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Exciton Transport Mechanism in 1,4-Dibromonaphthalene (DBN)–1-Bromo-4-chloronaphthalene (BCN) Mixed Crystal at 77 K

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The exciton transport in the presence of both orientational and substitutional disorders is investigated at 77 K. The systems of study include different compositions of 1,4-dibromonaphthalene (DBN) and 1-bromo-4-chloronaphthalene (BCN). In DBN, crystal phosphorescence emission is in conformity with quasi-one-dimensional exciton motion. Fluorescence emission from an impurity and phosphorescence emissions from the triplet state of DBN and from an impurity site present in the DBN crystal have been observed. However the fluorescence emission from the first excited singlet state of DBN is absent. In BCN-doped DBN crystal, the emission corresponding to first triplet of DBN disappears. With the increase of BCN concentration, fluorescence intensity of impurity S_1^{IMP} decreases, while the impurity phosphorescence emission intensity increases. The role of the deep trap present in DBN and the effect of orientational disorder due to BCN on the energy transfer processes have been discussed. The experimental results are explained quite satisfactorily in terms of the percolation model, which suggests a two-dimensional exciton transport topology in the mixed crystal.

The dynamics of energy transfer in disordered solids have received considerable attention in recent years.[1—5] Studies on exciton migration in substitutionally disordered mixed molecular crystals, especially isotopically mixed solid solutions as well as the orientationally disordered solids, have drawn extensive attention.[6—14]

The primary difficulty associated with substitutionally disordered solids is that the dopants perturb the host lattice to such an extent that they do not form proper solid solutions but separate out as two different components as the concentration of the dopant increases. Solid solutions of 1,4-dibromonaphthalene (DBN) as host and 1-bromo-4-chloronaphthalene (BCN) as guest of different compositions, where both substitutional and orientational disorder are present, are of great interest.[10,11,14] The system has a great advantage in that it forms excellent solid solutions over a wide range of their concentration composition, in spite of differences of their crystal structure.[16] A Raman phonon spectral study shows that at concentrations of DBN$\geq$42 mole percent, the crystal structure is that of DBN, whereas at lower concentrations BCN crystal structure prevails.[16] The structure of BCN-doped DBN system is a randomly distributed linked cluster of each components. Previous work on this system,[10,11] has shown that at 4.2 and 1.8 K the triplet exciton migration is acceptor concentration dependent and at a critical concentration the energy transfer efficiency is greatly enhanced. It has been established that a two dimensional exchange interaction mechanism is responsible for energy migration in this system.[10,11,14] The steady state studies in DBN–BCN mixed crystals at 4.2 and 1.8 K have also shown that Anderson localisation is absent and that the concentration behavior is consistent with the percolation model.

In an earlier paper,[15] we have studied the exciton migration in a disordered lattice using the Monte-Carlo technique. The concentration dependent excitation transport efficiency in two dimensions was found to be consistent with the percolation model. In this paper, we extend our studies to a well-known quasi-one-dimensional DBN–BCN system in order to investigate the role of a deep trap as well as the effect of orientationally disordered BCN of varying concentrations on energy transport at the relatively high temperature at 77 K. The percolation model is found to account for the experimental results. Analyses of the results indicate a two-dimensional exciton transport topology in the mixed crystal, in contrast to a one-dimensional topology in pure DBN and BCN crystal.[17]

Experimental

DBN obtained from Kodak Chemical Co. (U.S.A.) was vacuum sublimed and then repeatedly recrystallized from pure ethanol and finally chromatographed through a column of alumina using pentane as eluent. The chromatographed sample was then extensively zone-refined and a single crystal of DBN was grown by Bridgeman technique. BCN prepared by Sandmayer reaction discussed elsewhere[18] was extensively zone-refined and was used as a dopant. Mixed single crystals were grown with various concentrations of BCN. The emission spectra were recorded by Perkin–Elmer MPF 44A Spectrofluorimeter at 77 K.

Results and Discussion

The emission spectra of a pure DBN crystal at 77 K with excitation at 300 nm is shown in Fig. 1. Three distinct band systems in the emission spectra are observed. The first emission band, which we have assigned as impurity fluorescence because of its being at lower energy than the well recognized lowest singlet state of DBN (S_1^{DBN}) crystal, appears at 29776 cm^{-1}. The second band system is the usual T_1^{DBN}—S_0 (20199 cm^{-1}) phosphorescence. The assigned values of the 0–0 bands of T_1^{DBN} and the vibrational analysis of the emission spectra are found to be in good agreement with those reported in the literature.[20,21] We have identified the third band system with origin at 18903 cm^{-1} (T_1^{IMP}) to originate from an impurity site present in DBN crystal.[20] There is, however, no emission observed from the S_1^{DBN} state. It is noteworthy that the first band assigned to an impurity emission almost coincides energetically with the T_2^{DBN} state.[19,20] However it is unlikely that this is T_2 emission of DBN, as in such a case T_2–T_1 internal conversion should be very inefficient and its life time should be in the millisecond time domain, which is most unlikely.

In DBN crystal, the heavy atom effect suggests a very efficient intersystem crossing. It is thus very likely that on excitation at S_1^{*DBN} (S_1^{*DBN} being some higher vibronic level of S_1^{DBN}), the major part of the excitation will be transferred to T_2^{DBN} via S_1^{DBN} ($S_1^{*DBN}\rightarrow S_1^{DBN}\rightarrow T_2^{DBN}$). Absence of $S_1^{DBN}\rightarrow S_0$ fluorescence emission in pure DBN crystal is obviously due to strong $S_1^{DBN}\rightarrow T_2^{DBN}$ intersystem crossing. Heavy atoms in the molecules and small $S_1^{DBN}\rightarrow T_2^{DBN}$ (579 cm^{-1}) energy gap favor large intersystem crossing. The other part of the excitation is transferred to S_1^{IMP}. Thus our results in pure DBN suggest that on S_1^{*DBN} (300 nm) excitation, the deactivation routes are

$$\begin{tikzcd}
 & & S_1^{IMP} \arrow[rr] & & S_0+h\nu_{S_1}^{IMP} & \\
S_1^{*DBN} \arrow[r] & S_1^{DBN} \arrow[rr] \arrow[ur] & & T_2^{DBN} \arrow[r] \arrow[ul] \arrow[d] & T_1^{DBN} \arrow[r] & S_0+h\nu_{T_1}^{DBN} \\
 & & & T_1^{IMP} \arrow[r] & S_0+h\nu_{T_1}^{IMP} &
\end{tikzcd}$$

where $\nu_{T_1}^{DBN}$, $\nu_{S_1}^{IMP}$, $\nu_{T_1}^{IMP}$ are the frequencies of the emissions from T_1^{DBN}, S_1^{IMP}, and T_1^{IMP} levels respectively.

The origin of S_1^{IMP} and T_1^{IMP} seems to be a physical lattice defect. Indeed the vibronic structure of the impurity phosphorescence shows 1,4-DBN vibration.[20] Considering a statistical hopping model Montroll[22] has shown that the trapping efficiency of a linear chain system is much less, almost three orders of magnitude smaller than that in a higher-dimensional one. This has been assumed to be a reason why it is relatively easy to observe exciton phosphorescence emission in linear chains like DBN.

On doping the pure DBN with increasing concentrations of BCN, we observe that the emission corresponding to T_1^{DBN} vanishes and the emission from S_1^{IMP} and the trap T_1^{IMP} remain. On increasing the concentration of BCN, the intensity of S_1^{IMP} decreases while the im-

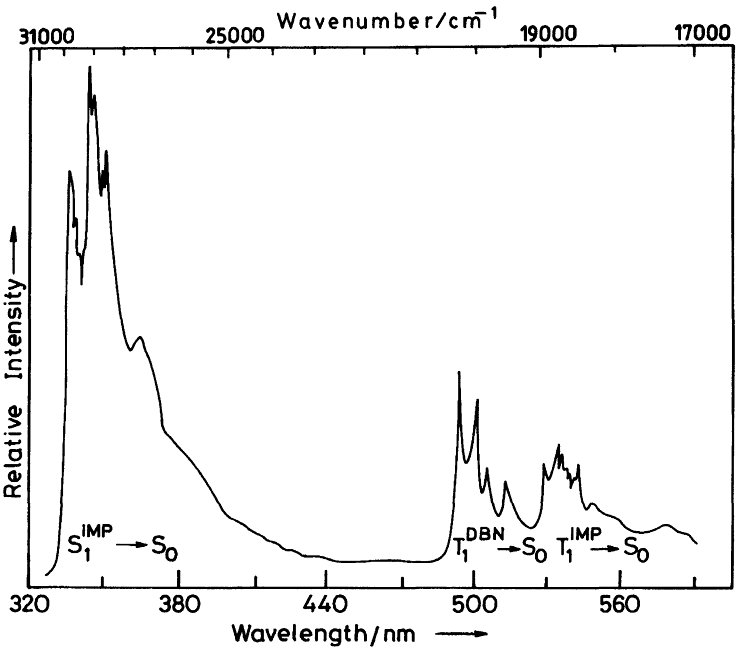

Fig. 1. Total emission spectra of DBN crystal at 77 K.

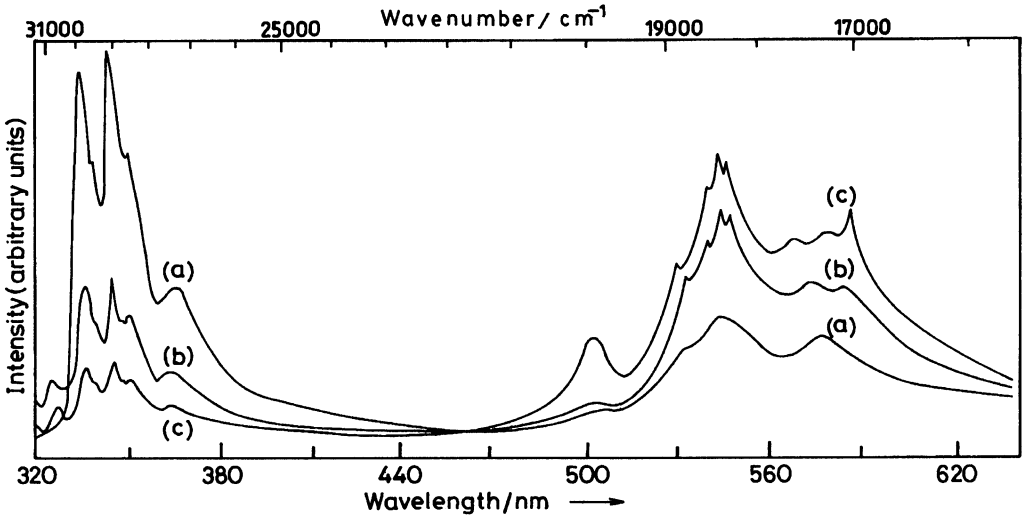

Fig. 2. Total emission spectra of the mixed crystal of DBN and BCN at different concentrations. (a) 13%, (b) 40%, (c) 57%.

purity phosphorescence intensity increases. The experimentally observed spectra are shown in Fig. 2. Furthermore with increase of BCN in DBN new bands appear at 30359 cm^{-1} and at around 20000 cm^{-1} and these gradually increase in intensity with increasing concentration of BCN. These new bands are likely to be the singlet and the triplet emissions of DBN.[19] A similar observation has also been reported for pyrene-doped DBN.[20] The energy level diagram of DBN–BCN mixed crystal is shown in Fig. 3. T_2^{DBN} and S_1^{IMP} are shown by a single level, as these two states are very close. This assignment, we believe is justified because with increasing concentration of BCN, DBN clusters (cages) get smaller and smaller and at a certain point trap free clusters (cages) are formed. DBN excitons then, after repeated reflections at the cage boundaries, may show exciton emissions.

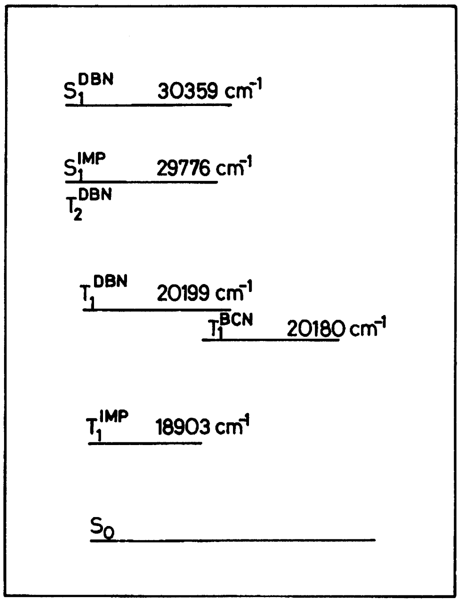

Fig. 3. Energy level diagram of the mixed crystal of DBN and BCN. S_1 and T_1 stand for the singlet and triplet states. S_1^{IMP} and T_2^{DBN} represented by the single line to indicate overlapping of the energy levels.

BCN exhibits orientational disorder with respect to the position of halogen groups, whereas the centers of the molecules are rather regular.[6] The orientational disorder leads to a profound broadening of the spectral profile of the electronic transition due to inhomogeneous distribution of the site energies.[10,11] The line width of the singlet–triplet absorption in BCN crystal is 83 cm^{-1} even at 4.2 K, which is about two orders of magnitude larger than the line width (1 cm^{-1}) for the corresponding transition in DBN.[23] To our knowledge, the energetic positions S_1^{BCN} and T_2^{BCN} are not reported, but it is expected from the similar nature of DBN and BCN structures that the energy levels are close to each other.

The lowest BCN triplet state is known to be located at about 20180 cm^{-1}, which is 20 cm^{-1} below the T_1^{DBN}. At 77 K, where all our studies have performed, the T_1^{DBN} is expected to fall well within the inhomogeneously broadened T_1^{BCN} profile. Furthermore, as already pointed out, with the introduction of guest (BCN) molecules in the host (DBN) lattice, the infinite chain of DBN breaks down and produces a random distribution of different-sized clusters (chains) of the host and guest respectively.

As the inter-chain nearest neighbor resonance interaction for the DBN is negative, the smaller the size of the chain is, the higher the transition energies are. With the increase of BCN concentration, the DBN chain breaks into smaller sizes of different n-mers. Thus the T_1^{DBN} band shifts to the higher energy side with increasing concentration of BCN. Also, due to the overlap of different-sized clusters, profiles of T_1^{DBN} gets broader and broader. On the other hand, the average cluster size of guest (BCN) increases with concentration, which also extends the absorption profile towards the lower energy. A similar situation is expected for the other states like S_1 and T_2. Thus the energy level of the mixed crystal system is very much concentration-dependent.

As discussed earlier, different clusters of guest and host have random spatial as well as energetic distribution over the crystal. The initially excited higher energy cluster can transfer its energy to a lower energy cluster. In our system, the process of energy migration corresponds to a transfer of excitation in real space from an initially excited cluster site to another nearby cluster site having lower energy than the donor. If it so happens that a impurity site resides either in a donor cluster or in an acceptor cluster, then the excitation will get trapped by the trapping center, which eventually gives rise to the impurity emission. Otherwise, the acceptor cluster may in turn act as a donor cluster for another low energy cluster. This energy cascading will continue until final donor clusters contain any trapping site. With this type of energy cascading any T_1^{DBN} or T_1^{BCN} triplet exciton always finds a trap site within the BCN cluster to dump their energy. As a consequence $T_1^{\mathrm{DBN}}\rightarrow S_0$ and $T_1^{\mathrm{BCN}}\rightarrow S_0$ emission do not appear in the mixed crystal spectra. The average size of the guest cluster increases as the size of the host cluster decreases with the increase of guest concentration. Thus the probability of a trap site situated inside a guest cluster increases. As the energy of the larger guest cluster is lower than the smaller one, the trapping efficiency increases with increase of guest concentration. These facts are reflected in the observation that in the mixed crystal spectra $S_1^{\mathrm{IMP}}\rightarrow S_0$ emission decreases whereas $T_1^{\mathrm{IMP}}\rightarrow S_0$ emission increases with the increase of guest BCN concentration. In Fig. 4, we have plotted the ratio of the integrated intensities of trap (I_{Trap}) and the total (I_{Total}) emission at different concentrations of the guest. I_{Trap} and I_{Total} have been evaluted from the observed spectral area. We observed a sigmoid type of behavior in the curve, where there is an indication of a critical concentration (C_{C}), above which the ratio $\alpha = I_{\mathrm{Trap}}/I_{\mathrm{Total}}$ changes abruptly.

The characteristics of the system and also the critical behavior of an abrupt change in energy transfer efficiency encourages us to use the percolation model to explain the energy transfer mechanism, the result shows this to be justified.

The percolation theory of energy transfer has been developed for the case where the sensor (trap or impurity) is in low concentration, as is the case in our system, so that it probes the divergence of the guest clusters. The entire theory of percolation has been treated by Stauffer.[24] Utilizing such theory, Kopelman et al.[1,25] have formulated that the donor/acceptor trapping probability, which is basically $\alpha = I_{\mathrm{Trap}}/I_{\mathrm{Total}}$ is related to C/C_{C} according to the following relations:

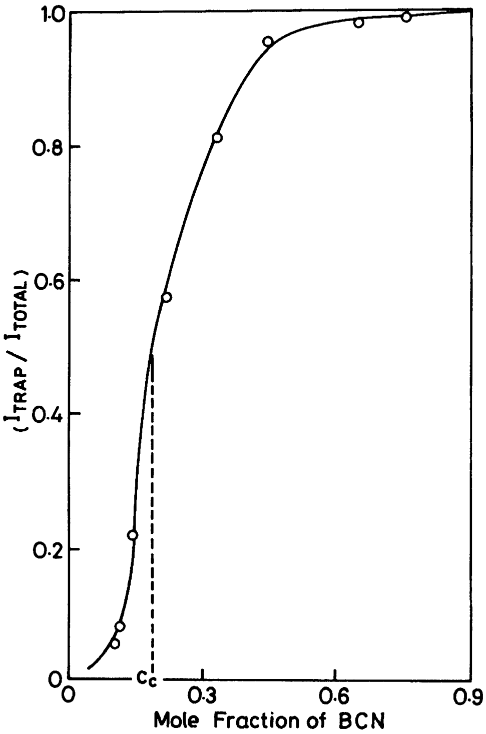

Fig. 4. Plot of the ratio of the intensity of trap emission to the total emission versus the concentration of BCN in DBN.

$$\begin{aligned} \alpha &= |C/C_{\mathrm{C}}-1|^{-\gamma} && C/C_{\mathrm{C}}<1 \\ &= C^{1/\delta} && C/C_{\mathrm{C}}=1 \\ &= |C/C_{\mathrm{C}}-1|^{\beta} && C/C_{\mathrm{C}}>1 \end{aligned}$$

where $\delta = 1+\gamma/\beta$, the critical exponents γ and β depend on the dimensionality of exciton transfer. We define the critical concentration, C_{C} as the concentration at which the energy transfer efficiency is 50%, which means $\alpha = 0.5$.

In Fig. 5, we have plotted log (α) against log $|C/C_{\mathrm{C}}-1|$, which shows two asymptotic straight lines above and below the critical concentration. From the slope of the two lines it is found that $\beta = 0.20$, $\gamma = 2.3$. These val-

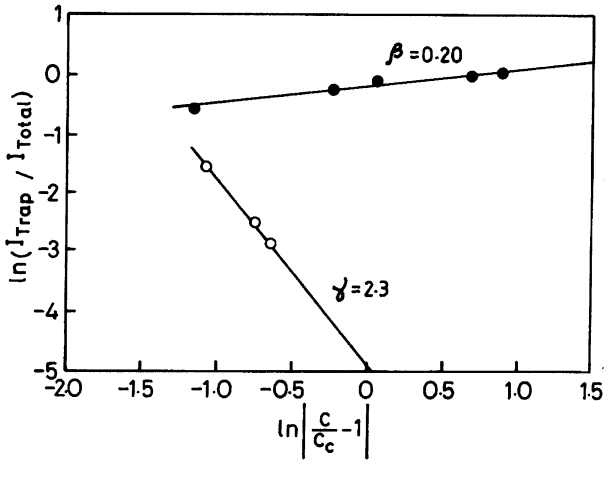

Fig. 5. Plot of ln (α) versus ln $|C/C_{\mathrm{C}}-1|$.

ues are well in agreement with the reported values of β and γ for the two-dimensional topology.[24,25] Hence it becomes evident that as a result of doping BCN in DBN, the unidimensional exciton transport topology is affected and goes over to a two-dimensional one.

In our opinion, the mechanism of percolation accounts well for our system even at a higher temperature (77 K) despite the fact that percolation is thought to erode at higher temperatures.[26] Although we did not consider the role of phonon-assisted long-range super exchange which may be important at 77 K, still the experimental results are quite satisfactorily explained in terms of percolation model and suggest a two-dimensional exciton transport topology for DBN–BCN mixed crystal.

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