

Raman scattering from a diamond at pressures up to 72 GPa

A. F. Goncharov, I. N. Makarenko, and S. M. Stishov

Institute of Crystallography, Academy of Sciences of the USSR

(Submitted 11 January 1985)

Pis'ma Zh. Eksp. Teor. Fiz. **41**, No. 4, 150–153 (25 February 1985)

The spectra of first-order Raman scattering from a diamond at static pressures up to 72 GPa were studied for the first time. The Grüneisen mode parameter γ for a diamond increases with pressure, in contrast with its behavior in silicon and germanium. It is concluded that a moderate compression stabilizes the tetrahedral structure of a diamond.

We have studied for the first time the spectra of first-order Raman scattering from a diamond at pressures up to 72 GPa.

The experiments were carried out in a cell with diamond anvils. This cell was specially designed for optical measurements in compressed xenon.¹ The diamond samples ($30 \times 40 \mu\text{m}$ and $10\text{--}40 \mu\text{m}$ thick) to be tested were compressed with a metal spacer made from Inconel-750 alloy. The initial thickness of the spacer was $\sim 50 \mu\text{m}$. The initial diameter of its bore was $150 \mu\text{m}$ and the final diameter (at higher pressures) was $90 \mu\text{m}$. The pressure was determined from the shift of the R_1 luminescence line of a small piece of ruby² which was placed in close proximity to the sample to be tested. The spectrum of Raman scattering from a diamond and the spectrum of ruby luminescence were pumped by a beam from an argon laser ($\lambda = 488 \text{ nm}$ and $\lambda = 514.5 \text{ nm}$) and recorded with a DFS-24 double diffraction spectrometer under photon-counting

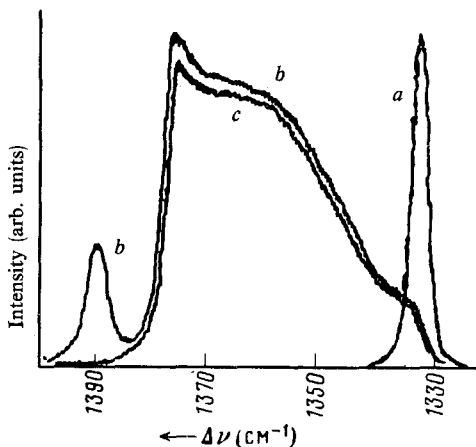


FIG. 1. Raman-scattering spectra of a diamond sample at atmospheric pressure (a), of a diamond sample situated in a diamond chamber at a pressure $P \approx 20$ GPa (b), and of diamond anvils without a diamond sample at the same pressure (c).

conditions. The spectral width of the monochromator slit was ~ 1.5 cm⁻¹. The frequencies of the Raman scattering bands were measured to within ± 0.5 cm⁻¹ and the pressure was measured to within ± 0.05 GPa.

We should emphasize that Raman scattering from a diamond sample in a high-pressure chamber is accompanied by a strong background scattering from diamond anvils. At a certain pressure (~ 6 GPa), however, the Raman-scattering band of a sample goes beyond the background limit (Fig. 1), allowing its spectral position to be determined. This effect is presumably a consequence of the highly nonuniform, load-induced strain on diamond anvils.³

Figure 2 shows pressure-dependent measurement results of the spectral location of the maximum in the band of a first-order Raman scattering from a diamond, and it also shows the half-widths of the corresponding peaks. We see that the frequency of the line for Raman scattering from a diamond increases monotonically with pressure, consistent with the "normal" behavior of stable materials. At pressures above 50 GPa, however, this curve exhibits a faint spectral feature (an inflection point), which is probably due to an increase in the nonhydrostatic component of the pressure in solid xenon. The fact that the hydrostatic conditions deteriorate significantly at $P > 50$ GPa

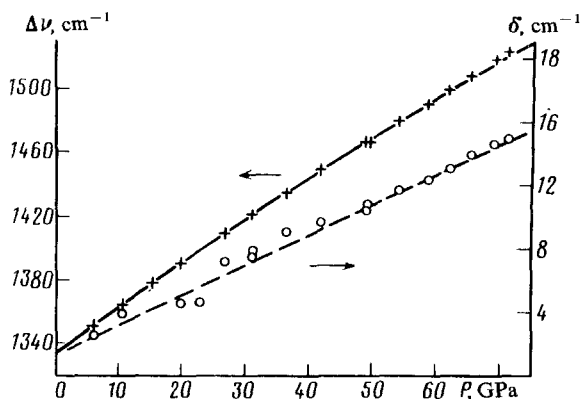


FIG. 2. A shift in the spectral position of a first-order Raman-scattering band ($\Delta\nu$) and the half-width of the corresponding peaks (δ) plotted as a function of pressure. +, o—Experimental points; —approximation based on expression (1).

TABLE I.

	P_c	K_0	$(\partial K / \partial P)_0$	γ_0	$(\partial \gamma / \partial P)_0$
C	$>172^a$	442^d	$4 \pm 0, 7^f$	$1.000 \pm 0.003^*$	$0.022 \pm 0.016^*$
Si	12.5^b	97.08^e	4.16^e	1.00 ± 0.03^i	$-(0.015 \pm 0.006)^i$
Ge	11^c	72.43^e	4.35^e	1.05 ± 0.03^i	$-(0.019 \pm 0.010)^i$

P_c —Pressure required for a transition to β -Sn structure (GPa); K_0 —GPa; $(\partial \gamma / \partial P)_0$ —(GPa) $^{-1}$; a – f —data of Refs. 6–11, respectively; i —calculated from experimental data of Refs. 7 and 8 which are represented in the form in Eq. (1); *—our data.

is indicated by the considerable broadening of the Raman-scattering band under study and by the distorted shape of the luminescence spectrum of ruby. We therefore had to restrict the quantitative analysis of our data to a pressure range below that indicated above.

Because the relative frequency shift $\Delta \nu / \nu_0$ is small over the entire pressure range under study, we can write the function $P(\nu)$ as an expansion

$$P / K_0 = A_1 (\Delta \nu / \nu_0) + A_2 (\Delta \nu / \nu_0)^2, \tag{1}$$

where P is the pressure, K_0 is the bulk rigidity modulus for a diamond at $P = 0$, $\nu_0 = 1332.4 \pm 0.3 \text{ cm}^{-1}$, and $\Delta \nu = \nu - \nu_0$. Expression (1) is a good approximation of the experimental data when $A_1 = 1.000 \pm 0.003$ and $A_2 = 1.02 \pm 0.05$. The mean square error of the approximation is 0.05 GPa in this case.

We immediately infer from this value of A_1 [note that $A_1 = (\nu_0 / K_0)(\partial P / \partial \nu)\nu_0 = 1 / \gamma_0$] that at atmospheric pressure and room temperature the Grüneisen mode parameter γ_0 for a diamond is 1 ± 0.003 . This result is in excellent agreement with the data of Refs. 4 and 5.

The coefficient A_2 in expression (1) allows us to determine the first derivative of the Grüneisen parameter with respect to pressure $(\partial \gamma / \partial P)_0$. Since $A_1 = 1$, we have $A_2 = (\nu_0^2 / 2K_0)(\partial^2 P / \partial \nu^2)\nu_0 = [(\partial K / \partial P)_0 - K_0 (\partial \gamma / \partial P)_0 - 1] / 2$. It follows, therefore, that

$$(\partial \gamma / \partial P)_0 = [(\partial K / \partial P)_0 - 2A_2 - 1] / K_0. \tag{2}$$

Substituting into (2) the known values of $(\partial K / \partial P)_0$ and K_0 (see Table I), we find $(\partial \gamma / \partial P)_0 = 0.022 \pm 0.016 \text{ GPa}^{-1}$. This result shows that the first slope of the $\gamma(P)$ curve for a diamond is, in contrast with that for silicon and germanium, a positive slope. This difference in the indicated slopes holds at high pressures (Fig. 3).

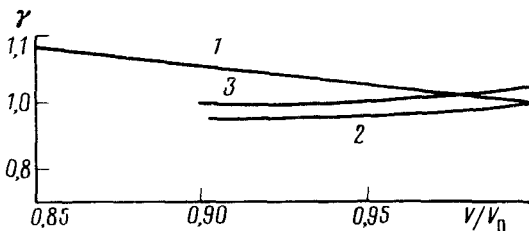


FIG. 3. The Grüneisen mode parameter γ for diamond, silicon, and germanium samples plotted as a function of volume. The values of γ were calculated from Murnaghan's equation. The data necessary for the calculation are listed in Table I. 1—Diamond sample; 2—silicon sample; 3—germanium sample.

We should emphasize, on the other hand, that since diamond, silicon, and germanium have approximately the same values of $(\partial K / \partial P)_0$ (see Table I), there must be a universal equation of state for these materials in the case of moderately high compression. The difference in the manner in which the parameter γ varies in diamond, silicon, and germanium is therefore contingent upon the difference in the volume dependences of noncentral forces that stabilize their tetrahedral structure¹² but contribute negligibly to volume compressibility.

Accordingly, a pressure-dependent increase in the parameter γ for a diamond might indicate that compression stabilizes the tetrahedral structure of a diamond, in contrast with silicon and germanium which undergo a phase transition to a β -Sn structure at relatively low pressures (see Table I). Lending support to this conclusion are the measurements of the γ parameter for the $TA(X)$ mode of diamond¹³ and the calculation results of Ref. 14.

¹I. N. Makarenko, G. Weill, J. P. Itie, and J. M. Besson, Phys. Rev. B **26**, 7113 (1982).

²H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

³M. H. Grimsditch, E. Anastassakis, and M. Cardona, Phys. Rev. B **18**, 901 (1978).

⁴S. S. Mitra, O. Brafman, W. B. Daniels, and R. K. Crawford, Phys. Rev. **186**, 942 (1969).

⁵E. Whalley, A. Lavergue, and P. T. T. Wong, Rev. Sci. Inst. **47**, 845 (1976).

⁶H. K. Mao and P. M. Bell, Science **200**, 1145 (1978).

⁷B. A. Weinstein and G. J. Piermarini, Phys. Rev. B **12**, 1172 (1975).

⁸D. Olego and M. Cardona, Phys. Rev. B **25**, 1151 (1982).

⁹H. J. McSkimin and W. L. Bond, Phys. Rev. **105**, 116 (1957); M. H. Grimsditch and A. K. Ramdas, Phys. Rev. B **11**, 3139 (1975).

¹⁰O. L. Anderson, J. Phys. Chem. Sol. **27**, 547 (1966).

¹¹H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **43**, 2944 (1972).

¹²M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 3259 (1982).

¹³B. J. Parsons, Proc. Roy. Soc. London **A352**, 397 (1977).

¹⁴M. T. Yin and M. L. Cohen, Phys. Rev. Lett. **50**, 2006 (1983).

Translated by S. J. Amoretty