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GAP REDUCTION OF C_{60} AND C_{70} AT HIGH PRESSURE.

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Abstract The absorption spectra of the C_{60} and C_{70} are measured at pressures up to 19 GPa. The pressure dependence of the fundamental absorption edge position E(P) is determined for both materials. The initial value of dE/dP=-0.15 eV/GPa for the stronger-absorption region of C_{60} decreases up to -0.019 eV/GPa at 12 GPa. The weaker-absorption region located near the fundamental absorption edge shifts slower dE/dP=-0.05 eV/GPa. For the C_{70} the initial value of dE/dP=-0.1 eV/GPa decreases up to -0.029 eV/GPa at 10 GPa. All pressure induced changes are reversible in this pressure range.

INTRODUCTION

The measurements and calculations of the energy spectrum of the fullerite C_{60} and C_{70} gave the basic features of the crystal band structure[1-3]. For the improvement of the calculations one has to know the band gap behavior at high pressure, which makes experimental study in this field quite essential.

EXPERIMENT

The initial material of C_{60} and C_{70} was prepared using Kratschmer's method[4]. A mass-spectral analysis has shown that the purity was better than 99% for C_{60} and 97% for C_{70}. The measurements were performed for the single crystals of C_{60} grown from the supersaturated solution in benzene. The grown crystals were platelets with thickness from 0.5 to 5 μm and 200×300 μm^2 dimensions. The measurements of the absorption spectra of the C_{70} were performed for the pellets of C_{70}. Pellets were made using a high pressure diamond anvil cell (DAC). The high-pressure measurements were carried out in a DAC; a mixture of alcohols was used as the pressure-transmitting medium. The pressure was determined from the luminescence in the R_1 line of a ruby crystal with accuracy 0.1 GPa[5].

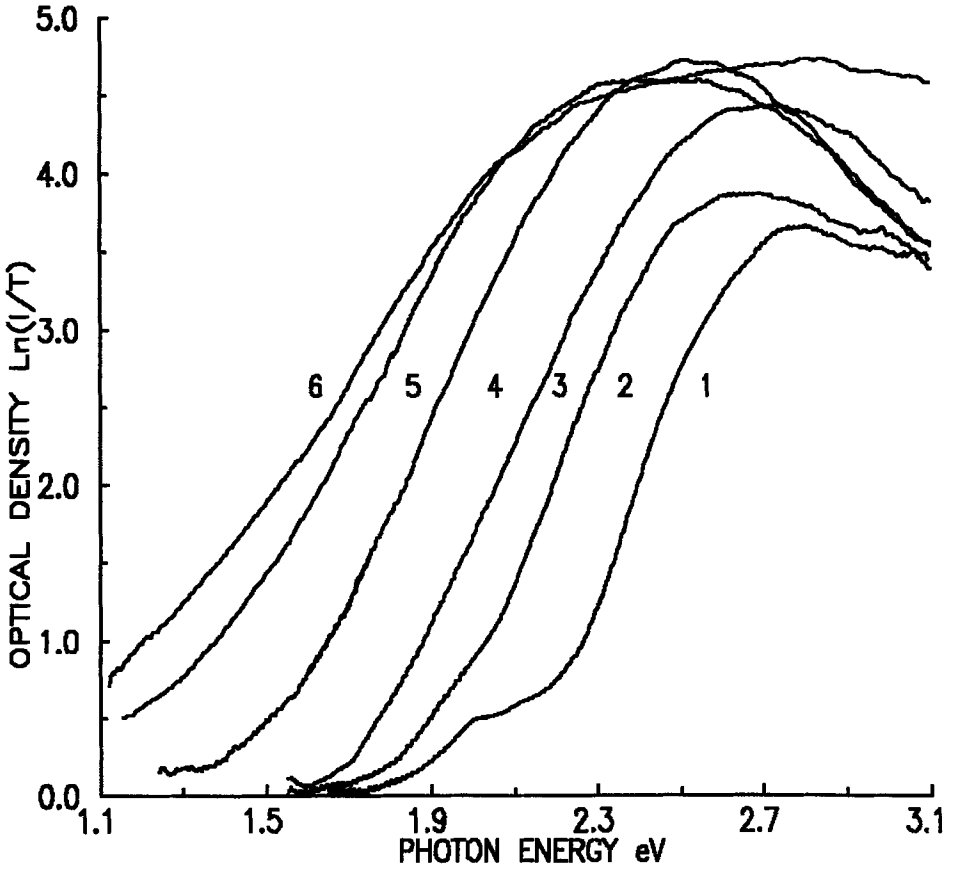

FIGURE 1 Absorption spectra of 0.7 μm thick C_{60} crystal at pressures up to 19 GPa. Curve 1 corresponds to normal pressure, curves 2, 3, 4, 5, and 6 to pressures 0.9, 3.1, 9.5, 14 and 19 GPa.

RESULTS

Fig. 1 depicts the absorption spectra of C_{60} crystal 0.7 μm in thickness at 300K and pressure up to 19 GPa. Curve 1 corresponds to the normal pressure, curves 2, 3, 4, 5, and 6 correspond to pressures of 0.9, 3.1, 9.5, 14 and 19 GPa, respectively. The growing of pressure gives rise to a strong red shift of the absorption spectrum. The spectrum form is invariable in pressure range from 2.0 GPa up to 12 GPa. One can observe a spectrum broadening connected with solidification of the alcohol mixture at pressure exceeding 12 GPa. Fig. 2 depicts the absorption spectra of 2.8 μm thick C_{60} crystal at ambient pressure (curve 1) and pressures of 0.9, 1.4, and 2.4 GPa (curves 2, 3, and 4, respectively). A pressure growth leads to a rapid decrease of the

width of the weaker-absorption region. It is connected with the difference in the pressure-induced shifts of the wea-

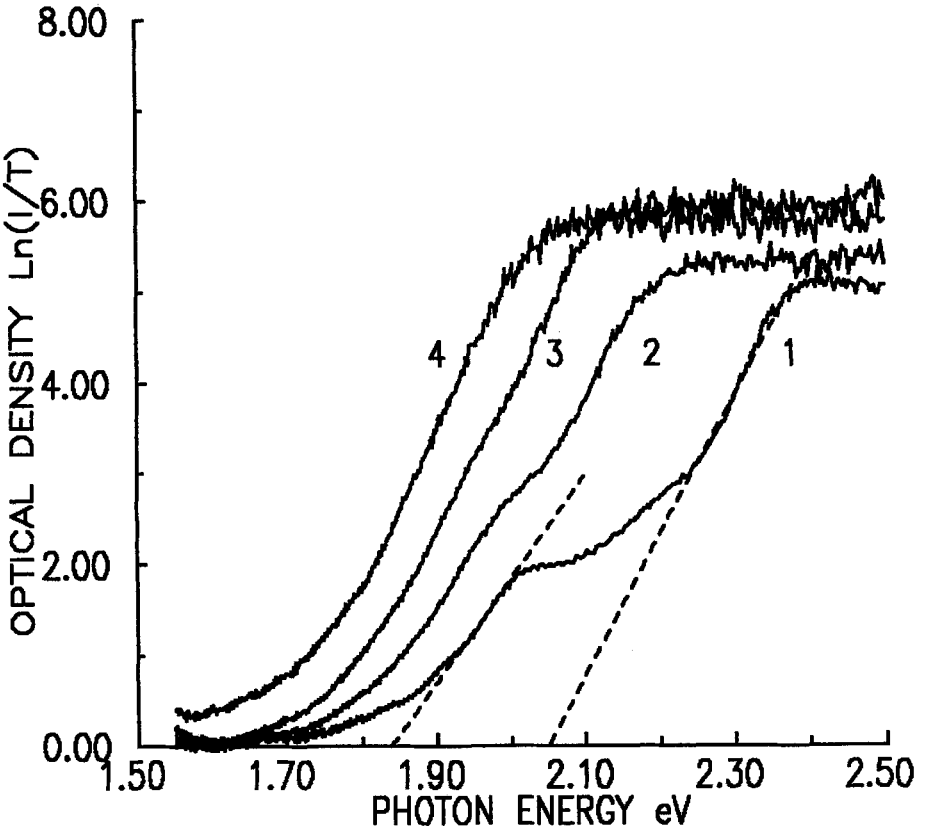

FIGURE 2 Absorption spectra of 2.8 μm thick C_{60} crystal at pressures 0.0001, 0.9, 1.4, and 2.4 GPa - curves 1, 2, 3, and 4, respectively. Dashed lines cut off on the energy axis the absorption edge position.

ker- and stronger-absorption regions. The dashed lines in Fig. 2 cut off on the energy axis the values corresponding approximately to the absorption edge position for weaker-absorption (1.83 eV) and stronger-absorption (2.04 eV) regions at ambient pressure.

In Fig.3 the absorption spectra of C_{70} pellets are shown in solid lines at pressures of 10.1 GPa (far left) and, accordingly, 8.0, 4.7, 1.4 and 0.2 GPa. The lover dashed curve corresponds to the absorption spectrum of the C_{70} solution in toluene and is given for comparison with the absorption spectrum of thin pellet of C_{70} (the upper

dashed curve). Measurements on pellets of various thickness yield the value of 1.78±0.005 eV for the fundamental absorption edge position of solid C_{70}.

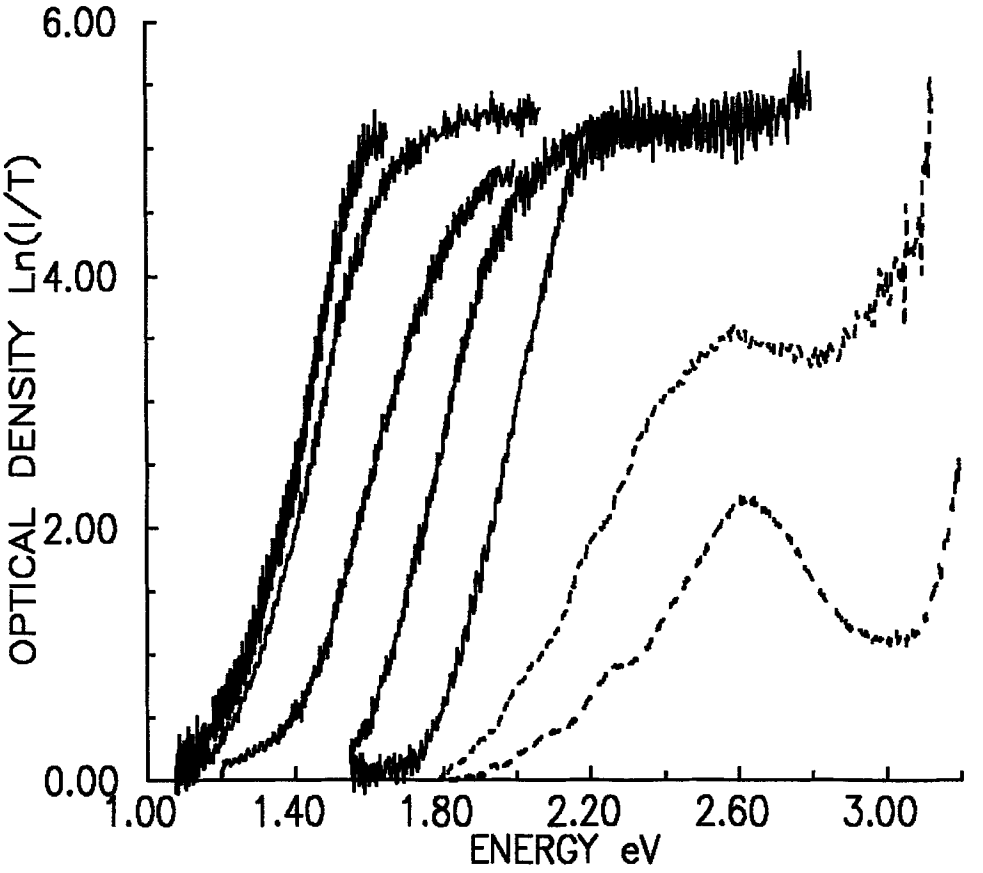

FIGURE 3 Absorption spectra of fullerite C_{70} pellets at pressures of 10.1, 8.0, 4.7, 1.4 and 0.2 GPa from left to right, respectively (solid lines). The upper dashed curve stands for thin pellet, the lower for C_{70} solution.

Fig.4 shows the pressure dependence of the absorption edge position of the C_{60} for the stronger-absorption (filled circles) and weaker-absorption (open circles) regions. As a whole, this dependence is reminiscent of the pressure dependence of a relative change of the volume V/V_0, obtained by Duclos et al. for C_{60} crystal[6]. The initial value of dE/dP=-0.15 eV/GPa for the stronger-absorption region decreases in absolute value up to -0.019 eV/GPa at 12 GPa. For the weaker-absorption region dE/dP=-0.055 eV/GPa. The absorption edge position of the C_{70} is shown in Fig.4 by triangles. For the C_{70} the initial value of dE/dP=-0.1

eV/GPa at ambient pressure decreases in absolute value up to -0.029 eV/GPa at 10 GPa.

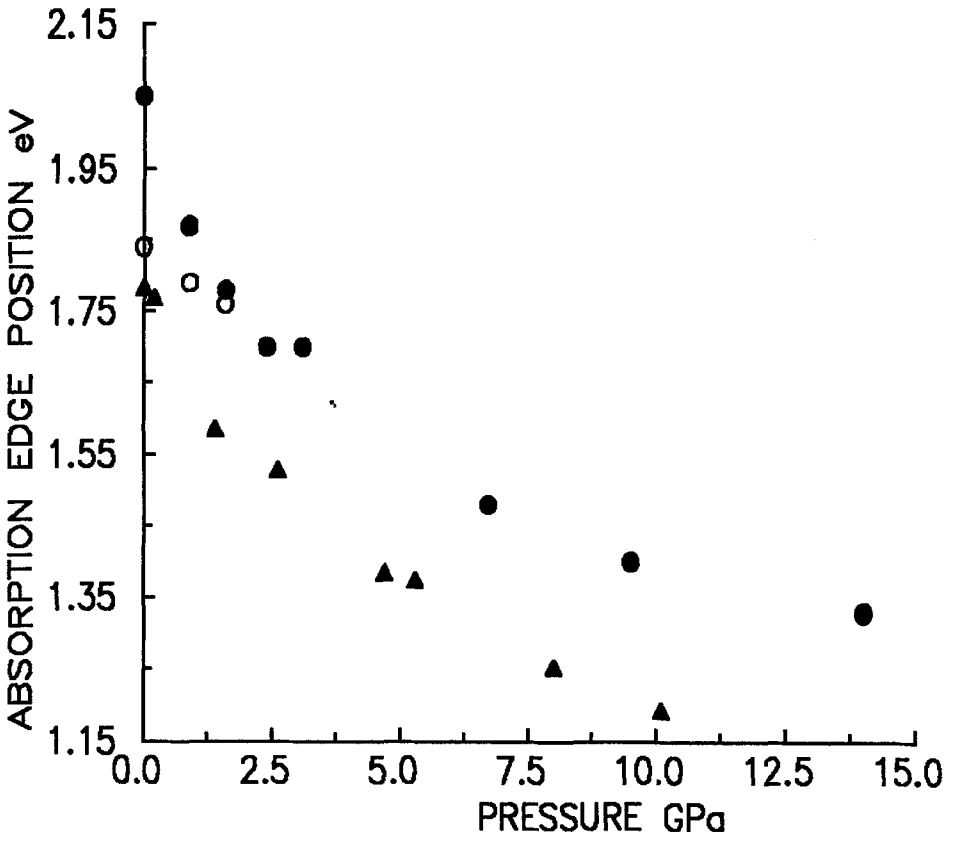

FIGURE 4 Absorption edge position vs the pressure for the C_{60} and C_{70} crystals. Filled and open circles correspond to the stronger- and weaker-absorption regions of C_{60}. Triangles correspond to the C_{70}.

DISCUSSION

The negative pressure shift of the absorption edge of C_{60} and C_{70} is characteristic also for molecular crystals of hydrocarbon compounds whose optical absorption is also governed by π-electron shells of carbon skeletons[7]. For these crystals the behavior of the absorption spectra at high pressure is connected with the specificity of Van der Waals intermolecular interaction and is markedly different

from those of traditional inorganic semiconductors[8]. The basic difference is that the pressure shift in C_{60} and C_{70} crystals is negative and its dependence is nonlinear not only on the pressure but on intermolecular distances as well. The latter circumstance complicates estimations of the pressure at which the band-gap may go to zero. The obtained data suggest that the pressure region >50 GPa is most interesting from this point of view. Measurements in this region are of particular interest since the distances between carbon atoms from neighboring fullerene molecules are comparable with intramolecular bond length. The interest to such a measurements is also related to the stability of fullerene molecule at high pressure since the results in this area are contradictory[9-11].

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