Graphite at high pressures: pseudomelting at 44 GPa

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A comparative study has been carried out of the Raman spectra (RS) at high pressures of graphite-like modifications of carbon: single-crystal graphite, glassy carbon, and pyrolytic graphite. A strong broadening of the RS bands of glassy carbon and pyrolytic graphite is observed at $P > 44$ GPa, similar to that found earlier (A. F. Goncharov, [JETP Lett. **51**, 418 (1990)]) in single-crystal graphite at $P > 23$ GPa. An anomaly (step) is found in the pressure dependence of the RS frequency in the latter at $P = 23$–45 GPa. At $P > 44$ GPa the Raman spectra of all three substances studied become practically indistinguishable from one another and from the spectra of amorphous carbon (a-C) at the same pressures. This result is attributed to the formation of a dense amorphous modification of carbon at these pressures.

Investigations of graphite at high pressures have recently started up again in connection with progress in high-pressure techniques. Results of several studies with diamond anvils have already been published, using methods of Raman-scattering spectroscopy (RS) in reflection and absorption and of x-ray diffraction.[1-5] These works agree in confirming the transformation of the graphite phase of carbon at $P > 14$ GPa, in agreement with the results of earlier work,[6] but differ appreciably in the characteristics of the high-pressure phase. There is mention of a crystalline diamond-like phase,[3,5] and also[1,2] of an amorphous phase.1) Results of shock-wave experiments[7] provide evidence of an anomaly on the compression curve at 22–42 GPa, which was interpreted as a graphite–diamond transition on the continuation of the graphite melting curve and the line of graphite-diamond direct transitions.

In the present work a comparative study has been carried out of the RS spectra of graphite-like modifications of carbon: single-crystal graphite, pyrolytic graphite, and glassy carbon at high pressures. As is known, the latter differ in their disordered structure and consist of fine crystals oriented with respect to the *c* axis in the case of pyrolytic graphite. The aim of the present work was to elucidate the extent to which the disordered structure influences the transformation of the graphite phase at high pressures.

The experimental technique had been described before.[1] We note that unlike others,[3-5] we used a pressure-transmitting medium (He) which achieved practically hydrostatic conditions in the high-pressure chamber. It is probable that this can explain the difference of the transition pressures of graphite single-crystals into the high-pressure phase: 23 GPa[1] and 14 GPa.[3-5]

The RS spectra of pyrolytic graphite and SU-2000 glassy carbon at different pressures are shown in Fig. 1. The corresponding pressure dependences of the frequency ν of the RS band maxima are shown in Fig. 2. Unlike single-crystal graphite, the intra-layer RS mode of which undergoes a sharp broadening for $P > 23$ GPa, the corresponding RS bands in these materials (broadened by structural disorder compared with the E_{2g} band of single-crystal graphite at $P = 0$ GPa) remain practically unchanged up to 44 GPa. A strong broadening of the RS bands, observed in both materials, occurs at higher pressures and the shape of the spectrum for $P > 44$ GPa practically coincides with the spectra of single-crystal graphite and amorphous carbon (a-C) at the same pressures (Fig. 3).

We will now consider the transformation of the spectra of single-crystal graphite over a wider pressure range compared with the measurements described before.[1,2] After a strong rearrangement of the spectrum, associated with the transition to a disordered state,[1] the position of the RS peak remains practically unchanged up to 45–50 GPa, after which an appreciable pressure shift is observed (Fig. 2). The form of the spectrum then remains unchanged up to the maximum achieved pressure 80 GPa.

Visual observations of the specimens in transmitted light showed that, unlike single-crystal graphite which becomes transparent to IR and visible radiation simultaneously with the reconstruction of the RS spectrum at 23 GPa, pyrolytic graphite and glassy carbon remain opaque up to the maximum pressures studied. Furthermore, some specimens of single-crystal graphite (mainly from natural deposits) remained opaque, although they also underwent a transformation of the RS spectra at 23 GPa.

The strong change in the form of the spectra of pyrolytic graphite and glassy carbon at $P > 44$ GPa indicates the breakdown of the wave-vector selection rules[8] as a result of the vanishing of long-range order. Since pyrolytic graphite and glassy carbon are at the outset strongly disordered materials with disrupted periodicity in the junction of the layers, this transformation of the structure must be associated with deformations of the hexagonal layer planes of carbon, which

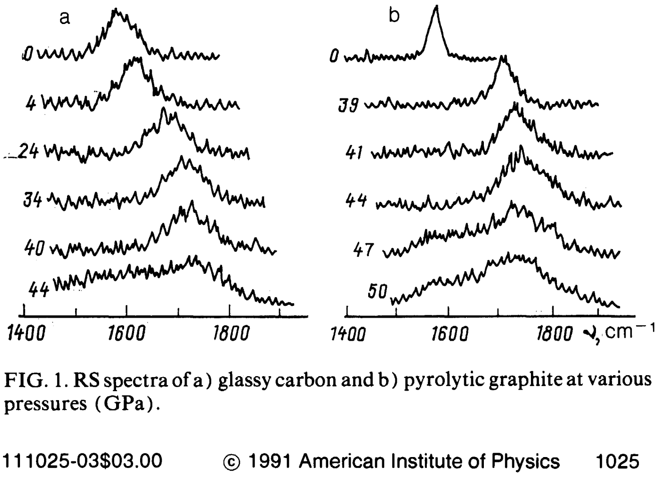

FIG. 1. RS spectra of a) glassy carbon and b) pyrolytic graphite at various pressures (GPa).

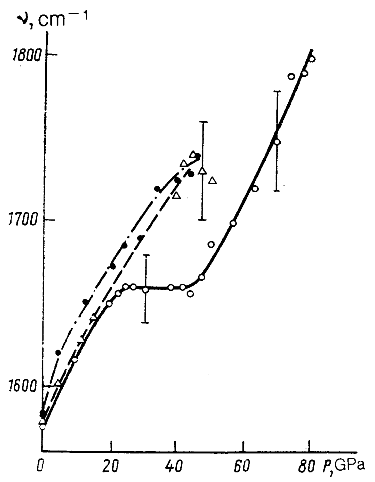

FIG. 2. Pressure dependence of the RS frequencies for (○) single-crystal graphite, (●) glassy carbon, and (△) pyrolytic graphite.

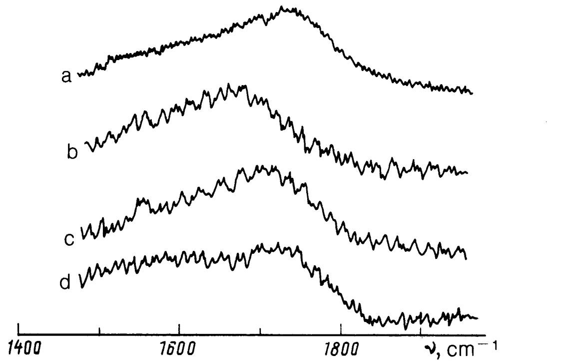

FIG. 3. Comparison of the RS spectra of different modifications of carbon at high pressures: a) a-C (50 GPa), b) single-crystal graphite (50 GPa), c) pyrolytic graphite (50 GPa), d) glassy carbon (44 GPa).

can be considered as pseudomelting of the graphite phase. The corresponding process in single-crystal graphite takes place gradually (Figs. 1 and 2) as the ensuing structural deformations accumulate. The similarity of the RS spectra of all the graphite-like modifications of carbon studied at $P > 44$ kPa to the spectrum of a-C (Fig. 3) is evidence that their structures are close. As is known, a-C is amorphous and according to calculation[9] is characterized by the presence of $\sim 15\%$ sp^3 bonding. The results of our measurements show that a complete transition to a state with sp^3 bonds, i.e. to the diamond phase, does not take place up to 80 GPa. Evidence of this is the fact that the maximum in the intensity of the RS spectrum of the high-pressure phase is situated much higher than the limiting phonon frequency of the diamond lattice spectrum, practically coinciding with the RS frequency of diamond, while the "diamond" band is not observed. This comment is also valid with respect to a possible transition to the hexagonal diamond structure (Lonsdaleite),[5,6] in the spectrum of which only a relatively small splitting of one peak into two components, due to the lifting of degeneracy, can be expected.[2]

We will discuss the results in connection with present ideas about the carbon phase diagram. The transition point found of graphite into the amorphous state (44 GPa, 300 K) occurs on the continuation of the melting curve of graphite and the line for the direct transitions from graphite to diamond,[10] which can be interpreted as the boundary of the absolute instability of the graphite phase. Similar phase diagrams have also been observed earlier for H_2O and SiO_2.[11,12] As has been noted,[11] the amorphous phases with an analogous structure can also be obtained as a result of the deposition of thin films from the gas phase. The specimen of a-C used in the present work for comparison was obtained by the first of the methods enumerated,[13] and the proximity of its spectrum to the spectra of the high-pressure phase is evidence of such an approach. We also note that the considerations described above about the structure of supercooled liquid lead to the conclusion that the diamond melting curve has a positive slope (the density of the a-C phase is less than the density of diamond),[10,14] which agrees with the existing experimental results.[15] It should be stressed that the transformation of graphite at high pressures into the amorphous phase, and not into diamond, is evidently explained by the high barrier for the graphite-diamond transition, as a result of which one should expect the corresponding direct transition at 60–80 GPa.[14,16] At the same time the transition to the amorphous phase probably does not require an appreciable collective regrouping of atoms and can be regarded as the consequence of instability of the graphite lattice at high pressures.[1]

We will finally discuss the possible nature of the irregularity in the $\nu(P)$ dependence for single-crystal graphite. According to earlier work,[1] a gradual broadening of the RS band takes place in the range 23–38 GPa, mainly due to the increase in the scattering intensity on the low-frequency side, where one can expect the manifestation of sp^3 bonding. At the same time the position of the maximum of the peak does not change. This can be qualitatively explained by the appearance of the amorphous state in the range 23–44 GPa, partly consisting of sp^3 bonding, thanks to which a reduction in the volume of the specimen occurs, without a reduction in the sp^2 bond length. In this connection we note that the observed picture, with some reservations, is similar to the "heat supplied vs temperature" diagram for usual melting, and the analogy becomes especially clear if we take into account the fact that no "plateau" is observed for disordered graphite-like modifications of carbon (Fig. 2) as in the case of the melting of amorphous materials. It thus seems justified to characterize the observed phenomenon as cold melting or pseudomelting.

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[1] Here and below, for convenience, we will use the term "phase," being aware of its applicability in some circumstances in relation to the amorphous state.

[2] Our measurements on natural (compacted) specimens and those synthesized at high pressures and temperatures with a high Lonsdaleite content showed the existence of one strongly broadened band.

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