"Direct" determination of the Grüneisen parameter of the LTO(Γ) mode of diamond at high pressures

I. V. Aleksandrov, A. F. Goncharov, and S. M. Stishov
Institute of Crystallography, Academy of Sciences of the USSR

(Submitted 14 October 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **44**, No. 10, 474–477 (25 November 1986)

The first-order Raman scattering spectra of diamond have been measured at pressures up to 42 GPa. The lattice constant was measured simultaneously. The results show that the Grüneisen parameter of the LTO(Γ) mode of diamond is essentially independent of the density.

The academic problem of the stability of diamond at high pressures has recently acquired practical value as well in connection with the use of diamonds to achieve very high pressures,[1,2] above 1 Mbar. The most interesting result of the recent theoretical research in this field has been the conclusion that diamond is stable with respect to transitions to a metallic phase with the white tin stucture.[3,4] This result means that the behavior of carbon during high compression is fundamentally different from the behavior of its closest analogs, silicon and germanium.[5–7] It is presently believed that a likely candidate for the post-diamond phase of carbon is a phase of the BC-8 type,[4,8] whose structure is again a slightly distorted tetrahedral coordination of carbon atoms.[9]

The suggested stability of the tetrahedral configuration of particles in carbon even at ultrahigh pressures forces an expanded search for possible mechanisms for an instability of the diamond phase of carbon. A study of optical vibrational modes is of interest in this connection.

The first-order Raman scattering spectra of diamond have been studied previously[10–12] at pressures up to 72 GPa. An attempt was made in Ref. 10 to work from experimental data to derive the bulk dependence of the mode Grüneisen parameter $\gamma_i = -d\ln\nu_i/d\ln V$ [here and below, we are talking about the longitudinal-transverse optical mode at the center of the Brillouin zone, LTO (Γ)]. It turns out that the parameter $\gamma_{\mathrm{LTO}(\Gamma)}$ of diamond, in contrast with that of Si and Ge, increases upon compression. However, the conclusions reached in Ref. 10 depend strongly on the particular form of the equation of state of diamond and on the high-pressure scale, which is not known accurately.

In the present letter we report new measurements of the first-order Raman scattering spectra of diamond and simultaneous measurements of its lattice constant, so that it becomes possible to calculate the Grüneisen "constant" and its dependence on the volume without using information of any sort regarding the equation of state of diamond or the high-pressure scale.

The experiments are carried out in a diamond pressure chamber designed to allow a single-crystal x-ray analysis. The sample, which is a single crystal with dimensions of $60\times30\times15\,\mu$m, and a ruby pressure gauge are placed in a hole in a metal spacer. The entire chamber is then inserted into a special vessel which is filled with compressed

helium. After an axial load is applied, and a sufficient contact pressure is reached, the chamber is extracted from the vessel and prepared for the corresponding experiments. In the present series of measurements, the medium that transmits the pressure is compressed helium; the effect is to approximate hydrostatic experimental conditions as closely as possible.[1)]

The technique by which the Raman spectra are measured is described briefly in Ref. 10. The determination of the frequency ν is based on several measurements in which the lines at 488 and 514.5 nm from an argon laser are used as exciting lines. The uncertainty in the determination of the spectral position of the Raman frequency is ~ 0.3 cm^{-1}.

The x-ray photography is carried out on a standard DRON 2.0 two-circle diffractometer with MoKα_1 radiation. The uncertainty in the determination of the lattice constant is $\sim 10^{-3}$ Å and is essentially independent of the pressure. The corresponding uncertainty in the determination of the volume or density is[2)] 0.1%.

The lattice constant and the frequency of the Raman scattering are measured with the same sample, at identical readings of the "ruby" pressure gauge, as pressure is applied to the chamber and also as the pressure is removed after a hold for the time required for the essential termination of relaxation processes associated with the change in the external load (usually, 1–3 days). All the measurements are taken at room temperature.

Figure 1 shows the results of a determination of the frequency of the LTO(Γ) mode of diamond as a function of the density. It can be seen from this figure that the dependence $\nu_{\mathrm{LTO}(\Gamma)}(\rho)$ is essentially linear up to a reduced density ~ 1.075 or a pressure ~ 35 GPa. At a higher compression, we observe deviations from the original linear dependence, accompanied by a broadening of the x-ray reflections[2)] and of the Raman scattering lines. On the other hand, the half-widths of the ruby luminescence

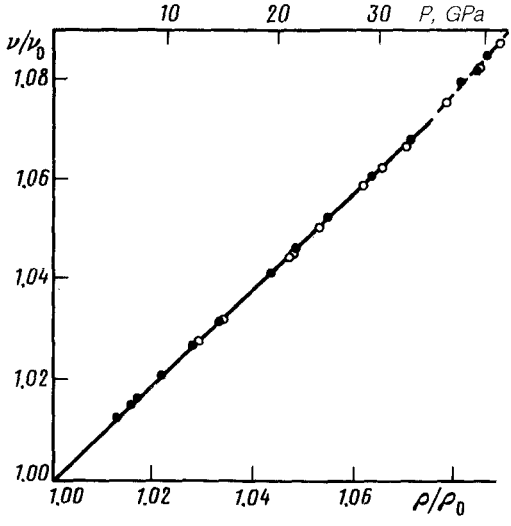

FIG. 1. Reduced Raman scattering frequency versus the reduced density of diamond ($\nu_0 = 1332.4$ cm^{-1}, $\rho_0 = 3.5116$ g/cm^3). The pressure scale is shown in accordance with a ruby calibration.[13] O—Forward path; ●—backward path.

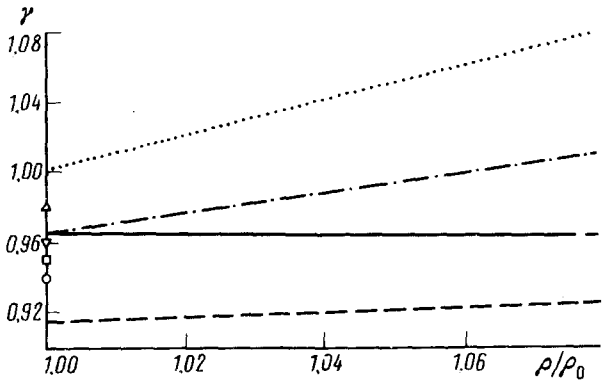

FIG. 2. The mode Grüneisen parameter of the LTO(Γ) mode versus the reduced density of diamond. Solid line—results of present studies; dotted line—Ref. 10; dashed line—Ref. 11; dot-dashed line—Ref. 15; ▽—Ref. 11; □—Ref. 12; △—Ref. 16; ○—Ref. 17.

lines R_1 and R_2 remain essentially the same. The effect is completely reversible. We believe that it is based on a nonuniform deformation of the thin, extended diamond plate represented by the sample under the influence of a nonhydrostatic component of the stress.

In one way or another, the observed anomaly in the behavior $\nu(\rho)$ restricts our further analysis of the density range to the interval $1<\rho/\rho_0<1.075$, which corresponds to hydrostatic conditions. Since the changes in the slope of the function $\nu(\rho)$ are small in any case, we seek an expression for $\gamma_{\mathrm{LTO}(\Gamma)}$ in the form

$$\gamma=\gamma_0+[\partial\gamma/\partial(V/V_0)]_{V=V_0}[(V/V_0)-1]. \tag{1}$$

The calculations yield the following values for the parameters in (1): $\gamma_0=0.958\pm0.005$ and $[\partial\gamma/\partial(V/V_0)]_{V=V_0}=-(0.20\pm0.19)$. Using $(\partial\gamma/\partial P)_0=-(1/K_0)[\partial\gamma/\partial(V/V_0)]_{V=V_0}$, where $K_0=-V_0(\partial P/\partial V)_{V=V_0}$, and assigning K_0 the value 4.42 Mbar or 442 GPa (Ref. 14), we find $(\partial\gamma/\partial P)_0=(4.5\pm4.3)\times10^{-4}\ \mathrm{GPa}^{-1}$. The numerical values of the errors correspond to a 65% confidence limit. It can be seen from these results that the uncertainty in the numerical values of the derivatives $(\partial\gamma/\partial P)_0$ and $[\partial\gamma/\partial(V/V_0)]_{V=V_0}$ is so great that we should apparently assume $\gamma=$ const over the interval $1<\rho/\rho_0<1.075$. A calculation in this approximation yields $\gamma=\gamma_0=9.965\pm0.005$.

Figure 2 shows the experimental and theoretical results which we have been able to find on the behavior of $\gamma_{\mathrm{LTO}(\Gamma)}$ during compression. Also shown here are several results from the literature on $\gamma_{\mathrm{LTO}(\Gamma)}$ at atmospheric pressure.

A comparison of the results of the present study with the data of Ref. 10 (Fig. 2) shows that an experimental determination of γ_i of a compressed substance in the absence of direct information on the density of the substance is an extremely subtle and not always reliable procedure.

In summary, despite the slight increase in $\gamma_{\mathrm{LTO}(\Gamma)}$ with increasing density, which

has been predicted by the theoreticians (Fig. 2), the "direct" experimental data indicate that $\gamma_{LTO(\Gamma)}$ most likely remains constant during compression to $\rho/\rho_0 \cong 1.075$. In this case, the simple Grüneisen law $\nu/\nu_0 = (V_0/V)^{0.965}$ evidently holds, so that we can take diamond to be an ideal "Grüneisen" object, at least in terms of the LTO(Γ) vibrations. Consequently, nothing has surfaced so far to imply an instability of diamond associated with the LTO(Γ) vibrational mode. Furthermore, since the force constant corresponding to the LTO(Γ) vibrations incorporates a contribution from noncentral interactions,[18,19] we should assume that the transverse acoustic modes in diamond are completely stable at moderate compression.

[1)]At room temperature, helium solidifies at a pressure of 12 GPa (120 kbar).
[2)]The details of the x-ray experiment will be published in a separate paper.

[1]P. M. Bell, H. K. Mao, and K. Goettel, Science **226**, 542 (1984).
[2]W. C. Moss, J. O. Hallquist, R. Reichlin, K. A. Goettel, and S. Martin, Appl. Phys. Lett. **48**, 1258 (1986).
[3]M. T. Yin and M. L. Cohen, Phys. Rev. Lett. **50**, 2006 (1983).
[4]R. Biswas, R. M. Martin, R. J. Needs, and O. H. Nielson, Phys. Rev. B **30**, 3210 (1984).
[5]J. C. Jamieson, Science **139**, 762 (1963).
[6]B. A. Weinstein and G. J. Piermarini, Phys. Rev. B **12**, 1172 (1975).
[7]D. Olego and M. Cardona, Phys. Rev. B **25**, 3680 (1982).
[8]M. T. Yin, Phys. Rev. B **30**, 1773 (1984).
[9]J. C. Kasper and S. M. Richard, Acta Cryst. **17**, 752 (1964).
[10]A. F. Goncharov, I. N. Makarenko, and S. M. Sgishov, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 150 (1985) [JETP Lett. **41**, 184 (1985)].
[11]M. Hanfland, K. Syassen, S. Fahy, S. G. Louie, and M. L. Cohen, Phys. Rev. B **31**, 6896 (1985).
[12]H. Boppart, J. van Straaten, and I. F. Silvera, Phys. Rev. B **32**, 1423 (1985).
[13]H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).
[14]H. J. McSkimin and P. Andreatch, J. Appl. Phys. **43**, 2944 (1972).
[15]O. H. Nielsen, Preprint NORRDITA-85/40, 1985; Phys. Rev. B, 1986.
[16]E. Whalley, A. Lavergne, and P. T. T. Wong, Rev. Sci. Instrum. **47**, 845 (1976).
[17]S. S. Mitra, O. Brafman, W. B. Danield, and R. K. Grawford, Phys. Rev. **186**, 942 (1969).
[18]M. T. Yin and M. I. Cohen, Phys. Rev. B **26**, 3259 (1983).
[19]H. Wendel and R. M. Martin, Phys. Rev. B **19**, 5251 (1979).

Translated by Dave Parsons