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Band structure model and electrostatic effects in third and fourth stages of graphite acceptor compounds

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Résumé. — Nous décrivons la structure des niveaux électroniques dans les composés d’accepteur de stades 3 et 4, en utilisant le modèle des sous-systèmes indépendants. Les effets électrostatiques, dus à la non-équivalence des couches de graphite internes et externes, induisent une distribution de charge non uniforme dans chaque système mais aussi modifient considérablement la structure de bandes. Les transitions optiques interbandes sont analysées dans ce modèle. Pour un transfert de charge comparable à celui qui a été obtenu pour les premiers stades des composés d’accepteur, les énergies des transitions intervale peuvent être en bon accord avec les données expérimentales.

Abstract. — The model of independent graphite subsystems is extended to describe the electronic states in stages 3 and 4 of GAC. The electrostatic effects related to the nonequivalence of the internal and external graphite layers are proved to induce a non uniform charge distribution in the system, and also to modify drastically the band structure. Interband optical transitions are analysed within this model. With a charge transfer coefficient comparable to the value obtained for lowest stages of GAC, the expected energies of the intervalence transitions are close to the energies of the reflectivity structures observed experimentally.

1. Introduction. — In our previous paper [1], denoted further by I, we have shown that the optical reflectivity spectra of 1st and 2nd stage graphite acceptor compounds (GAC) can be well interpreted within the model of independent graphite subsystems. In this model the nth stage GAC is treated as a set of equivalent, independent subsystems of n graphite layers limited by intercalated layers. It is assumed that the charge transfer from graphite to acceptors introduces free delocalized holes in each graphite subsystem, whereas the negative charge is treated as rigidly bound to acceptors. The potential energy fluctuations produced within graphite subsystems by the charged acceptors are neglected. These fluctuations are expected to be considerably screened out due to large density of free holes. The secondary role of these fluctuations seems to be confirmed by very small changes of the electrical conductivity in intercalated graphite accompanying the ordered-disordered phase transitions within intercalated layers [2].

The electronic states of graphite subsystems have been calculated in I by the simplest tight-binding method, taking into account only the interactions between nearest carbon atoms. A similar model of independent graphite subsystems, but using a more refined method of band structure calculations, has been proposed recently by Holzwarth [3]. However this model neglects entirely the electrostatic effects due to the presence of the excess charge on the graphite layers. These effects are not important in 1st and 2nd stage compounds studied in I, in which all graphite layers are equivalent, and the same excess charge is accumulated on each layer. The situation is quite different however in GAC of the stage \( n \geq 3 \). The layers are no longer electrostatically equivalent and the electrostatic forces affect the equilibrium excess charge distribution of the system. The only existing quantitative analysis of the excess charge distribution in GAC is due to Pietronero et al. [4]. These authors applied the Thomas-Fermi model to determine the excess charge distribution in a parallel slab of continuous polarizable medium with the density of states and the background dielectric constant of 3D graphite. Pietronero et al. [4] use locally the 3D rigid band model, and neglect entirely the fact that the band structure of a system of a few layers is principally different from that of a graphite crystal of macroscopic dimension. In a system of a few layers, instead of the 3D continuum of electronic states, there exists a number of 2D bands. Each band corresponding in general to different electron localization is affected
in a specific way by the electrostatic potential energy variations in the system. The band structure and the excess charge distribution have to be in principle determined in a self-consistent way.

The purpose of the present paper is to investigate the band structure of independent graphite subsystems of 3 and 4 charged graphite layers. We focus our attention on electrostatic effects, and thus we adopt the same simplified tight-binding method as we already used for lowest stages of GAC in 1.

2. The model Hamiltonian. — We consider \( n \) graphite layers \((n = 3\) or 4\) in the coordinate system shown in figure 1. The full and open circles in figure 1 represent the nonequivalent lattice sites A and B. The A and B positions in the \( j \) level are defined by vectors \( p_m + \tau_{2j-1} \) and \( p_m + \tau_{2j} \) where \( p_m \) is the vector of the Bravais lattice in the layer 1. The vectors \( \tau_i \) are:

\[
\begin{align*}
\tau_{2j-1} &= (j - 1) d e_x \\
\tau_{2j} &= (j - 1) d e_x - (- 1)^j b e_x
\end{align*}
\]  

where \( e_x \) and \( e_z \) are the unit vectors of \( x \) and \( z \) axes respectively. \( d \) is the interlayer distance and \( b \) the nearest neighbour distance.

The basis tight-binding functions constructed from atomic \( \phi_n(r) \) functions localized at the atomic sites \( p_m + \tau_i \) are:

\[
u_{ik}(r) = \sqrt{Q} \sum_{p_m} \phi_n(p_m + \tau_i) \phi_i(r - p_m - \tau_i)\]

\( i = 1, \ldots, 2n \)

\( Q = 3 \sqrt{3} h^2 / 2 \) is the area of the 2D elementary crystal cell and \( \Sigma \) is the area of the system in \( xy \) plane. The 2D wavevector \( \mathbf{k} \) is restricted to the first Brillouin zone.

By a straightforward generalization of the approximate procedure used in 1 for two layer systems, we get the secular equations determining the band structure at point \( \mathbf{k} \), in the vicinity of the U point of the 2D Brillouin zone, in the systems of 3 (eq. (3)) and 4 (eq. (4)) layers. Concerning the charged acceptor layers, we use the same approximations as Pietronero et al. [4] i.e. we treat these layers as planes (or slabs) with the uniform charge distribution. Consequently, they do not introduce any potential variation within the graphite subsystems.

\[
\begin{bmatrix}
\delta + \delta_1 - E & -x & \gamma_1 & 0 & 0 & 0 \\
-x^* & \delta - \delta_1 - E & 0 & 0 & 0 & 0 \\
\gamma_1 & 0 & -\delta + \delta_2 - E & -x^* & \gamma_1 & 0 \\
0 & 0 & -x & -\delta - \delta_2 - E & 0 & 0 \\
0 & 0 & \gamma_1 & 0 & \delta + \delta_1 - E & -x \\
0 & 0 & 0 & 0 & -x^* & \delta - \delta_1 - E
\end{bmatrix}
= 0
\]  

and

\[
\begin{bmatrix}
\delta + \delta_1 - E & -x & \gamma_1 & 0 & 0 & 0 & 0 \\
-x^* & \delta - \delta_1 - E & 0 & 0 & 0 & 0 & 0 \\
\gamma_1 & 0 & -\delta + \delta_2 - E & -x^* & \gamma_1 & 0 & 0 \\
0 & 0 & -x & -\delta - \delta_2 - E & 0 & 0 & 0 \\
0 & 0 & \gamma_1 & 0 & -\delta + \delta_1 - E & -x & \gamma_1 \\
0 & 0 & 0 & 0 & -x^* & -\delta - \delta_2 - E & 0 \\
0 & 0 & 0 & 0 & \gamma_1 & 0 & \delta + \delta_1 - E & -x^* \\
0 & 0 & 0 & 0 & 0 & 0 & -x & \delta - \delta_1 - E
\end{bmatrix}
= 0
\]
where, in the vicinity of U point \( |x| = \frac{3}{2} \gamma_0 b k \), \( k \) being the distance from \( k \) to the U point. \( \gamma_0 \) and \( \gamma_1 \ll \gamma_0 \) are the resonance integrals defined in 1

\[
2 \delta = \frac{E_1 + E_2 - E_3 - E_4}{2}
\]

\[
2 \delta_1 = E_1 - E_2
\]

\[
2 \delta_2 = E_3 - E_4
\]

where

\[
E_i = \int \varphi_i^2(r - \tau_i) |V(r)|^2 d^3r, \quad i = 1, 2, 3, 4.
\]

The potential energy differences \( 2 \delta_i, 2 \delta_1, 2 \delta_2 \) depend, via the crystal potential \( V(r) \), on the excess charge distribution which in turn is a function of the band structure, wavefunctions and band population.

The direct construction of the total crystal potential \( V(r) \) is beyond the possibilities of our model. We represent \( V(r) \) in the form:

\[
V(r) = V_0(r) + V(r) - V_0(r)
\]

where \( V_0(r) \) is the auxiliary potential produced by \( n \) neutral graphite layers with the rigid charge distribution of 2D graphite. The difference \( V(r) - V_0(r) \) can be related to the excess charge distribution \( \Delta \rho(r) \) defined as the difference between the actual charge distribution and the distribution in a system of neutral noninteracting layers.

We approximate \( \Delta \rho(r) \) by a sum of the excess charge distributions localized on atomic sites. We attribute to an atom of \( \tau_i \) the charge \( e_i \), the dipole moment \( p_i \), and the quadrupole moment tensor \( Q_\alpha \) for \( x \neq (3) \). The number of different \( e_i \), \( p_i \), and \( Q_\alpha \) is restricted by the symmetry of the system, e.g. \( e_1 = e_5 \) in stage 3, \( e_1 = e_7 \) in stage 4, etc.

We assume that the excess charge distribution around each atom is essentially of the same form as for \( \varphi_z \) atomic state of carbon, but proportional to \( e_i \) instead of \( e \). In writing down eqs. (3) and (4) we neglected \( \sigma - \pi \) band mixing, thus the induced dipole moments cannot be related to any quantity introduced up to now. We treat the induced dipole moments as entirely independent quantities given by the classical formulae derived in the Appendix.

By direct computer summation (described in the Appendix) of the contributions to \( E_i \) from consecutive layers (neglecting small quadrupole-quadrupole interactions) we get the following formulae for the potential energy differences:

\[
2 \delta_1 \approx E_{10} - E_{20} - e(e_1 - e_2) \left( J - \frac{1.53}{b} - \frac{1.16 q}{b^3} \right)
\]

\[
2 \delta_2 \approx E_{30} - E_{40} - e(e_3 - e_4) \left( J - \frac{1.53}{b} - \frac{1.16 q}{b^3} \right)
\]

\[
2 \delta = \frac{E_{10} + E_{20} - E_{30} - E_{40}}{2} - e(e_1 + e_2 - e_3 - e_4) \left( J - \frac{3.32}{b} - \frac{3.29 q}{b^3} \right) + 2 \pi d e - 2 \pi |\sigma_d| e
\]

where \( E_{10} \) are given by (6) with \( V(r) \) replaced by \( V_0(r) \). \( -ee_j J \) represents the electrostatic energy interaction of the electron in the state \( \varphi_z(r - \tau_j) \) with the excess charge distribution at the atom at \( \tau_j \). \( -eq \) is the \( zz \) component of the quadrupole moment tensor for the state \( \varphi_z(r) \). The numerical factors result from the geometry of graphite lattice. \( \sigma_e \) is the total surface density of the excess charge on the internal layers. \( \sigma_d \) is the sum of the surface densities of induced dipole moments in layers 1 and 2 related to the surface charge densities by eqs. (A.5)-(A.7) of the Appendix. If we represent \( \varphi_z(r) \) by the Slater orbital

\[
\varphi_z(r) = \sqrt{\frac{\alpha^3}{\pi}} z e^{-\alpha z} \quad \text{with} \quad \alpha = 1.59/a_b [5]
\]

where \( a_b \) is the Bohr radius, we obtain

\[
J = \frac{501}{1280} \alpha = 0.622 a_b
\]

One result of the \textit{ab initio} band structure calculations by Painter and Ellis [6] is that the crystal potentials in 3D and 2D graphite differ little from each other. One can thus expect that the differences \( E_{10} - E_{20} \) and \( E_{30} - E_{40} \) are of the order of the corresponding parameter \( \Delta = -0.009 \text{ eV} [7] \) in 3D graphite and can be neglected. Within the tight-binding method, the potential energy of the electron \( (E_{30} + E_{40})/2 \) at a neutral graphite layer can be identified with the average valence band energy at point K in the B.Z. of 3D graphite. From the Painter and Ellis results one can conclude that this energy is lower by about 0.2 eV than the energy at U point in an isolated graphite layer. Taking into account that the external layer has a neighbouring layer on one side only, the difference \( \frac{1}{2}(E_{10} + E_{20} - E_{30} - E_{40}) \) can be expected to be about 0.1 eV.
Using the formulae of the Appendix and substituting numerical values for \( J \) and \( q \), we get finally:

\[
2 \delta_1 = \frac{e_1 - e_2}{e} \cdot 2.5 \text{ eV} \tag{8}
\]

\[
2 \delta_2 = \frac{e_3 - e_4}{e} \cdot 2.5 \text{ eV}
\]

\[
2 \delta = 0.1 \text{ eV} + \frac{f}{I} (z \cdot 57.6 \text{ eV} - 2.7 \text{ eV}),
\]

for 3rd stage \( (9) \)

and

\[
2 \delta = 0.1 \text{ eV} + \frac{f}{I} (z \cdot 53.5 \text{ eV} - 2.7 \text{ eV}),
\]

for 4th stage \( (10) \)

where \( f \) is the charge transfer coefficient per intercalated molecule in the compound \((\text{C}_2)_{n} X\), \( z \) denotes the fraction of the excess charge accumulated on internal layers. For uniform charge repartition \( z = \frac{1}{3} \) for the 3rd stage and \( z = \frac{1}{2} \) for the 4th stage.

However approximate, the formulae \( (9) \) and \( (10) \) indicate that the electrostatic potential energy difference between external and internal layers is quite important and must be taken into account in any band structure calculation. In particular, it is easy to see from eqs. \( (9)-(10) \) that the assumptions concerning the excess charge distribution in two models previously used to interpret the experimental data are not realistic:

1) the uniform charge repartition assumed in the rigid band model \( [7] \) leads to the values of \( 2 \delta \) larger or comparable to the hole Fermi energy (even if we neglect the constant term \( 0.1 \text{ eV} \) in eqs. \( (9)-(10) \)). This evidently contradicts the assumption of the uniform charge distribution,

2) the localization of the excess charge in external layers only, assumed in the metallic sandwich model \( [8] \) leads to very small or even negative values of \( 2 \delta \), whereas such a localization would require very large and positive values of \( 2 \delta \).

Eqs. \( (8)-(10) \) form in principle a basis for the self-consistent band structure calculations for a given value of \( f/I \). Taking into account the approximate character of our model, it seems more reasonable however to treat \( 2 \delta_1, 2 \delta_2 \) and \( 2 \delta_3 \) as phenomenological parameters and use eqs. \( (8)-(10) \) only as approximate tests for the self-consistency.

3. 3rd stage. — If we adopt the simplifying hypothesis that \( b_1 \) and \( \gamma_2 \) are negligible as compared to \( \gamma_1 \) (which seems plausible in view of eqs. \( (8) \)); the secular eq. \( (3) \) can be solved analytically. The band energies in the vicinity of the U point are :

\[
E_{1}\nu = \delta \pm |x|
\]

\[
E_{2}\nu = \pm \sqrt{\delta^2 + \gamma_1^2} + |x|^2 - \sqrt{\gamma_1^2 + (4 \delta^2 + 2 \gamma_1^2)} |x|^2 = \pm E_-
\]

\[
E_{3}\nu = \pm \sqrt{\delta^2 + \gamma_1^2} + |x|^2 + \sqrt{\gamma_1^2 + (4 \delta^2 + 2 \gamma_1^2)} |x|^2 = \pm E_+
\]

These energies are plotted in figure 2a, b, c for the arbitrary values of \( \delta = 0, \gamma_1/3, 2 \gamma_1/3 \) respectively.

The wavefunctions associated with each band are linear combinations of the tight-binding basis functions :

\[
\psi = \sum_{i=1}^{6} a_i \psi_{i}(x).
\]

For the linear bands \( E_{i}\nu \) (Fig. 2), the electrons are localized entirely on the external layers. Whatever the value of \( \delta \),

\[
a_1 = -a_5 = \frac{1}{2}; \quad a_2 = -a_6 = \mp \frac{x^*}{2 |x|}; \quad a_3 = a_4 = 0
\]

the upper and lower signs correspond to the conduction and valence band respectively.

The wavefunctions for all other bands are localized on both external and internal layers. In the case \( \delta = 0 \), the linear combination coefficients are

\[
a_1 = \frac{E}{2 \sqrt{E^2 + |x|^2}}
\]

\[
a_2 = -\frac{E}{2 \sqrt{E^2 + |x|^2}}
\]

\[
a_3 = \pm \frac{E}{\sqrt{2} \sqrt{E^2 + |x|^2}}
\]

\[
a_4 = \mp \frac{x}{\sqrt{2} \sqrt{E^2 + |x|^2}}
\]

where \( E \) is the corresponding band energy. The upper sign is for the bands 3c and 2v, the lower sign for 2c and 3v.

We first discuss the case \( \delta = 0 \).

In figure 3 we plotted the probabilities for interband transitions induced by unpolarized light propagating along the c-axis as a function of \( |x| \). The probability for \( 1v \rightarrow 1c \) transitions is the same as in the 1st stage GAC studied in I, i.e. independent of \( k \) in the whole region of linearity of these bands. The probabilities for other transitions between symmetrical bands \( (3v \rightarrow 3c, 2v \rightarrow 2c) \), forbidden at \( k = 0 \), increase rapidly with \( x \).
Fig. 2. Band structure near the U point in the third stage GAC (\(|x| = \frac{\gamma_0}{2} \). a) \( \delta = 0 \); b) \( \delta = \gamma_3/3 \); c) \( \delta = 2 \gamma_3/3 \).

Fig. 3. Relative probabilities for interband transitions in stage 3.

\[
\begin{align*}
\delta = 0 & \quad \delta = \gamma_3/3 \\
1 : 1v \to 1c & \quad 1 : 1v \to 1c \\
2 : 2v \to 2c & \quad 4 : 2v \to 2c \\
3 : 3v \to 3c & \quad 5 : 3v \to 3c \\
6 : 3v \to 2v & \\
7 : 3v \to 2c & \quad 2 : 3v \to 2c \\
\end{align*}
\]
and become comparable for \( x > \gamma_1 \) with the probability of \( 1v \rightarrow 1c \) transitions. On the contrary, the probability for transitions \( 2v \rightarrow 3c, \ 3v \rightarrow 2c \) and \( 3v \rightarrow 2v \), allowed for \( k = 0 \), decrease rapidly to zero with increasing \( k \). All other interband transitions are forbidden for any \( k \).

Experimental reflectivity spectra of stage 3 GAC [9] exhibit a strong structure near 0.56 eV which may correspond to the intervalence transition \( 3v \rightarrow 2v \) predicted in the present model at

\[
\hbar \omega = \sqrt{2} \gamma_1 = 0.53 \text{ eV}
\]

(for \( \gamma_1 = 0.377 \text{ eV} \) [7]). As well-pronounced plasma edges with a low reflectance minimum are observed in the vicinity of 1 eV, we must exclude the occurrence in this region of interband transitions (contrarily to the case of pure graphite) which would completely smear out the plasma minimum. This observation implies that the onsets of the principal \((2v \rightarrow 2c, \ 3v \rightarrow 3c)\) valence to conduction transitions are located at higher energies, which leads to \( E_F > \sqrt{2} \gamma_1 \).

This condition is satisfied for a charge transfer coefficient of the same order of magnitude as those determined in I for stage 2 compounds.

The comparison of the model predictions in the case \( \delta = 0 \) with the experimental reflectivity data seems to be quite encouraging.

The assumption \( \delta = 0 \) is not satisfactory however from the point of view of the self-consistency of the model. The examination of the electron localization for valence band states proves that whatever the position of the Fermi level in the case \( \delta = 0 \), at least 1/4 of the total excess charge has to be localized on internal layers. Each hole in the bands \( 3v \) and \( 2v \) contributes a half of the elementary charge \( e \) to the charge on internal layers. As the total number of holes in these bands is always larger than the number of holes in the band \( 1v \), we get \( z > \frac{1}{4} \). With \( z = \frac{1}{4} \), and with the charge transfer \( f/l \) corresponding to \( E_F \gtrsim \sqrt{2} \gamma_1 \), one obtains from (9) the value

\[
2 \delta > 0.4 \text{ eV}
\]

which considerably differs from the starting value \( 2 \delta = 0 \).

The band structure for \( \delta = \gamma_1/3 \) and \( 2 \gamma_1/3 \) is shown in figure 2b and 2c.

With increasing \( \delta \), the valence band is pushed up and the number of holes localized exclusively in external layers increases. The band \( 2v \) acquires the camelback shape at small \( k \), crosses the band \( 1v \) at \( |x| = 2 \delta \) and becomes practically linear for larger \( k \). The band \( 3v \) is slightly pushed down and the number of holes in this band decreases. The distance between the bands \( 3v \) and \( 2v \) varies from \( \sqrt{2} \gamma_1 + \delta^2 - \delta \) at \( k = 0 \) to \( \sqrt{2} \gamma_1 + 4 \delta^2 \) at large \( k \) where both bands become parallel. As long as \( \delta \) remains smaller than \( \gamma_1/2 \), the optical properties of the system are not very different from the case \( \delta = 0 \). The transition probabilities, plotted in figure 3, are quite similar for \( \delta = \gamma_1/3 \) and \( \delta = 0 \). The modifications of the optical spectrum result mainly from the change in the dispersion laws. The bands \( 2v \) and \( 3v \) are no longer parallel, and the absorption peak at \( \hbar \omega = \sqrt{2} \gamma_1 \) is now replaced by the absorption band ranging from about \( \sqrt{2} \gamma_1 + 0 \delta^2 - \delta \) to about \( \sqrt{2} \gamma_1 + 4 \delta^2 \) (the accurate values of the energy limits being dependent on the hole Fermi energy \( E_F \)). The absorption increases rapidly in the vicinity of the upper energy limit, i.e. for transitions between almost parallel bands and the asymmetric absorption peak is expected slightly below \( \sqrt{2} \gamma_1 + 4 \delta^2 \) which equals 0.56-0.57 eV for \( \delta = 0 \).

In figure 4, we present the results of the approximate iterative calculations of \( 2 \delta \) and \( z \) as a function of the charge transfer \( f/l \) for the 3rd stage. The approximations consist in the assumption that the essential contribution to \( z = \frac{I}{2 f} (e_3 + e_4) \) comes from the vicinity of the points \( U \) and \( U' \) of the B.Z. Consequently, we have neglected the overlaps and we calculated the linear combination coefficients \( a_i \) with the use of eq. (3). To get analytical formulae for these coefficients and band energies, we assume

\[
2 \delta_1 = 2 \delta_2 = 0.
\]

The solid and broken lines in figure 4 correspond to two values of \( \gamma_0 \), 2.4 eV and 3.12 eV [1], respectively. If the charge transfer is the same as in the 2nd stage compounds studied in I, the expected value of \( 2 \delta \) will be 0.24-0.28 eV for Br3, 0.25-0.32 eV for ICl and SbCl3 and 0.35-0.42 eV for AsF5-graphite. (The lower and the upper limit corresponds to \( \gamma_0 = 3.12 \text{ eV} \) and \( 2.4 \text{ eV} \) respectively.)
The two values of \( z \) obtained here are smaller than those obtained for the same charge transfer in third stage by Pietronero et al. [4]. The detailed comparison is not instructive because these authors used the unrealistically large value 5.4 for the background dielectric constant (see the discussion on the dielectric constant in the Appendix).

These roughly estimated values of \( 2 \delta \) are in most cases not far from the value of \( 2 \delta = 0.2-0.22 \) eV, which reproduces exactly the experimental absorption peak position. The only exception is the AsF₅-graphite, for which \( 2 \delta \) is much larger than for other compounds, and consequently the intervalence transitions are expected at higher energies. This last conclusion disagrees with the data of Hanlon et al. [10] who observed in the 3rd stage of AsF₅ graphite the reflectivity minimum at 0.56 eV.

4. 4th stage. — In the new basis \( \omega_j^\pm (j = 1, 2, 3, 4) \) related to \( u_{jk} \) (\( j = 1, 2, ..., 8 \)) by:

\[
\begin{align*}
\omega_1^+ &= \frac{1}{\sqrt{2}} (\pm u_{3k} + u_{7k}), \\
\omega_2^+ &= \frac{1}{\sqrt{2}} \left( \pm \frac{x^*}{|x|} u_{2k} + \frac{x}{|x|} u_{6k} \right), \\
\omega_3^+ &= \frac{1}{\sqrt{2}} (\pm u_{3k} + u_{5k}), \\
\omega_4^+ &= \frac{1}{\sqrt{2}} \left( \pm \frac{x}{|x|} u_{4k} + \frac{x^*}{|x|} u_{6k} \right).
\end{align*}
\]

Eq. (4) factorizes into the product of two \( 4 \times 4 \) determinants

\[
\det \begin{bmatrix}
\delta + \delta_2 - E & - |x| \\
- |x| & \delta - \delta_1 - E \\
\gamma_1 & 0 \\
0 & 0
\end{bmatrix} = 0. \tag{11}
\]

Even for \( \delta_1 = \delta_2 = 0 \), eq. (11) can not be solved analytically unless \( \delta = 0 \). Both equations are however biquadratic with respect to \( |x| \) and the \( |x| \) values for fixed \( E \) can be calculated. The figure 5a, b, c shows the band structures for the arbitrarily chosen values \( \delta = 0, \gamma_1/2, \gamma_1 \) respectively (with \( \delta_1 = \delta_2 = 0 \)). The wavefunctions for the «+» and «-» bands are linear combinations of the functions \( \omega_1^+ \) and \( \omega_1^- \) respectively. For typical values of the charge transfer considered above, the valence band \( 2\nu^- \) is completely

![Fig. 5. — Band structure near the U point in the fourth stage GAC \((|x| = \frac{2}{3} \gamma_0 b\bar{k})\). a) \( \delta = 0 \); b) \( \delta = \gamma_1/2 \); c) \( \delta = \gamma_1 \).](image-url)
filled whatever the value of $\delta$ and the hole Fermi energy shown schematically in figure 5 is smaller than in the 3rd stage.

In the case $\delta = 0$, the distances between parallel bands are $\sqrt{5} + \frac{1}{2} \gamma_1$ for $1v^+$ and $2v^-$; $\sqrt{5} - \frac{1}{2} \gamma_1$ for $1v^-$ and $2v^+$. The interband transition $2v^+ \rightarrow 1c^+$, $2v^- \rightarrow 1c^-$ and $2v^- \rightarrow 1v^+$, $2v^+ \rightarrow 1v^-$ are allowed at $k = 0$ but their probabilities decrease rapidly with increasing $k$. The probabilities for the transitions between symmetrical bands $1v^+ \rightarrow 1c^-$, $2v^+ \rightarrow 2c^-$, $1v^- \rightarrow 1c^+$, $2v^- \rightarrow 2c^+$, forbidden at $k = 0$, increase rapidly with $k$ and tend to the probability of interband transitions in 2D graphite for large $k$. All other interband transitions are strictly forbidden for all $k$ values.

The analysis of the wavefunctions shows that the carriers in all bands are partially localized on both external and internal layers. Each hole in the bands $1v^+$ and $2v^-$ contributes the charge $e \left(1 + \frac{1}{\sqrt{5}}\right)$ to the excess charge on the internal layers. The hole in the bands $1v^-$ and $2v^+$ contributes the charge

$$e \left(1 - \frac{1}{\sqrt{5}}\right).$$

Consequently for $\delta = 0$, the fraction $z$ of charge localized on internal layers is even higher than in the 3rd stage. Thus, in view of eq. (10), the case $\delta = 0$ has to be excluded and one can expect for the 4th stage higher values of $\delta$ than for the 3rd stage.

For $\delta \neq 0$, the valence bands $1v^+$ and $1v^-$ acquire the camelback shape for small $k$. For larger $k$, the distance between both bands decreases and the dispersion relations for both bands can be reasonably approximated by $E = \delta - |x|$, as if the holes in both bands were entirely localized on external layers, decoupled from the interior of the system.

For $\delta < \gamma_1/2$, the bands $1v^+$ and $1v^-$ are degenerate at $k = 0$. For $\delta > \gamma_1/2$, a finite gap between both bands appears but at the same time $1v^-$ becomes degenerate at $k = 0$ with the band $2v^+$.

For finite $\delta$, all interband transitions become allowed for a general value of $k$. One can expect however two strong absorption peaks resulting from the transitions between quasi parallel valence bands with the finite states above the Fermi level. For $\delta = \gamma_1/2$, the peak positions should be at about $0.37$ eV and $0.74$ eV. The last energy coincides well with the structure observed [9] in several 4th stage GAC. (The region below $0.5$ eV has not been experimentally studied in most compounds.) In addition, weaker structures are expected at about $0.35$ eV and $0.91$ eV which result from the transitions $2v^- \rightarrow 1v^-$ and $2v^- \rightarrow 1c^-$ near $k = 0$. As in the case of the 3rd stage, the actual experimental data [10] for AsF$_5$-graphite cannot be explained within the present model.

5. Concluding remarks. — The present model involves numerous simplifying assumptions and approximations. Nevertheless, it allows us to explain several optical properties of stages 3 and 4 GAC in the near IR and visible regions. The charge transfer coefficients $f/l$ involved are quite comparable to those deduced previously for the lowest stage compounds [1] leading to hole Fermi energy of the order of $0.5$ eV. Consequently the strong interband absorption from valence to conduction bands, dominating the spectrum of pure graphite, is now shifted in the photon energy range $\hbar \omega > 2 E_F$. This allows us to observe well pronounced plasma edges below this threshold.

The interband transitions at lower energies between the quasi parallel valence bands explain some resonant structures observed below the plasma edges. The model, however, does not explain the reflectivity structure positions observed by Hanlon et al. [10] in AsF$_5$-graphite.

The inclusion of electrostatic effects induces important modifications of the band structure which should be reflected in both magnetoreflectivity and magneto-transport phenomena. For $\delta \neq 0$, one can expect — even for relatively large transfer coefficient — the existence of interband transitions in the low energy region.

These intervalence transitions ($3v \rightarrow 2v$ for stage 3, $2v^+ \rightarrow 1v^-$ for stage 4), occurring near $k = 0$, with the final states in the camelback region, may give rise in an applied magnetic field to low energy oscillatory magnetoreflectivity spectra. These transitions may be invoked in order to explain the experimental observation reported by Mendez et al. [11]. The low energy onset and the shape of the expected absorption depend however crucially on the exact position of the Fermi level with respect to the valence bands at $k = 0$. This position and the whole band structure at small $k$ are very sensitive functions of all model parameters, in particular to $\delta_1$ and $\delta_2$ which we neglected in our simplified treatment.

The present model also predicts the coexistence of large and small frequencies of magnetotransport oscillations, without any Brillouin zone folding effects. Due to the potential energy difference originating from electrostatic effects, between external and internal layers, the predominant majority of holes occupy the states of the two upper valence bands.

The corresponding wavefunctions are mainly localized on the external layers. The Fermi level intersects these bands in the region where their dispersion relations $E(k)$, almost linear, are very similar. Consequently, the highest frequencies are practically insensitive to the small parameters $\delta_1$ and $\delta_2$. For the typical values of $f/l$ reported in I for SbCl$_3$ — and halogens — graphite compounds, the expected values of the highest frequencies are in the range $5 \times 10^6$ G (for $\gamma_0 = 2.4$ eV) or $3 \times 10^6$ G (for $\gamma_0 = 3.12$ eV) and should be almost independent of stage for $n \geq 3$. These values compare well with the largest experimen-
natural frequencies of MTO observed by Batallan et al. [12] in several GAC. The lower frequency corresponding to the lowest populated valence band (3v in stage 3, 2v⁺ in stage 4) should vary with the stage and depend drastically on the exact position of the Fermi level and the parameters δ₁, δ₂.

APPENDIX

Polarization effects in graphite and GAC. — In the absence of external fields, the macroscopic electric field in GAC vanishes. Nevertheless, due to the excess charge on graphite layers, the carbon atoms are in general strongly polarized along the c-axis and the polarization state changes rapidly from one layer to another.

We performed the computer analysis of the electric field at various distances from the 2D hexagonal Bravais lattice of point charges. The analysis shows that, already at distances larger than the lattice constant a, the field is highly uniform, the relative field variations do not exceed one percent and drop below 10⁻⁴ at distances larger than 1.5 a. In graphite, the distance d = 3.35 Å between the layers is considerably larger than both the lattice constant a = 2.46 Å and the spatial extent of the 2p atomic functions of carbon. One can thus conclude that, whatever the detail of the charge distribution, the electric field produced by the charged graphite layer acting on atoms of adjacent layers can be approximated by the uniform field

\[ E = 2 \pi e \sigma_e \]  \hspace{1cm} (A.1)

where \( \sigma_e \) is the surface density of the excess charge on the layer.

One can expect that the local polarization properties of the graphite layers are determined essentially by the atomic properties of the carbon atoms modified by the relatively strong interactions between the nearest neighbour atoms in the layer. The effect of weak short range interlayer interactions and of the excess charge on the layers are secondary and will be neglected. Note that the excess charge in GAC is always very small (< 10⁻²) in comparison with the total charge of electrons in the layer.

We consider first the crystal of pure graphite in an external electric field \( E_{\text{ext}} \) along the c-direction. (To leave aside the free carrier effects we assume that the frequency of \( E_{\text{ext}} \) is higher than the plasma frequency of free carriers in graphite.) In the case of spatially uniform field \( E_{\text{ext}} \), the induced dipole moment \( \sigma_d \) per unit surface of each graphite layer is given by the simple formula:

\[ \sigma_d = \frac{d(c - 1)}{4 \pi e} E_{\text{ext}} \]  \hspace{1cm} (A.2)

where \( e \) is the optical dielectric constant of graphite in the c-direction. Eq. (A.2) in general does not apply to the case of \( E_{\text{ext}} \) varying in space: the effective field acting on electric charges in the crystal is a non-local function of the perturbed charge density distribution. We show however that in graphite eq. (A.2) can be used to relate the dipole moment induced on a given layer to the electric field produced by the excess charge localized on the other layers. Our arguments are based on the classical model of localized dipole moments but the result seems to be more general that the model itself.

In the spatially uniform field \( E_{\text{ext}} \parallel c \) the local field \( E_{\text{loc}} \) acting on an atomic dipole in the layer \( z = 0 (z \parallel c) \) can be written as:

\[ E_{\text{loc}} = E_{\text{ext}} + E_{\text{dip}} \]  \hspace{1cm} (A.3)

where \( E_{\text{dip}} \) is the field produced by all other atomic dipoles in the crystal. \( E_{\text{dip}} \) can have two different values \( E_{\text{dip}}^A \) and \( E_{\text{dip}}^B \) at two nonequivalent sites A and B. As the nonequivalence between A and B sites originates only from the weak interlayer interaction we attribute the same polarizability \( \gamma \) to all atoms. The atomic dipole moments on the lattice sites A and B are therefore:

\[ P_A = \gamma E_{\text{loc}}^A, \quad P_B = \gamma E_{\text{loc}}^B \]  \hspace{1cm} (A.4)

The dipole fields \( E_{\text{dip}}^A \) and \( E_{\text{dip}}^B \) are linear functions of \( P_A \) and \( P_B \) with the coefficients \( C_{ij} \) determined solely by the crystal structure. We calculated these coefficients by the direct computer summation of electric fields produced by the atomic dipoles in consecutive graphite layers \( z = 0, z = \pm d, \) etc. For each layer, the summation was carried up to 600th nearest neighbours (5 665 atoms). For more distant regions of each layer the continuous approximation was adopted. (The same method was also used to calculate the coefficients in eq. (7).)

It turned out that all layers, except \( z = 0 \), behave as if the dipole moments were uniformly smeared out and produce almost no electric field in \( z = 0 \) plane. This is due to the large interlayer distance as compared to the interatomic spacing in the layer. The total contribution to \( C_{ij} \) from all \( z \neq 0 \) layers represents about \( 10^{-3} \) of the total value of \( C_{ij} \) and can be practically neglected. One gets \( C_{AA} = C_{BB}, \quad C_{AB} = C_{BA} \) and consequently \( P_A = P_B \). In the uniform field \( E_{\text{ext}} \parallel c \) the polarization state of a graphite layer is not affected by the existence of other layers.

Now, consider the case of electric field \( E_{\text{ext}}(z) \parallel c \parallel z \) varying from one layer to another but independent of \( x \) and \( y \) coordinates. The induced dipole moments are then different in each layer but the dipole field \( E_{\text{dip}} \) is still almost exclusively determined by the dipole moments localized in one layer. The dipole moment in each layer depends only on the local value of external field \( E_{\text{ext}}(z) \). This dependence is identical as in the case of a spatially uniform field \( E_{\text{ext}} \) and eq. (A.2) can be applied.
The above result is a direct consequence of the strong anisotropy of the graphite lattice. For a cubic crystal the formula (A.2) is rigorously restricted to the case of uniform electric fields because the calculation of $E_{\text{dip}}$ involves at least three layers.

Eqs. (A.1) and (A.2) allows us to relate the surface densities $\sigma_4$ of dipole moments in GAC to the surface densities $\sigma_0$ of the excess charge on different layers. Let $\sigma_{c1}$ and $\sigma_{c2}$ denote the surface charge densities on the external and internal layers, respectively. For the third stage compound the surface density $\sigma_{d1}$ of dipole moments induced on external layers is then:

$$\sigma_{d1} = \pm \frac{d(e - 1)}{2e} (\sigma_{c1} + \sigma_{c2}). \quad (A.5)$$

For the fourth stage compound

$$\sigma_{d1} = \pm \frac{d(e - 1)}{2e} (\sigma_{c1} + 2 \sigma_{c2}) \quad (A.6)$$

and

$$\sigma_{d2} = \pm \frac{d(e - 1)}{2e} \sigma_{c2} \quad (A.7)$$

for external and internal layers, respectively.

There are few measurements of the dielectric function of graphite in the c-direction. From direct measurements of the reflectivity for light polarized along the c-axis, Venghaus [13] obtained the value $\varepsilon = 5.4$. This value has been recently contested by Zanini et al. [14] who established that $\varepsilon$ is lower than 3.2.

The dipole field $E_{\text{dip}} = (C_{AA} + C_{AB}) P$ resulting from our computer calculation can be expressed in the form:

$$E_{\text{dip}} = - C \frac{4\pi}{3} NP$$

where $N$ is the number of atoms per unit volume and $C = 4.81$ is the constant dependent on the lattice geometry. From eqs. (A.2) and (A.3) one obtains the relation between the dielectric constant $\varepsilon$ and the atomic polarizability $\gamma$:

$$\varepsilon = \frac{1 + C(4\pi N\gamma/3)}{1 + (C - 3)(4\pi N\gamma/3)} \quad (A.8)$$

For cubic crystals $C = 2$ and (A.8) is equivalent to the Clausius Mossotti formula. In the case of graphite, independently of the value of $\gamma$, we obtain the inequality

$$\varepsilon \leq \frac{C}{C - 3} = 2.66$$

which is well consistent with the value $\varepsilon = 2.34$ but is in contradiction with $\varepsilon = 5.4$.

References