

Observation of amorphous phase of carbon at pressures above 23 GPa

A. F. Goncharov

Institute of Crystallography, Academy of Sciences of the USSR

(Submitted 23 February 1990)

Pis'ma Zh. Eksp. Teor. Fiz. **51**, No. 7, 368–370 (10 April 1990)

The Raman spectra of first and second orders and the transmission spectra of graphite single crystals have been measured at pressures up to 38 GPa. At $P \approx 23$ GPa, a transition to a transparent phase is detected. The Raman spectra of this transparent phase are similar to those of amorphous carbon (*a*-C). It is concluded from any analysis of the measured second-order Raman spectra at $P < 23$ GPa that a deformation of the graphite lattice precedes the transition to an amorphous state.

The phase diagram of carbon at high pressures and temperatures is largely unexplained, primarily because of the lack of reliable experimental data (Ref. 1, for example). It has been assumed that crystalline graphite converts into hexagonal diamond (lonsdaleite) at $P = 15\text{--}20$ GPa. However, the observation of an in-layer band in the Raman scattering of graphite at $P > 20$ GPa was reported in Ref. 3; the diamond band was not detected in the Raman scattering.

In this letter we are reporting the first observation of the transition of crystalline graphite into an amorphous state, which is detected from sharp changes in the Raman spectra and the absorption spectra in the visible and near-IR parts of the spectrum.

The high pressures were produced with a diamond-anvil cell, whose design made it possible to collect the emission over a wide angular interval ($\pm 20^\circ$) around the optical axis. The pressure was determined from the spectral position of the R_1 luminescence line of a ruby detector placed beside the sample, in an aperture in a metal spacer between the anvils.⁴ The medium used to transmit the pressure was compressed helium, which provided approximately hydrostatic conditions inside the pressure chamber (Ref. 5, for example). The experiments were carried out on samples of highly oriented single-crystal graphite produced by hot pressing from pyrolytic graphite. The initial dimensions of the sample were $35 \times 25 \times 5 \mu\text{m}$.

The Raman spectra were recorded by a triple spectrometer with multichannel recording. This spectrometer was developed from a home-made double monochromator (filter), a Jobin-Yvon THR-1000 spectrograph, and an OSMA optical multichannel analyzer. The spectrum was excited ($\lambda_i = 514.5 \text{ nm}$), and the scattered light collected, with the help of a laser microscope constructed on the basis of an Amplival (GDR) microscope.

Transmission spectra in the region 0.4–0.9 eV were measured with a modernized FS-01 Fourier spectrometer equipped with an IR microscope and a PbS detector. The spectra were normalized to the transmission of the pressure chamber without the sample.

All the measurements were carried out at room temperature.

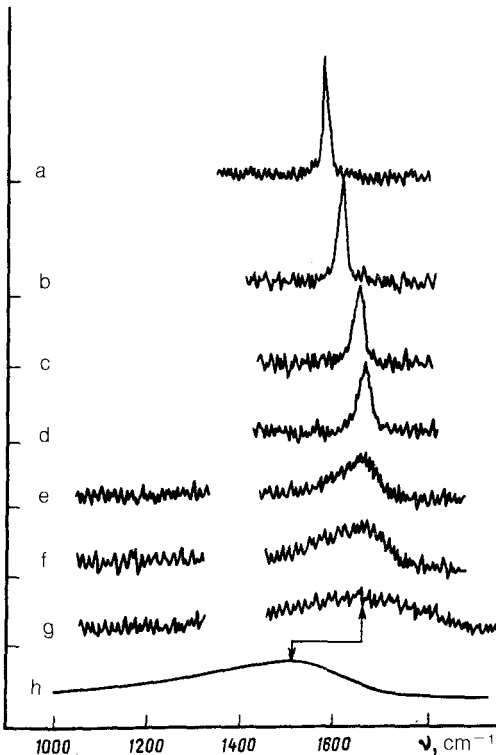


FIG. 1. Evolution of the Raman spectra of single-crystal graphite. a—0.01; b—9.3; c—19.9; d—22.6; e—23.2; f—30.2; g—37.6 GPa; h—Raman spectrum of *a*-C (Refs. 6 and 7).

Figure 1 shows Raman spectra at various pressures for scattering by the in-layer E_{2g} mode of the original graphite. Beginning at $P \approx 6$ GPa, and continuing up to $P = 22.6$ GPa, we observe a gradual broadening of the band. At $P = 23.2$ GPa, the line becomes much broader, and its shape changes. A further increase in the pressure results in a further, gradual broadening of this band. The position of its peak does not change. At the point $P = 23$ GPa, at which the Raman spectrum changes shape, the optical properties also undergo some dramatic changes: The originally opaque samples become transparent in the near-IR region (with a transmission coefficient ~ 0.5), and visual observations reveal a dark brown color. As the pressure is raised to 26.1 GPa, the samples become completely transparent in the IR and visible parts of the spectrum.

Consequently, a dielectric gap appears, and the Raman spectra change markedly, at the point $P = 23$ GPa (Fig. 1). The shape of the spectrum at $P > 23$ GPa is typical of scattering in amorphous substances lacking a long-range order. In this case, the shape of the spectrum reflects the spectrum of the density of phonon states, because of a violation of the selection rules in terms of the wave vector (Ref. 6, for example). Allowing for the baric shift,¹⁾ we see that the spectrum observed at the highest pressures correspond to the spectra of amorphous carbon [Fig. 1(h)] produced through ion bombardment of graphite or diamond⁶ and of amorphous diamond-like films syn-

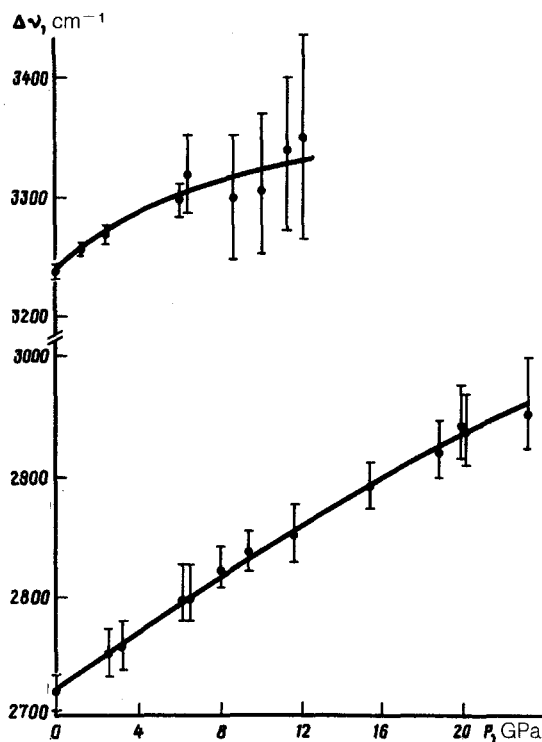


FIG. 2. Pressure dependence of the frequencies of the second-order Raman bands of single-crystal graphite. The large scatter in the data at high pressures stems from the broadening of the bands (see the text proper).

thesized by chemical deposition (Ref. 7, for example). It is also interesting to note that the peak of the dispersive branch of in-layer planar vibrations is at the center of the Brillouin zone, as can be seen from a comparison of the spectra at 22.6 and 23.2 GPa, while that in graphite at $P = 0$ is shifted along the [100] and [110] directions.⁸ To follow the dynamics of this restructuring, we studied the pressure dependence of the second-order Raman spectra of graphite, represented by the bands at 2720 cm^{-1} (1) and 3240 cm^{-1} (2), which correspond to overtones of respectively the minimum and maximum of the optical branch of in-layer planar vibrations. Figure 2 shows the pressure dependence of the frequencies of these bands. Band 1 is observed over the entire range in which the crystalline phase exists; it then become much broader and unobservable. At $P > 6.1$ GPa, band 2 becomes substantially broader, and above 12.2 GPa it can no longer be detected. According to a simple dynamic model which incorporates only central interactions between first and second neighbors, the dispersion relation for this branch is $\omega^2 = [4k(1 - \cos 2qa) + 2f(1 + \cos qa)]/m$, where f and k are the interactions between first and second neighbors, respectively. In the case $8k > f$, the maximum of the dispersion branch shifts away from the point $q = 0$. Analysis of the experimental data on the basis of the model leads to the conclusion that the interactions between second neighbors become relatively weaker as the pressure is raised, probably because of a progressive corrugation of the plane layers of carbon atoms before the formation of an amorphous state.

In summary, graphite in the stability field of diamond undergoes a gradual structural conversion which results in the formation of an amorphous at $P = 23$ GPa. This phase is related to the α -C phase, which arises at low pressures as a result of nonequilibrium processes.

I wish to thank S. M. Stishov for interest in this study and for useful discussions of the results. I thank V. N. Denisov, B. N. Mavrin, and V. B. Podobedov, from the Institute of Spectroscopy, Academy of Sciences of the USSR, for furnishing drawings of a preliminary monochromator and for useful consultations. I thank A. Viskovatykh, A. Chelnokov, V. A. Vagin, and A. A. Balashov of the UP Central Design Bureau, Academy of Sciences of the USSR, for assistance in, and consultations regarding, the startup, upgrading, and use of the Fourier spectrometer. Finally, I thank M. A. Sheindlin for furnishing the single-crystal graphite samples.

¹A corresponding estimate based on the known values of dv/dP in graphite³ and diamond⁵ yields $\Delta\nu = 110\text{--}150\text{ cm}^{-1}$, in agreement with experiment [Figs. 1(g) and 1(h)].

¹A. F. Goncharov, Usp. Fiz. Nauk **152**, 317 (1987) [Sov. Phys. Usp. **30**, 525 (1987)].

²F. P. Bundy and J. S. Kasper, J. Chem. Phys. **46**, 3437 (1967).

³A. F. Goncharov *et al.*, Zh. Eksp. Teor. Fiz. **96**(2), 670 (1989) [Sov. Phys. JETP **69**, 380 (1989)].

⁴H. K. Mao *et al.*, J. Chem. Phys. **49**, 3276 (1978).

⁵I. V. Aleksandrov *et al.*, Zh. Eksp. Teor. Fiz. **93**(2), 680 (1987) [Sov. Phys. JETP **66**, 384 (1987)].

⁶M. H. Brodsky, in *Light Scattering in Solids* (ed. M. Cardona), Springer-Verlag, New York, 1975.

⁷W. Zhu *et al.*, J. Vac. Sci. Technol. **7**, 2315 (1989).

⁸R. J. Nemanich and S. A. Solin, Phys. Rev. B **20**, 392 (1979).

Translated by Dave Parsons