Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 21 Mar 2007.

To cite this article: H. Chojnacki (1968): Temperature Dependence of Current Carriers Mobilities in Anthracene, Molecular Crystals, 3:3, 375-383

To link to this article: http://dx.doi.org/10.1080/15421406808083452

Molecular Crystals. 1968. Vol. 3, pp. 375–383

Printed in Great Britain

Temperature Dependence of Current Carriers Mobilities in Anthracene

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Received August 28, 1967; *Revised November* 8, 1967

Abstract—Components of the mobility tensor for electron and hole have been calculated in the tight binding approximation for 95°K and 290°K in anthracene crystal. The results for the temperature dependence of mobilities are in fair agreement with experiment. It follows from the performed calculations that, considering exchange effects, the application of the Hartree-Fock wave functions instead of those of the STO's (and possibly the potential of neutral hydrogens) should give good agreement with experiment for the anisotropy of the mobilities in both crystallographic planes.

In the study of semiconductivity of organic compounds made hitherto, anthracene is known as a model substance among the conjugated aromatic systems. The results of the study of its electrical conductivity[14, 15] indicate that in the cleavage plane (001) the conductivity is rather isotropic while in the (010) plane the current observed was 2.1–3.6-fold greater along the a axis than in the c' direction. The mobilities of current carriers are of the order of 1 cm^2/V sec at room temperature and appear anisotropic for holes and electrons both.[9–11] There are no complete data concerning the temperature dependence of anisotropy of current carriers for all crystallographic directions. It follows, however, from experiment that the dependence in question may be presented by the equation: $\mu = A.T^n$ with $0 > n > -3$.

The theoretical explanation of electronic transport processes in molecular organic solids appears to be a problem complicated by a number of subtle interrelated effects. The nature of interactions in a molecular crystal lattice, different in principle from that of inorganic semiconductors, renders the application of the band

model questionable. On the other hand, however, the band model in the tight binding approximation appears to be adequate in case of a narrow bandwidth leading to results which are not inconsistent with experiment[1,4] Calculations in such approximation were begun by LeBlanc[12] and later carried out for other compounds with the same crystal structures by Thaxton *et al.*[17] and Katz and collaborators.[6] Similar calculations have been made considering effects such as phonon-electron interaction,[2] exchange effects[16] and atomic polarization.[3]

One of the fundamental criteria for the applicability of a semiconductor model is the possibility of the theoretical prediction of the temperature dependence of current carrier mobilities. Until recently this problem for organic semiconductors has only been mentioned in the resonance transfer model[7] and it has been studied more exactly in the tunneling transfer.[8] The recent literature, however, dealing with organic semiconductors lacks calculations concerning the above-mentioned question using the tight binding approximation. Since complete X-ray data for anthracene at 95°K and 290°K have been published lately, it seemed desirable to perform calculations according to the one-electron approximation for both temperatures.

The numerical calculations were performed for 95°K and 290°K on the basis of Mason's crystallographic data.[13] In contrast with LeBlanc's calculations, allowance has been made for the existence of the two band branches corresponding to the two molecules per unit cell. In the calculations single Slater orbitals characterized by an orbital exponent of 3.08 were used. The molecular orbitals of a positive or negative ion were approximated by a linear combination of neutral carbon $2p_z$ wave functions with Hueckel coefficients without overlap. The two-center resonance integrals between the molecule in position 1 (Fig. 1) and, in contrast with most recent calculations, between the other molecules were calculated without approximation including all integrals between molecules containing carbon atoms closer than 10 Å from each other. Thus allowance was made for a number of integrals neglected in the LeBlanc method.[12]

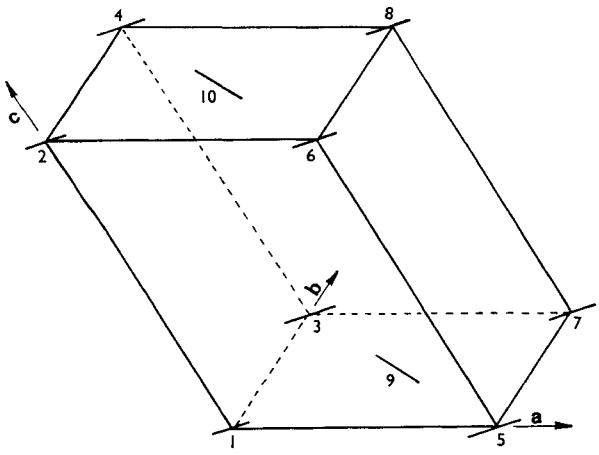

Figure 1. Schematic representation of the base-centered crystal structure showing the numbering of the molecules used in this paper.

The evaluated intermolecular resonance integrals (in units of 10^{-4} ev) are presented for both temperatures in Table 1. The components of the mobility tensor calculated in an orthogonal coordinate system for constant isotropic relaxation time are listed

TABLE 1. Intermolecular Resonance Integrals in Units of 10^{-4} eV

Molecule number	$T = 95°K$		$T = 290°K$	
	Hole	Electron	Hole	Electron
3	−3.81	17.57	−23.20	17.60
6	−0.19	−0.04	−0.10	−0.03
9	8.25	−32.74	−17.43	−25.00
10	−7.52	0.78	−1.69	−0.58

(in units of 10^{10} cm^2/sec^2) in Table 2. Table 3 shows the calculated anisotropies for holes and electrons and that of LeBlanc [12] and Silbey *et al.*[16] at 290°K. Here we also introduce for the sake of comparison the experimental values of anisotropy at 290°K after Kepler,[10] and in parentheses the results of anisotropy calculated

TABLE 2. Components of the Mobility Tensor in the Constant-free-time Approximation in Units of 10^{10} cm^2/sec^2.

Component	$T = 95°K$		$T = 290°K$	
	Hole	Electron	Hole	Electron
$\langle v_a v_a \rangle$	1.12	17.63	5.14	10.58
$\langle v_b v_b \rangle$	0.72	14.04	11.62	10.47
$\langle v_{c'} v \rangle$	4.27	0.05	0.22	0.03

TABLE 3 Calculated and Experimental Values of the Anisotropy of the Current Carrier Mobilities in Anthracene at 290°K

	Calculated						Experimental	
	Hole[a]	Electron[a]	Hole[b]	Electron[b]	Hole[c]	Electron[c]	Hole	Electron
μ_{aa}/μ_{bb}	0.52	1.13	0.39	2.6	0.44	1.01	0.67 (0.49)	1.55 (1.92)
$\mu_{c'c'}/\mu_{aa}$	0.25	0.0035	0.44	0.01	0.04	0.0025	0.67 (0.86)	0.24 (0.21)

[a] See ref. 12.
[b] See ref. 16.
[c] This paper.

TABLE 4 Calculated Values of the Anisotropy of the Current Carrier Mobilities in Anthracene at 95°K and 290°K

	$T = 95°K$		$T = 290°K$	
	Hole	Electron	Hole	Electron
μ_{aa}/μ_{bb}	1.55	1.26	0.44	1.01
$\mu_{c'c'}/\mu_{aa}$	3.81	0.0026	0.04	0.0025

by the least-square method based on the Kepler's other paper.[9] In Table 4 we display the calculated anisotropies of mobilities for both temperatures. In Table 5 are listed the theoretical and experimental values of n in the equation $\mu = A.T^n$. The excess

TABLE 5 Calculated and Experimental Values of n in the Equation $\mu = A.T^n$

Direction	Calculated		Experimental[9]	
	Hole	Electron	Hole	Electron
a	+1.37	−0.46	—	−0.68
b	+2.49	−0.26	—	−0.29
c'	−2.65	−0.50	−1.78	+0.22 (−1.10)

hole and electron band structures in reduced Brillouin zone are illustrated in the reciprocal crystal axis directions in Figs. 2–7.

It should be noted that for all crystallographic directions there is an appreciable effect of temperature on a bandwidth both for holes and electrons. This effect is most distinct along the a^{-1} and

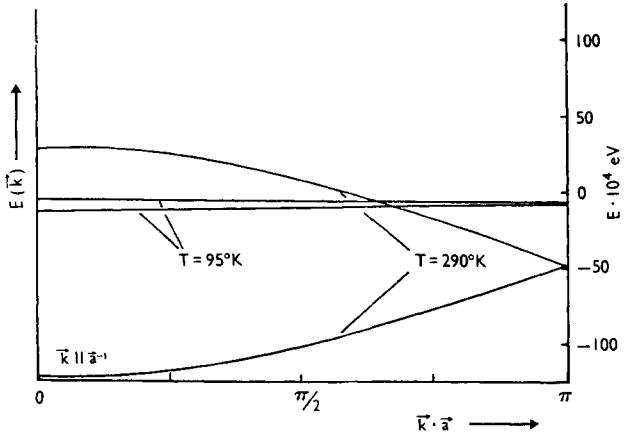

Figure 2. Shape of the excess hole band in the a^{-1} direction at 95°K and 290°K.

b^{-1} directions (Figs. 2–4) but at 95°K the hole bandwidth is extremely small. The widest band of the order 0.025 eV appears along the above directions for electrons (Figs. 3 and 5). As it can be seen from Fig. 6 the shape of the c^{-1} band for holes is distinctly dependent on temperature.

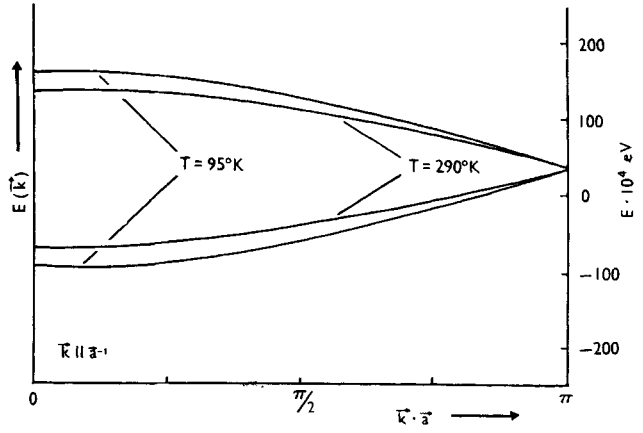

Figure 3. Shape of the excess electron band in the a^{-1} direction at 95°K and 290°K.

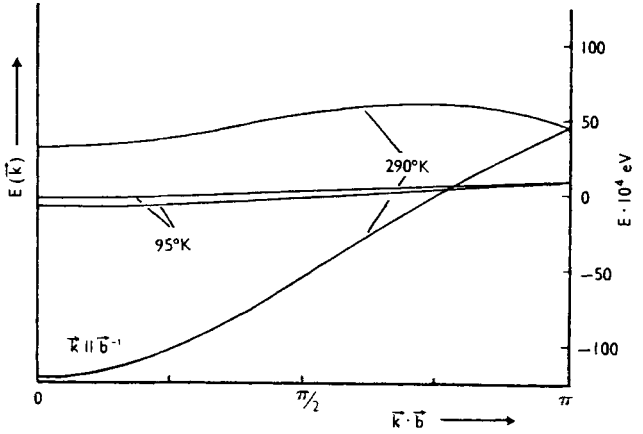

Figure 4. Shape of the excess hole band in the b^{-1} direction at 95°K and 290°K.

Comparing the values of the components of the mobility tensor calculated via several approximations[12, 6, 16, and this paper] with experimental data, as well as each with the other, the following conclusions can be drawn:

1. On the (001) plane reasonable values of anisotropy are obtained in all methods. Although the use of the SCF wave functions

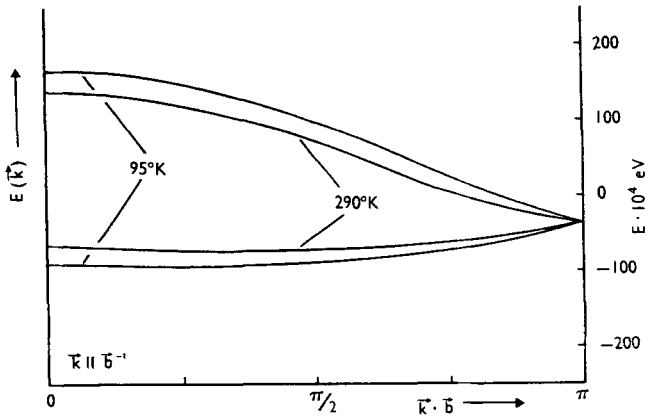

Figure 5. Shape of the excess electron band in the b^{-1} direction at 95°K and 290°K.

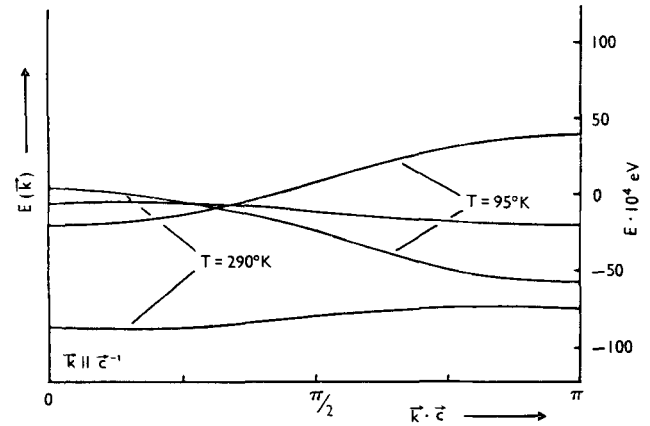

Figure 6. Shape of the excess hole band in the c^{-1} direction at 95°K and 290°K.

instead of the Slater ones is more justified, the correctness of the structural data seems to be of great importance. The results of our calculations based on the Slater orbitals differ from the experimental data to the same extent as those published by Silbey *et al.*[16] who used the SCF wave functions. This con-

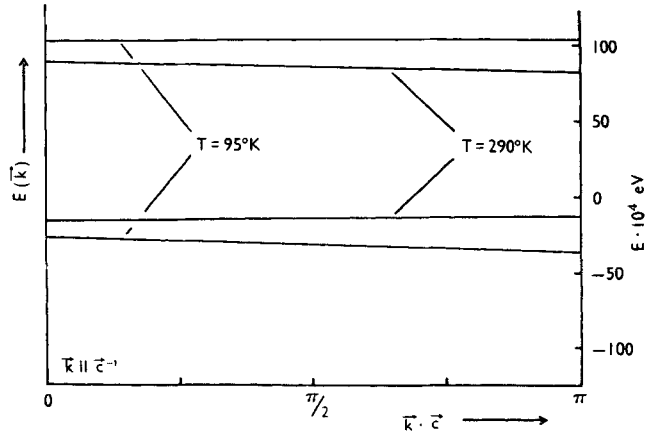

Figure 7. Shape of the excess electron band in the c^{-1} direction at 95°K and 290°K.

clusion is of practical importance as in the calculations by the method of[16] high speed computer is necessary.

2. None of the methods gives reasonable values of the component of the mobility tensor in the c' direction. Some improvement in this direction could be obtained if allowance were made for the contribution of hydrogen atoms in the neutral molecule potential.[5] The field of a proton is probably not completely shielded by its single electron making, in this way, a significant contribution to the molecular potential. This effect may appear most distinct in the direction of the c' axis along which the intermolecular contacts occur through hydrogen atoms. The interaction between hydrogens and π-orbitals of neighbouring molecules may cause the lowering of the barrier height for the transport of electron and raise at the same time its height for the hole. As a result this effect should improve the calculated anisotropy of mobilities.

In spite of some differences in anisotropy over the STO's and the SCF wave functions the temperature coefficient should be approximately correct in both cases. The lack of more complete experimental information about the temperature dependence of current

carrier mobilities for all crystallographic directions makes it impossible to discuss the problem more fully. However, the comparison of the calculated values of n with existing experimental data shows the correctness of the results of calculations. This fact is in agreement with Friedman's results [2] indicating that there is not any appreciable effect of phonon-electron interaction on the anisotropy of current carrier mobilities. The results also point to the correctness of the calculations made so far in the approximation of the isotropic relaxation time and indicate that the relaxation time is rather independent of temperature.

The author wishes to express his gratitude to Dr. K. Pigoń for many helpful discussions and to Dr. A. Gołębiewski for valuable help in accomplishing this work. It is also a pleasure to record indebtedness to Dr. L. Sobczyk for computations on the digital computer Elliott 803.

REFERENCES

1. Friedman, L., *Phys. Rev.* **133A**, 1668 (1964).
2. Friedman, L., *Phys. Rev.* **140A**, 1649 (1965).
3. Glaeser, R. M. and Berry, R. S., *J. Chem. Phys.* **44**, 3797 (1966).
4. Glarum, S. H., *J. Phys. Chem. Solids* **25**, 1577 (1963).
5. Gołębiewski, A., private information.
6. Katz, J. L., Rice, S. A., Choi, S., and Jortner, J., *J. Chem. Phys.* **39**, 1683 (1963).
7. Kearns, D., *J. Chem. Phys.* **35**, 2269 (1961).
8. Keller, R. A. and Rast, H. E., Jr., *J. Chem. Phys.* **36**, 2640 (1962).
9. Kepler, R. G. in Brophy, J. J., Buttrey, J. W., *Organic Semiconductors*, The Macmillan Company, New York, 1962.
10. Kepler, R. G., *Org. Semocond. Proc. Inter.-Ind. Conf., Chicago*, 1961, 1 (1962).
11. LeBlanc, O. H., Jr., *J. Chem. Phys.* **33**, 626 (1960).
12. LeBlanc, O. H., Jr. *J. Chem. Phys.* **35**, 1275 (1961).
13. Mason, R., *Acta Cryst.* **17**, 547 (1964).
14. Mette, H. and Pick, H., *Phys. Z.* **134**, 566 (1953).
15. Pigoń, K. and Chojnacki, H., *Acta Phys. Polon.* **31**, 1061 (1967).
16. Silbey, R., Jortner, J., Rice, S. A. and Vala, M. T., Jr., *J. Chem. Phys.* **42**, 733 (1965); ibid. **43**, 2925 (1965).
17. Thaxton, G. D., Jarnagin, R. C. and Silver, M., *J. Phys. Chem.* **66**, 2461 (1962).