

AsF₅-INTERCALATED GRAPHITE:
SELF-CONSISTENT BAND STRUCTURE, OPTICAL PROPERTIES AND STRUCTURAL ENERGY

G. Campagnoli ^{a)*} and E. Tosatti ^{b)}

a) Laboratory of Inorganic Chemistry
University of Groningen
The Netherlands
and
Istituto di Fisica
University of Pavia, Italy

b) GNSM-CNR, Istituto di Fisica Teorica
University of Trieste
and
ICTP, Trieste, Italy

Calculations have been made of the electronic structure of a model stage-1 AsF₅-intercalated graphite, and of its optical and energy loss properties. Information is also obtained about total energy changes with respect to some distortions of the intercalated AsF₅ lattice.

I. Introduction

We report here preliminary results of a series of calculations of the electronic, optical and vibrational properties of a model acceptor graphite intercalate, as typified by stage-1 AsF₅-intercalated graphite. Their purpose is a) to set up a simple but self-consistent scheme to calculate the charge fraction on each different carbon site; b) to obtain the related band structure and Fermi surface of the intercalate (assumed to be ordered in some simple and plausible structure) including from first principles all intra- and inter-site electrostatic mean fields; c) to derive from this band structure an accurate frequency-dependent dielectric function, along with optical and energy loss properties for comparison with experiment; d) to get the total energy changes for (uniform and/or periodic) AsF₅-lattice deformations, thus allowing a first-principles evaluation of some interesting phonon frequencies, as well as of the stability of the assumed structure. The main novelty of the calculation - as compared to other recently published approaches [1,2] - is in its self-consistency. This does involve solving a few rather delicate problems [3], but it has much more predictive power, and no less simplicity, which renders it preferable for many purposes. As in previous calculations [1,2] the principal adjustable parameter of the theory is the average electron fraction f transferred to each AsF₅ molecule. This we cannot calculate, as the intercalated molecule is not described in any detail, being just represented by one orbital located between the graphite layers. The value of f is fixed, as in [1], by comparison of our optical results with reflectance experiment [4], yielding $f = 0.4$, as discussed later on.

II. Model and Calculations

We assume a C₈X (2a × 2a × c) superlattice, with $a = 2.46 \text{ \AA}$ and $c = 8.1 \text{ \AA}$ [5], and each X molecule (X stands for AsF₅) sits in the hollow between adjacent carbon layers (see Fig.(1)). Questions have been raised about the detailed validity of this geometry [6], but no better model seems to exist to date. To some extent, indications as to what a better structure might be like could come precisely as a result of calculations of this type. Our electronic structure assumes one p_z-like π -orbital per carbon, ϕ_i ($i = 1, \dots, 8$) and one orbital ϕ_x for the intercalated molecule. A Huckel-type hopping $\beta = -2.3 \text{ eV}$ [7] is taken

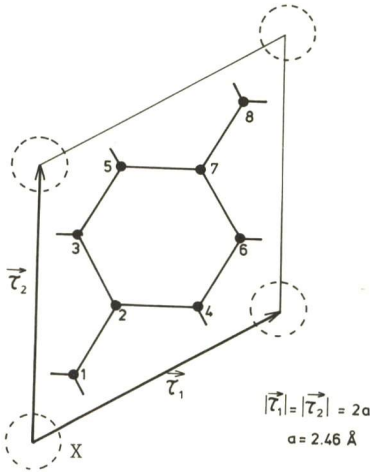


Fig.1 C_8X geometry: The carbon sites are numbered 1 to 8

between first-neighbour carbons, while hopping between C and X, X and X, and C's on different layers is neglected. The function φ_x is supposed to be such that the charge f is concentrated in two point-like lumps $f/2$, located at $(0,0,\pm h)$, with the distance from the graphite plane h taken to be ≈ 2 Å from geometrical considerations. The electron unbalance on each C-atom

$$\rho_i = \sum_{k\ell, \text{occupied}} |\langle \psi_{k\ell} | \varphi_i \rangle|^2 - 1 \quad (1)$$

(here $\psi_{k\ell}$ denotes a Bloch function) distinguishes two types of sites, $\rho_1 = \rho_3 = \rho_4 = \rho_5 = \rho_6 = \rho_8$ and $\rho_2 = \rho_7$, with $6\rho_1 + 2\rho_2 = -f$. The π -electronic structure is calculated by diagonalizing an (8×8) matrix, where each diagonal element is

$$\mathcal{H}_{ii} = -e\rho_i \sum_j V_{ij} + (1/2)\rho_i U \quad (2)$$

where $\sum_j V_{ij}$ is a Madelung-type lattice sum (each $|\varphi_i(r)|^2$ is supposed to be point-like, for this purpose), and U is an on-site energy, fixed at 10.96 eV [8]. One delicate point is the screening of V_{ij} due to the σ -orbitals [3], which are otherwise left out of the calculation. The φ_x level is decoupled from the φ_i 's and will be flat and pinned at E_F , if f is different from 0 or 2.

The self-consistent cycle consists of assuming $\rho_i = -f/8$; calculating $\mathcal{H}_{ii}$ from eq.(1) and diagonalizing (the only k -dependence comes from off-diagonal terms proportional to β); finding the Fermi level E_F with $8-f$ electrons in the π -bands; recalculating ρ_i from eq.(1) and iterating to convergence.

III. Electronic Structure

We obtain, for $f = 0.4$, the self-consistent charges $\rho_1 = -0.06$ and $\rho_2 = -0.02$. This should reflect, e.g., in a core-level difference between two types of carbons. The corresponding π -band structure of Fig.(2) is rather close to the folded-in 2-d bands of pristine graphite [7]. (Note, however, the δ -function-like X level pinned at E_F .) There is an overall shift of the bands of ~ 0.25 eV and a splitting of the saddle-points, due to two different carbons, by somewhat less than this amount.

IV. Optical Properties

For $\omega < 10$ eV, our optical dielectric function ($q \rightarrow 0$) is taken to be

$$\epsilon(\omega) = \epsilon_\pi(\omega) + \frac{4\pi n_\sigma e^2/m}{\omega^2 - \omega_\sigma^2 - i\omega\gamma} \quad (3)$$

where $n_\sigma = 3$ electron/carbon, $\omega_\sigma \approx 13$ eV [7]. The complex $\epsilon_\pi(\omega)$ is calculated numerically by expressing the k -dependent $\tilde{P}$ matrix element exactly through the f -sum rule [3]. Its imaginary part has a Drude-like intraband piece as well as an interband term both apparent in Fig.(3). The calculated low-frequency normal reflectivity is shown on Fig.(4) for a few values of the charge transfer parameter

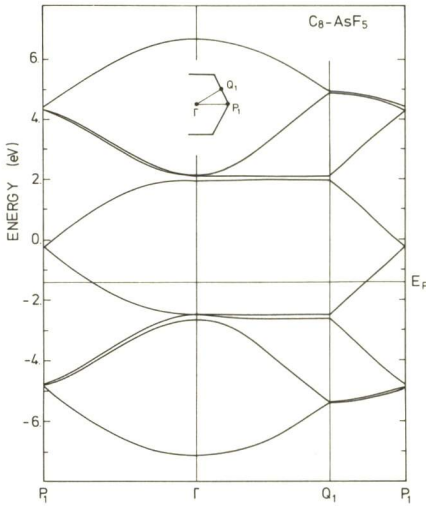


Fig.2 Band structure of our model intercalate, for $f = 0.4$

f . Comparison with experiment⁵ suggests for stage 1 AsF₅ intercalated graphite $f = 0.4 \pm 0.02$. This is basically the same value found in [1], but it is substantially larger than 0.24 as suggested by ESR [9]. Finer modifications of the true band structure from that of Fig.(2) near E_F , due to some structural distortion and/or disorder might well account for this disagreement. However, our result hardly depends on any such details and should constitute a much more reliable evaluation of the average charge transfer.

The energy loss function $-\text{Im } \epsilon^{-1}(\omega)$ has also been calculated. The π -plasmon of pristine graphite is shifted from 7 to 6.5 eV. A new intraband plasmon similar to that observed in C_6FeCl_3 [2] is predicted for C_8AsF_5 at ± 1.5 eV.

V. Energy Change with Lattice Distortion

The total electronic energy is, in our approximation,

$$E_{\text{tot}} = fE_F + 2 \sum_{k \text{ occ}} \epsilon_k - \frac{1}{2} \sum_{i=1}^8 \rho_i \sum_j V_{ij}, \quad (4)$$

where $i = 1, \dots, 8$ denotes carbon sites, $i = 9$ is the X-site, and j runs over all sites in the crystal. Here fE_F accounts for the one-electron energy of the charge localized on the X-molecule.

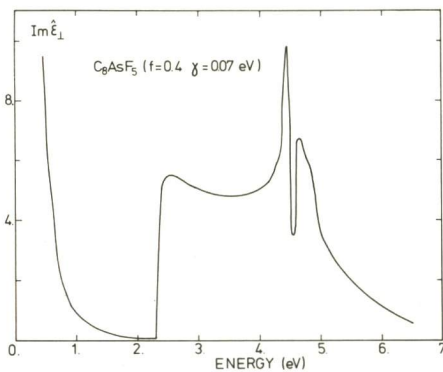


Fig.3 Imaginary π -dielectric function: Note the sharp Fermi edge at 2.3 eV, and the split $\pi \rightarrow \pi^*$ peak at 4.6 eV

This energy can be used to calculate phonon frequencies and also to judge on stability of the structure assumed. So far, we have tried only to change the position of the X centre-of-mass from the central hollow site $(0,0,c/2)$ to off-centre $(\delta,0,c/2)$ and $(0,\delta,c/2)$. An energy increase $\Delta E_{\text{tot}} = \frac{1}{2} k \delta^2$ is obtained, with $k \approx 2 \times 10^4 \text{ g} \cdot \text{sec}^{-2}$ for $f = 0.4$. From $\omega^2 = k/M_{\text{AsF}_5}$ we estimate about 5.5 meV for the frequency of an (optically active) phonon where the AsF₅ layers vibrate along (x,y) out of phase with the graphite layers. This $q = 0$ value corresponds of course only to an average between actual longitudinal and transverse frequencies at $q \rightarrow 0$.

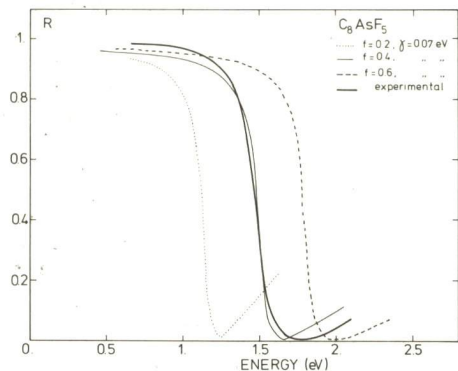


Fig.4 Calculated normal reflectivity for C_8-AsF_5 . The experimental curve is shown for comparison

Interestingly, this is precisely the main superlattice feature seen by X-rays⁶. It seems also possible that a partial Fermi-surface assisted disproportionation, of which the proposed $3AsF_5 \rightarrow AsF_3 + 2AsF_6$ represents an extreme limit, could take place. The intricacies of the new Fermi surface expected for this situation will be investigated in subsequent work.

Our approach is also suitable for a study of stability of superlattice distortions, which we are presently planning. For the time being, qualitative indications as to what kind of superlattice might be favored can be extracted from the (undistorted) Fermi surface. As can be readily argued from Fig 2, this consists of six carbon hole cylinders centered at P_1 , plus one AsF_5 electron cylinder centered at Γ . (These electrons are localized in the present approximation, but would become spread into a narrow band by a small X-X or C-X hopping). This Fermi surface has considerable $\Gamma \rightarrow P_1$ electron-hole nesting, suggesting a $\sqrt{3} \times \sqrt{3}$ charge-density wave superlattice.

References

- * Work supported by the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (ZWO).
- 1) J. Blinowski, Nguyen Hy Hau, C. Rigaux, J.P. Vieren, R. Le Toullec, G. Furdin, A. Herold and J. Melin: J. Physique 41 (1980) 47.
- 2) J.J. Ritsko and E.J. Mele: Physica 99 B+C (1980) 425.
- 3) G. Campagnoli and E. Tosatti: to be published.
- 4) L.R. Hanlon, E.R. Falardeau, D. Guerard and J.E. Fischer: Mat. Sci. Eng. 31 (1977) 161.
- 5) E.R. Falardeau, L.R. Hanlon and T.E. Thompson: Inorg. Chem. 17 (1978) 301.
- 6) N. Bartlett, B. McQuillan and A.S. Robertson: Mat. Res. Bull. 13 (1978) 1259.
- 7) F. Bassani and G. Pastori Parravicini: Electronic States and Optical properties in Solids, Pergamon Press (1975), Ch. 4 & 5, and references therein.
- 8) R. Pariser: J. Chem. Phys. 24 (1956) 250.
- 9) B.R. Weinberger, J. Kaufer, A.J. Heeger, M.J. Moran, J.E. Fischer and N.A.W. Holtzwarth: Phys. Rev. Letters 41 (1978) 1417.