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Molecular Crystals

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

On the Tight Binding Calculations for Anthracene Crystal

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Version of record first published: 21 Mar 2007.

To cite this article: H. Chojnacki (1969): On the Tight Binding Calculations for Anthracene Crystal, Molecular Crystals, 5:3,

313-315

To link to this article: http://dx.doi.org/10.1080/15421406908083466

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Molecular Crystals. 1969. Vol. 5, pp. 313-315 © Copyright 1968 Gordon and Breach Science Publishers Printed in Great Britain

On the Tight Binding Calculations for Anthracene Crystal

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Received October 25, 1968

The problem of the theoretical prediction of the temperature dependence of current carriers mobilities in molecular solids has been studied in general within the framework of the band theory for both narrow and broad band cases giving n < 2 in the relation $\mu \sim T^{-n}$ when only single acoustic phonon scattering processes are considered. A possible role of the intermolecular resonance integrals (transfer integrals T.I.) for an explanation of the temperature dependence of mobilities in anthracene crystal has also been studied recently.³

We have found an error in the former machine computation process and the recalculated values of T.I. obtained for 290 °K and 95 °K with the same assumptions as before³ are listed in Table 1. The results are also compared with those obtained for Sinclair et al.¹² crystal structure of anthracene. It will be noted that the LeBlanc's T.I. cited by Delacôte⁵ were evaluated by an incorrect formula⁷ (also in Thaxton et al.¹⁴ calculation). A small divergence between the results of Delacôte and ours may arise from another set of Mason's coordinates¹⁶ taken in (5). We have shown that the differences are within the limits of the accuracy of the anthracene crystal structure determination.

The new values of n in the equation $\mu \sim T^{-n}$ are quoted in Table 2 both with the existing experimental data. The theoretical slopes seem to be correct except the c' direction for electron. The comparison made between the results of experiments with one

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Table 1 Values of Transfer Integrals (in Units of 10⁻⁴eV) between the Molecule Situated at the Origin of Coordinate System and Molecules Described by the Indices (010), (0.5 0.5 0), and (0.5 0.5 1) Respectively

Temp.	(010)		$(0.5\ 0.5\ 0)$		$(0.5 \ 0.5 \ 1)$	
	Hole	Electron	Hole	Electron	Hole	Electron
Room ¹²	- 20.72	15.64	- 18.34	- 24.80	4.13	0.67
290 °K10†	- 23.20	17.60	-17.43	- 25.00	4.40	0.71
95°K10+	- 23.84	17.59	-26.33	- 33.41	6.07	0.78
290 °K10‡	- 23.04	17.57	- 16.95	- 25.16	4.47	0.77
95°K10‡	- 23.32	17.10	-26.48	- 33.07	5.95	0.73

[†] Calculated for the arithmetic mean of the Mason's coordinates.

Table 2 Calculated and Experimental Values of n in the Equation $u \sim T^{-n}$

D'acciden	Calc	ulated	Experimental		
Direction -	Hole	Electron	Hole	Electron	
a	0.7	0.5		1.18	
b	0.2	0.3		0.88	
· c ′	0.6	0.2	1°; 2°; 1.1°(?)	$1^9; -0.3^8; \\ 1.8^8(?)$	

another and with those of Bepler for the pyrene crystal¹ suggests, however, that the temperature dependence of electron mobility along the c'-axis is not ascertained. A scattering parameter may also play a role but for this effect allowance is not made on our calculation.

The tight binding model may be inadequate for molecular solids especially with the use of not good in tail STO's.⁷ In such a case only a few atomic components in the T.I. are usually taken into account for the (0.5 0.5 1) molecule of anthracene. The SCF 2p functions (e.g. Clementi-Roothaan orbitals⁷ seem to be much better but then the three-center integrals are of great importance⁷

[‡] Calculated for the "complete" Mason's coordinates.

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revised¹¹). On the other hand the approximation is only a π -electron approach. The results of Schmidt's orthogonalization for naphthalene¹³ point out (as well as our calculations for anthracene⁴ do) that the crystal field of the form

$$V(\mathbf{r}) = \sum_{l} V^{C}(\mathbf{r} - \mathbf{r}_{l}) + \sum_{l,m} V^{H}(\mathbf{r} - \mathbf{r}_{lm})$$

where not only carbon potentials ($V^{\rm C}$) but also m hydrogen potentials each of l molecules ($V^{\rm H}$) are taken into account may be a better approach for hydrocarbon crystals. The hydrogen potentials seem to be most of importance just along the c'-axis where intermolecular interactions are realized greatly by hydrogens. Hence, this may be another reason that the transport properties are more difficult to explain along the c' direction.

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