

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.

Recently ^{13}C enriched diamonds has 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 on compression? Any 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 high pressure that the quantum effects in diamond do increase on compression.

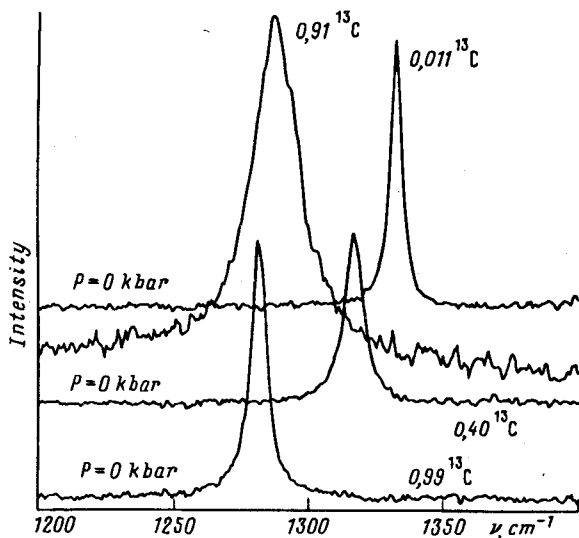


Fig.1. The first order Raman spectra of the diamond samples at normal pressure

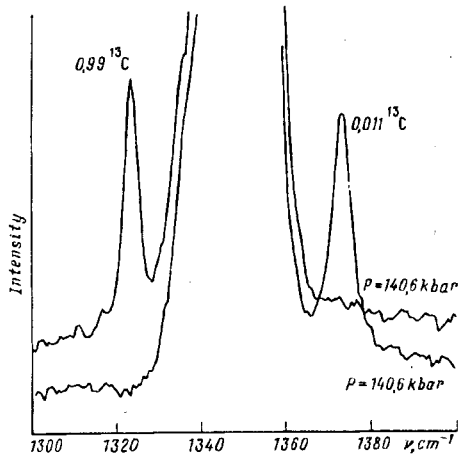


Fig. 2.

Fig. 2. The 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

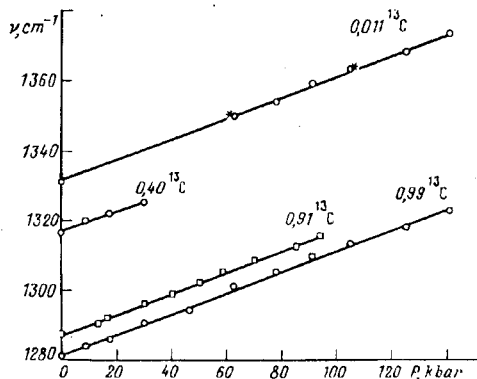


Fig. 3.

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

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 4880Å lines of an argon-ion laser and analyzed in back scattering 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 Fig's 1-5. The zero pressure values of the corresponding frequencies are: natural diamond (1.1% ^{13}C) - 1332.1cm^{-1} , high pressure grown diamond (40% ^{13}C) - 1316.5cm^{-1} , high pressure grown diamond (99% ^{13}C) - 1281.2cm^{-1} , CVD polycrystalline diamond film (91% ^{13}C) - 1287.3cm^{-1} .

To estimate the quantum contribution to the first order Raman frequency and the ν^{12}/ν^{13} -ratio we use the quasi harmonic approach. First, we find the volume contribution on the basis of the simple Debye model of solids. The volume expansion due to quantum effects can be written in the form [1]:¹⁾

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

¹⁾ The formulae (1) follows from the trivial relation $\Delta V/V = P/k$, if we define pressure P as $P_x = -(\partial E_x / \partial V)_T$, where $E_x = (9/8)\theta_D$ is the zero point energy. Note that the formulae (1) looks like the well known expression for thermal expansion where the thermal energy is replaced by the zero point energy.

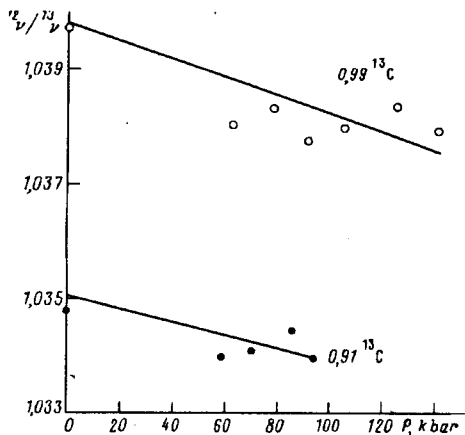


Fig. 4.

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

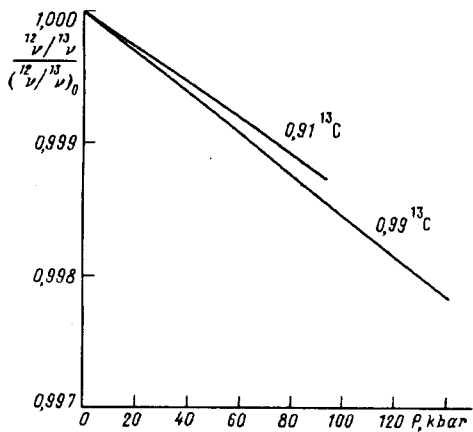


Fig. 5.

Fig. 5. The reduced frequency ratio of the first order Raman lines of natural and ^{13}C enriched diamonds as a function of pressure

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

Using the numerical values:

$$^{12}\theta_D = 2200 \text{ K}, \quad ^{13}\theta_D = 2114 \text{ K}, \quad \gamma \approx 1, \quad k \approx 4.42 \text{ Mbar}, \quad V = 3.42 \text{ cm}^3/\text{mole},$$

we obtain for ambient pressure and temperature $T \ll \theta_D$,

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

From (2) follows, that,

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

where a is the lattice constant. This value agrees with experimental data in Ref. [1,2].

Then taking into account the result in Ref.[3], that in case of diamond the ideal Gruneisen law $(\nu/\nu_0) = (V_0/V)^{0.965}$, holds, we easily get,

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

or $(^{12}\nu/^{13}\nu) \approx 1.04025$ at $P = 0$ (note that the classical value for the frequency ratio is 1.04083) Thus the quasi harmonic quantum contribution to the frequency ratio is too small to be reliably measured due to 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 do influence the frequency ratio, it may be detected from its pressure dependence. In the given case the

$^{12}\nu/^{13}\nu$ ratio drops with pressure which indicates the growth of the quantum contribution. On the basis of Eq.(3) one may expect the value of

$$\frac{^{12}a - ^{13}a}{^{13}a} \approx 1 \cdot 10^{-3}$$

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 the general case, changes with pressure as a result of tradeoff between 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 interacting with the pair potential $(r) \sim \frac{1}{r^n}$ the quantum effects increase on compression if $n < 2$. That is what we expect for the systems with Coulomb interaction. It is not clear enough how useful that kind of approach might be in case of diamond, but at least the growth of quantum effects in diamond with pressure probably tells us that a system with highly delocalized electrons behaves in some ways like a free electron system.

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