0.1–0.2% larger than that for ^{12}C diamond.

Contrary to the interpretation of the Brillouin scattering data, measurements of diamond compressibility by x-ray diffraction [3] to pressures of 22 GPa suggested that the

bulk modulus ^{12}C diamond should be larger than that of ^{13}C diamond by 1.5%, i.e., the quantum effects in a diamond should increase under compression. However, the accuracy of measurements of bulk moduli in Ref. [3] was 2–3%, bringing this conclusion into question.

Raman studies seem to be promising for accurate examination of the quantum effects in diamond isotopes at high pressures. A study of various diamond isotopes under pressure up to 14 GPa by the Raman spectroscopy was carried out in Ref. [7]. It was found by the authors of Ref. [7] that at ambient pressure the frequency ratio $^{12}\nu / {}^{13}\nu \approx 1.0395$ was less than the classical value 1.04083. It was claimed by the authors of Ref. [7] that the frequency ratio decreased with pressure. Accordingly, it was suggested that the quantum effects in the diamond get stronger under compression, although the accuracy of the measurement [7] likely did not justify this conclusion.

Of special interest is the Raman study of crystals with a mixed isotope composition. The isotopic disorder in crystals leads to an increase in phonon damping and the corresponding Raman scattering peak broadening. The vibration frequency for a crystal with isotopic disorder corresponds to a certain effective atomic mass, which does not coincide with the mean mass [10]. The effect of pressure on Raman scattering of crystals with isotopic disorder was earlier examined for Ge crystals [11]. The difference between the effective and mean masses in the natural Ge crystal was assumed to increase under pressure, but the differences in effect was within the measurement error. The $^{12.6}$C diamond crystals of mixed isotope composition were earlier investigated by the Raman scattering to 3 GPa [7].

It should be emphasized that in high-pressure studies a pressure-transmitting medium is of paramount importance. The shear stresses in the medium can affect significantly results of measurements. In most studies argon and nitrogen are used as a pressure medium, which leads to the development of strong nonhydrostatic stresses in samples under pressures above 10 GPa. At the same time one should mention Refs [7,12], where the Raman scattering and x-ray diffraction studies of

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diamond were carried out with helium as a pressure-transmitting medium (natural diamonds were studied in Ref. [12]).

The present research is aimed at clarifying the behavior of quantum effects in diamond isotopes under pressure. We report accurate measurements of Raman scattering for diamonds ^{12}C, ^{13}C, and $^{12.5}$C over the extended pressure range up to 75 GPa at room temperature and of isotopically pure ^{12}C and ^{13}C samples at pressures up to 17 GPa at 80 K.

Isotopically pure high-quality single crystals of diamond ^{12}C, ^{13}C, and $^{12.5}$C were produced by high-pressure synthesis in a belt-type apparatus from an amorphous carbon source. The details of this method are described in Ref. [13]. The quality of both ^{12}C and ^{13}C is quite high [much better in comparison with chemical vapor deposition (CVD) pure isotopic diamonds]. The total impurity content is less than 0.01%.

Raman measurements were performed using a 488-nm Ar+ laser line for excitation and a triple-grating spectrometer (Princeton Instruments TriVista 555) with a liquid-nitrogen-cooled CCD detector. The spectral width of the slits used was about $1 \, \text{cm}^{-1}$. We used a 50 times objective (N.A. = 0.50) Olympus BX51 microscope to focus the laser and to collect the Raman signal. We estimated the size of excitation volume as 3–7 micron in diameter and 2–4 micron in depth, and at high pressures the excitation volume of the sample was 10–20% of the excitation volume of the anvil. The laser output power in front of the DAC was less than 1.5 mW. High pressure was generated by a diamond anvil cell (DAC) with a culet's diameter of 300 μm.

The pressure-transmitting medium was helium, which provides good hydrostatic conditions in the whole pressure range. The hole in a stainless steel gasket serving as the sample chamber was set to about 100 μm in diameter and 60 μm in thickness. The pressures were determined from the pressure-dependent shift of the ruby fluorescence R_1 line. The samples of ^{12}C and ^{13}C were placed into the DAC together, with a ruby chip positioned near the center of the hole. Samples sizes were 10–15 microns and the samples were placed to the cell close to each other (almost touching). At low pressures, up to 10 GPa, it was indeed easy to obtain separate spectra for each sample using 1.5–2 micron laser spot. At pressures higher than 12 GPa (solidification of He) the optical contrast becomes poor and we preferred to collect the spectra from both samples together using 3–7 micron laser spot. Before the high-pressure experiment we checked the quality of the Raman spectra from the different sample regions and found that there is no degradation of the spectra on the edge regions of the samples. $^{12.5}$C samples of mixed isotope composition were investigated in a separate series of experiments. Low-temperature measurements were taken with the use of Oxford Optistat SMX cryostat.

We carried out special experiments, which showed that the random errors were rather small ($\sim$0.05 cm^{-1}) over the measured Raman mode frequencies. The random errors, connected with uncertainties of the pressure coordinates, were negligible as well. The main uncertainty of the data caused by systematic factors, e.g., shear stresses, which were somewhat different in each experimental series. We estimated the errors of the Raman frequency measurements in the all pressure range to be about ±0.2 cm^{-1} for ^{12}C and ^{13}C and ±0.5 cm^{-1} for $^{12.5}$C.
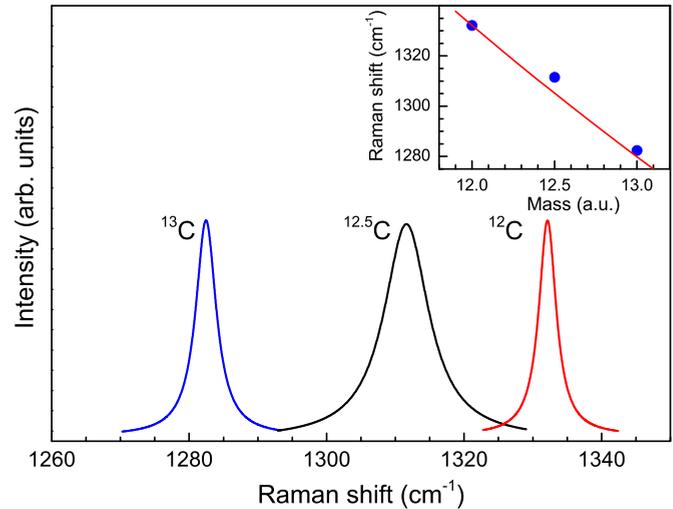
FIG. 1. The first-order Raman spectra of diamond specimens for ^{13}C, $^{12.5}$C, and ^{12}C at ambient pressure and room temperature. In the inset the Raman frequency as a function of the average mass for isotopically enriched and disordered diamond samples is shown. The red solid line is a calculation with $\nu = 1332.1 * (12/m)^{0.5}$ cm^{-1} (VCA).

The first-order Raman scattering lines corresponding to isotopically pure ^{13}C, $^{12.5}$C and ^{12}C diamonds are located at, respectively, 1282.5, 1311.5, and 1332.1 cm^{-1} (see Fig. 1). As it is seen in Fig. 1, ^{13}C diamonds have a slightly larger Raman peak half-width, which possibly is associated with larger values of stresses and defects. For the isotopically mixed sample, the line half-width is increased greatly compared to the isotopically pure samples, which is caused by the isotopic disorder. Note that the Raman scattering from an isotope mixture can be interpreted as the scattering from a homogeneous medium with an effective mass. Consequently, the scattering line position for an isotope mixture deviates noticeably from the position that might be expected for the arithmetic average mass [virtual crystal approximation (VCA)] Fig. 1 [10].

It is known that studies of diamond isotopes encounter additional difficulties with DACs. The intense first-order Raman scattering line from diamond anvils itself can mask the scattering from the samples in a certain pressure range. Figure 2 presents the Raman spectra of diamond isotopes ^{12}C, ^{13}C, and $^{12.5}$C together with DAC recorded with increasing pressure. The mutual positions of the Raman line for samples and diamond anvils shift with applied pressure. For the ^{12}C isotope, the signal of the sample in a DAC is completely hidden by the strong Raman scattering of the anvils below 13 GPa. Fortunately, the change in the Raman profile of the strained anvils differs sufficiently from the change due to the hydrostatic pressure, so that the Raman peak from the sample can be clearly seen above 13 GPa. In the case of the ^{13}C isotope the problem arises over the pressure range of 13–34 GPa, where the signal of the sample in a DAC becomes hidden by the strong Raman scattering of the anvils. For the isotopically mixed $^{12.5}$C diamond sample the first-order Raman line can be traced well up to pressures of 6 GPa, and then, because of the background scattering of diamond anvils, the accuracy in
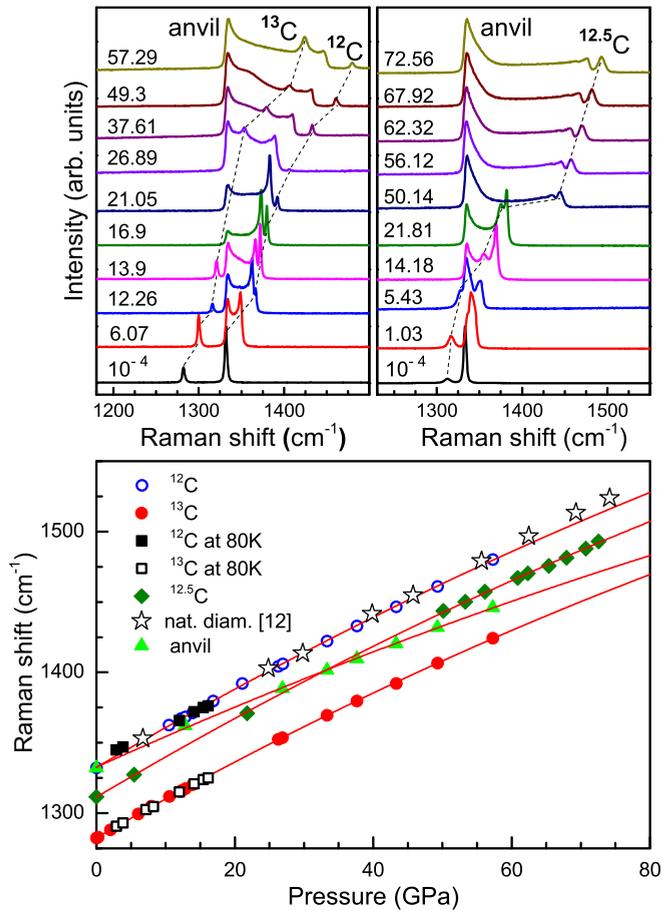
FIG. 2. The pressure evolution of the Raman spectra of diamond ^{12}C, ^{13}C (upper left panel), and $^{12.5}C$ (upper right panel) at room temperature. The numbers show the pressure in GPa. Dashed lines represent peak positions of carbon isotopes. The unlabeled peak in both panels is due to the strained interface of the anvil. Pressure dependence of the Raman shift of isotopically enriched (both at room and low temperatures), isotopically disordered diamond samples, and for diamond anvil (bottom panel). Solid lines are the polynomial fits with seconnd order for ^{12}C, ^{13}C, $^{12.5}C$, and anvil at room temperature.

FIG. 3. (a) The reduced frequency of the LTO(G) mode in isotopically different diamond samples versus pressure is presented. The data points show the measured frequency for the diamond ^{12}C. For diamonds ^{13}C and $^{12.5}C$ measured frequency multiplied by a factor of $k_1 = 1.03883$ and $k_2 = 1.01568$, respectively, to make coincidence of the Raman frequencies for different isotopes at room pressure. The inset of Fig. 3(a) shows the frequency ratio of the first-order Raman peaks of ^{12}C and $^{12.5}C$ diamonds as a function of pressure. The value for the frequency ratio for average mass $(^{12.5}m/^{12}m)^{0.5} = 1.02062$ (VCA) is shown by a dotted black line. The red solid line is a linear fit of our experimental data. (b) The disorder-induced shift of the Raman phonon of diamond as a function of the ^{13}C concentration is shown. The open and filled symbols correspond to our data at ambient pressure and pressures 60 and 73 GPa for ^{13}C and $^{12.5}C$, respectively. The solid line is a fit to all previous experimental data, taken from Ref. [15]. The dotted and dashed lines represent the fits to theoretical values obtained from *ab initio* and CPA calculations, respectively [15].

the determination of the line position worsens markedly up to pressures of 40–50 GPa, while above 50 GPa the Raman line for the $^{12.5}C$ diamond becomes available again for accurate measurements.

The pressure dependence of the Raman frequencies for the isotopes, and the diamond anvil at $T = 296$ K is displayed in Fig. 2. The pressure dependence obtained by fitting all the results is given by the polynomials: $\nu(P) = \nu_{RT} + b_1 * P + b_2 * P^2$, where $\nu_{RT} = 1282.5 \pm 0.1 \, \mathrm{cm}^{-1}$ and $b_1 = 2.81 \pm 0.01 \, \mathrm{cm}^{-1}/\mathrm{GPa}$, $b_2 = (-5.96 \pm 0.2) * 10^{-3} \, \mathrm{cm}^{-1}/\mathrm{GPa}^2$ for diamond ^{13}C; $\nu_{RT} = 1332.3 \pm 0.3 \, \mathrm{cm}^{-1}$ and $b_1 = 2.91 \pm 0.02 \, \mathrm{cm}^{-1}/\mathrm{GPa}$, $b_2 = (-5.9 \pm 0.4) * 10^{-3} \, \mathrm{cm}^{-1}/\mathrm{GPa}^2$ for diamond ^{12}C; and $\nu_{RT} = 1311.4 \pm 0.6 \, \mathrm{cm}^{-1}$ and $b_1 = 2.91 \pm 0.04 \, \mathrm{cm}^{-1}/\mathrm{GPa}$, $b_2 = (-5.75 \pm 0.5) * 10^{-3} \, \mathrm{cm}^{-1}/\mathrm{GPa}^2$ for diamond $^{12.5}C$. Linear coefficients in the polynomials are quite close to the data of Ref. [14]. Our data for ^{12}C diamonds almost coincides with the data for the natural diamond from [12] up to 50 GPa. A slight deviation at higher pressures may be connected with larger errors of the data found in Ref. [12]

or inapplicability of the current polynomic approximation at higher pressures. The temperature dependencies of Raman frequencies in diamond are very small in our temperature range [14] because of the high value of the Debye temperature. So the data taken at temperatures of 80 and 300 K cannot be distinguished in Fig. 2.

Figure 3(a) presents the pressure dependencies of Raman frequencies of ^{12}C diamonds and normalized frequencies of ^{13}C and $^{12.5}C$ diamonds in a way that makes all three frequencies equal at ambient pressure (using multiplicative corrections). At first sight all three dependencies lie on the same curve. However, more detailed analysis shows that the ^{13}C to ^{12}C isotope frequency ratio decreases weakly up to 25–30 GPa and then increases weakly during further compression (Fig. 4). The possible minimum in the pressure dependence of the ratio of Raman frequencies is weak and
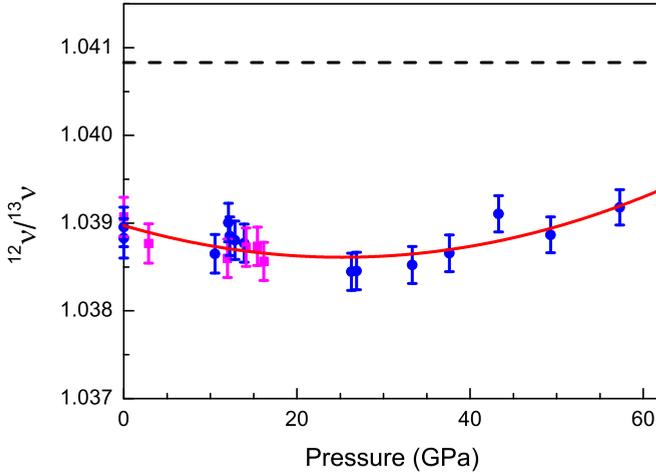
FIG. 4. The frequency ratio of the first-order Raman peaks of ^{12}C and ^{13}C diamonds as a function of pressure. The blue circles and magenta squares represent our experimental data at $T = 296$ K and $T = 80$ K, respectively. The red solid line is the polynomial fit with second order which revealed inversion of the pressure dependence of quantum isotope effects under compression. The classical value for the frequency ratio for average mass $(^{13}m/^{12}m)^{0.5} = 1.04083$ is shown by a dotted black line.

only several times larger than the experimental error, as shown in Fig. 4. However, from an approximation of the mean square error the data common sense supports the hypothesis that there is a minimum of the pressure dependence of the ratio of Raman frequencies of ^{12}C and ^{13}C diamond isotopes.

The data obtained imply that the quantum effects in diamond have a small increasing trend over compression up to 30 GPa (6% density increase) and a decreasing trend at higher pressures. This variation of quantum effects is an order of magnitude less than the previous estimations [3–5,7].

The ratio of the Raman frequency of the isotopically mixed $^{12.5}$C diamond to the frequency for the pure ^{12}C isotope changes with pressure slightly. However, the value of the effect significantly exceeds the measurement error [see inset to Figs. 3(a) and 3(b)]. This change is not due to the quantum effects and is caused by the effective mass variation under compression. The difference between the arithmetical average and the effective mass increases with pressure. At ambient pressure the effective mass for $^{12.5}$C isotope is equal to 12.38 $\pm$ 0.01 a.u. and at 73 GPa to 12.33 $\pm$ 0.02 a.u.. The increase of the difference between the effective and average masses for the natural germanium isotope under pressure was hypothesized previously in Ref. [11]. Enhancement of the isotopic disorder effects under compression is clearly seen in Fig. 3(b), showing the disorder-induced shift of the Raman frequency of diamond with respect to the VCA. The figure also presents the integrated results of previous examinations of diamond with isotopic disorder and the results of theoretical calculations from Ref. [15]. The coherent potential approximation gives rather good agreement with the experimental results with allowance for the additional contribution from quantum effects. Note that the theoretical calculations ignored the quantum contribution to the disorder-induced shift of the Raman frequency, which for the ^{13}C isotope makes up 2.5–3 cm^{-1} [see Fig. 3(b)]. The
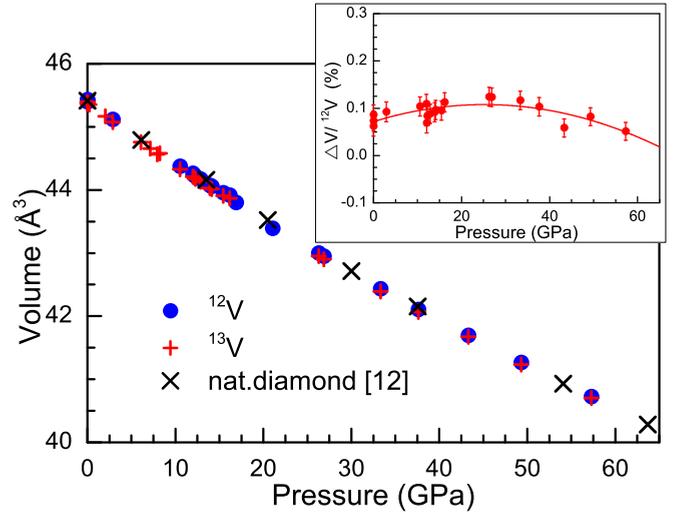
FIG. 5. Pressure dependencies of the calculated cell volume of isotopes ^{12}C, ^{13}C, and cell volume of natural diamond from Ref. [12]. Relative difference of the calculated cell volumes for ^{12}C, ^{13}C isotopes of diamond is shown in the inset.

variation of the effective mass under compression is obviously associated with the change in the effective interparticle interaction. To the best of our knowledge, no calculations concerning the effect of pressure on the effective mass in diamond-like semiconductors with isotopic disorder have been carried out to the present time.

Next we would like to remind readers that once diamond was named an "ideal Gruneisen body," which implied that the relationship $V/V_0 = (\nu_0/\nu)^\gamma$ was held with $\gamma = 0.97$ over a broad range of pressure [16]. The current Raman measurements allow us to estimate the pressure dependencies of the relative volume of both isotopes. Figure 5 presents these dependencies together with the experimental data for natural diamond from Ref. [12]. The inset to Fig. 5 shows the pressure dependence of the relative volume change between ^{12}C and ^{13}C diamonds. One can conclude that the difference of bulk moduli of ^{12}C and ^{13}C isotopes changes in sign at 30 GPa and does not exceed 0.15%. This difference cannot be measured by direct methods.

Lastly, at megabar pressures, one of the most reliable pressure sensors is the Raman frequency of diamond [14,16–20]. In particular, in Ref. [14] ^{12}C and ^{13}C diamond isotopes were employed as pressure sensors. The theoretical description of the equation of state and Raman frequency for diamond under pressure was presented in Ref. [20]. The data of the present study were obtained in an extended pressure range with the use of the hydrostatic medium and can be also employed for high-pressure measurements (see also the data from Refs. [12,16–20] obtained for natural diamond). A high-pressure scale based on the diamond equation state was suggested in Ref. [16].

Thus, we may conclude that the accurate measurements of the Raman spectra in different diamond isotopes under hydrostatic conditions over a broad pressure range revealed inversion of the pressure dependence of quantum isotope effects under compression. It was discussed early on that, depending on the type of interparticle interaction, the quantum

effects (and the contribution of zero energy) can either decrease (for substances with Lennard-Jones-type molecular interaction) or increase (for Coulomb systems) [1]. Diamond seemingly behaves like a Coulomb system at moderate pressures, as was proposed in Ref. [7]. However, measurements over higher pressures show different features, which can be tentatively connected with the repulsive non-Coulomb part of the interaction. Anyway, the experimental results obtained can serve as a test for *ab initio* calculations of the relative contribution of zero point energy in diamond to the total energy under compression. The experimentally revealed significant pressure-induced effective-mass variation

for diamonds with isotopic disorder also requires theoretical explanation.

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