Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Bandgap-Determination from Autoionization Data in Molecular Crystals

H. Baessler [a] & H. Killesreiter [a]

[a] Fachbereich Physikalische Chemie der Universität, Marburg Biegenstrasse 12 D, 3550, Marburg/Lahn, West Germany

Version of record first published: 21 Mar 2007.

To cite this article: H. Baessler & H. Killesreiter (1973): Bandgap-Determination from Autoionization Data in Molecular Crystals, Molecular Crystals and Liquid Crystals, 24:1-2, 21-31

To link to this article: http://dx.doi.org/10.1080/15421407308083385

Molecular Crystals and Liquid Crystals. 1973. Vol. 24, pp. 21–31

Printed in Great Britain

Bandgap-Determination from Autoionization Data in Molecular Crystals

H. BAESSLER and H. KILLESREITER

Fachbereich Physikalische Chemie der Universität Marburg
Biegenstrasse 12
D 3550 Marburg/Lahn, West Germany

Received December 29, 1972

Abstract—An interpretation of action spectra for intrinsic photo-conduction in crystalline anthracene and tetracene is presented. It is shown (i) that the primary dissociation probability of a molecular excited state does not depend on photon energy as long as its energy exceeds the energy of the charge-transfer state and (ii) that excess energy of the excited state is dissipated during thermalization of the generated electron-hole pair in course of a random-walk process. The energy balance for the complete autoionization process allows precise determination of the band-gap. The values $E_g = 4.00 \pm 0.02$ for anthracene and $E_g = 3.11 \pm 0.03$ eV for tetracene are obtained.

1. Introduction

If an electron is injected into a molecular crystal from an electronic state in the contact whose energetic location is somewhat above the crystal conduction band, energy relaxation occurs. The vast majority of injected carriers loose their excess energy by interaction with molecular or lattice vibrations. They get thermalized before having escaped from the zone in which the attractive coulombic potential built up by the countercharge in the contact dominates the electrostatic potential distribution. It was shown(1) that the field dependence of the extrinsic, contact-limited photo-currents can be used as a probe to get information on the thermalization process.

Energy relaxation also occurs if an excited molecular state of sufficient energy forms a pair of charge carriers inside the crystal in course of an autoionization process.(2–4) It will be shown that the spectral response curve of intrinsic photoconductivity is determined by thermalization of the generated electron-hole pair and its thermally activated separation against attractive coulombic forces. It therefore contains information on the intermediate steps between molecular excitation and formation of a free carrier and allows accurate determination of the crystal bandgap.

2. Description of the Model

In crystalline anthracene intrinsic photoconduction becomes noticeable at photon energies beyond 3.9 eV. The action spectrum displays peaks at 4.4, 5.2 and 6.3 eV.(2–4) Geacintov and Pope(3) have explained its structure in terms of transitions from lower lying valence states: The autoionization (AI)-efficiency drops when the photon energy reaches a value at which optical transitions from the penultimate orbital to the lowest unoccupied, but non-autoionizing level can effectively compete with transitions from the highest filled orbital to a vibrationally excited singlet state isoenergetic with the conducting state of the crystal. Further increase of the total AI-yield φ is observed when the photon energy is sufficient to cause transitions from the penultimate orbital to an autoionizing state.

Batt, Braun and Hornig(5) have measured the activation energy of intrinsic photoconduction in anthracene crystals. They concluded that it has to be identified with the coulombic binding energy $e^2/\epsilon r_{th}$ of an electron-hole pair at a mutual thermalization distance $r_{th}.r_{th}$ and, concomitantly, also the photoelectric quantum yield depends on the initial photon energy $h\nu$ (Fig. 1). In the photon energy range $4.2 < h\nu < 5.04$ eV r_{th} was found to be almost constant. This observation was taken as evidence for the existence of a well-defined autoionizing state which is reached during cooling-off of the vibrationally excited first singlet state, irrespective of the initial photon energy. The increase of r_{th} at higher photon energies was attributed to the onset of prompt ionization, in course of which part of the initial excitation energy is converted into kinetic energy of the generated electron-hole pair.

There is, however, no spectroscopic evidence for the existence of a discrete autoionizing state. Moreover, it is difficult to see why autoionization should require a definite vibrational configuration of an excited molecule. Therefore an alternative model will be presented to explain AI-data. Its basic assumptions are:

i) Any vibrationally excited $S_1{}^v$ state, whose energy exceeds a critical value E_c, is able to primarily dissociate into a pair of charge

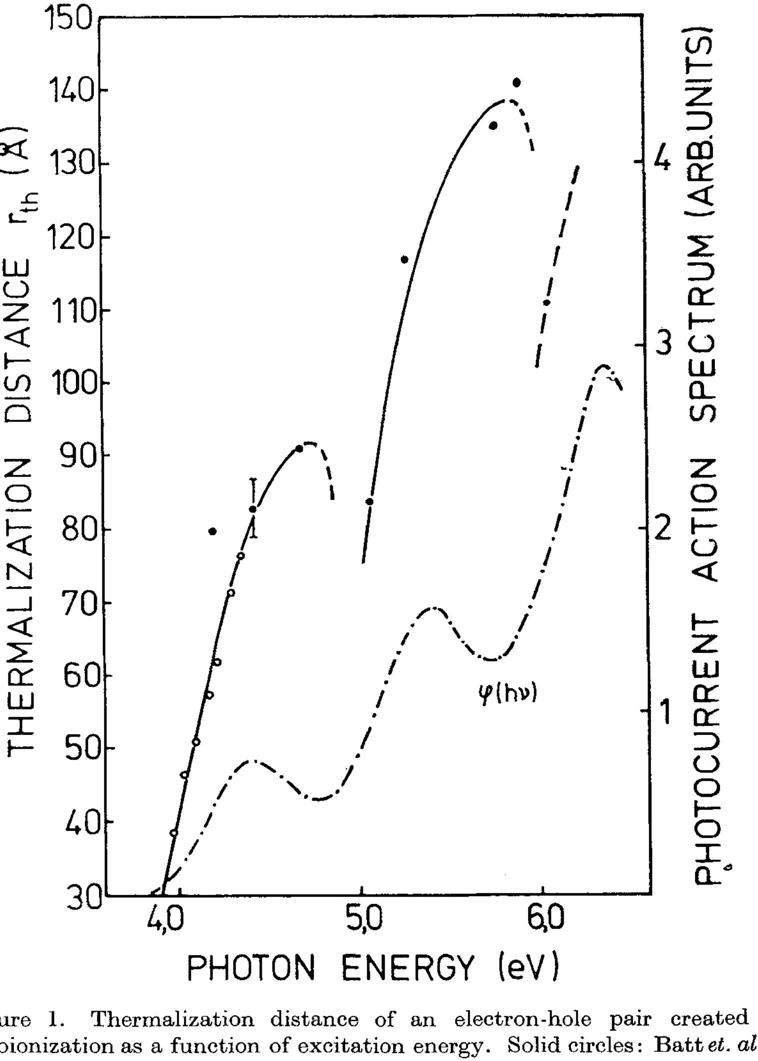

Figure 1. Thermalization distance of an electron-hole pair created by autoionization as a function of excitation energy. Solid circles: Batt *et. al's*[5] data derived from activation energy measurements. Open circles: Values calculated from Geacintov and Pope's spectral response curve.[3] —·—·—: Action spectrum of intrinsic photoconduction in anthracene.

carriers at a rate constant k_{AI} which is independent of the excess energy $h\nu - E_c$. E_c can be identified with the energy required to create a pair of charge carriers at neighboring molecules, i.e. it should be identical with the energy of the charge transfer state. Autoionization competes with vibrational relaxation of $S_1{}^v$ state (rate constant k_r). Therefore the probability that a $S_1{}^v$ state will primarily dissociate is $k_{\mathrm{AI}}/(k_{\mathrm{AI}}+k_r)$ independent of $h\nu - E_c$.

ii) If the energy of the autoionizating state exceeds the energy of the final ionized state the excess energy is transferred to the electron-hole pair in form of kinetic energy. Energy relaxation occurs in course of a random walk process determined by inelastic collisions between carriers and molecular or lattice vibrations. Assume that during one scattering event an average energy E_0 is dissipated, and that the total amount of energy to be converted into heat is ΔE $(h\nu)$. Then electron and hole will in total suffer $n = \Delta E/E_0$ scattering events. If the scattering mean free-path is l_0 the carriers get thermalized at an average mutual distance⁽⁶⁾

$$r_{th} = l_0(n/3)^{1/2} = l_0(\Delta E/3E_0)^{1/2} \tag{1}$$

If $r_{th} < e^2/\epsilon kT$, a thermalized carrier pair is still under the influence of attractive coulombic forces, the binding energy being

$$E_{\mathrm{coul}} = \frac{e^2}{\epsilon r_{th}} \tag{2}$$

At a given photon energy r_{th}- and E_{coul}-values must in principle form a distribution, since (i) thermalization of the carrier-pair is a statistical process and (ii) an initially excited $S_1{}^v$-state of energy $E = h\nu$ will undergo vibrational relaxation in course of which lower $S_1{}^v$ states are intermediately populated which should also autoionize—as long as $h\nu > E > E_c$—and thus yield carrier pairs at $r_{th} < r_{th}$ $(E = h\nu)$. The experiment, however, shows,⁽⁵⁾ that at a given photon energy the photocurrent is associated with a discrete activation energy. This means, that the distribution of r_{th} $(h\nu)$-values can be approximated by a δ-function. It indicates that after a $S_1{}^v$ state is produced, it decays preferentially to S_1 instead of passing through all the intervening vibrational states, or that generation of a state $S_1(\nu_k)$ by relaxation from a state $S_1(\nu_{k+1})$ is a different process from the excitation of $S_1(\nu_k)$ directly by light as far as autoionization is concerned. The probability that a S_1^v state dissociates into a pair of completely free carriers can therefore be approximated by

$$\varphi(h\nu) = \frac{k_{\mathrm{AI}}}{k_{\mathrm{AI}} + k_r} \exp\left[- \frac{E_{\mathrm{coul}}(h\nu)}{kT} \right] \tag{3}$$

Equation (3) describes the photocurrent action spectrum.

3. Comparison with Experimental Results

In this section the applicability of Eqs. (1) and (3) and, concomitantly, of the above assumptions will be checked using literature data on intrinsic photoconduction in crystalline anthracene.

i) If $k_{\mathrm{AI}}/(k_{\mathrm{AI}} + k_r)$ is independent from $h\nu$ as long as $h\nu > E_c$, the dependence of the intrinsic photocurrent on $h\nu$ must completely be determined by the dependence of E_{coul}, respectively r_{th}, on $h\nu$ provided that the number of S_1^v states with $E > E_c$ remains constant. Consequently the photocurrent action spectrum allows calculation or $r_{th}(h\nu)$. For normalization purposes E_{coul} must be known for a single photon energy because $k_{\mathrm{AI}}/(k_{\mathrm{AI}} + k_r)$ is unknown. Data listed in Table 1 are derived from Geacintov and Pope's spectral response curve measured for anthracene and Batt *et. al*'s(5) value E_{coul} ($h\nu = 4.43$ eV) = 0.058 eV.

Figure 1 shows that the shape of the $r_{th}(h\nu)$-curve calculated for the photon energy range $3.9 < h\nu < 4.4$ eV is identical with the *shape*

TABLE 1 Data for coulombic binding energy and thermalization distance r_{th} of carrier pairs formed by autoionization in crystalline anthracene, derived from photocurrent action spectra reported in Ref. 3. r_{th} is calculated on the assumption of an isotropic dielectric constant $\bar{\epsilon} = 3.02$[5]. A change in ϵ affects r_{th} and the parameter E_0/l_0^2 (see Eq. 1) but leaves the computed E_g-value unchanged.

h (eV)	E_{coul} (eV)	r_{th} (Å)
4.42	0.058	83.0
4.35	0.0628	76.6
4.29	0.0672	71.6
4.21	0.0775	62.0
4.17	0.0837	57.5
4.10	0.0945	51.0
4.03	0.1035	46.5
3.97	0.123	38.5

of the curve $r_{th}(h\nu)$ derived from direct activation energy measurements in the range $5.0 < h\nu < 6.0$ eV, which corresponds to the second peak in the $\varphi(h\nu)$-curve. Apparently the approximate constancy of $r_{th}(h\nu)$ for $4.2 < h\nu < 5.04$ eV is incidental. This indicates that the same set of autoionizing $S_1{}^v$ states is populated by transitions from the first and second filled molecular orbital and that the same autoionization mechanism operates throughout the photon-energy range investigated.

The upswing of the curve $\varphi(h\nu)$ after having passed the minimum at 4.8 eV occurs when excitation of the penultimate orbital also leads to population of an autoionizing state, which however, has less excess energy to be converted into kinetic energy of the carrier pair. Consequently for $h\nu > 4.8$ eV an additional photocurrent component appears, associated with a smaller thermalization distance. This means that the average thermalization distance drops when $\varphi(h\nu)$ passes a minimum.

ii) The essential confirmation of the above assumptions is provided by the dependence of the energy balance for the complete ionization process on photon energy. The total amount of energy converted into heat (ΔE) must be the difference between the energy supplied both optically and thermally ($h\nu + E_{\text{coul}}$) and the energy E_g necessary to create a free electron-hole pair,

$$\Delta E(h\nu) = h\nu + E_{\text{coul}}(h\nu) - E_g \tag{4}$$

ΔE can only be calculated if the band gap E_g is known. However, if k_{AI} is independent of excess photon energy $h\nu - E_c$ and if cooling-off of the hot carrier-pair occurs during a random walk process, also the square law relationship $\Delta E(h\nu) \sim [r_{th}(h\nu)]^2$ as predicted by Eq. (1) must be fulfilled. It is therefore a critical test of the present model whether or not it is possible to find a reasonable E_g-value which in combination with experimental $h\nu$- and E_{coul}-values yields a functional dependence between ΔE and r_{th} which is in accord with Eq. (1). Using the data for anthracene a good fit can indeed be obtained for a bandgap $E_g = 4.00 \pm 0.02$ eV. A plot of calculated ΔE-values is presented in Fig. 2 which also shows how sensitive the functional dependence of $\Delta E(r_{th})$ reacts on variation of E_g. The values of the parameter $E_0/(\epsilon^2 l_0{}^2)$ is found to be 2,3 × 10^{-6} eV Å^{-2}. Extrapolation of $\Delta E(r_{th})$ and $E_{\text{coul}}(r_{th})$ to r_{th}-values which are of the order of the

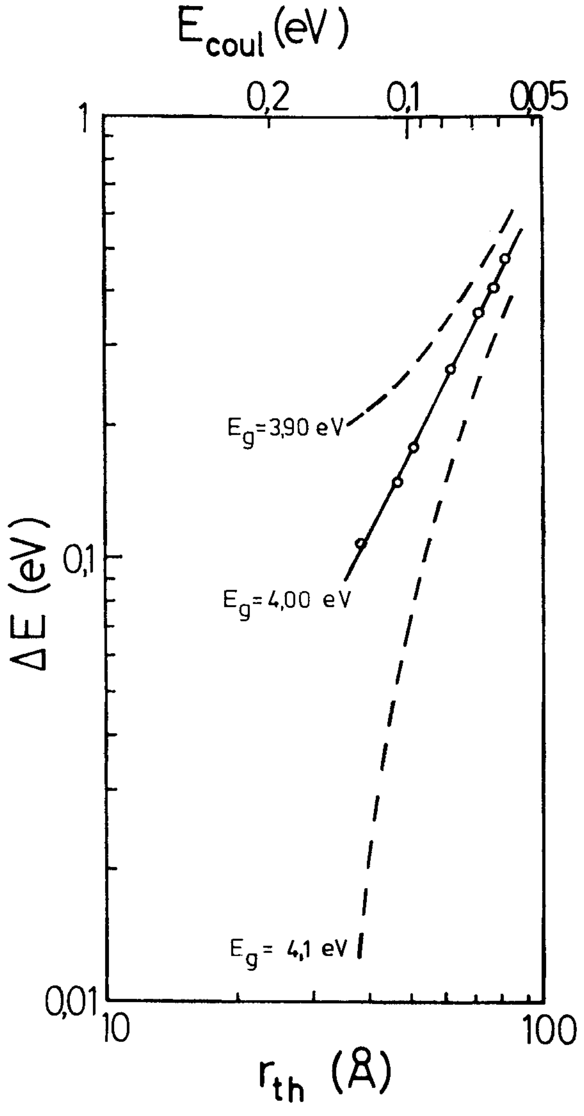

Figure 2. Dependence of the energy ΔE dissipated during thermalization of an electron-hole pair as a function of thermalization distance r_{th}. ΔE is calculated according to Eq. (4) for various E_g-values.

lattice parameter i.e. about 10 Å yields the critical energy $E_c = 3{,}5\,\text{eV}$. As expected it is identical with the energy of the charge transfer state in anthracene.(8,9)

4. Application

The calculated value for the bandgap in crystalline anthracene agrees with the commonly accepted literature value (see also next section). Moreover, application of the above model, the essence of which is thermalization of a carrier pair in course of a random walk process, allows a self-consistent interpretation of intrinsic photoconductivity data. This confirms the present model and suggests that the assumptions presented in Sec. 2 constitute a reasonable basis to interpret autoionization data in molecular crystals in general. It is then possible to calculate the bandgap of molecular crystals from photoconductivity action spectra with high accuracy, even if the temperature dependence of the photocurrent has not been determined. This will be illustrated for tetracene as an example.

Let i_m be the photocurrent measured at the first maximum of the spectral response curve and i the photocurrent at lower photon energies, then

$$i/i_m = \exp\left[-\frac{E_{\text{coul}} - E_{\text{coul},m}}{kT}\right]$$

and

$$E_{\text{coul}}(h\nu) = -kT\ln[i(h\nu)/i_m] + E_{\text{coul},m} \tag{5}$$

Inserting Eq. (5) to Eq. (4) and expressing ΔE in terms of E_{coul} (see Eqs. 1 and 3) yields

$$E_g = h\nu - kT\ln\frac{i}{i_m} + E_{\text{coul},m} - \frac{3e^4E_0}{\epsilon^2 l_0^2}\left[E_{\text{coul},m} - kT\ln\frac{i}{i_m}\right]^{-2} \tag{6}$$

$E_{\text{coul},m}$ and $E_0/\epsilon^2 l_0^2$ are adjustable parameters which in course of a fitting procedure have to be chosen such as to make the right side of Eq. (6) independent of photon energy. Equation 6 shall be applied to determine E_g for crystalline tetracene, using Geacintov and Pope's photocurrent data(3) (see Table 2). It is fulfilled for the following choice of parameters: $E_{\text{coul},m} = 0.06\,\text{eV}$ and $E_0/(\epsilon l_0)^2 = 4.3 \times 10^{-6}\,\text{Å}^{-2}$. A bandgap $E_g = 3.11 \pm 0.03\,\text{eV}$ follows. The electron affinity

TABLE 2 Intrinsic Photocurrent Data for Crystalline Tetracene. i/i_m is taken from Ref. 3. E_g data are computed according to Eq. (5) using the parameters $E_{\mathrm{coul},m} = 0.06$ eV and $E_0/(\epsilon l_0)^2 = 4.3 \times 10^{-6}$ eV Å^{-2}.

h (eV)	i/i_m	$-kT\ 1_n(i/i_m)$	E_g (eV)
3.06	0.025	0.093	3.105
3.14	0.0675	0.063	3.10
3.26	0.1875	0.0423	3.10
3.37	0.363	0.0256	3.10
3.38	0.325	0.0284	3.105
3.51	0.508	0.0171	3.15
3.57	0.60	0.0129	3.12
3.60	0.775	0.0065	3.10
3.70	0.90	0.0027	3.10
3.76	1.00	0	3.09
3.82	0.89		

of the crystal is therefore $A_c = I_c - E_g = 2.14$ eV, I_c being the ionization energy of the crystal ($I_c = 5.25$ eV(10)). It seems noteworthy that the difference between the electron affinities of solid tetracene ($A_{c,tc} - A_{c,ac} = 0.49 \pm 0.04$ eV) is about the same as the difference between the theoretical A_g-values calculated for the gaseous molecules ($A_{g,tc} - A_{g,ac} = 0.6$ eV(10)).

5. Conclusions

From action spectra for photoemission of electrons and holes from an evaporated cerium (or magnesium) contact into anthracene a bandgap of 3.72 eV has been deduced.(11) However, because of image potential corrections this value is lower than the energy difference E_g between the states of a free electron and a free hole at infinite separation. To obtain E_g, the activation energies for positive (E^+) and negative (E^-) photoemission currents have to be added to the above value. From recent measurements $E^+ + E^- = 0.4 \pm 0.1$ eV follows(1). Therefore $E_g = 4.1 \pm 0.1$ eV eV is obtained.

The agreement between E_g values determined by two completely different methods strongly favors acceptance of the 4.0 eV value as the correct bandgap in anthracene. This is of importance, since Ishihara and Nakada(12) recently have questioned the validity of this value. Their statement was based upon photoconductivity measurements using tetracene-doped anthracene crystals. Illumination in the spectral range of guest absorption gave rise to both a positive and negative photocurrent associated with activation energies E^+ and E^-. It was concluded that it was due to dissociation of the lowest excited guest singlet state of energy E_{ex}. The bandgap of the host crystal should then be $E_g = E_{ex}+E^+ +E^-$ yielding $E_g = 3.0$ eV. The true origin of the photocurrent in this experiment is not clear. It can only tentatively be suggested that photoemission of carriers from the contact metals played an important role. On the other hand doubts on the reliability of the Ishihara–Nakada-method for bandgap determinations were also raised by the observation by Donnini(13) that $E_{ex}+E^+ +E^-$ strongly depends on the nature of the dopant, whereas the bandgap of the host crystal should be independent of the dopant.

The constant $E_0/\epsilon^2 l_0^2$ yields some information on the way the hot carrier pair looses its excess energy. Assuming that the scattering mean freepath is the same as has been found for electrons photoemitted from a metal contact, i.e. $l_0 = 11$ Å, the average amount of energy lost during one scattering event is $E_0 = 3 \times 10^{-3}$ eV. However, the l_0-value quoted above also includes elastic scattering. In the case that $l_{0,\text{inelastic}} > l_{0,\text{elastic}}$ the characteristic energy loss would be higher. It should be mentioned that the energy change a molecular out-of-plane mode experiences upon interaction with a chargecarrier is of the order of 10^{-2} eV. Munn and Siebrand have shown(14) that it is this interaction which limits the mobility of free chargecarriers.

An interesting, yet unresolved question is how a carrier pair can initially have kinetic energy of several tenths of an eV in a molecular crystal in which highest valence and lowest conduction band are only a few hundredths of an eV wide. Since the second and broader conduction band is located 0.6 eV above the lowest conduction band(15,16) there should be no allowed states with an *electronic* excitation energy of less than that value. The same problem was also encountered in course of the interpretation of low temperature photoemission data:(1) It was found that a photoemitted metal electron with excess kinetic energy has a small but finite chance to reach the potential maximum, formed by superposition of the external potential and the image potential, without being scattered. Energetically during its motion it passes a zone which does not contain allowed states.

Acknowledgement

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

REFERENCES

1. Baessler, H. and Killesreiter, H., *phys. stat. sol.* (*b*) **53**, 183 (1972) and Killesreiter, H. and Baessler, H., *phys. stat. sol.* (*b*) **53**, 193 (1972).
2. Castro, G. and Hornig, J. F., *J. Chem. Phys.* **42**, 1459 (1965).
3. Geacintov, N. and Pope, M., *J. Chem. Phys.* **50**, 814 (1969).
4. Chaiken, R. F. and Kearns, D. R., *J. Chem. Phys.* **45**, 3966 (1968).
5. Batt, R. H., Braun, C. L., and Hornig, J. F., *J. Chem. Phys.* **49**, 1967 (1968).
6. This is only correct for isotropic diffusion. Owing to the anisotropy of the dielectric constant (see N. Karl, D. Rohrbacher and D. Siebert, *phys. stat. sol.* (*a*) **4**, 105 (1971)) this condition is not fulfilled. Since, however, corrections would only modify the numerical factor in Eq. (1), anisotropy effects will not be considered here.
7. Pope, M. and Burgos, J., *Mol. Cryst.* **1**, 395 (1966).
8. Webman, I. and Jortner, J., *J. Chem. Phys.* **50**, 2706 (1969).
9. Pope, M., Burgos, J. and Giachino, J., *J. Chem. Phys.* **43**, 3367 (1965).
10. Becker, R. S. and Chen, E., *J. Chem. Phys.* **45**, 2403 (1966).
11. Vaubel, G. and Baessler, H., *Phys. Letters* **27A**, 328 (1968).
12. Ishihara, Y. and Nakada, I., *J. Phys. Soc.* (*Japan*) **28**, 667 (1970).
13. Donnini, J., *J. Phys. Soc.* (*Japan*) **32**, 455 (1972).
14. Munn, R. W. and Siebrand, W., *J. Chem. Phys.* **52**, 6391 (1970).
15. Baessler, H. and Vaubel, G., *Phys. Rev. Letters* **21**, 615 (1968) and Baessler, H., Riehl, N. and Vaubel, G., *Mol. Cryst. and Liquid Cryst.* **6**, 249 (1968).
16. It should be mentioned that J. Dresner (*Phys. Rev. Letters* **21**, 356 (1968)) from the same type of experiments as reported in Ref. 15 has deduced an energy gap between first and second conduction band of only 0.05 eV.