

П И С Ь М А  
В ЖУРНАЛ ЭКСПЕРИМЕНТАЛЬНОЙ  
И ТЕОРЕТИЧЕСКОЙ ФИЗИКИ

ОСНОВАН В 1965 ГОДУ  
ВЫХОДИТ 24 РАЗА В ГОД

ТОМ 63, ВЫПУСК 2  
25 ЯНВАРЯ, 1996

Pis'ma v ZhETF, vol.63, iss.2, pp.73 - 77

© 1996 January 25

PRESSURE DEPENDENCE OF LATTICE CONSTANT OF  
DIAMOND: ISOTOPIC EFFECTS

*H.Fujihisa*<sup>1)</sup>, *V.A.Sidorov*<sup>2)</sup>, *K.Takemura*, *H.Kanda*, *S.M.Stishov*\*<sup>□</sup>

*National Institute for Research in Inorganic Materials  
Tsukuba, Ibaraki 305, Japan*

*\*Institute for High Pressure Physics, RAS  
142092 Troitsk, Moscow distr., Russia*

*□ Institute of Crystallography RAS  
117333 Moscow, Russia*

Submitted 8 December, 1995

The pressure dependence of lattice constants of the <sup>13</sup>C enriched diamond and the diamond of natural isotopic composition have been studied by using x-ray synchrotron radiation and imaging plate technique. The compression curves reveal features which indicate the inversion of the isotope effect at high pressure.

PACS 35.10.Bg, 64.30.+t, 62.50.+p

1. Introduction. Recently much attention has been paid to studying physical properties of isotopically pure diamonds. One of the most interesting finding of the studies was a discovery of slight but distinct quantum effect on various properties of diamond, including lattice and elastic constants [1-3], Raman scattering [4], indirect gap [5], optical absorption [6], etc. Raman scattering in <sup>12</sup>C and <sup>13</sup>C diamonds at high pressure was reported in Ref.[7]. It was found that the ratio  $\nu^{12}/\nu^{13}$ , where  $\nu$  is the frequency of the first order Raman line, decreases with pressure. This kind of behavior means that the quantum contribution to the physical properties of diamond increases with density. A simple analysis, which was carried out in Ref.[7] on the basis of Debye-Gruneisen model of solids, has

<sup>1)</sup>Present address: National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan.

<sup>2)</sup>Present address: Institute for High Pressure Physics, Russian Academy of Sciences, 142092 Troitsk, Moscow region, Russia.

shown that the volume ratio  $^{12}V/^{13}V$  for  $^{12}\text{C}$  and  $^{13}\text{C}$  diamonds might drastically increase with pressure. Thus a little chance has appeared that the difference in the corresponding lattice constants could be measured by conventional x-ray techniques at high pressure.

In the present study, the lattice constants of  $^{12}\text{C}$  and  $^{13}\text{C}$  diamonds were measured up to pressure about 37 GPa. Contrary to the expectations, the difference in lattice constants of isotopes decreases at high pressure and changes sign at about 10 GPa .

2. Experimental. The crystals of  $^{13}\text{C}$  diamond was produced by high pressure synthesis in the belt type apparatus from the amorphous carbon source containing 99% of  $^{13}\text{C}$  carbon. The details of this method are described in Ref.[6]. The powder samples were prepared by crushing the diamond crystals with tungsten carbide (WC) rollers and subsequent separation of the diamond powder by the sinking method. The final product had approximately  $1\ \mu\text{m}$  grain size. The sample of natural diamond (99%  $^{12}\text{C}$ ) was prepared in the same way from the synthetic crystals of  $30\ \mu\text{m}$  size produced by General Electric. Pressures were generated in the gasketed diamond anvil cell and measured by the ruby fluorescence method [8]. The gasket geometry and the ruby sensor position ( $15\ \mu\text{m}$  spot of fine ruby powder in the center of  $150\ \mu\text{m}$  gasket hole) were the same in all experiments. A 4:1 mixture of methanol and ethanol was used as a pressure transmitting medium. As is known this mixture freezes at pressure around 10 GPa, which causes nonhydrostatic stresses to appear. The latter may create certain problems at comparison of data, obtained in different runs.

Angle-dispersive powder x-ray diffraction patterns were obtained by using synchrotron radiation from the bending magnet on the beamline BL-6B at the Photon Factory, National Laboratory for High Energy Physics (KEK). The incident beam was monochromatized to a wavelength of  $0.6888\ \text{\AA}$  (18.00 keV) by Si(111) sagittally focused double monochromator. The imaging plate technique was used to record diffraction pattern. Two-dimensional image was converted to an ordinary one-dimensional diffraction pattern with the method reported in Ref.[9]. Two experimental runs were done for  $^{13}\text{C}$  samples (one in the pressure range 0-14 GPa and other in the range 10-40 GPa). Two similar runs were also done for  $^{12}\text{C}$  samples.

3. Results and Discussion. Diffraction peaks (111) and (220) of diamond were clearly observed in the all runs. Much wider peaks of hexagonal WC, the source of which is the the crushing rollers, were also seen. Since the strongest (111) diamond peak was located far from WC peaks, the lattice constant of diamond was calculated by using the (111) single peak.

The pressure dependence of the lattice constants of  $^{13}\text{C}$  (closed squares) and  $^{12}\text{C}$  (open squares) diamonds are shown in Fig.1. The size of the square mark corresponds to the experimental errors of the determination of the lattice constants and pressure, which are  $0.001\ \text{\AA}$  for the lattice constants and 0.5 GPa for the pressure values. Unfortunately we can not account properly for the errors introduced by nonhydrostatic environment at pressures above 10 GPa. The extrapolation of our data for  $^{13}\text{C}$  and  $^{12}\text{C}$  diamonds gives the zero pressure values of the lattice constants fairly close to those observed in Ref.[1, 2] (closed and open circles). Fitting the experimental data by the Birch-Murnaghan equation [10] of

state gives the values of the bulk moduli<sup>3)</sup>. The value of  $B_0$  for  $^{12}\text{C}$  diamond was found to be  $B_0 = 440 \pm 4$  GPa in good agreement with commonly accepted value 442 GPa [11-13]. For  $^{13}\text{C}$  diamond, the fit gave  $B_0 = 457 \pm 4$  GPa.

The bulk modulus of  $^{13}\text{C}$  diamond is very close to but slightly (4%) larger than that of  $^{12}\text{C}$  one. This result is in qualitative agreement with the experimental data on the elastic properties of  $^{13}\text{C}$  diamond at normal pressure [3,14-16]<sup>4)</sup>.

The present data should be compared with the results of Ref.[11], where the single crystal x-ray diffraction study of natural diamond at high pressure were carried out with making use of helium pressure medium (dashed curve in Fig.1). Both sets of the data agree well up to pressure about 15 GPa. The difference becomes noticeable at higher pressure, which is undoubtedly result of different mechanical properties of the solidified alcohol mixture and solid helium [17]. That kind of effect was observed for the first time at the study of the equation of state of CsJ, when using different pressure media [18].

Now we will discuss the experimental data in more specific way. As is seen in Fig.1 the experimental compression curves which are almost indistinguishable at low pressures, obviously can be separated at high pressures. The puzzle is that the lattice parameter of the light  $^{12}\text{C}$  diamond appeared to be lower than that of the heavier  $^{13}\text{C}$  diamond at pressures above 20 GPa. But because it is known that at normal pressure the light isotope has the higher volume [1,2], the behavior of the compression curves observed actually means their crossing at some pressure as a result of inversion of the quantum isotope effect. It is well illustrated by Fig.2, where the difference of the corresponding lattice constants versus pressure is plotted. From Fig.2 also follows that the present experimental data completely contradict to the prediction which was made on the basis of the Raman scattering experiment in the framework of quasiharmonic Gruneisen model [7]. It was expected that the difference in lattice constants of  $^{12}\text{C}$  and  $^{13}\text{C}$  diamonds will strongly increase on compression (curve 1 in Fig.2).

However it is too early to discuss the reason of this contradiction. Keeping in mind, that the pressure medium (alcohol mixture) is solid above 10 GPa, one might expect that the present experimental data are strongly influenced by the somewhat random stress conditions in the cell. This may make doubtful conclusion derived by comparison of the data, obtained in different runs. Fortunately, there is a rather strong argument against of that kind of extreme assumption. Fig.3

<sup>3)</sup>The fitting procedure includes the determination of three parameters: zero pressure volume  $V_0$ , zero pressure bulk modulus  $B_0$ , and its pressure derivative  $B'_0$ . Fitting with free parameters gives too large range of values for these parameters due to scattering of experimental data. Namely, the pressure should be well above 40 GPa to determine  $B'_0$  with high precision for low compressible diamond. Thus we fixed  $V_0$  and  $B'_0$  parameters to obtain  $B_0$ . The values of  $V_0$  for  $^{13}\text{C}$  ( $45.369 \text{ \AA}^3$ ) and  $^{12}\text{C}$  diamond ( $45.389 \text{ \AA}^3$ ) were taken from Ref.[2], and are very close to extrapolation of our high pressure data. The value of  $B'_0$  was chosen to be  $B'_0 = 4$ . The arguments in favor of this choice based on analogy with other group IV elements possessing diamond like structure (Si and Ge) are presented in Ref.[11]. The choice of  $B'_0$  value did not influence appreciably the fitted value of  $B_0$ .

<sup>4)</sup>Note some quantitative disagreement between the results Brillouin scattering (Ref.[3]) and ultrasonic (Ref.[15]) experiments. The effective elastic constant  $c_{eff} = (c_{11} + 2c_{12} + 4c_{44})/3$  exhibits 5% rise when going from  $^{12}\text{C}$  to  $^{13}\text{C}$  diamond according to Hurley et al. (Ref.[15]) but only 0.5% rise according to Ramdas et al. (Ref.[3]). Recent Brillouin scattering experiments (Ref.[16]) revealed the difference in  $c_{eff}$  between  $^{12}\text{C}$  and  $^{13}\text{C}$  diamonds to be less than 0.2%. The only available value of bulk modulus for  $^{13}\text{C}$  diamond (Ref.[15]) looks surprisingly high (17% increase compared to  $^{12}\text{C}$ ). In this situation further experiments are required to obtain more consistent information on the elastic properties of isotopes of diamond.

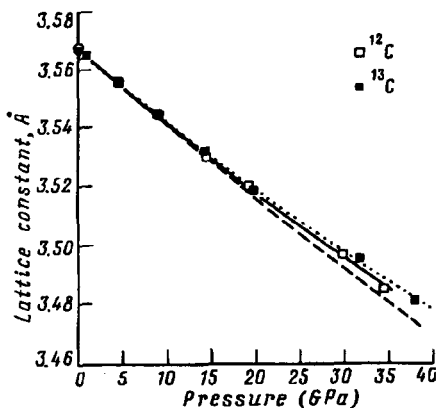


Fig.1. Pressure dependence of diamond lattice constant. Circles - lattice constants at normal pressure from Ref.[2]; squares - our data. Open symbols -  $^{12}\text{C}$ , filled symbols -  $^{13}\text{C}$ . Dashed line - data for  $^{12}\text{C}$  from Ref.[11]. Solid and dotted lines - Birch-Murnaghan fit for  $^{12}\text{C}$  and  $^{13}\text{C}$  diamonds respectively

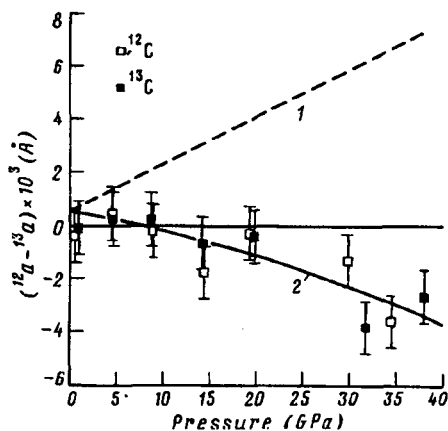


Fig.2. Difference of lattice constants of isotopes of diamond: 1 - prediction made on the basis of the Raman scattering experiment and quasiharmonic model (Ref.[7]); 2 - difference of fitted curves for  $^{12}\text{C}$  and  $^{13}\text{C}$  diamonds based on present experiment; filled and open symbols - difference between experimental points and corresponding fitted curve related to curve 2

shows the halfwidth of the (111) diffraction peak plotted as a function of pressure. As is seen the width of the peaks started to increase on freezing the pressure medium, which certainly shows emerging nonhydrostatic stresses. At the same time it should be emphasized that there is no systematic difference in the halfwidth of peaks in four different runs, which indicates that the sample environment was in fact quite reproducible. So we believe that the experimental data under discussion are qualitatively correct though the values of pressure in the region above freezing the alcohol mixture are certainly in error.

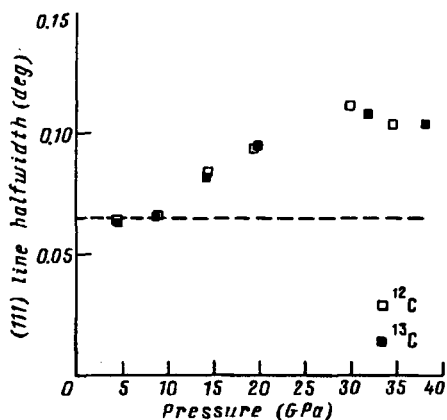


Fig.3. Pressure dependence of (111) line halfwidth (Lorenz curve fitting) for diamond. Increase of line width at pressures above 10 GPa indicates nonhydrostatic component of stress

Another way of the interpretation of the data is to claim that there is no significant influence of pressure on the difference of the corresponding lattice

constants. This interpretation would also mean that the behavior of the quantum contribution to the lattice properties of diamond at high pressure is not trivial and can not be described by the simple quasiharmonical approach.

Probably the explanation required could be found at the anharmonic treatment of the problem (see e.g. Ref.[3]). It should be added that the experimental data and theoretical calculations on  $^3\text{He}$  and  $^4\text{He}$  properties at high pressures also indicate the inversion of the isotope effect [19,20].

Summarizing, the experimental data on the influence of pressure on the lattice constant of  $^{12}\text{C}$  and  $^{13}\text{C}$  diamonds are reported. The pressure dependence of lattice constant of  $^{13}\text{C}$  diamond was measured for the first time. A comparison of the data on  $^{13}\text{C}$  and  $^{12}\text{C}$  diamonds leads to conclusion of inversion of the quantum isotope effect in diamond at high pressure.

This study was performed as a part of COE project of NIRIM, Science and Technology Agency of Japan. The x-ray diffraction experiments were done under the proposal numbers 94G110 and 94G112 of the Photon Factory.

The authors (HF and VAS) are grateful to Science and Technology Agency of Japan for possibility to work under COE fellowship. One of the authors (SMS) thanks Russian Fund for Fundamental Research for partial support of this work (Grant 93-02/2330). We thank Dr. M.Grimsditch for useful discussion of the problem and for information on the elastic properties of  $^{13}\text{C}$  diamond prior to publication.

- 
1. H.Holloway, K.C.Hass, M.A.Tamor et al., *Phys. Rev. B* **44**, 7123 (1991).
  2. T.Yamanaka, S.Morimoto, and H.Kanda, *Phys. Rev. B* **49**, 9341 (1994).
  3. A.K.Ramdas, S.Rodriguez, M.Grimsditch et al., *Phys. Rev. Lett.* **71**, 189 (1993).
  4. R.M.Chrenko, *J.Appl. Phys.* **63**, 5873 (1988).
  5. A.T.Collins, S.C.Lawson, G.Davies, and H.Kanda, *Phys. Rev. Lett.* **65**, 891 (1990).
  6. A.T.Collins, G.Davies, H.Kanda, and G.S.Woods, *J. Phys. C:Solid State Phys.* **21**, 1363 (1988).
  7. M.Muinov, H.Kanda, and S.M.Stishov, *Phys. Rev. B* **50**, 13860 (1994).
  8. H.K.Mao, P.M.Bell, J.W.Shaner, and D.J.Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).
  9. O.Shimomura, K.Takemura, H.Fujihisa et al., *Rev. Sci. Instrum.* **63**, 967 (1992).
  10. F.Birch, *J.Geophys. Res.* **83**, 1257 (1978).
  11. I.V.Aleksandrov, A.F.Goncharov, A.N.Zisman, and S.M.Stishov, *Zh. Eksp. Teor. Fiz.* **93**, 680 (1987) [*Sov. Phys. JETP* **66**, 384 (1987)].
  12. H.J.McSkimin and P.Andreatch Jr., *J. Appl. Phys.* **43**, 2944 (1972).
  13. M.H.Grimsditch and A.K.Ramdas, *Phys. Rev. B* **11**, 3139 (1975).
  14. T.Anthony and W.Banholzer, *Diamond Relat. Mater.* **1**, 717 (1992).
  15. D.C.Hurley, R.S.Gilmore, and W.F.Banholzer, *J. Appl. Phys.* **76**, 7726 (1994).
  16. M.Grimsditch, private communication.
  17. V.V.Avilov and R.G.Arhipov, *Solid State Commun.* **48**, 933 (1983).
  18. I.V.Aleksandrov, A.F.Goncharov, I.N.Makarenko, and S.M.Stishov, *Phys. Rev. B* **43**, 6194 (1991).
  19. P.Loubeyre, R.Letoullec, and J.P.Pinceaux, *Phys. Rev. Lett.* **69**, 1216 (1992).
  20. M.Boninsegni, C.Pierleoni, and D.M.Ceperley, *Phys. Rev. Lett.* **72**, 1854 (1994).