BAND THEORY OF PYROCARBONS AND COKES

by Oscar GONZALEZ* and Alphonse CHARLIER

Laboratoire de Physique du Solide, Université de Metz (France)

I. Introduction.

We present a two dimensional model which gives good agreement with observed experimental results [1] on pyrocarbons and cokes near the graphitization zone.

It is based on Wallace's [2] calculations, supplementary terms are provided by including overlapping integral between nearest neighbouring atoms and exchange integral between second neighbouring atoms in the layer.

II. Energy.

By linear combination of Bloch atomic orbitals we construct the following secular determinant

$$0 = \begin{vmatrix} E_0 - \gamma_0' f(k) - E & F(k)(E_0 S_{AB} - \gamma_0 - E S_{AB}) \\ (E_0 S_{AB} - \gamma_0 - E S_{AB}) F^*(k) & E_0 - \gamma_0' f(k) - E \end{vmatrix}$$

The energy values obtained by determinantal resolution, the energy E_c and the dispersion formula near the corner of the first Brillouin zone are respectively :

$$E(k) = E_0 \pm \frac{\gamma_0 |F(k)| \mp \gamma_0' f(k)}{1 \mp S_{AB} |F(k)|}$$

$$E_c = E_0 + 3\gamma_0'$$

$$|E - E_c| = \pm \frac{(9\gamma_0' S + \gamma_0)\sqrt{3}\pi a |k - k_c|}{1 - 3a\sqrt{3}\pi S |k - k_c|}$$

III. State's density.

The number of electronic states in the energy interval dE is

$$N(E) = \frac{4Am}{27\pi a^3 S^2}\left(\frac{|E - E_c|}{\frac{1}{m} + |E - E_c|}\right)$$

$$m = \frac{3S}{9\gamma_0' S + \gamma_0}$$

this seems to be a reasonable curve intermediate between the Wallace's theoretical linear form and the Coulson more experimental one.

IV. Electrical conductivity

In order to estimate the electrical conductivity parallel to the graphitic layer, the general current density

$$\vec{j} = 2e \int \vec{v} f(\vec{k}) d^3k$$

and the Fermi-Dirac distribution function :

$$f(\vec{k}) = f_0 + g(\vec{k})$$

f_0 undisturbed function

$$g(\vec{k}) = -\frac{e\tau}{\hbar c} \vec{\varepsilon} \cdot \vec{\nabla}_k f_0 \qquad \text{supplementary}$$

term due to applied electrical field, are used and lead us to

$$\vec{j} = -\frac{4e^2\tau}{\hbar^2 c} \int \frac{\partial f_0}{\partial E}\left[\int (\vec{\nabla}_k E)(\vec{\varepsilon} \cdot \vec{\nabla}_k E)\frac{d\sigma_k}{|\vec{\nabla}_k E|}\right] dE$$

After integral evaluations we obtain

$$\sigma_{//} = \frac{16\pi e^2 \tau KT}{\hbar^2 c}\left[\log 2 - m\pi KT\right]$$

This result may be regarded as the sum of two terms : Wallace's one and a supplementary correction $\Delta\sigma_{//}$ with

$$\Delta\sigma_{//} = -\frac{48\pi^2 e^2 \tau (KT)^2 S}{\hbar^2 c (9\gamma_0' S + \gamma_0)}$$

A theory of the mean free path has been given by Mott and Gurney [3] ; according to this calculation

$$\tau = \frac{\ell}{v} \qquad \ell = C\left(\frac{T}{\theta}\right)^{1/2}\left(e^{\frac{\theta}{T}} - 1\right)$$

θ is the Debye temperature of the sample.

The agreement with experimental measurements is good if we assume a dependance between high temperature treatment and the Debye temperature

V. Diamagnetic susceptibility.

The value of the diamagnetic susceptibility is obtained by a similar procedure as that used by Mc Clure.

$$\chi = \chi_{\text{Mac Clure}} \left(1 + \frac{9 \gamma_0' S}{\gamma_0} \right)^2$$

$$\chi_{\text{Mac Clure}} = - \frac{0,010}{T} \, \text{sech}^2 \frac{\xi}{2KT}$$

The comparaison with Ganguli and Krishnan's [4] experimental results permits the evaluation of the parameter γ_0' ; the numerical value is 0,02 eV.

VI. Conclusion.

This rough theoritical model may be completed with better calculation of the relaxation time and its dependance with graphitization.

VI. References.

(1) KLEIN C.A, J. of App. Phys. 33,11, (1962)
SHARMA S.K., SEN GUPTA. S.K, J. Sci. Industr. Res. Vol 20 D, 247-251 (1961)

(2) WALLACE P.R., Phys. Rev. 71, 9, 622-634 (1947)

(3) MOTT & GURNEY Electronic Processes in Jonic Crystals, 107, University Press

(4) MAC CLURE J.W, Phys. Rev 104, 666-671 (1956)

* Present adress "Universidad de Oriente", Physics Department
CUMANA (Sucre) VENEZUELA