

HIGH PRESSURE STUDY OF THE ABSORPTION EDGE OF CRYSTALLINE FULLERITE C60

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The absorption spectra of the thin fullerite crystals C60 have been measured in the energy range 1.1–3.1 eV at room temperature and pressures up to 19 GPa. The mean rate of the pressure shift of the absorption spectra dE/dP has been estimated for strong- and weak-absorption regions. It has been found that in the strong-absorption region its value at initial pressure is -0.15 eV/GPa, and then its absolute value decreases up to 0.019 eV/GPa at 12 GPa. The weaker-absorption region located at the red edge shifts much slower ($dE/dP = -0.05$ eV/GPa) and coalesces with the strong-absorption region at pressure exceeding 2.0 GPa. The $T = 4.2$ K measurement indicate the presence of a fine structure in the weak-absorption region of C60, that transforms to a step at room temperature. The dependence of the absorption edge shift on the intermolecular distances has been determined and shown to be governed by the Van der Waals forces of the intermolecular interaction.

I. Introduction. After the elaboration of highly productive method for synthesizing of fullerenes, considerable advances have been achieved in investigation of the crystalline structure, phase transitions, quasi-particle excitation spectrum, electrical properties of C60 and M_x C60 compounds [1]. In particular, measurements of optical spectra of solutions, films, and crystals of C60 have made it possible to define the basic features of the energy spectrum and the adequacy of the theoretical models [2–4]. However, for the detailed estimations of the energy spectrum of molecular and the band spructure of C60 crystal one has to have precise data on the fundamental absorption edge position, band gap width and intermolecular interaction, which, in our opinion, make experimental studies in this field quite actual.

We have measured the absorption spectra of thin C60 crystals at 4.2 K and at 300 K in the pressure range up to 19 GPa. The data have been obtained on the position of the fundamental absorption edge, and its pressure dependence has been determined. It has been shown that the fundamental absorption edge shift with a change in intermolecular distances is governed by the Van der Waals forces.

II. Experiment. The measurements were performed for C60 single crystals grown from the oversaturated solution in benzene. As suggested by mass-spectrometry data, the purity of the initial material was not worse than 99%. The grown crystals were platelets $0.5\text{--}5\text{ }\mu\text{m}$ in thickness and $\sim 200 \times 300\text{ }\mu\text{m}^2$ dimensions. Their colour varied from golden-yellow to black, depending on the thickness. The have X-ray measurements have shown that the crystals the symmetry, and the developed plane coincided with an (111) plane of the crystal. The high-pressure studies were carried out at 300 K in a high-pressure chamber with diamond anvils, the working aperture of the gasket was about $160\text{ }\mu\text{m}$ in dia. The pressure-transmitting medium was a methanol-ethanol mixture (4:1). The pressure was deduced from the shift of the R_1 luminescence line of a ruby crystal with the accuracy to 0.05 GPa [5].

The spectral measurements were carried out using a projecting microscope which made it possible to produce a $\times 20$ intermediate image from which a crossed slit selected the part of $50 \times 50\text{ }\mu\text{m}^2$ dimensions, that was then projected to the input slit of the spectrometer. The spectral resolution of the instrument was $2 \cdot 10^{-3}$ eV,

the maximal level of the scattered light did not exceed $2 \cdot 10^{-3}$. The low-temperature measurements were carried out by means of helium optical thermostat, the temperature was maintained at an accuracy of 1 K.

III. Experimental results. Fig. 1 depicts the absorption spectra of C60 crystal 0.7 μm in thickness at 300 K and pressure up to 19 GPa. Curve 1 corresponds to the normal pressure and, with allowance for the difference in thickness is coincident with the spectra of fullerite films obtained by other authors [6] though one has noted the film spectra broadening due to mechanical stresses. Curves 2, 3, 4, 5 and 6 correspond to pressures of 0.9, 3.1, 9.5, 14 and 19 GPa, respectively. The growing pressure gives rise to a strong red shift of the absorption spectrum. Visually, the crystal colour varied from golden-yellow to magenta and then to black at pressure > 4 GPa. The spectrum form is invariable in a wide range of pressures, excluding the initial region up to 2.0 GPa, and also, $P > 12$ GPa, where one can observe a spectrum broadening related to the disturbance of hydrostatic conditions of pressurization upon solidification of the alcohol mixture. The pressure drop down to the normal one leads to the recovery of the initial spectrum, that is somewhat broadened because of the residual stresses.

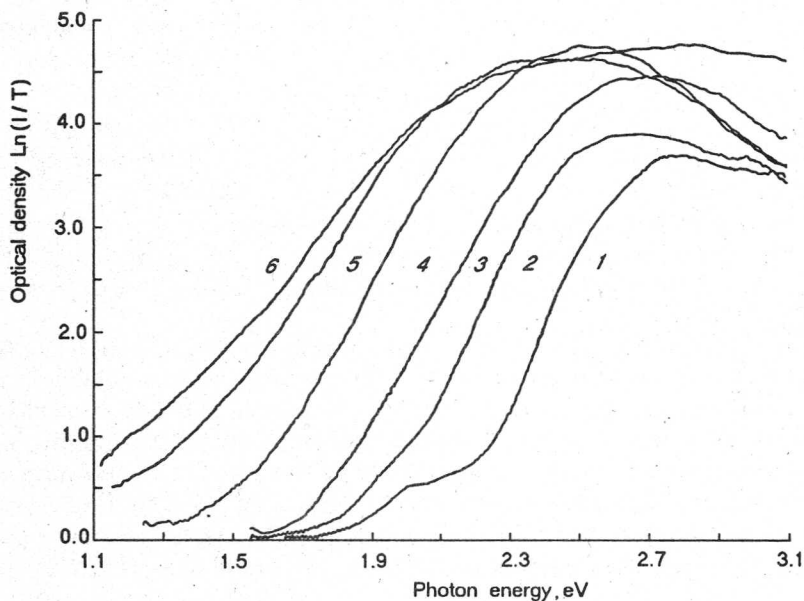


Fig. 1. Absorption spectra of 0.7 μm thick C60 crystal at room temperature and pressures up to 19 GPa. Curve 1 corresponds to normal pressure, curves 2, 3, 4, 5, and 6 to pressures of 0.9, 3.1, 9.5, 14, 19 GPa, respectively

The change in the spectrum form in the initial pressure region is most intriguing. Fig. 2 depicts the absorption spectra of 2.8 μm thick C60 crystal at room temperature and normal pressure (curve 1) and pressures of 0.9, 1.4, and 2.4 GPa (curves 2, 3 and 4, respectively). Figs. 1 and 2 prompt that pressure growth leads to a rapid decrease of the width of the 2 eV step, until it disappears at pressures $P > 2$ GPa, which is followed by an increase of the absorption coefficient. A small increase of the absorption is observed with a further compression of the crystal: it is related to an increase in the 2D density of the absorbing centers N of C60 molecules with increasing pressure ($N \sim (a_0/a)^2$), where a is the constant of the fcc lattice.

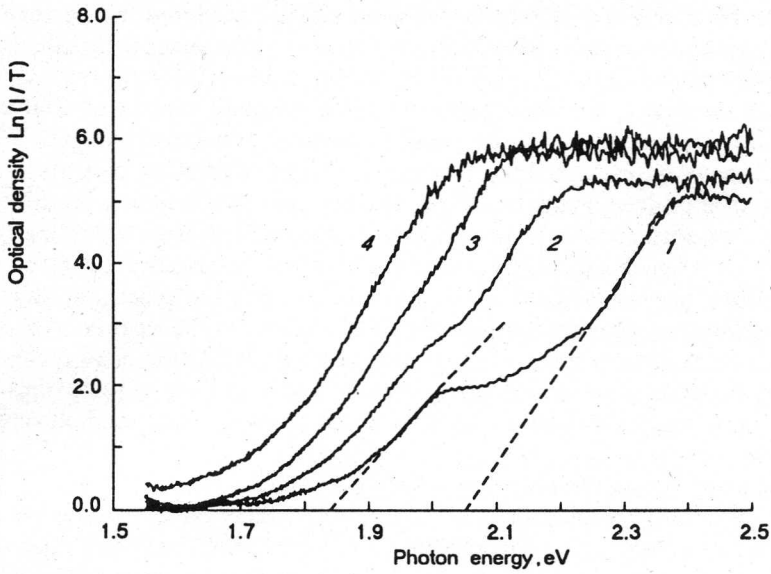


Fig. 2. Absorption spectra of $2.8 \mu\text{m}$ thick C60 crystal at $T = 300 \text{ K}$ at pressure 0.0001, 0.9, 1.4, and 2.4 GPa — solid curves 1, 2, 3, and 4, respectively. Dashed lines cut off the absorption edge position for the weak and strong absorption regions

A decrease of the step width in the absorption spectrum is due to the difference in the shift rate of two spectral regions: the stronger-absorption region, located at the back of the step overlaps the weaker-absorption region. The dashed line in Fig. 2 cuts off on the energy axis the values corresponding approximately to the absorption edge position for these spectral regions under normal pressure.

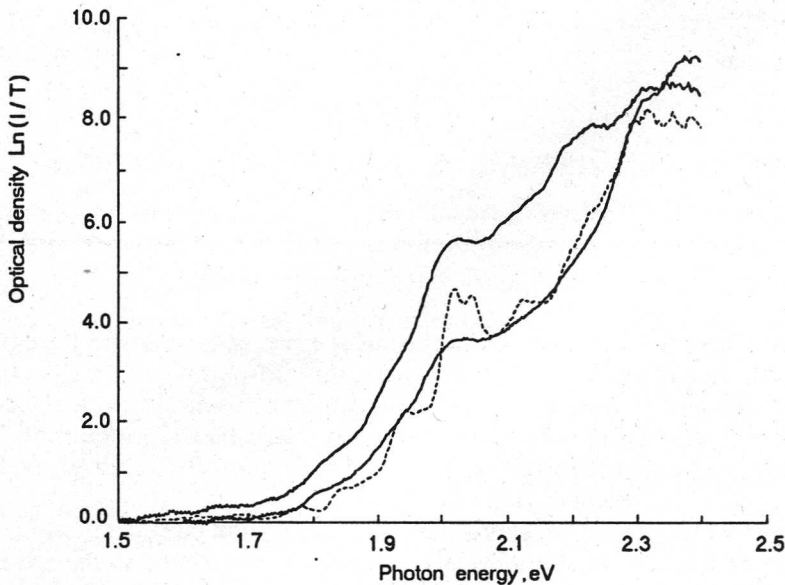


Fig. 3. Absorption spectra of C60 crystals at $T = 300 \text{ K}$ and normal pressure (thickness $5 \mu\text{m}$ — top solid curve, and $3 \mu\text{m}$ — bottom solid curve). The dashed curve — the absorption spectrum of the $3 \mu\text{m}$ thick crystal at $T = 4.2 \text{ K}$ and normal pressure

It should be noted that the spectrum form change occurred in the region of pressures approximately corresponding to the orientational phase transition in C60 crystal (0.3 GPa at $T = 300$ K) [7]. In order to elucidate whether it is related to the phase transition or not, we have measured the absorption spectra of C60 under normal pressure before and after the phase transition at temperatures 300, 55 and 4.2 K. Fig. 3 shows in solid lines the absorption spectra of two C60 crystals at room temperature and under normal pressure. The top curve corresponds to the $5\text{ }\mu\text{m}$ thick crystal, the bottom curve to $3\text{ }\mu\text{m}$ thick one, the dashed curve is the absorption spectrum of the $3\text{ }\mu\text{m}$ thick crystal at $T = 4.2$ K, which is virtually invariable with the temperature increase to 55 K. The main difference in the spectra at room and helium temperatures is the appearance of a fine structure in the weaker-absorption region, whereas the step itself and the position of the absorption edge for the two spectral regions remain invariant. This implies that a change in the form of the absorption spectrum under pressure is not related to the orientational phase transition.

The fine structure at the absorption spectrum edge of C60 films at $T = 4.2$ K was earlier observed by C. Reber et al. [3], and it is interesting to compare their results with those obtained by us. Like in [3] all the peaks but the first one are doublets, the red component of the doublet being always stronger and more prominent. The peak positions, determined in our work from the double differential spectra d^2I/d^2E , are listed in Table.

Table. Fine structure peaks position in the region of the weak absorption edge of fullerite C60 crystal

Peak position		
cm^{-1} [3]	cm^{-1} [this work]	eV
14420	14435 ± 15	1.778
14870	14850 ± 10	1.842
15100	15155 ± 10	1.880
15640	15640 ± 10	1.940
15880	15870 ± 10	1.965
16260	16255 ± 10	2.022
16500	16515 ± 10	2.049
17100	17110 ± 10	2.123
17320	17330 ± 10	2.150

The position of the peaks, with the exclusion of three, coincides with the data of [3] within the error of measurements. However, this difference and the associated lack of correspondence between the peak-to-peak distances and the intramolecular vibration frequencies make a vibronic analysis, proposed in [3], doubtful. The interpretation of the fine structure of the spectrum is interesting indeed, and we shall come back to this problem in the due course.

Fig. 4 shows the pressure dependence of the absorption edge position for the region of strong (filled circles) and week (open circles) absorption in the pressure range up to 14 GPa. The experimental results for the pressure 19 GPa are excluded from consideration because of large error related to the spectrum broadening. The mean rate of the absorption edge shift dE/dP is governed by the slope of the tangent

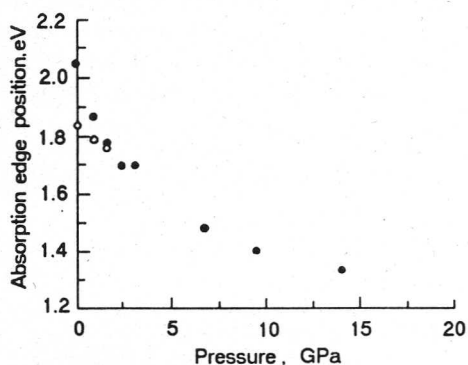


Fig. 4. Absorption edge position vs the pressure for the C60 crystal. Filled and open circles correspond to the strong and weak absorption region

absorption edge alone will be present in the absorption spectrum, and the mean shift rate dE/dP with small pressures will be confined only to this region. Inasmuch as the pressure dependence of the position of the absorption edge is markedly nonlinear, then the determination by a method of simple extrapolation of the pressure value, at which the band gap width vanishes, may lead to its strong underestimation [9].

IV. Discussion of the results. For molecular crystals, to which fullerite belongs, the intermolecular Van der Waals interaction is much weaker than the intramolecular one, and the optical spectrum of crystal is as a rule very similar to that of molecule. At present the theory of excitonic states in molecular crystals, that describes the transformation of the electronic spectrum of the molecule in going over to the crystal, is most developed. In this case the principal changes are the so-called crystalline shift and the formation of band states corresponding to collective excitations [10,11]:

$$E^{\mu} = E_0^{\mu} + D^{\mu} + L_k^{\mu} \quad (1)$$

Here E^{μ} is the energy of the μ -th electronic transition in the crystal, E_0^{μ} is the same for a free molecule, D^{μ} is the crystalline shift equal to the energy difference of the Van der Waals interaction of the molecule in the ground and the excited states, and L_k^{μ} is the term responsible for the excitation transfer and the occurrence of the collective states. The crystalline shift D is regularly red and equals to the difference in the energies of the electronic transition in the crystal and unsplit molecular level, and its magnitude grows with an increase of the electronic transition dipole moment [10]. A decrease of the intermolecular distances upon the crystal pressurization leads to an enhancement of the interaction and an increase of the crystalline shift, therefore the pressure shift of the electronic levels in molecular crystals is negative ($dE/dP < 0$) and its magnitude is also proportional to the dipole moment of the electronic transition. The experimental results on the pressure shift of the exciton bands and impurity levels, obtained by the present time for a number of molecular crystals have the form of the power function of the type $\Delta_p = A + B \times (R_0/R_p)^n$, where R_0 and R_p are intermolecular distances at the

to this function and, as seen from the Figure, its magnitude is strongly diminished with the growing pressure. As a whole, this dependence is reminiscent of the pressure dependence of a relative change of the volume V/V_0 , obtained by S. J. Duclos et al. for C60 crystals [8]. The initial value of the shift rate dE/dP is -0.15 eV/GPa and -0.055 GPa for the region of strong and weak absorption, respectively, and for $P = 12$ GPa its absolute value decreases to 0.019 eV/GPa. It should be noted that in the case of thick C60 crystals, due to limitation of the maximally measurable value of the optical density $Ln(I/T)$ related to the scattered light, the region of the weak

corresponding pressures. The exponent n varies from 8 for the strong transition in anthracene crystal to 15 for the weak transition in a benzene crystal [12–14]. The London's dispersion effect theory that explains the attraction of two electrically neutral molecules lacking the dipole moment allows for the Coulomb interaction alone, and the main dipole-dipole contribution to the interaction energy is proportional to $(R_0/R_p)^6$ [15]. The high exponents in the experimental function may be due both to the contribution of high multipoles and the electron exchange interaction.

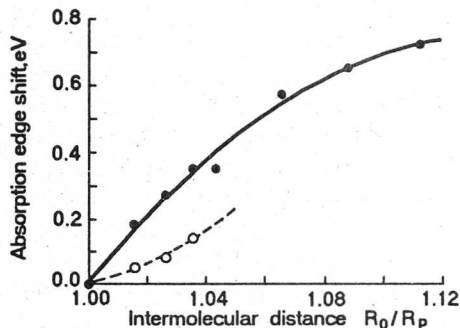


Fig. 5. Absorption edge shift of the C60 crystal vs the intermolecular distance. The filled circles and the solid line are the experimental data and the approximation by function of the form $\Delta_p = A + B \times (R_0/R_p)^6 + C \times (R_0/R_p)^{12}$ for the strong absorption region, the open circles and the dashed line are the same for the weak absorption region ($\Delta_p = A + B \times (R_0/R_p)^6$)

The obtained experimental results enable one to determine the absorption edge shift of C60 $\Delta_p = E_0^\mu - E_p^\mu$ as a function of the intermolecular distance. Inasmuch as the crystalline lattice of fullerite is cubic, a relative change in the intermolecular distances R_0/R_p for every pair of molecules coincides with a relative change of the cell parameters a_0/a_p , and can be deduced directly from the X-ray data under high pressure [8]. Fig. 5 illustrates the absorption edge shift of C60 as a function of the intermolecular distances for the strong and weak absorption regions (filled and open circles, respectively). The experimental results for weak absorption region can be described by the equation:

$$\Delta_p = E_0^1 - E_p^1 = A + B \times (R_0/R_p)^6, \quad (2)$$

where $A = -0.6$ eV, $B = 0.6$ eV. It should be noted that in contrast with the weak absorption region for which the dependence of the shift on the intermolecular distances is similar to the corresponding functions for molecular crystals of anthracene, naphthalene, and benzene, in the strong absorption region this function has a qualitatively different form: the experimental results cannot be described by the power function of the form (2) with reasonable n values in terms of London's theory ($n > 6$). When using the approaches employed so far for the description of the electron-spectrum shift in molecular crystals, one has, probably, to allow for the contribution of the higher terms in the power expansion of the interaction (R_0/R_p) . For the strong absorption region the Δ_p function can be described as

$$\Delta_p = E_0^2 - E_p^2 = A + B \times (R_0/R_p)^6 + C \times (R_0/R_p)^{12}, \quad (3)$$

where $A = -2.35$ eV, $B = 3.21$ eV, and $C = -0.84$ eV, i. e. by the function analogous to the Lennart-Jones potential.

The difference in the functional dependence of the shift for the weak and strong absorption bands, and the fine structure of the low-temperature spectrum in the

weak-absorption region indicate the different origin of these spectral regions. The obtained experimental data make it possible to consider three possible versions of the weak-absorption region origin:

1. The weak-absorption region complies with exciton transitions near the absorption edge. This version is supported by the fine spectral structure at low temperature, in this case, however, one should expect the occurrence of the shift in this region with the growing pressure synchronously with the edge of the strong absorption region, which contradicts the experimental data.

2. This region complies with the impurity absorption. In this case the difference in the shift rates and the fine spectral structure at low temperature are explainable. Certain doubts are cast by the observation of this region virtually in all the works available by the present time, including those carried out for sufficiently pure materials. In any case, the absorption coefficients in this region are very high for the crystals of the used purity, and the unambiguous answer can be obtained only for ultra pure crystals.

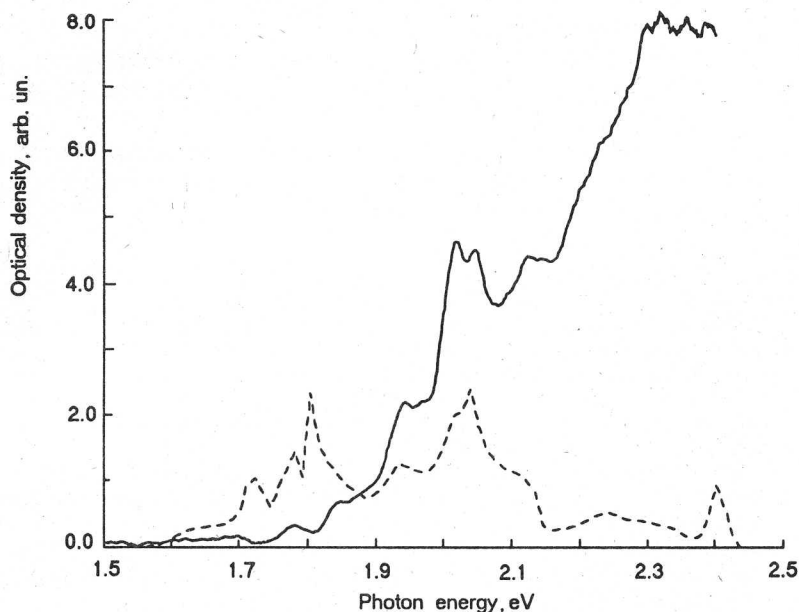


Fig. 6. Absorption spectrum of the C60 crystal at $T = 4.2$ K and the normal pressure (solid line), and 0.17 eV shifted to the violet spectrum region imaginary part of the dielectric permeability ϵ , calculated for the C60 crystal in the work [16] (dashed line)

3. All the absorption is truly crystalline, and the fine spectral structure is stipulated by Van Hove's singularities of the density of states. In this case the question is: Why do the rates of the pressure shift differ for the two spectral regions? The answer may be that these regions comply with different molecular electronic transition with different dipole moments and therefore they have different rates of the pressure shift.

We shall consider the latter version at greater length in view of the recent results obtained by W. Y. Ching et al. in their calculations of the band structure of C60 [16]. They have calculated the spectral density of the band states, determined the spectral dependence of the real and imaginary parts of the dielectric permeability

ϵ and have shown that the absorption spectrum of C60 near fundamental edge was formed by two different electronic transitions. It consists of two sequential regions: 1.4 eV weak absorption region and a strong 2.4–4 eV absorption region. The spectral dependence of ϵ governs the absorption spectrum form, and in Fig. 6 the dashed line shows the imaginary part of the dielectric permeability in the weak absorption region, calculated in [16], and the solid line stands for the absorption spectrum at low temperature. The curve of the imaginary part of ϵ was shifted by 0.17 eV towards higher energies, that led to the energy superposition of the strongest features of the experimental and calculated spectra. Fig. 6 demonstrates a correlation between the spectral position for other maxima as well. The distinct structure of the curve is stipulated by Van Hove's singularities of the density of states. In contrast to ordinary semiconductors for which these singularities are bent-shaped in molecular crystals they have the form of sharp peaks due to the small band width stipulated by a weak intermolecular interaction. Remembering that ϵ reflects the principal features of the transmission spectrum and, also, that there is a certain correlation between the fine absorption spectrum structure and the ϵ curve, then being optimistic, we should prefer the third version. However, the strongest proof of such origin of the weak absorption region would be, in our opinion, the confirmation of the experimental data on the pressure shift of weak and strong absorption regions by the calculations of the band structure and transmission spectra of C60 at high pressure.

In conclusion we note that the data on the position of fundamental absorption edge, pressure shift of the absorption spectrum of C60 and intermolecular interaction may be useful for correction of band structure calculations.

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