# Electronic Density of States of Graphite

John E. Hove

# Electronic Density of States of Graphite*

JOHN E. HOVE

*Nuclear Engineering and Manufacturing, North American Aviation,
Inc., Downey, California*

(Received January 10, 1955)

I T has been shown by Carter and Krumhansl[1] that the electronic density of states of graphite near the top of the filled band is asymmetric about the energy where this band touches the next, unfilled, band. This conclusion is based on a modification of the Wallace[2] band structure. This modification consists of recognizing the difference in the number of neighbors between the four atoms in the unit cell and thus assigning two of Wallace's diagonal matrix elements a different value than the other two. The discontinuity of the density of state at the band edge is proportional to the difference $(H_{11}-H_{22})$ and if this is large enough (greater than $2\gamma_1$) the bands need not touch at all. It should be mentioned that asymmetry in the energy contours is a necessary feature to explain the sizeable negative Hall coefficient.[3]

The purpose of the present note is to point out that the effect of including next-nearest neighbors (in the basal plane) is to introduce an asymmetry in the density of states in the same qualitative fashion as above. Next-nearest neighbors in the plane are easily taken into consideration and, in fact, Wallace[2] has already done so, although he neglects such terms when calculating the density of states. From reference 2, the energy of a state **k**, including nearest and next-nearest neighbors in the plane and nearest neighbors out of the plane, is:

$$\epsilon = -\gamma_1 \cos\tfrac{1}{2}ck_z \pm [\gamma_1^2 \cos^2\tfrac{1}{2}ck_z + \tfrac{3}{4}\gamma_0^2 a^2 \kappa_{xy}^2]^{\frac{1}{2}} - \tfrac{3}{4}\gamma_0' a^2 \kappa_{xy}^2. \quad (1)$$

Here $\kappa_{xy}^2 = \kappa_x^2 + \kappa_y^2$, where $\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}$(corner), $\epsilon$ is measured from the band edge, and $\gamma_0$, $\gamma_0'$, and $\gamma_1$ are the resonance integrals involving coplanar nearest and next-nearest and interplanar nearest neighbors, respectively. The only effect of including $\gamma_0'$ is a term in $\kappa_{xy}^2$. In the two-dimensional approximation ($\gamma_1 = 0$) the $\gamma_0'$ term does not affect the density of states to a first order.

However, when $\gamma_1$ is retained, the terms in $\gamma_0'$ and in $\gamma_0$ are of the same order for small $\kappa_{xy}$ and the density of states curve is altered markedly. The calculation for this case can be readily performed with the assumption that $\gamma_0' \ll \gamma_0$, which is certainly true. The result for the density of states per atom to a second order in the energy is given below, where $\eta_0 = \gamma_0'/\gamma_0$ and $\eta_1 = \gamma_1/\gamma_0$.

(1) For $0 < \epsilon < 2\gamma_1$,

$$N(\epsilon) \simeq \frac{2\gamma_1}{\sqrt{3}\pi^2\gamma_0^2}\left[1 + \frac{\pi}{2}\eta_0\eta_1 + \frac{\epsilon}{2\gamma_1}(\pi + 12\eta_0\eta_1)\right.$$
$$\left. + \left(\frac{\epsilon}{2\gamma_1}\right)^2 (\tfrac{3}{2} + 6\pi\eta_0\eta_1)\right]. \quad (2)$$

(2) For $-2\gamma_1 < \epsilon < 0$,

$$N(\epsilon) \simeq \frac{2\gamma_1}{\sqrt{3}\pi^2\gamma_0^2}\left[1 - \frac{\pi}{2}\eta_0\eta_1 + \frac{|\epsilon|}{2\gamma_1}(\pi - 12\eta_0\eta_1)\right.$$
$$\left. + \left(\frac{\epsilon}{2\gamma_1}\right)^2 (\tfrac{3}{2} - 6\pi\eta_0\eta_1)\right]. \quad (3)$$

The effect of $\gamma_0'$ is seen in Fig. 1. There is a discontinuity in $N(\epsilon)$ at zero and both its value and slope are less for the lower band. This is the same qualitative feature found by Carter and Krumhansl. The next-nearest neighbor effect may be of equal or greater importance than the effect of coordination number, although estimates of relative magnitude are difficult to make. It is, however, significant that these two modifications (dissimilar in nature) have similar effects on the density of states curve. This is probably a general property of the graphite lattice symmetry in that if the correct matrix elements were expanded in a Fourier series the above asymmetry would generally appear. The coefficients in the series would be disposable constants and not directly identifiable with any particular overlap integral by itself. The effects considered above and by Carter and Krumhansl would, however, be a major part of the first order coefficients. This change in the density of states is in the correct direction to explain the negative Hall coefficient.

The author would like to acknowledge discussions of this topic with J. A. Krumhansl.

[1] J. L. Carter and J. A. Krumhansl, J. Chem. Phys. **21**, 2238 (1953).
[2] P. R. Wallace, Phys. Rev. **71**, 622 (1947).
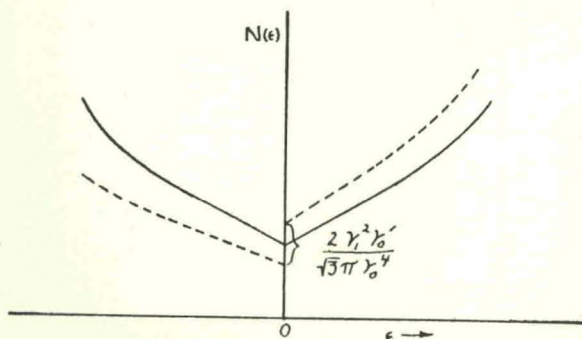[3] G. Hennig, J. Chem. Phys. **20**, 1438 (1952).



FIG. 1. The graphite density of states (the solid line is for $\gamma_0' = 0$).