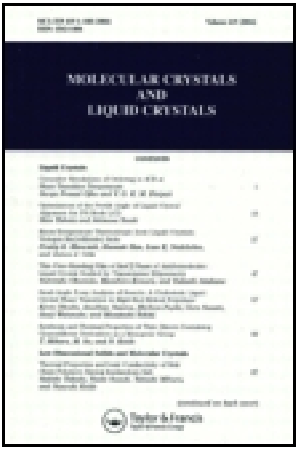

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: A. Eilmes & P. Petelenz (1994): Charge Transfer Induced Local Exciton States at High Dopant Concentration, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 257:1, 251-257

To link to this article: http://dx.doi.org/10.1080/10587259408033781

Mol. Cryst. Liq. Cryst., 1994, Vol. 257, pp. 251–257
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Charge Transfer Induced Local Exciton States at High Dopant Concentration

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(Received May 24, 1993)

The model attributing the occurrence of local Frenkel exciton levels in doped naphthalene crystals to charge transfer effects is investigated for dopant concentrations high enough to enable a host molecule to interact with multiple impurities. The predictions are compared with those of the conventional model where the local levels are explained in terms of a substantial perturbation of the diagonal exciton energy, and found to differ for some deep local states. In view of existing ambiguities in the experimental data, new experiments are suggested to establish the mechanism of local state creation.

Keywords: Excitons, charge transfer, local states, doped crystals

1. INTRODUCTION

It is well known that some benzene derivatives, when embedded in naphthalene, give rise to local Frenkel exciton states. Considerable evidence[1–5], partly experimental and partly theoretical, suggests that the effect the impurity molecules have on the host is mediated by the off-diagonal (in the local basis) charge transfer interactions. This mechanism of local level formation is different from the normally invoked modification of the Frenkel exciton transfer integral[6–9] or of its diagonal energy[10–12] in the vicinity of a dopant molecule.

For this latter, more conventional, mechanism, further changes in the spectrum of a doped crystal are expected at high dopant concentration[11,12], i.e., when the probability that one host molecule is affected by two or more impurity molecules becomes appreciable, producing new types of local levels.

On that view, it is natural to ask whether a similar effect would be expected if the local states are due to charge transfer interactions. It is our present objective to answer this question.

2. MODEL

To our knowledge, no systematic experimental study of the dependence of CTILFES (Charge Transfer Induced Local Frenkel Exciton States) spectra on dopant concentration has been published.

The only experimental studies that are of direct relevance to the problem in hand pertain to the naphthalene (Naph) crystals doped with indole (Ind[11,12]) or thionaphthene (TNP[12]). The occurrence of local levels in those systems was interpreted in terms of the modification of the host Frenkel exciton diagonal energy due to the perturbation by the guest. As the conclusion about the CTILFES nature of local levels for crystals doped with benzene derivatives was based on the study of a series of similar dopants with different ionization potentials[1–5] and such studies are absent for Naph/Ind and Naph/TNP, the available experimental data are insufficient to assess whether the spectra observed for those systems could be re-interpreted as due to CTILFES.

Leaving this question temporarily open, we will use the Naph/Ind crystal as a model system. The theoretical results obtained by Ostapenko, Sugakov and Shpak[11,12] within the conventional model mentioned above will provide a reference to compare with the conclusions obtained from the calculations based on the assumption that the local states in that system are induced by charge transfer effects. The present calculations are performed within the finite cluster model presented in our previous papers[4,5], to which the Reader is referred for details.

3. PARAMETRIZATION

The input parameters characterizing the host naphthalene crystal are the same as in Reference 5.

The diagonal energies of the charge transfer (CT) states engaging the indole molecule are estimated in the same way as it was done for other dopants[5], based on the vertical ionization potential of indole[13,14] ($I_a = 7.90$ eV), and its electron affinity assumed arbitrarily to be the same as that of the dopants we have studied in the past[1], i.e., about 1 eV.[15]

As usually, the transfer integrals involving the impurity molecule are not known. In previous papers,[3–5] we assumed them to be the same as for a pair of naphthalene molecules. This approach, although crude, avoided the need to introduce adjustable parameters and was justified as long as we were interested in general features of the solutions for a series of crystals containing different dopants, rather than in the energies of specific levels for a single dopant. We retain it for the Frenkel exciton transfer integrals (M and W).[5]

In the present context, a higher accuracy is necessary to differentiate between the results of the approach invoking the CT interaction and those of the conventional model.[10–12] As in the calculations of References 10–12 and empirical parameter was introduced, it is reasonable to introduce one in our approach as well. Otherwise, the discrepancies between the two sets of results might be due to a different quality of the input data rather than the physical differences between the models.

Of all parameters, the Frenkel exciton dissociation integrals are the least certain, so they are the logical choice for empirical scaling.

The "basic" local level (L_1), due to an isolated impurity and observed even for very low concentrations of the dopant, is located in Naph/Ind at 31462 cm^{-1}, i.e., 14 cm^{-1} below the A band of the neat crystal. Its stabilization energy, calculated within the cluster model of Reference 5 with the dissociation integrals appropriate for naphthalene–naphthalene interaction (as used previously), is overestimated by 8 cm^{-1}. The correct value is recovered if all the dissociation integrals are uniformly reduced by the factor of 0.92, which in that case is the sole adjustable parameter of the model. The data set that ensues will be referred to as Parametrization 1.

The above scaling of the dissociation integrals is the simplest but by no means the only reasonable one. As an alternative, we have tested the case where the dissociation integrals D for the (0, 1, 0) direction are reduced by 0.90 and at the same time the dissociation integrals D' for the (1/2, 1/2, 0) direction are increased by 1.20 (with respect to naphthalene). This data set (referred to as Parametrization 2) seems physically better founded: for geometric reasons, the lone electron pair of the heterocyclic nitrogen atom is likely to increase the intermolecular overlap integral between translationally inequivalent nearest neighbour molecules, while the overlap in the (0, 1, 0) direction is likely to be smaller for the five atom pyrrole ring (in indole) than for the six atom benzene ring (in naphthalene).

However, Parametrization 2 involves in fact two arbitrary scaling parameters instead of one, and consequently suffers from a higher degree of arbitrariness. Therefore, it will be only briefly mentioned, the presentation being focused primarily on the results obtained for Parametrization 1.

4. CALCULATIONS

As in heavily doped crystals the local bands originate from various configurations of impurities, one should take into account all possible relative arrangements of dopant molecules with appropriate statistical weights. The simplest way to do this is to repeat the calculations for a series of clusters containing randomly located impurities.

The calculations have been done for series of 20 to 50 clusters (depending on concentration—higher concentrations require longer series to achieve stability of the results) containing 342 molecules (cluster size 19 × 18). For each molecule a random draw decided whether it was to represent naphthalene or indole, with the probability corresponding to the actual concentration of the dopant. The calculations have been done for average indole concentration 0.5, 2.5, 5 and 10%.

Each predicted energy level has been represented by a Gaussian curve with the width $\alpha = 5 \times 10^{-5}$ eV, and the results have been averaged over the series of clusters.

The results are displayed in Figure 1.

In each panel, the simulated absorption spectrum represents our results, and the solid vertical bars below the horizontal base line show the energies of the local levels calculated be Ostapenko *et al.*[11,12]. The broken lines in the upper part of each plot correspond to the bands observed experimentally in fluorescence.[11,12] In consecutive panels the intensity scale is reduced proportionally to the concentration.

In order to have an insight into the interactions operative in the doped crystal we have tried to match the obtained peaks to the main impurity configurations which produce them. The results of the analysis are shown in Figure 2. They may be summarized as follows: The most intense broad band at about 31470 cm^{-1} corresponds to the A band of the pure naphthalene crystal. The band at about 31460 cm^{-1}

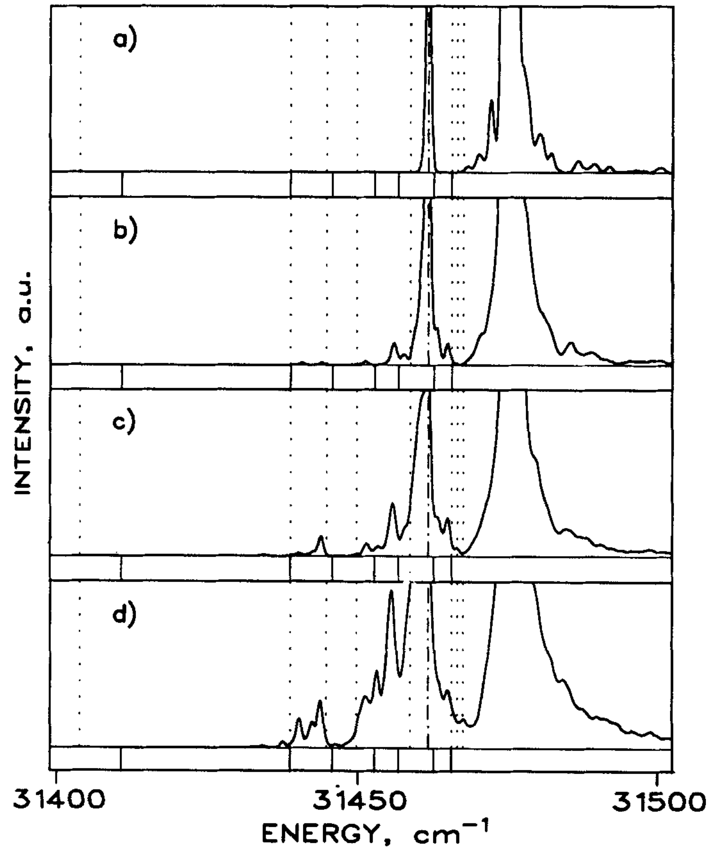

FIGURE 1 Absorption spectrum of Naph/Ind resulting from cluster calculations for different dopant concentrations: a) $\simeq 0.5\%$, b) $\simeq 2.5\%$, c) $\simeq 5\%$, d) $\simeq 10\%$. Vertical bars below the horizontal base line—energies of local levels calculated by Ostapenko *et al.*[11,12]; broken lines— bands observed experimentally in fluorescence[11,12]. The dash-dot line represents the L_1 state, used to scale the dissociation integrals.

represents the "basic" L_1 impurity centre. Other bands represent the cases where two closely spaced impurities affect the same naphthalene molecule.

Due to the smaller CT integrals, the effect of the impurity on the naphthalene molecules in the (1/2, 1/2, 0) direction is rather weak.[5] In effect, the geometric arrangements where one naphthalene molecule interacts with two impurities lead to peaks close to the "basic" L_1 local band, except for the case where both indole-naphthalene interactions are in the (0, 1, 0) direction. Generally, the deepest local levels energe from the configurations of three or four indole molecules interacting with one host molecule (L_3 and L_4 centres[11,12]) especially when two of the relevant interactions are in the *b* crystalographic direction. These arrangements of impurities also contribute additional intensity in the region where the shallowest local levels caused by two-impurity interactions appear (31460–31470 cm^{-1}).

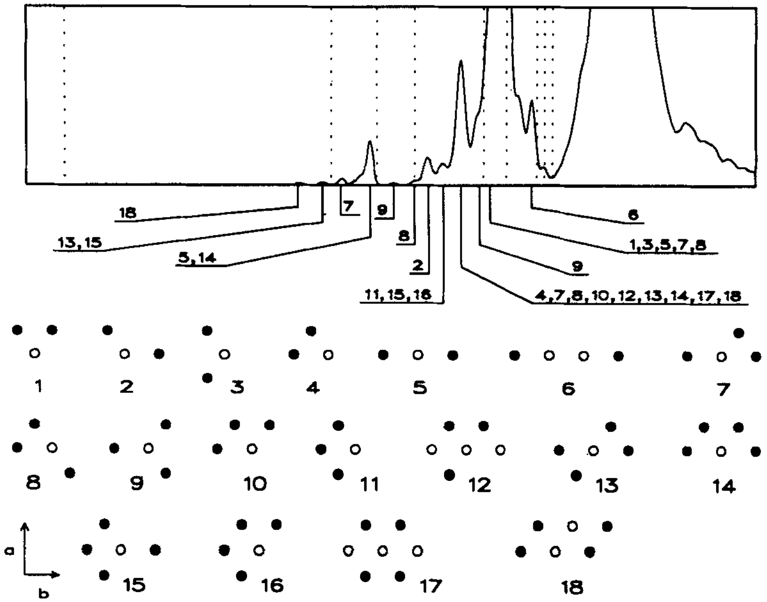

FIGURE 2 Main impurity configurations contributing to the absorption spectrum. The circles represent naphthalene, the black dots–indole molecules.

5. DISCUSSION

It is readily seen that with increasing indole concentration new peaks appear at lower energies. The intensity of existing bands shifts in the same direction.

In the region between $31430\,\mathrm{cm}^{-1}$ and the A' band of the neat crystal ($31476\,\mathrm{cm}^{-1}$) the correspondence between the simulated spectra and the positions of local levels predicted by the conventional theory is surprizingly good. The intensities evidently accumulate close to the local level energies calculated by Ostapenko *et al.*[11,12]. The actual number of maxima is not a reliable criterion of agreement, since it depends on the width of individual bands, assumed in the calculations. In order to minimize the number of new parameters, we have set this width at the same value as was used in our previous calculations.[5] In reality, it is very likely that the quality of heavily doped crystals is poorer, which would justify a larger width and probably wipe out some maxima, making the coincidences more evident.

However, the similarity of the spectra predicted by the two approaches for this energy range seems to be purely accidental. In fact, in most instances the arrangement of impurity molecules attributed by the conventional theory[11,12] to a local level shown in the lower part of the panels in Figure 1, is quite different from the percentage of the levels contributing in our calculations to the nearby intensity maximum. Even the direction of maximum host-guest interaction is differently identified: it is (0, 1, 0) in our calculations, but (1/2, 1/2, 0) according to Ostapenko *et al.*[11,12].

As has been mentioned before, the deepest levels predicted by our treatment derive from the configurations where a naphthalene molecule has two impurity molecules as nearest neighbours in the (0, 1, 0) direction. In the conventional theory, the local level corresponding to a similar arrangement along the (1/2, 1/2, 0) direction (referred to as the $2L$ level[11,12]) is predicted at a much lower energy (about 31400 cm^{-1}).

In this respect, our results are in acute conflict with those of References 11, 12: the very deep local level ($2L$) predicted by Ostapenko *et al.* at about 31400 cm^{-1} has no counterpart in our results.

Our tentative calculations for naphthalene doped with thionaphthene lead to a similar conclusion.

The difference is probably due to the fact that in our model the stabilization of the local levels is due primarily to the *off-diagonal* interaction with the CT manifold, while in the model of Ostapenko *et al.*[11,12], the *diagonal* Frenkel exciton energy is affected.

The model of References 11, 12 predicts that the stabilization energy of the $2L$ local level should be twice as large as that of the L_1 level, whose stabilization energy is Δ (which is the adjustable parameter of that theory). Consequently, the $2L$ state is expected to split off by 2Δ *from the diagonal naphthalene energy.*

In our approach, the effects of the two dopant molecules are also roughly additive, but the net effect has to be counted (approximately) *from the position of the A band.* As the A band is located well below the diagonal energy of a naphthalene molecule in the crystal, the "stabilization energy" of the L_1 level, calculated in this way, is smaller than in the approach of References 11, 12. Accordingly, the "stabilization energy" of the $2L$ level is also much smaller.

The presence or absence of the deep level seems to be the crucial test that may allow to discriminate experimentally which of the two models is physically more appropriate for the description of a given doped crystal.

Unfortunately, the only experimental data known to us were obtained from fluorescence,[11,12,16,17] not absorption spectra. In effect, at least the intensities of different transitions cannot be interpreted within our model, since they would be determined partly by (unknown) radiationless characteristics like the cross section of various multiple-impurity centres for exciton capture, which are beyond the scope of our model.

On the face of it, the experimental results for Naph/Ind,[11,12] where the deep local level attributed to the $2L$ centre has been observed, seem to support the interpretation of Ostapenko *et al.* and contradict the one we are proposing. However, we do not consider this evidence as conclusive. According to References 12 (p. 76), the relevant band appears only at very high dopant concentration and is very weak. Statistically, there is no obvious reason why it should not start to be observable at the same concentration as other local centres involving two closely spaced dopant molecules (e.g., the centre denoted as L_2^n – cf. p. 25 of Reference 12). It should be certainly more prominent than the L_3 and L_4 centres.

The above considerations suggest that the band attributed originally to the $2L$ centre may in fact be due to an uncontrolled impurity. Other experiments done so far failed to confirm the existence of that band[16]; its coincidence with a band often observed in commercial naphthalene and disappearing upon purification[16] may also be considered as suggestive.

Other bands observed experimentally have their counterparts in our results, and the agreement may be further improved by a slight modification of the input data (Parametrization 2).

Our tentative results suggest that a similar situation is encountered for naphthalene doped with thionaphthene. Although the calculations are less reliable (due to the uncertainties concerning the dissociation integrals for a sulphur containing compound) and the agreement is generally worse than for Naph/Ind, the major conflict of our results with the experimental data of Reference 12 concerns the lowest energy transition, reported at about $31360\,\text{cm}^{-1}$ and originally attributed[12] to the $2L$ centre. That band has no counterpart in our results, its stabilization energy being roughly twice as large as the model based on CT interactions predicts for the deepest local level.

Apparently, there is again some disagreement between the relevant experimental data, since in References 17 that band is reported to disappear upon purification of the crystal.

On that view, it seems that a very thorough experimental investigation of the concentration effects in Naph/Ind and Naph/TNP, with a search for the deep $2L$ levels, could resolve the existing doubts. We hope that this paper will provoke such a study.

Acknowledgements

This research was supported by Grant No 2 0669 91 01 (1723/2/91) from the State Committee for Scientific Research (Poland). The authors express their gratitute to Dr I. V. Brovchenko for suggesting the problem, for access to unpublished experimental data and for valuable comments.

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