

Vladimir M. Shatalov

FINE STRUCTURE AND PRESSURE DEPENDENCE OF FULLERITE OPTICAL ABSORPTION EDGE IN TERMS OF INTERBAND TRANSITIONS

Донецкий физико-технический институт НАН Украины, 340111, г. Донецк, ул. Розы Люксембург, 72

Статья поступила в редакцию 23 ноября 1993 года

Recently reported fine structure of the optical absorption edge of pure fullerite and its pressure dependence have been reproduced in terms of interband transitions within a simple tight binding model. It is shown that the fine structure originates from the lowest intra-molecular excitations which are forbidden in an isolated C₆₀ but allowed in a crystal due to the inter-molecular hopping. The structure is added to a tail of the on-site dipole-allowed transitions. The observed ratio of intensities, edge shift rates and pressure dependence of the spectral shape have been explained in terms of the exponential behavior of the hopping integrals.

There exists still unresolved problem of the true bandwidth value W in fullerite. An analysis of the available photoemission and inverse photoemission data [1], thermopower estimations [2] and *ab initio* calculations [3] give the values of W from 0.2 to 1.0 eV but the upper and lower critical field measurements [4] predict much smaller values of $W \approx 200$ K. Calculations within a tight binding method [2] give similar results, so W is definitely unknown.

Recently a weak fine structure of optical absorption edge of pure fullerite has been discovered at $T=4.2$ K [5,6] and pressure dependence of it has been measured at room temperature [6]. At room temperature it looks like a weak feature at 1.8 eV on the tail of a strong feature at 2.1 eV. The spectrum shape differs to a marked degree from the calculated one [7] and no proved interpretation of the fine structure and pressure dependence of it has been given.

To clarify the above problems in this paper we report the results of our calculations of the spectrum as a function of hydrostatic pressure. The calculations were carried out on the basis of Slater atomic orbitals within a simple tight binding model based on the freezing molecular states and intermolecular hopping integrals. Only π -electrons were included in the consideration.

The tight binding model of C₆₀ in general use [2,3] deals with a minimal basis of atomic p_z -orbitals $\varphi_a(\vec{r})$ atom a of C₆₀ unit, so the l -th molecular orbital (MO) is a linear combination of atomic orbitals (LCAO),

$$\psi_l(\vec{r}) = \sum_{a=1}^{60} \varphi_a(\vec{r}) C_{al} \quad (1)$$

C_{al} are the eigenstates of the molecular hamiltonian written usually in the nearest neighbor approximation:

$$\hat{h}_{TB} = \sum_{\langle ij \rangle}^h V_h a_i^+ a_j + \sum_{\langle ij \rangle}^p V_p a_i^+ a_j + \text{h.c.} \quad (2)$$

where a_i is an annihilation operator of p_z -electron in the i -th atom; the sum labeled with h (or p) is taken over the pairs of atoms neighboring along the hexagon-hexagon (or pentagon-hexagon) edges; and V_h and V_p are the hopping integrals taken from molecular data or adjusted to an experiment. LCAO coefficients C_{ai} of the minimal basis are determined by the icosahedral symmetry of fullerene and do not depend on the values of the hamiltonian parameters V_h and V_p [3].

Interaction between molecules in solid C_{60} mixes up the MO's into the Bloch sum

$$\Psi_{nk}(\vec{r}) = \sum_l A_{lk} \sum_R e^{i\vec{k}\vec{R}} \psi_l(\vec{r} - \vec{R}) \quad (3)$$

and splits MO levels E_l into the energy bands E_{nk} which are solutions of the generalized eigenvalue problem,

$$\text{DET} |\hat{H} - E\hat{S}| = 0 \quad (4)$$

where \hat{H} and \hat{S} are the hamiltonian and overlap matrix. It should be noted that a solution of the non-linear Eq.(4) depends on the absolute value of E while the model hamiltonian (2) produces just a splitting of energy. Therefore using the solutions of Eq.(2) we ought to take into account in Eq.(3) only degenerated MO's believing for simplicity that the Bloch states from the different MO levels are not mixed up. In this case one may calculate the energy E from the corresponding molecular level E_l by replacing \hat{H} in Eq.(4) by the screened Coulomb potential V_{sc} ,

$$H_{lm} = \sum_R e^{i\vec{k}\vec{R}} \sum_{a=1}^{60} \sum_{b=1}^{60} C_{al} C_{bm} \langle \varphi_a(\vec{r}) | V_{sc} | \varphi_b(\vec{r} - \vec{R}) \rangle \quad (5)$$

Taking into account the large distances between the neighboring atoms of adjacent molecules only two-site integrals may be included in Eq.(5). Each of the integrals expressed in terms of σ - and π -hopping integrals has the form [3,8]:

$$V_{ab} = \langle \varphi_a | V_{sc} | \varphi_b \rangle = - (V_\sigma + V_\pi) (\hat{R}_a d) (\hat{R}_b d) + V_\pi (\hat{R}_a \hat{R}_b) \quad (6)$$

where $\hat{R} \equiv \vec{R}/R$ is a unit vector in the radial direction and $\hat{d} \equiv \vec{d}/d$ is a unit vector in the direction from atom a to atom b . The overlap matrix has the same form.

To obtain the electron spectrum as a function of separation between the molecules in a solid C_{60} one needs to state a distance-dependence of the hopping integrals V_{ab} and $S_{ab} = \langle \varphi_a | \varphi_b \rangle$. Note the very importance of this step because it states the structural and macroscopic properties of a crystal. Gunnarsson *et al.* [9] omitted S_{ab} and used in Eq.(6) the following formula

$$V_{\sigma}(d) = -4V_{\pi}(d) = (d/d_0) V_0 \exp [-(d-d_0)/L] \quad (7)$$

The parameter values $V_0=0.90\text{eV}$, $L=0.505\text{\AA}$ and $d_0=3.00\text{\AA}$ were adjusted by fitting $V_{\pi}(d)$ to the matrix elements of hamiltonian (2) $V_h=-2.78\text{eV}$ and $V_p=-2.59\text{eV}$ at distances d equal to the hexagon $b_h=1.391\text{\AA}$ and pentagon $b_p=1.455\text{\AA}$ edge respectively. Such a choice gives for the lowest unoccupied molecular orbital (LUMO) a bandwidth close to the result of the *ab initio* local density approximation (LDA) $W=0.50\text{eV}$ [3]. The distance-dependence of Eq.(7) originates from an exponential tail of the atomic potential. However the ratio V_{π}/V_{σ} as a function of d varies from -1 at $d=0$ to 0 at $d \rightarrow \infty$. The equation $V_{\sigma}(d) = -4 V_{\pi}(d)$ was justified at the valence bond distance of 1.5\AA but it seems to be doubtful at $d>3\text{\AA}$ in the van der Waals crystal.

Gelfand and Lu [2] used analytical forms of the hopping integrals V_{σ} and V_{π} derived [8] for the screened Coulomb potential of carbon on the basis of the Slater atomic orbitals

$$\varphi_a(\vec{r}) = (\zeta^5/\pi)^{1/2} z \exp(-\zeta r). \quad (8)$$

The bandwidth of LUMO level was found to be $W=0.03\text{eV}$ in the order smaller than the LDA one. Such an underestimation was due to the Slater parameter value $\zeta a_0=1.64$ which does not reproduce well the asymptotic behavior of the atomic orbital (here a_0 is Borh radius). Nevertheless the LUMO density of states [2] coincided with LDA result [3] at an appropriate energy scaling that was used to explore the effect of orientation disorder on the normal- state electronic transport of fullerite [2].

In the present band structure calculations we use the analytical forms of hopping integrals V_{σ} and V_{π} [8] and take into account the corresponding overlap integrals. The parameter $\zeta a_0=1.27$ was determined by fitting the Slater orbital Eq.(8) to the precise atomic wave function [10] at actual distances. It differs to a marked degree from the Slater value 1.64 and the single $-\zeta$ [10] approximate value 1.57. The latter one was obtained by the variational procedure of Hartree-Fock-Roothan which was not able to produce any true asymptotic behavior of a trial function. Our calculations give LUMO band structure and density of states shapes which are very close to the *ab initio* results [3]. Howeve in our case the bandwidth $W=0.2\text{eV}$ is a factor of 2.5 less.

The optical absorption edge corresponds to the forbidden intra-molecular transition between the highest occupied molecular orbital (HOMO) h_u and LUMO t_{1u} level which is displayed in a crystal spectrum as a low absorption band due to the ability of inter-molecular transitions. To calculate the spectrum we also take into account the second lowest on-site transition from HOMO h_u to the next unoccupied t_{1g} level which is allowed and gives rise to a high absorption band. The corresponding energy differences [9] $E_1=2.223$ and $E_2=2.870$ eV are the centres of gravity of the low and high absorption bands and depend on the hamiltonian (2) parameter values.

The oscillator strength of interband transition is $f_{ik} = 2 |\vec{P}_{ik}|^2 / (3E_{ik})$ (in

a.u.) where $i=1$ or 2 for the low or high absorption band and \vec{k} is a wave number, E_{ik} is the interband difference and \vec{P}_{ik} is the momentum matrix element. The latter one was obtained on the basis of Slater orbitals. The imaginary part of the dielectric constant (in atomic units)

$$\varepsilon_2(E) = 2\pi^2 \sum_i \sum_k f_{ik} \delta(E - E_{ik})/E \quad (9)$$

was calculated using the full-zone tetrahedron method where the 240 irreducible k -point set of fcc lattice was multiplied twice by $\pi/4$ rotation about the four-fold crystal axis to take into account the lowering of the fcc symmetry in fullerite. Note the importance of the last operation which changes drastically some features of the spectrum. The real part of dielectric constant was obtained from the dispersion relation

$$\varepsilon_1(E) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_2(E') dE'}{E'^2 - E^2} \quad (10)$$

Since the used $\varepsilon_2(E)$ includes just the above-mentioned transitions, then Eq.(10) gives an approximate $\varepsilon_1(E)$. The omitted upper band transitions would add near constant term to the $\varepsilon_1(E)$ in the absorption edge region. This approximation is sufficient for our purposes to estimate the shifts of the bands under pressure.

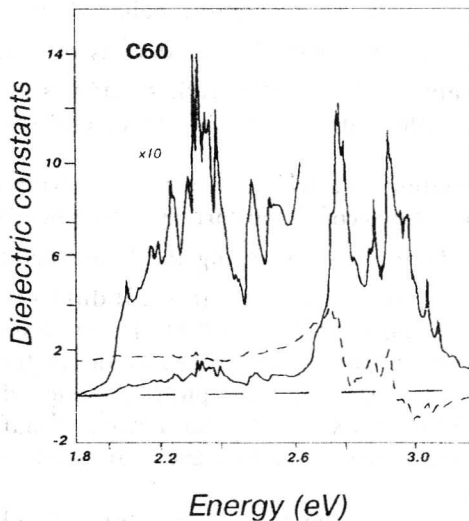


Fig. 1. Real (dashed line) and imaginary (solid lines) parts of dielectric constant as a function of energy for fcc lattice constant $a=14.1 \text{ \AA}$

The resulting curves are presented in Fig.1. The absorption appears at the energies exceeding 1.9 eV as a number of sharp peaks. Some of them are doublets originated from the known double peak structure of LUMO density of states [3]. The low absorption band is superimposed on the high one at $E=2.6$ eV. Note the close values of these band widths caused by a splitting of the molecular levels while their ratio of intensities is equal in the order of magnitude to MO's intersite overlap integral. The last one increases exponentially if the molecules are drawn together.

Getting ε_1 and ε_2 one can obtain the absorption coefficient $\alpha = 4\pi\kappa/\lambda$ where λ is the wave length of light and κ is the imaginary part of the refractive index

$$\kappa = \{[(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1] / 2\}^{1/2} \quad (11)$$

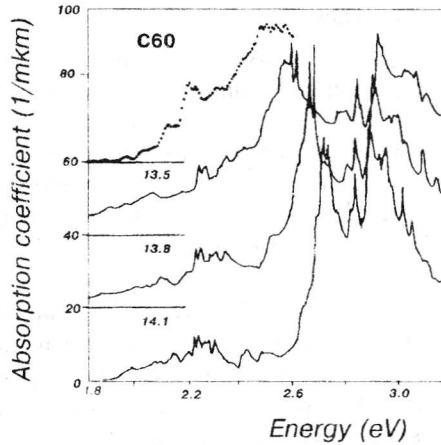


Fig. 2. Absorption coefficients for various fcc lattice constants are pointed at the curves in A (solid lines) and experimental one [6] for zero pressure and $T=4.2K$ (dotted line in arbitrary units, 0.2 eV shifted the to right). The origins of every curve are shifted by 20 units up

The calculated absorption coefficients as a function of energy in the cases of normal and compressed crystals are shown in Fig.2. In the framework of the model the low and high absorption bands are expanded exponentially if the intermolecular distance decreases because the band splitting is proportional to the hopping integral. The structures in the centers of the bands at $E_1=2.223$ and $E_2=2.870$ eV are keeping their place while the others are shifted proportionally to their distances from the corresponding center of band. That explains the observed differences of the red shifts under pressure of the low and high absorption equal to -0.055eV/GPa and -0.15eV/GPa , respectively. The last value recalculated via intermolecular distance [6] is equal to $1\text{eV}/A$ which is close to our estimation of the near 2.6 eV threshold shift which is equal to $0.6\text{eV}/A$. The calculated shift of the lower edge is close to the upper one and much exceed the observed value. Note that the lower edge is not well defined (see Fig.2) and should be smoothed out at room temperature. These are the reasons why the experimentally observed weak feature [6] seems to be not the lower edge but should be related with a singularity inside the “forbidden” band which is closer to the E_1 level and must have lesser shift then the edge has.

Comparing the parameter $\zeta a_0=1.27$ adjusted here to $a_0/L=1.05$ from Eq.(7) one may obtain that the shift of the absorption edge in the model of Ref.3 is equal to $1.2\text{eV}/A$ which is close to the experimentally quoted number. However the absorption bands in that model would have a factor of 2.5 larger widths.

The experimental [6] absorption curve shape, Fig.2, is close to the results of our calculations. However to consist the energy position of bands with the observed values in framework of the model used one needs to reduce E_1 to 2.0

and E_2 to 2.4eV that contradict to the well known experimental value of $t_{1u} \rightarrow t_{1g}$ splitting equal to 1eV. Both this contradiction and the previous estimation of shifts brings us to the conclusion that the bandwidth W in our model is underestimated 2.5 times. So enlarging the $t_{1u} \rightarrow t_{1g}$ splitting from 0.4eV of ours to 1eV of Ref.3 and correspondently multiply the bandwidth 2.5 times one may obtain a result which satisfies the different experiments.

Unfortunately we cannot compare all the details of the fine structure with the experimental one since of the phase transition from the fcc to simple cubic lattice with four non-equivalent positions of C_{60} units takes place at low temperature. As it was shown in [3] that causes drastic changes in LUMO density of states but keeps the value of bandwidth. That partially explains inconsistency between the measured [6] and calculated in Ref.[7] spectrum. The other reason may be that the sum in Eq.(9) was calculated in [7] without the lowering of the fcc symmetry.

As is shown in Fig.2 the pressure increasing produces a broadening, smoothing out and overlapping of the bands that is in accordance with the experiment [6]. The absolute values of the absorption coefficient are also in a reasonable range.

To sum up, we have reproduced the experimentally observed fine structure, differences of intensities, shifts and pressure dependence of the absorption spectrum shape of fullerite in terms of the exponential behavior of the hopping integrals. The applied pressure expands the absorption spectrum in such a way that the shift of a singularity in each absorption band is proportional to the distance from the level of molecular excitation energy. This shift being free from various broadening factors should be used for an experimental estimation of the bandwidth.

Acknowledgements Fruitful discussions with Dr. M.Gelfand and Dr. O.Gunnarsson are acknowledged. The author thanks Drs. V.A.Telezhkin and A.V.Ovodenko for their help at early stage of the work and the authors of Ref.6 for providing the experimental data.

1. T.Takahashi, S.Suzuki, T.Morikawa, S.Hasegawa & H.Inokuchi, Phys. Rev.Lett. 68, 1232 (1992).
2. M.P.Gelfand & J.P.Lu, Phys. Rev. B 46, 4367 (1992).
3. S.Satpathy, V.P.Antropov, O.K.Andersen, O.Jepsen, O.Gunnarsson & A.I.Liechtenstein, Phys. Rev. B 46, 1773 (1992).
4. K.Holczer, O.Klein, G.Gruner, J.D. Thompson, F.Diederich, R.L.Whetten, Phys. Rev. Lett. 67, 271 (1991).
5. C.Reber, L.Yee, J.McKiernan, J.I.Zink, R.S.Williams, W.S.Tong, D.A.A.Ohlberg, R.L.Whetten & F.Diederich, J.Phys. Chem. 95, 2127 (1991).
6. K.P.Meletov, V.K.Dolganov, O.V.Zharikov, I.N.Kremenskaya & Yu.A.Ossipyan, Journal de Physique I, 2, 2097 (1992).
7. W.Y.Ching, H.Ming-Zhu, Xu Yong-Nian, W.G.Harter & F.T.Chan, Phys. Rev. Lett., 67, 2045 (1991).
8. O.H.LeBlanc, J.Chem. Phys. 35, 1274 (1961).
9. O.Gunnarsson, S.Satpathy, O.Jepsen & O.K.Andersen, Phys. Rev. Lett., 67, 3002 (1991).
10. E.Clementi & C.Roetti, Atomic Data and Nuclear Data Tables 14, 177 (1974).