

Raman scattering in diamond at high pressure isotopic effects

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The first-order Raman scattering in natural and ^{13}C -enriched diamonds was measured at high pressures up to 150 kb in a diamond anvil cell. The ratio ν^{12}/ν^{13} , where ν is the frequency of the first-order Raman line, decreases with pressure. The deviation of the frequency ratio from the limiting classical value of $(m^{13}/m^{12})^{0.5}=1.0408$, where m is the isotopic mass, becomes stronger at high density. This kind of behavior means that the quantum contribution to the physical properties of diamond increases with density. This is typical of systems with Coulomb interaction, e.g., metals, high-density plasma. © 1994 *American Institute of Physics.*

Recently ^{13}C -enriched diamonds have become available and their physical properties are studied extensively. The data obtained show the subtle but quite distinct quantum contribution to the physical properties of diamond. The question arises whether the quantum effects in diamond become more or less pronounced as a result of compression? The answer to this question may contribute greatly to our understanding of covalent solids. In the present paper we show on the basis of the Raman scattering study of ^{13}C -enriched and natural diamonds at a high pressure that the quantum effects in diamond increase as a result of compression.

A diamond anvil cell was used. Compressed helium gas was utilized as a pressure medium. Pressure was measured by the shift of the ruby fluorescence line. The appropriate samples with dimensions $\sim 50 \times 50 \times 15 \mu\text{m}^3$ were selected among the fragments of crushed single crystals of natural and ^{13}C -enriched diamonds. A polycrystalline CVD 91% ^{13}C diamond was used also as one of the samples.

Raman spectra were excited with the 5145 and 4880 Å lines of an argon-ion laser and analyzed in a backscattering geometry. The spectra were measured with a triple polychromator and a multichannel detector. The precision of the determination of a spectral position of the Raman lines was $\sim 0.5 \text{ cm}^{-1}$.

The results are shown in Figs. 1–5. The zero pressure values of the corresponding frequencies are: natural diamond (1.1% ^{13}C)—1332.1 cm^{-1} , high-pressure grown diamond (40% ^{13}C)—1316.5 cm^{-1} , high-pressure grown diamond (99% ^{13}C)—1281.2

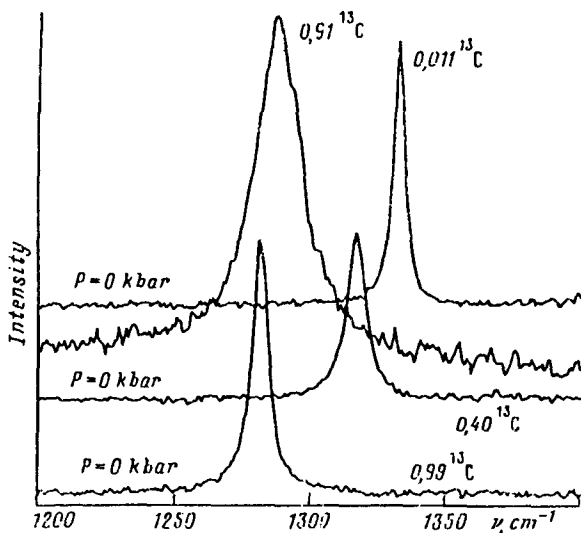


FIG. 1. The first-order Raman spectra of the diamond samples at normal pressure.

cm^{-1} , CVD polycrystalline diamond film (91% ^{13}C)— 1287.3 cm^{-1} .

To determine the quantum contribution to the first-order Raman frequency and the ν^{12}/ν^{13} ratio, we used the quasi-harmonic approach. First, we found the volume contribution on the basis of a simple Debye model of solids. The volume expansion due to quantum effects can be written in the form¹⁾

$$\frac{\Delta V}{V_0} = \frac{9}{8} \gamma \frac{\theta_D}{k_0 V_0}, \quad (1)$$

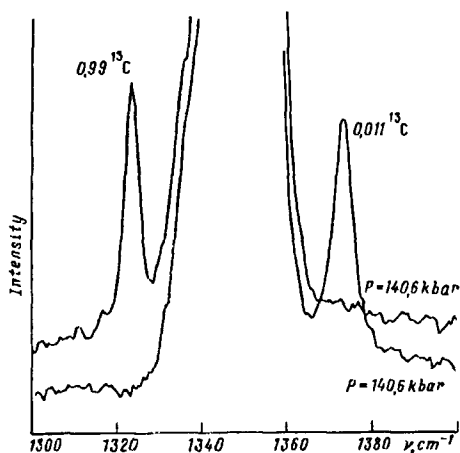


FIG. 2. Raman spectra of the diamond samples as they appear in the diamond anvil cell at high pressure. The wide band is the scattering by the stressed diamond anvils.

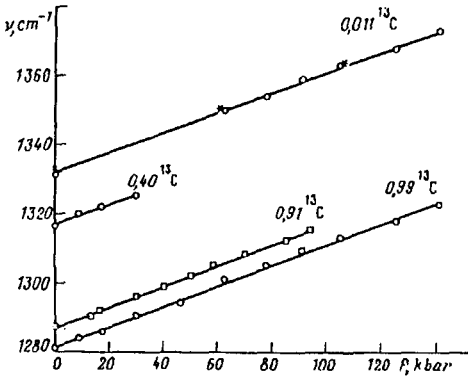


FIG. 3. The pressure dependence of the frequencies of the first-order Raman lines for diamonds of different isotopic compositions. The solid lines are linear fits of the experimental data.

where $\Delta V = V - V_0$, V is the molar volume, V_0 is the molar volume in the classical limit, θ_D is the Debye temperature, $k_0 = -V_0(\partial P/\partial V)_T$ is the bulk modulus, and γ is the Gruneisen constant.

Using the numerical values

$$^{12}\theta_D = 2200 \text{ K}, \quad ^{13}\theta_D = 2114 \text{ K}, \quad \gamma \approx 1, \quad k \approx 4.42 \text{ Mbar},$$

$$V = 3.42 \text{ cm}^3/\text{mole},$$

we obtain the following values for the ambient pressure and the temperature $T \ll \theta_D$:

$$^{12}V/V_0 = 1.01362, \quad ^{13}V/V_0 = 1.01309, \quad ^{12}V/^{13}V = 1.00053. \quad (2)$$

From (2) it follows that

$$\frac{^{12}a - ^{13}a}{^{13}a} = 1.75 \times 10^{-4},$$

where a is the lattice constant. This value agrees with the experimental data in Refs. 1 and 2.

Since in the case of diamond the ideal Gruneisen law $(\nu/\nu_0) = (V_0/V)^{0.965}$ holds,³ we easily obtain

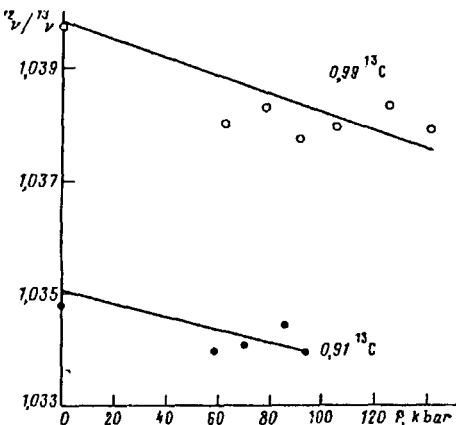


FIG. 4. Frequency ratio of the first-order Raman lines of the nature and the ^{13}C -enriched diamonds as a function of pressure. The solid lines are calculated from the linear fits of the experimental data (Fig. 3).

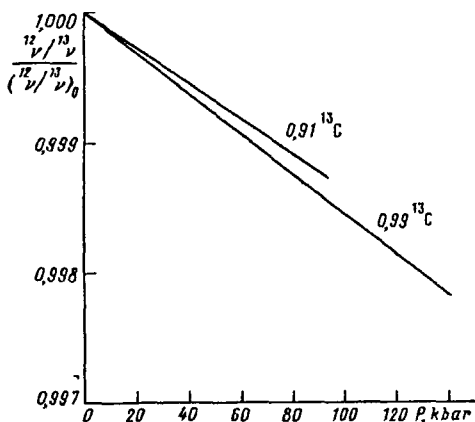


FIG. 5. Reduced frequency ratio of the first-order Raman lines of the natural and the ^{13}C -enriched diamonds as a function of pressure.

$$({}^{12}\nu/{}^{13}\nu) \cong (13/12)^{0.5} ({}^{13}V/{}^{12}V) \quad (3)$$

or ${}^{12}\nu/{}^{13}\nu \approx 1.04025$ at $P=0$ (note that the classical value of the frequency ratio is 1.04083). Thus the quasi-harmonic quantum contribution to the frequency ratio is too small to be reliably measured because of the various kinds of uncertainties (chemical and isotopic composition, experimental errors, etc.). On the other hand, it follows from Eqs. (1) and (3) that if quantum effects influence the frequency ratio, then the ratio can be detected from its pressure dependence. In our case the ratio ${}^{12}\nu/{}^{13}\nu$ decreases with pressure, which indicates the growth of the quantum contribution. On the basis of Eq. (3) we expect the value

$$\frac{{}^{12}a - {}^{13}a}{{}^{13}a} \cong 1 \times 10^{-3}$$

at a pressure of 150 kb, which make it possible to measure this quantity at high pressure using conventional x-ray techniques.

In conclusion, we emphasize [cf., Eq. (1)] that the role of quantum effects, in general, changes with pressure as a result of the tradeoff between the Debye temperature and the total energy (the product kV is proportional to the total energy). It is easy to show,⁴ that for a system of particles which interact with the pair potential $(r) \sim 1/r^n$ the quantum effects increase as a result of compression if $n < 2$. This behavior is expected for the systems with a Coulomb interaction. It is not clear how useful that kind of approach might be in the case of diamond, but at least the growth of quantum effects in diamond under pressure probably tells us that a system with highly delocalized electrons behaves in some ways like a free electron system.

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¹Equation (1) follows from the trivial relation $\Delta V/V = P/k$, if we define the pressure P as $P_z = -(\partial E_z / \partial V)_T$, where $E_z = (9/8)\theta_D$ is the zero-point energy. Note that Eq. (1) resembles the well-known expression for thermal expansion, in which the thermal energy is replaced by the zero-point energy.

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