FUNDAMENTAL GAP OF DIAMOND UNDER HYDROSTATIC PRESSURE

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The hydrostatic pressure dependence of the fundamental gap of diamond has been measured up to 7 GPa. dE_g/dP = 6.9 meV/GPa, in good agreement both with other experiments and the theoretical work [Surh et al. Phys. Rev. B45, 8239 (1992)] which has successfully accounted for the pressure dependence of the dielectric constant.

Introduction. There are two reasons for making direct measurements of the fundamental gap in diamond as a function of hydrostatic pressure. Optical measurements in diamond anvil cells (DAC) in the megabar region indicate that the absorption gap of diamond inside the anvils decreases under pressure [1]. However, ab initio calculations in the local density approximation (LDA) [2] predict an increase of the indirect gap (5.3–6.6 meV/GPa). This is an exception to Paul's rule (negative dE_g/dP) for the group IV and A3B5 semiconductors.

For many years, there was only one published experimental measurement [3] of the fundamental gap of diamond as a function of quasihydrostatic pressure up to 4.5 GPa; the value of dE_g/dP deduced was 5 meV/GPa. Very recently the optical absorption edge of diamond was measured [4] up to 2.3 GPa (dE_g/dP was found to be 6 meV/GPa) in a sapphire cell under hydrostatic pressure.

Structurally, diamond is one of the simplest materials, and its band structure, including the dependence on lattice parameters [2], has been calculated frequently. In recent work [5], the band structure of diamond was calculated in detail using the GW method: the band gaps were found to increase with hydrostatic pressure. In particular $dE_{g_{min}}/dP$ was calculated to be 6.7 meV/GPa. As a result of the positive dE_g/dP, the dielectric constant decreases under pressure. It was shown that the energy spectrum of diamond is sensitive to uniaxial stresses; the smallest gap decreases on the application of additional [001] stress. This result explains the above-mentioned differing behaviour of the fundamental absorption of diamond under hydrostatic pressure and in the complex stresses inside diamond anvils. We have performed measurements of the absorption edge of diamond under truly hydrostatic pressure up to 7 GPa.

The result obtained, dE_g/dP = 6.9 meV/GPa, agrees both with [4], and, together with our measurements of the refractive index of diamond under pressure [6], with theory [5].

Experiment. Measurements were made on type IIa natural diamond samples, which contain the smallest concentrations of impurities. This allows us to analyze the behaviour of the diamond absorption coefficient down to wavelengths of 220 nm. The platelets with [100] surfaces were mechanically polished and then ion beam etched to thickness 10–13 μm, 50–100 μm in diameters.

A pair of sapphire anvils, each with a flat tip of 0.6 mm diameter, with rounded edges, was used with DAC [7]. The diamond platelets and a ruby chip were placed in a gasket (brass) hole of diameter 200 μm. Helium was used as a hydrostatic pressure transmitting medium. The transmission spectra were recorded by a mirror optical system with a spectrograph and CCD detectors. Such a system permits us to record spectra in the range 220–230 nm. This is necessary in order to obtain data for the whole range of pressures achieved. The spectra were measured with a

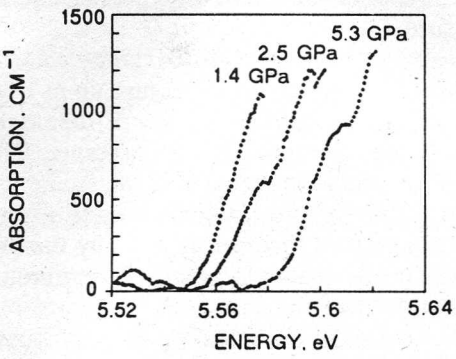
spectral resolution of 0.25Å. The pressure was determined from the red shift of the ruby luminescence with an accuracy of ± 0.3 kbar.

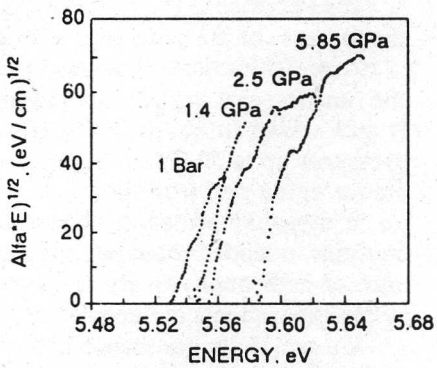
Results and discussion. The transmission spectra were obtained as a ratio of the intensity passed through the sample to a reference signal. The absorption coefficient as a function of photon energy was calculated taking into account the pressure contraction of the diamond [8] (Fig. 1). The absorption edge in diamond is due to indirect transitions. The indirect absorption follows [9]

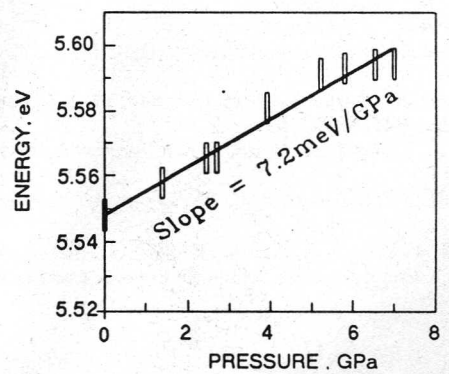
$$\text{Alfa}^{*}E_{\text{phot}} = C^{*}(E_{\text{phot}} - E_{\text{gap}} - E_{\text{phon}})^{2}, \qquad (1)$$

where C — a constant, E_{phot} — the energy of light, E_{phon} — the phonon energy.

The start point of the abrupt change in absorption coefficient was taken as the energy of the absorption edge (Fig. 2). The linear region near the absorption edge







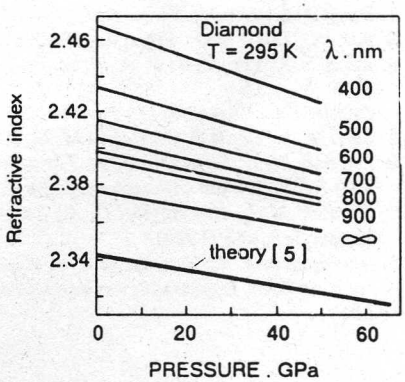


Fig. 1. Absorption spectra of a diamond sample of 13 μm thickness (295 K) under different hydrostatic pressures

Fig. 2. The square root of the left part of equation (1) versus the photon energy

Fig. 3. Fundamental absorption edge of diamond as a function of pressure

Fig. 4. The pressure dependence of the refractive index of diamond at different wavelengths; two lower lines — static limit (experimental data from [6])

justifies the formula (1). The pressure dependence of the energy corresponding to the start point of the absorption edge is shown in Fig. 3. The linear least-square fit gives a slope value 7.2 meV/GPa.

However, the pressure dependence of the diamond phonons responsible for the indirect transitions must be taken into account. Only the pressure dependence of the zone-centre phonon (0.31 meV/GPa) is known [8].

If the off-centre phonons corresponding to the lowest conduction band minimum of diamond have a similar pressure coefficient, this should be subtracted to obtain $dE_g/dP = 6.9$ meV/GPa. This value agrees well both with experiments [4] and with theory [5].

The theory [5] apparently describes not only the behaviour of the fundamental gap but also other energy gaps in the band structure very well. We have compared the behaviour of the dielectric constant calculated in [5] and data obtained in our previous experiments using pressures up to 50 GPa [6], (Fig. 4); the agreement is good.

The decrease of the refractive index (dielectric constant) with pressure reflects the increase of the band gaps with pressure.

Conclusions. Both previous experiments [3,4] and the present study show that the fundamental gap of diamond increases with hydrostatic pressure up to 7 GPa. It was shown in [6] from measurements of the refractive index of diamond in pressures up to 50 GPa that the average band gap increases with pressure. These results agree well with theory [5], which predicts the increase of the energy gaps up to megabar pressures. Therefore the shift of the absorption edge to lower energies in loaded diamond anvils [1] is explained theoretically [5] by the influence of high nonhydrostatic components in the diamond anvils. Direct uniaxial stress experiments are needed to verify this assertion.

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