RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 50, NUMBER 18 1 NOVEMBER 1994-II

Rapid Communications

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Raman scattering in diamond at high pressure: Isotopic effects

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(Received 14 July 1994; revised manuscript received 26 August 1994)

First-order Raman scattering in natural and ^{13}C-enriched diamond was measured at high pressures up to 15 GPa in a diamond anvil cell. The ratio $^{12}\nu/^{13}\nu$, 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 $(^{13}m/^{12}m)^{0.5}=1.0408$, 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 and high-density plasma.

The pressure dependence of first-order Raman scattering in natural diamond has been studied in a number of experimental and theoretical works.$^{1-6}$ Recently ^{13}C-enriched diamond has become available and its physical properties have been studied extensively (see, e.g., Refs. 7–10). The data obtained show a 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 a Raman-scattering study of ^{13}C-enriched and natural diamond at high pressure that the quantum effects in diamond do increase on compression.

EXPERIMENTAL

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 $\sim 50\times 50\times 15\ \mu\mathrm{m}^3$ were selected among the fragments of crushed single crystals of natural and ^{13}C-enriched diamond. A polycrystalline CVD 91% ^{13}C diamond was used also as one of the samples.

Raman spectra were excited with the 514.5- and 488-nm lines of an argon-ion laser and analyzed in 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 $\sim 0.5\ \mathrm{cm}^{-1}$.

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

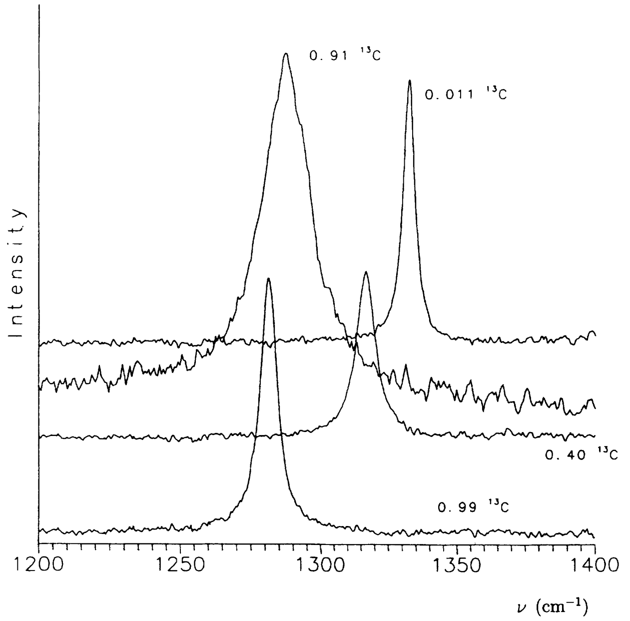

FIG. 1. The first-order Raman spectra of the diamond samples at normal pressure.

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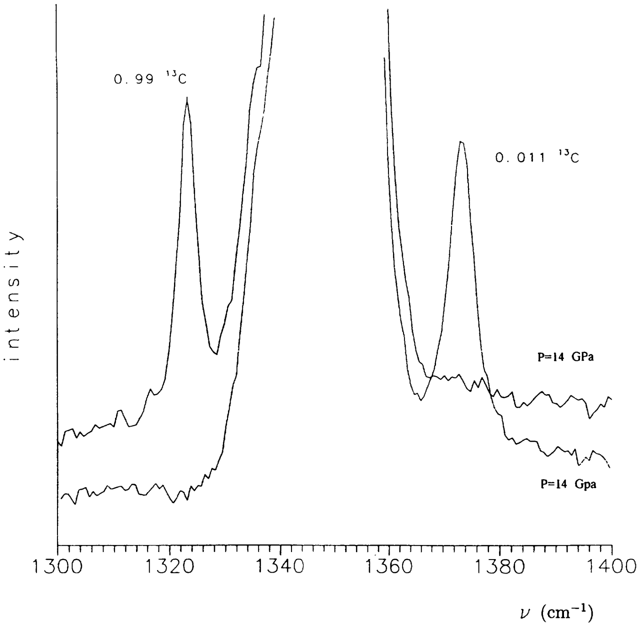

FIG. 2. The Raman spectra of the diamond samples as they appear in the diamond anvil cell at high pressure. The wide band is the scattering by the stressed diamond anvils.

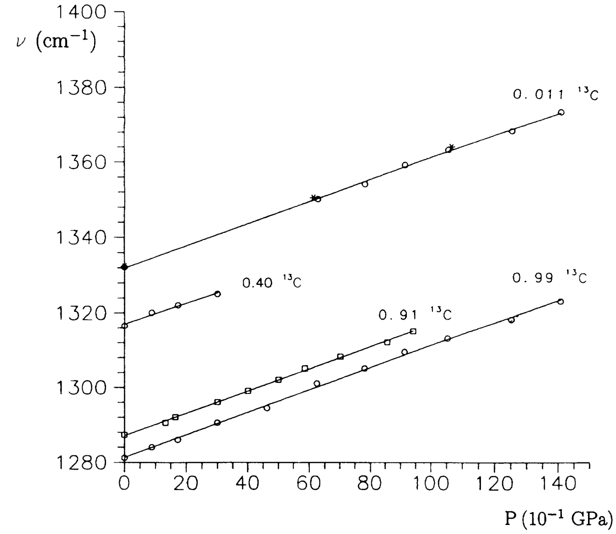

FIG. 3. The pressure dependence of the frequencies of the first-order Raman lines for diamond of different isotopic compositions. The solid lines are linear fits of the experimental data. (○) Present data. (∗) Data from Ref. 5.

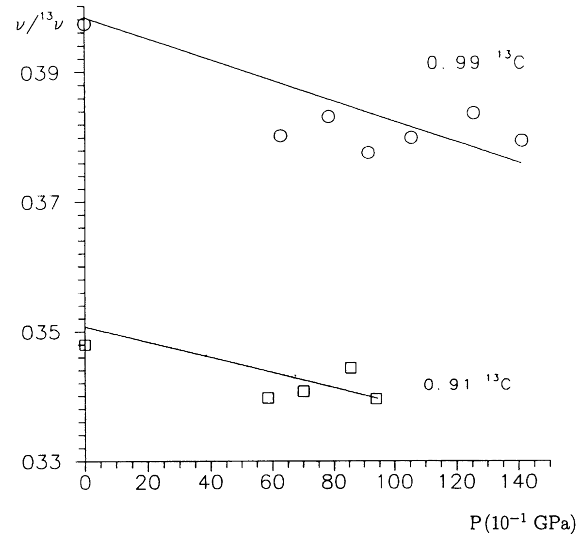

FIG. 4. The frequency ratio of the first-order Raman lines of natural and ^{13}C-enriched diamond as a function of pressure. The solid lines are calculated from the linear fits of the experimental data (cf. Fig. 3).

(99% ^{13}C), 1281.2 cm^{-1}; CVD polycrystalline diamond film (91% ^{13}C), 1287.3 cm^{-1}.

DISCUSSION

To analyze the data we try to estimate the quantum contribution to the LTO(Γ) Raman frequency and the $^{12}\nu/^{13}\nu$ ratio, using the quasiharmonic 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[11]

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

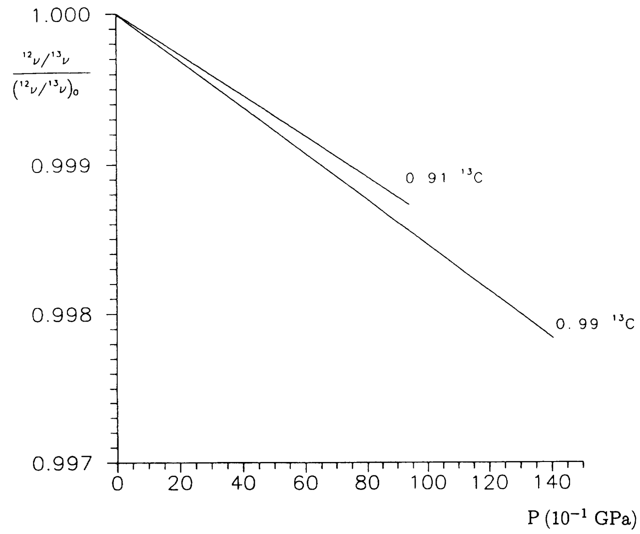

FIG. 5. The reduced frequency ratio of the first-order Raman lines of natural and ^{13}C-enriched diamond as a function of pressure.

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

Using the numerical values: ${}^{12}\Theta_D = 2200$ K, ${}^{13}\Theta_D = 2114$ K, $\gamma \approx 1$, $k \cong 4.42$ Mbar, $V = 3.42$ cm^3/mole, we obtain for ambient pressure and temperature $T \ll \Theta_D$,

$$^{12}V/V_0 = 1.013\,62, \quad ^{13}V/V_0 = 1.013\,09,$$

or

$$^{12}V/^{13}V = 1.0005. \tag{2}$$

From (2) follows, that $({}^{12}a - {}^{13}a)/{}^{13}a = 1.75 \times 10^{-4}$, where a is the lattice constant. This value agrees with experimental data in Refs. 9 and 10.

Then taking into account the result in Ref. 5, that in case of diamond the ideal Gruneisen law $(\nu/\nu_0) = (V_0/V)^{0.965}$ holds, we easily get

$$({}^{12}\nu/{}^{13}\nu) \cong (\tfrac{13}{12})^{0.5} \times ({}^{13}V/{}^{12}V), \tag{3}$$

or $({}^{12}\nu/{}^{13}\nu) \approx 1.040\,25$ at $P = 0$ (note that the classical value for the frequency ratio is 1.040 83).

Thus the quasiharmonical 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 (cf. Figs. 4 and 5), which indicates the growth of the quantum contribution. On the basis of Eq. (3) one may expect the value of $({}^{12}a - {}^{13}a)/{}^{13}a \cong 1 \times 10^{-3}$ at a pressure of 15 GPa, which makes 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[12] that for a system of particles interacting with the pair potential $\Phi(r) \sim 1/r^n$ 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 the 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.

ACKNOWLEDGMENTS

We are grateful to Dave Schiferl for providing us with ^{13}C CVD diamond film and Bob VonDreele for reading the manuscript.

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