Graphite at pressures up to 55 GPa: optical properties and Raman scattering—amorphous carbon?

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We have investigated the optical properties and Raman spectra (RS) of single-crystal graphite, using a cell with a diamond anvil to apply pressures up to 55 GPa under quasi-hydrostatic conditions. In the pressure range 15 to 35 GPa we observed a sharp decrease in the reflection coefficient and a simultaneous broadening of the intralayer RS band. For $P > 35$ GPa we observed an absorption edge in the visible region which shifts with pressure towards the large-energy side and gives rise to a "bleaching" effect in the samples. These data lead us to conclude that graphite is converted to a new form of carbon for $P \gtrsim 20$ GPa.

It is well-known that the thermodynamic characteristics of a material have no singularities at a first-order phase transition point. For this reason, the region in which a phase of the material exists can in principle be extended up to the boundary of absolute instability, where global or local stability conditions are violated. In general, it appears to be impossible to predict what will happen to a material once it has lost its stability. It is known that in a number of cases a stable phase which corresponds to the given thermodynamic conditions appear in place of the unstable phase. However, in what follows we will see that this is not the most general situation.

We have found that graphite, which lies in the stability field of diamond, is reversibly converted to a semitransparent material when subjected to pressures considerably in excess of the equilibrium transition pressure; this material is obviously unstable with respect to diamond.

Let us turn to a discussion of the experimental data. We recall that the graphite-diamond equilibrium curve intersects the room temperature axis at a pressure of ~2 GPa.[1,2] However, direct conversion of graphite to diamond cannot take place at this low temperature for kinetic reasons; in fact, the conversion of graphite to diamond is impossible even at temperatures of ~2000 °C without the use of catalysts. The direct transition from graphite to diamond takes place at $T \approx 3500$ °K and $P \approx 12$ GPa.[3] Thus, by compressing graphite at room temperature, we should be able to count on a significant tendency for the material to enter the metastable region.

In the course of the present work we investigated the absorption and reflection spectrum and Raman scattering (RS) spectrum for pressures up to 55 GPa. The experiments were carried out in a high-pressure cell with diamond anvils, using helium or xenon as a medium to transmit the pressure. The pressure in the chamber was determined using a ruby manometer.[4] We investigated cleaved samples of natural monocrystalline graphite from Russia and Ceylon. Starting dimensions of a sample were $60 \times 40 \times 10\,\mu$m.[3] The RS spectrum was excited using an argon laser ($\lambda_i = 488$ and 514.5 nm) and was measured with a DFS-24 double monochromator furnished with a cooled photomultiplier and recording system operating in the photon counting regime. In order to obtain the absorption and reflectivity spectra we used an automated diffraction spectrometer (KSVU-23) linked to an imaging microscope. The absorption and reflection measurements for the samples under study were normalized by the corresponding spectra of the diamond anvils. All measurements were taken at room temperature.

By observing the light in transmission, we found that graphite samples which were completely opaque in their original state would transmit light in the visible wavelength range when subjected to pressure. As the pressure increased, they acquired a dark-brown color; then they gradually would turn clear, eventually becoming transparent and colorless. In very thin cleaved layers (from the sample edge) this effect was noticeable starting at a pressure of ~35 GPa. The transparency of such samples reached 15% at $P = 55$ GPa; this "bleaching" effect in graphite under pressure is well-illustrated by the absorption spectra measured on one of the samples and shown in Fig. 1. As the pressure decreased the bleached graphite samples remained transparent down to ~5 GPa, below which they darken sharply.

This dramatic variation is also observed in the reflection of light: for $P > 20$ GPa the graphite samples lose their characteristic metallic luster. The reflection coefficient of the samples under study, when measured in the visible region of the spectrum, had a value of ~25% for $P = 15$ to 20 GPa; it then gradually decreased with pressure, amounting to less than 2% for $P > 35$ GPa.

In our study of the RS spectra of graphite under high pressures, we followed the intralayer mode E_{2g} with an initial frequency of 1580 cm^{-1} (see Fig. 2). Under pressure this band shifts to the high-energy side, and for $P > 15$ GPa it undergoes significant broadening. In the region $P > 35$ GPa

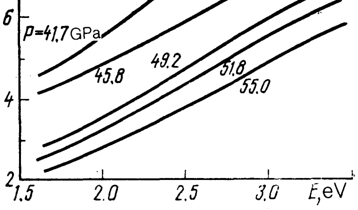

FIG. 1. Absorption spectra of graphite at various pressures.

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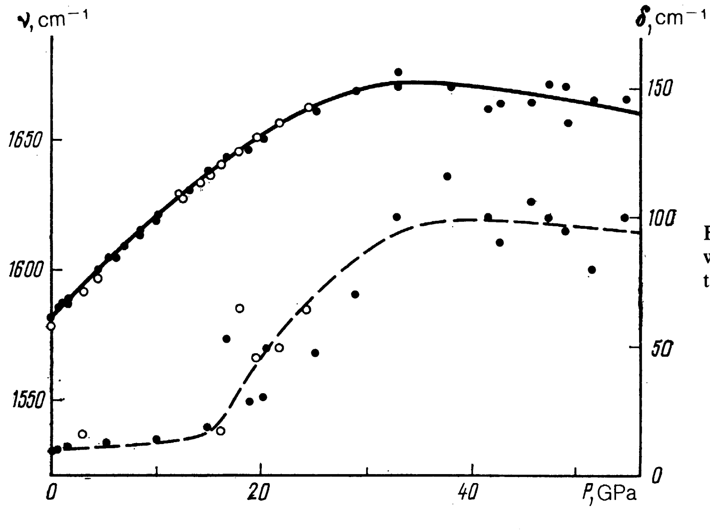

FIG. 2. Pressure dependence of the E_{2g} frequency (solid trace) and half-width (dashed trace) of the RS band in graphite: ●—He as the pressure transmitting medium, ○—Xe as the pressure transmitting medium.

the frequency and half-width of this band practically ceases to depend on pressure. As the pressure is decreased the width of the "graphite-like" RS band is preserved down to a pressure of ~5 GPa (at which the sample under study loses its transparency) and then decreases sharply. It is important to emphasize that no new bands (for example, no "diamond-like" bands) were observed in any of the RS spectra obtained, i.e., none which were not "graphite-like." Note also that the effects pointed out above cannot be explained by variations of the mechanical and optical properties of the medium transmitting the pressure, since the results of experiments carried out in different media (Xe and He) show no significant disagreement.

In terms of the character of the experimental data obtained (see Figs. 1 and 2) the pressure interval we investigated can be divided into two regions. For $P < 15$ GPa the properties of single-crystal graphite exhibit the "normal" behavior of materials under pressure. In this region of frequencies ν the RS bands (Fig. 2) increase monotonically with pressure (as a consequence of compression of the crystal lattice), and there is no sharp variation in the absorptivity and reflectivity in the near-IR and UV spectral ranges. At higher pressures a significant change in the RS spectrum occurs (Fig. 2): a characteristic semiconductor absorption edge appears, which shifts with pressure to the high-energy side (Fig. 1). The pressure at which this forbidden band appears in graphite can be estimated from the absorption data by extrapolating the lines of equal optical density to their zero energy value. As a result of these estimates (Fig. 3) we obtain a value of ~22 GPa. We note that this extrapolated value is close to the pressure at which graphite loses its metallic luster and the sharp broadening of the observed RS band takes place.

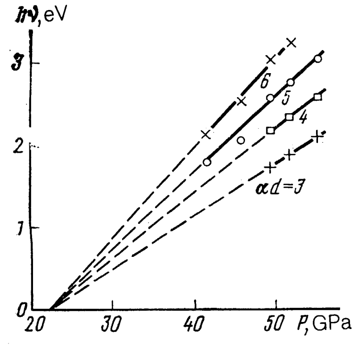

FIG. 3. Lines of identical optical density (the numbers next to the lines) for the absorption spectra shown in Fig. 1.

Thus, our results (including the hysteresis mentioned above) allow us to assert that at pressures above 20 GPa graphite is converted into a new semiconducting form of carbon. Analogous conclusions were arrived at in Ref. 5, in which a discontinuous change in the electrical resistivity of graphite was observed at pressures of 15 to 20 GPa. The authors of Ref. 5 associated this discontinuity with the formation of the hexagonal diamond phase. However, our measurements do not support this conjecture, because the RS spectrum of graphite at high pressures does not contain "diamond-like" bands. Furthermore, the existence of a "graphite-like" mode, whose intensity does not change with pressure, attests to a certain closeness of the high-pressure phase to the graphite structure. On the other hand, the significant broadening of the observed RS band for $P > 15$ GPa indicates the presence of strain, and possibly amorphization of the original structure as well, which leads to the appearance of the new "hybrid" form of carbon.[1] We emphasize that the authors of Ref. 6, who investigated the RS spectrum of strongly-compressed quartz (SiO_2) placed in the stability field of stishovite, were led to a similar conclusion. Thus, we cannot rule out the possibility that compression of a given class of covalent materials at sufficiently low temperatures may occur along a path which is appreciably far from equilibrium.

[1] It is conceivable (see Ref. 5) that heating this "phase" of carbon to $T \approx 1000$ °C results in the formation of hexagonal diamond without the use of catalysts.

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