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ANALOG OF THE DAVYDOV SPLITTING IN CARBON GRAPHITE-LIKE STRUCTURES

The brief analysis of the origin of Davydov splitting (DS) of phonon, electron, etc. spectra is presented. The problem how to increase the DS value is still important. So, in addition to molecular crystals, the layered crystals are perspective candidates. In particular, the bilayer graphenes (BG) are suitable structures for that. The calculation of the values of analogous DS in the nonstationary dipole approximation (electron exchange model) demonstrates the giant electron band splitting for all k of the Brillouin zone. The experimental results for distorted multicrystal ultrathin carbon layers demonstrate the new possibilities for increasing this splitting.

Keywords: Davydov splitting, bilayer graphene, Brillouin zone.

1. Theory

Davydov splitting was discovered experimentally by the optic group at the Institute of Physics in Kyiv and was explained theoretically by A.S. Davydov (1948) [1]. The essence of this effect is the splitting of phonon, electron and mixed spectra in molecular crystals with weak inductive (van-der-Waals) bonds between two neighboring molecules with different dipole orientations, that belong to one primitive cell, and the migration of the excitation energy inside the crystal. The values of DS for molecular crystals appear to be very small (1–10 meV). To increase DS, the inorganic layered crystals (As_2S_3, ZnP_z, CdP_z, *etc.*) have been studied, when "elementary cells of the neighboring layers" create a translation non-equivalent structure with van-der-Waals bonds between them, but with larger values of DS than that for molecular crystals (in particular, due to smaller interlayer distances, larger energy of bonds, *etc*). Bilayer graphene (BG) is characterized by one of the smallest values of $d_1 \sim (3.4–4)$ Å. There is the translation nonequivalence of A and B layers in BG, which are twisted at $2\pi/6$ relative to each other, Fig. 1 [2, 3].

Due to this, the Davydov-like splitting of the electron spectrum for BG can be predicted for all critical points of the Brillouin zone: K, Γ, M. The interaction through the p_z orbital removes the band degeneration, which leads to the splitting of the electron spectrum of a bilayer and transforms the material into a multivalley semiconductor. The splitting takes place for the whole Brillouin zone. So, we call this effect as an analog of the Davydov splitting. In addition, the effective variation of a band structure is also possible due to the elastic deformation and structural defects [2–6].

In fact, the DS mechanism due to the resonance interaction between two neighboring similar (but twisted relative to each other) "molecular clusters" is realized through the weak interaction of the ground state of one layer (Ψ_0) and the excited state of another one (Ψ_n). This "dynamical dipole" produces an energy correction in the first approximation of the exciton theory [1]:

$$\Delta E = \frac{e^2}{R^3}\langle|\Psi_n|H|\Psi_0\rangle\Phi(1,2) \sim f.$$

Here, $\Phi(1,2) = F(\Delta\theta_{1,2})$ is the geometric factor of a dipole disorientation of both layers, and f is the oscillator strength. At $\theta = 0$, we have $\Delta E = 0$; so, DS disappears.

The matrix element of the dipole transition is determined by the oscillator (dipole) strength f and the interlayer distance R. Our calculation of the band spectrum [2, 4, 5] was performed within the theory of strong bonding in the non-stationary (exchange mechanism) dipole approximation with regard for the π-interactions (i.e., the electron transition in optical spectra occurs only between π-bands). More weak σ (i.e. $-p_z$) bonds are also important due to a distortion of the planar (longitudinal) sp^2 bonds. The interlayer bonds are responsible for a splitting of the bands. Both terms related to the strong interaction in the limits of each of the longitudinal graphene-like layers and the weak interlayer interaction are taken into account in the Hamiltonian H [2, 5]. Band energy levels can be calculated as a solution of the secular equation

$$\det(H_{ij} - E\delta_{ij}) = 0,$$

where δ_{ij} is the deformation (distortion) factor, and

$$H_{ij} = \sum_{d} e^{ik(d+R_\nu+R_{\nu'})} \int \Phi^*(r{-}R_\nu) H \Phi(r{-}d{-}R_{\nu'}) dr.$$

Then we consider (for simplicity) the interactions with the nearest atoms only, by retaining only two types of the operator H: $V_0 = (pp\pi)$ – for a shift deformation, and $V_1 = (pp\tau)$ – for the interlayer interaction. We have obtained the energy values for all the principal points of the Brillouin zone (K, Γ, M) of BG with the use of the general form of the matrix H, which demonstrates the essential splitting of the bands, see Fig. 2 [2]:

$$\varepsilon_1 = \varepsilon_p + H_{13}^0 + \Delta_k + \frac{1}{2(V_1 + \Delta_k)} V_0^2 \delta^2,$$

$$\varepsilon_2 = \varepsilon_p + \frac{1}{2(V_1 + \Delta_k)} V_0^2 \delta^2,$$

$$\varepsilon_3 = \varepsilon_p - \frac{1}{2(V_1 + \Delta_k)} V_0^2 \delta^2,$$

$$\varepsilon_4 = \varepsilon_p - H_{13}^0 - \Delta_k - \frac{1}{2(V_1 + \Delta_k)} V_0^2 \delta^2.$$

The gaps for optical transitions were predicted with the parameters presented in the Table, which demonstrates the giant band splitting.

2. Experimental Results

The experimental procedure has included the low-energy chemical vapor deposition (CVD), which had produced the semiordered composition of carbon layered nanocrystallites with (1–3) layers in each with interlayer distances $d \sim 0.35$–0.4 nm. Optical spectra for these films are presented in Figs. 3 and 4. The widths of the spectra are proportional to a distortion.

Experimental dependence of E_g on the energy as a function of the distortion degree and $E_g = f(N_t)$ are presented in Fig. 4.

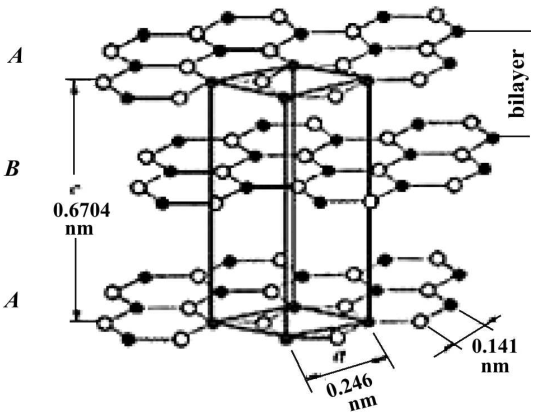

Fig. 1. Graphite and bilayer graphene

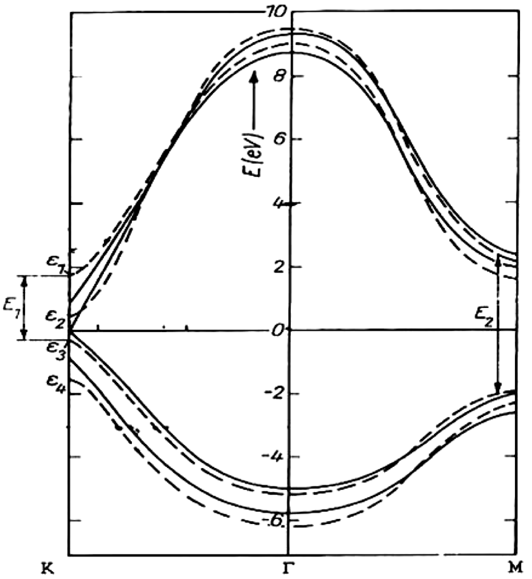

Fig. 2. Electronic energy structure of bigraphene (solid curves) and deformed bigraphene (dashed curves). The structural parameters θ and δ are determined from experimental data

ΔE splitting (in eV) for different energy band critical points. Indices c, v, and g are related to the conductive and valence bands and the gap, D – deformed films obtained experimentaly [2]

Type of point	ΔE_c	ΔE_v	ΔE_g	ΔE_{cD}	ΔE_{vD}	ΔE_{gD}
K	1	–0.8	1.8	1.2	–1.3	2.9
Γ	–0.6	–0.9	0.3	–0.7	–1.4	–0.7
M	–0.5	–0.7	0.2	–0.7	–0.5	–0.2

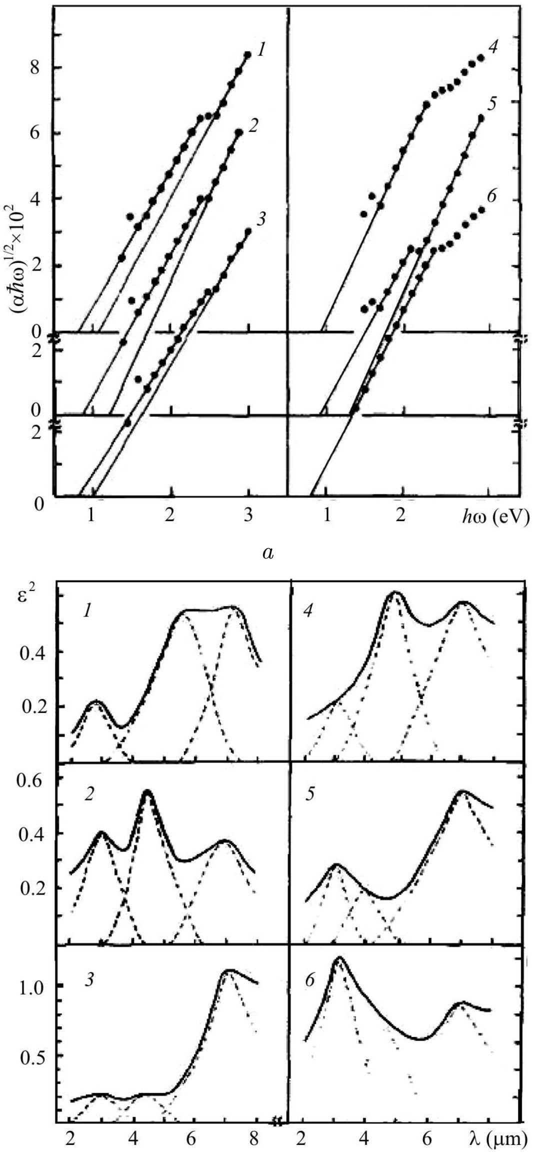

Fig. 3. Spectral dependence of the function $(\alpha\hbar\omega)^{1/2}$ for different samples, where α is the absorption coefficient [4] (*a*). Spectra of the imaginary part $\varepsilon_2(\hbar\omega)$ of the dielectric permittivity for different samples noted in Fig. 3, (*a*); (dotted lines – deconvolution into elementary oscillators) [4] (*b*)

The linear dependence of the width of the optical absorption spectrum was demonstrated at the bottom of the Brillouin zone.

The question arises about the origin of the gap appearing in zero-gap materials, like sp^2 carbon due to a deformation. In our previous publications [2,

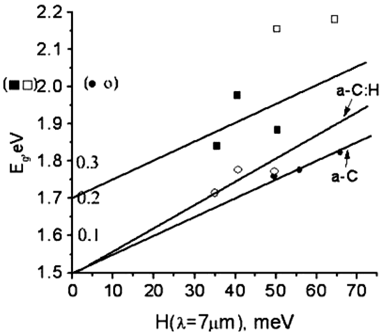

Fig. 4. Dependence of the energy gap in bigraphene on the defectness (proportional of the optical spectra presented in Fig. 3). Upper line – $E_{g1} = \varepsilon_1 - \varepsilon_3$, lower line – $E_{g2} = \varepsilon_2 - \varepsilon_3$

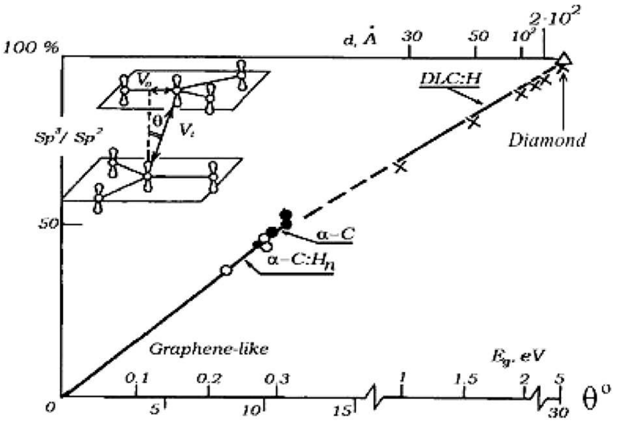

Fig. 5. Dependence of the energy gap E_g (splitting of bands) on the angle θ and on sp^3/sp^2 for various modifications of carbon (nondoped *a*-C, H-doped, diamond-like (DLC)) [4–6]

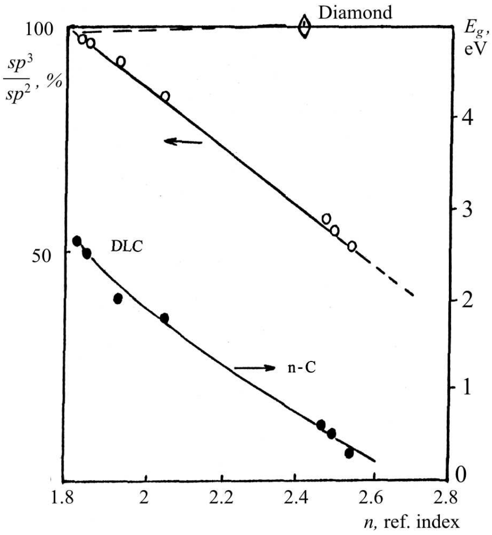

Fig. 6. DLC – diamond-like carbon, *n* – nanocarbon

4], we qualitatively discussed a peculiar mechanism for the atomic band structure of such polymorphous material as carbon. The possible appearance of the substances with different valence (sp) orbital orientations is expected: diamond-like sp^3, layer-graphite-like sp^2, linear sp, mixed like $(sp^3)_x - (sp^2)_{1-x}$ *etc.* In the last case, the different values of band gap were predicted: from near zero to about 5.5 eV (pure diamond). Depending on x, the intermediate phase was called as "diamond-like" with $E_g \geq 1$ eV; whereas, at $E_g \leq 0.5$–0 eV, it was called as graphite like [4]. The values of x for, in particular, sp^3 (or sp^2) can be determined experimentally by ellipsometric measurements of the effective refractive index n. The absorption spectra give the energy gap E_g by the empirical relation $n(sp^3/sp^2)$, $E_g(sp^3/sp^2)$ (see Figs. 5 and 6). The values presented in Figs. 3–5 were obtained from measurements for different samples.

In addition, the theory yields the deformation angle θ for different values of E_g. In such a way, we obtain the combine picture with x (sp^3/sp^2), the energy gap E_g, and deformation angle θ for carbon substances of different atomic configurations, including graphene-like and diamond-like. A deformation of sp^2 bands leads to the appearance of the partial sp^3 bands, increases the effective gap, and creates a family of narrow gap semiconductors, whereas a deformation of sp^3 gives the opposite effect: a decrease of the diamond gap and the creation of a family of wide gap semiconductors (Fig. 5). The experimental data are demonstrated in Fig. 5 by different points for

$$x\left(\frac{sp^3}{sp^2}\right) = 100 - \frac{\partial x}{\partial n}[n - n_{\min}],$$

$$E_g[\mathrm{eV}] = E_{g\,\max} - \frac{\partial E_g}{\partial n}[n - n_{\min}],$$

$$\frac{\partial x}{\partial n} = 120, \quad \frac{\partial E_g}{\partial n} = 3\ \mathrm{eV}.$$

3. Conclusion

The gigantic Davydov splitting for different layered structures (including bilayer graphene studied here) represents the new possibility for the engineering of new types of spectra and new semiconductors for different useful applications (such as IR sensors, laser bodies, *etc*).

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АНАЛОГ ДАВИДОВСЬКОГО РОЗЩЕПЛЕННЯ У ВУГЛЕЦЕВИХ ГРАФІТОПОДІБНИХ СТРУКТУРАХ

Резюме

Наведено короткий аналіз природи давидовського розщеплення (ДР) фононного, електронного та ін. спектрів. Підкреслено, що все ще важливою проблемою є задача збільшення величини ДР. Тому, крім молекулярних кристалів перспективними кандидатами є шаруваті структури. Зокрема двошаровий графен (ДГ) є для цієї мети підходящою структурою. Щоб це продемонструвати, були проведені розрахунки величини ДР методом нестаціонарного дипольного наближення (обмінна електронна модель), які демонструють гігантське розщеплення електронних спектрів для всіх значень k зони Бріллюена. Експериментальні результати на деформованих мультикристалічних надтонких вуглецевих плівках дають додаткові можливості для збільшення описаного розщеплення.