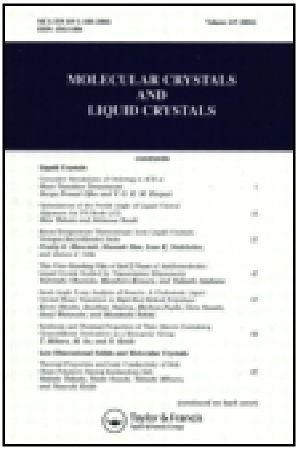

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High Pressure Studies of Critical Concentration Triplet Energy Transfer in Naphthalene: Percolation or Anderson Delocalization?

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Previous work has shown that ternary mixed crystals of naphthalene-h_8 (N-h) and betamethylnaphthalene (BMN) guests in a naphthalene-d_8 (N-d) host exhibit a critical concentration effect in which the phosphorescence intensity of BMN, which is present in very small concentration, rises sharply as the concentration of N-h traps passes through 13%. In the present investigation, high pressure is applied to test the validity of theoretical models for this critical concentration effect, and it is shown that at 4 kbar, the apparent critical concentration is lowered from 13% to 11%. High pressure also enhances supertrap capture and exciton fusion rates, as determined from phosphorescence decay measurements. It is tentatively concluded that the observed lowering of the critical concentration is consistent with a diffusive, dynamic percolation model, if one allows for reasonable increases in the exchange interaction β and the supertrap capture efficiency with pressure. The applicability of an Anderson-Mott description is not excluded by our results, but is considered unlikely on the basis of probable substantial increases in inhomogeneous broadening under pressure.

INTRODUCTION

In the past several years, it has been demonstrated that a number of organic molecular crystals show a "critical concentration" effect, in which the energy transfer efficiency, as monitored by the capture efficiency of a dilute, energetically low lying sensor species or "supertrap," rises abruptly when a certain critical concentration of energy conducting traps is reached. Such an effect has been observed in the triplet manifold in isotopically mixed phenazine[1] and benzene.[2] The most extensively studied crystal of this type is naphthalene, in which the host is perdeuterated naphthalene (N-d), the trap is perprotonated naphthalene (N-h) and the energy transfer sensor is betamethylnaphthalene (BMN), which is typically present in a mole fraction of ca. 10^{-4}. A schematic energy level diagram for the triplet species in this crystal system is shown in Figure 1. Kopelman and coworkers,[3,4] by monitoring the relative phosphorescence of the N-h trap and the BMN supertrap, as a function of N-h concentration, have shown that the phosphorescence of the

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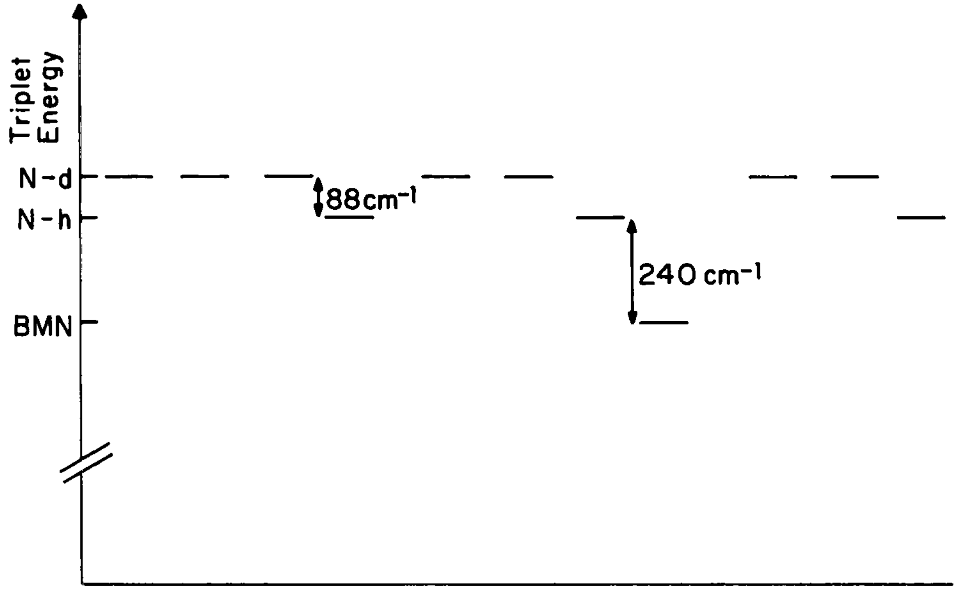

FIGURE 1 Energies of the principal triplet species in the ternary mixed naphthalene crystals studied in this work. The host is perdeuterated naphthalene, N-d, whose phosphorescence (0,0) lies at 21,296 cm^{-1} (Reference 3). The mole fraction of perprotonated naphthalene, N-h, is varied from 0.06 to 0.25, while the concentration of betamethylnaphthalene, BMN, *relative* to N-h is held at ca. 0.001.

very dilute BMN supertrap rises sharply as the N-h concentration is increased beyond a few percent, so that when the N-h concentration is above ca. 25%, almost all of the phosphorescence arises from BMN. The "critical concentration" for triplet transfer, defined as the concentration where the phosphorescence (0,0) intensities of N-h and BMN are equal, is found to be in the range 9–20%, depending on conditions such as the temperature and supertrap concentration.

A persistent question in the literature has concerned the proper theoretical description of this phenomenon. Kopelman and coworkers have employed a percolation description, in which the energy transfer yield of BMN depends on the existence of a pathway of N-h traps, whose interconnections are extended beyond nearest neighbor jumps by the superexchange interaction,[5] so that the triplet exciton can reach a BMN supertrap within its lifetime. Since this mechanism depends crucially on the time, it has been called "dynamic percolation".[6]

It should be mentioned that it is assumed throughout this work, as is commonly done in studies of isotopically mixed (proto in deutero) organic crystals, that the isotopic impurities enter the lattice randomly and substitutionally, since the host and trap are nearly chemically identical. Thus there are no inhomogeneous domains of protonated or deuterated species; whatever connections exist between traps are assumed to arise stochastically because of the random placement of traps near each other.

Klafter and Jortner (KJ) a number of years ago proposed an alternative interpretation[7] of the critical concentration effect in terms of an Anderson-Mott transition, in which the onset of efficient trap to supertrap transfer occurs when the lattice-averaged superexchange interaction (which is *also* taken to be the intertrap coupling mechanism in the KJ model) becomes comparable to the inhomogeneous broadening at the N-h trap sites. Other theoretical descriptions include the average rate constant kinetic approach of Blumen and Silbey,[8] and the master equation approach of Loring, Andersen, and Fayer,[9] which shows that the "sharp" rise in BMN relative luminescence yield depends on the distance dependence of the interaction which gives rise to trap to trap energy transfer.

In this work we employ high pressure as a test of the validity of the above theoretical models, specifically the Anderson-Mott description vs. the percolation model. Spectroscopic measurements of the triplet Davydov splitting in anthracene[10] have previously indicated that applied pressure in the range of 1–6.8 kbar (0.1–0.68 GPa) can increase the triplet exchange interaction β by up to 40%. We would expect that naphthalene, which has a qualitatively similar crystal structure to anthracene and a similar compressibility, would show similar increases in β at comparable pressures. If the interaction which leads to efficient population of the supertrap depends primarily on connections between N-h traps, then we would expect high pressure to have a relatively smaller effect on the observed critical concentration than in the case of the Anderson description, which depends on the longer-range averaged interaction. This expectation is obvious in the case of classical percolation, in which only nearest neighbor steps are allowed; since pressure moves molecules closer together but does affect their identity, it should not change the percolation threshold at all in this limit. However, even in the case where the superexchange interaction allows for longer than nearest neighbor jumps among traps, it can still be shown (see below) that a given increase in β will lead to a much greater lowering of the critical concentration in the Anderson model than in the case of "dynamic percolation", *provided no other parameters in the models are changed by the pressure.*

We have previously demonstrated[11] that a pressure of 4 kbar, applied to a 13% N-h crystal, which corresponds to the critical concentration threshold at ambient pressure, causes a dramatic enhancement of the BMN supertrap phosphorescence relative to the N-h trap emission, and thus makes the 13% crystal at 4 kbar comparable to a 16% N-h crystal at ambient pressure, in terms of supertrap/trap phosphorescence yields. (See Figure 2 and discussion below.) In the present work, we report additional measurements at several N-h concentrations, which show that the critical concentration, defined as the concentration at which the above ratio of phosphorescence intensities equals unity, is lowered from 13% (ambient) to 11%. We then discuss the significance of these results in terms of the expected increase in the exchange interaction β induced by this pressure, and the predicted resultant effects on the critical concentration, in the dynamic percolation and Anderson descriptions. It is tentatively concluded that our results are consistent with the dynamic percolation model, if one allows for an alteration of the "trapping efficiency" parameter in this model at high pressure. We also report some initial measurements of N-h trap phosphorescence decays in previously pressurized crystals which suggest the enhancement of supertrap capture rates and triplet-triplet annihilation by pressure, and discuss these results and the above steady state phos-

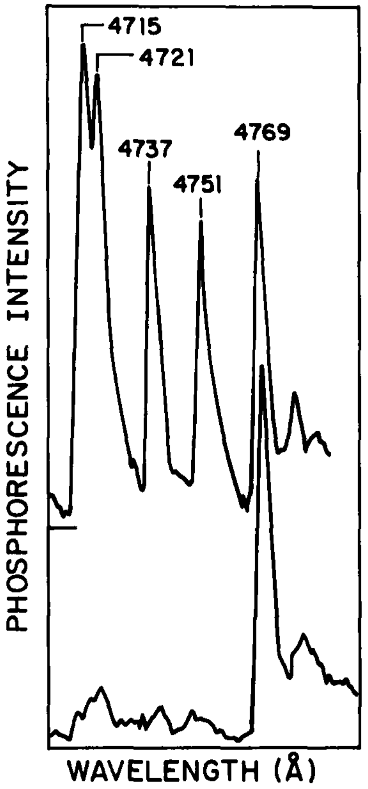

FIGURE 2 Phosphorescence spectra of 13% perprotonated naphthalene (N-h) and betamethylnaphthalene (BMN) in a perdeuterated naphthalene host. The BMN concentration, relative to N-h, was 0.0011, and the spectrometer slit widths were ca. 350 μm. The ordinate of the top spectrum has been offset vertically for ease of comparison. The 4 kbar spectrum (bottom) shows dramatic enhancement of the BMN phosphorescence at 4769 Å relative to the N-h emission at 4715 Å, as trap to trap transfer is enhanced. Adapted with permission from *J. Phys. Chem.*, **90** (1986) 8, American Chemical Society.

phorescence data in terms of recent work which has indicated that the networks of interacting traps in these crystals have fractal properties.

EXPERIMENTAL

Perdeuterated naphthalene (99% deuterium, Merck), perprotonated naphthalene (Baker) and betamethylnaphthalene (Baker) were all sublimed and extensively zone refined (at least 150 passes). The mixed crystals were grown by standard Bridgman techniques. The method of Ahlgren[12] was used to keep the ratio of BMN to N-h reasonably constant; a "standard" crystal, made by doping N-h with 0.1 mole % BMN was first grown, and then portions of this crystal were added to N-d to make ternary mixed crystals of the desired concentrations. The N-h concentrations in the grown crystals were determined by low resolution mass spectrometry.

High pressure phosphorescence measurements were performed using a piston-cylinder cell.[13,14] The crystal samples were attached by stopcock grease to a split polyurethane ring which was then inserted into the cell in contact with the pressure chamber. Ruby chips were placed near the crystal sample so that the ultimate pressure in the cell at low temperatures could be determined by the pressure-induced spectral shift of the R_1 fluorescence line at ca. 693.6 nm,[15] excited by the Xe lamp used to excite the naphthalene samples. Spectroscopic grade glycerol was added to the pressure chamber and used as the pressure transmitting medium. Pressure was applied at room temperature using a conventional hydraulic press to load the piston, and the pressure was "locked in" by tightening a nut around the piston. The cell was then mounted inside a Janis Model 10-DT variable temperature cryostat, where it was slowly cooled (4–5 hours) to liquid helium temperatures. A germanium resistor in contact with the cell was used to monitor the pumped helium temperatures.

The sample was excited with a 1000 W Xe lamp, whose ouput was filtered by a nickel sulfate/cobalt sulfate solution and a Corning 7-54 filter. Excitation of the sample and detection of phosphorescence through the single window of the pressure cell was accomplished with an arrangement of two 45° mirrors mounted below the cell window and aligned in the optical windows of the cryostat. Phosphorescence was detected at 90° with respect to the excitation beam, spectrally resolved with a 0.75 m Spex monochromator, and detected photoelectrically by a Bailey Centronics P4283 photomultiplier tube.

The measurements of phosphorescence decay curves were made with a 13% N-h crystal which had been previously exposed to 4 kbar pressure. In this sample, as noted in our previous report,[11] the pressure-induced changes in luminescence intensities persisted after the pressure was released, and it was more convenient experimentally to measure the decay with such a sample, rather than with a sample mounted in the pressure cell. This retention of pressure-induced changes has been seen with other samples near the critical concentration,[14] and is probably a result of plastic deformation[16]; annealing at 70–75°C largely restores the spectra to their characteristics at ambient pressure, when the samples are then re-examined at cryogenic temperatures.

This 13% sample was irradiated in a separate optical dewar with a 100 W Hg lamp (Osram), filtered in the same way as was the 1000 W Xe lamp cited above. A chopper phosphoroscope, operating at 133 Hz, was used to isolate the phosphorescence from prompt emission and scattered light. A Uniblitz programmable shutter was employed to terminate the excitation (closing time ~5 msec) and repetitive decays were accumulated with a Tracor Northern 570A signal averager.

RESULTS AND DISCUSSION

A. Phosphorescence intensity changes under steady illumination

1. *Summary of observations*

a) *Dopant traps: N-h and BMN*

The top section of Figure 2 (adapted from reference 11) shows the phosphorescence peaks for N-h (4715 Å) and BMN (4769 Å) in a 13% N-h crystal. The intermediate

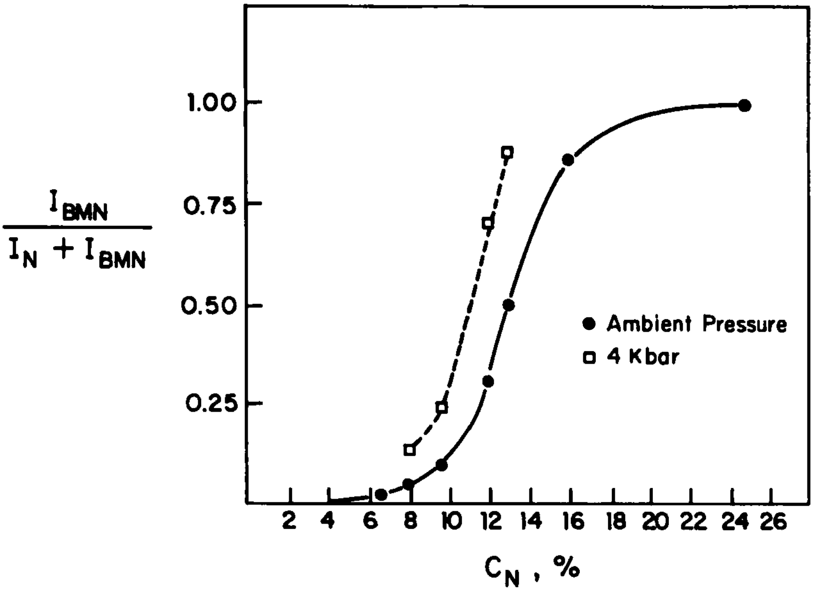

FIGURE 3 Relative phosphorescence yields of betamethylnaphthalene (BMN) and naphthalene-h_8 at 1.7 K in a naphthalene-d_8 host crystal, as a function of N concentration. The data illustrate a shift to a lower critical concentration at 4 kbar.

peaks have been assigned to defect traps, and will be discussed in more detail below. The main point to notice is that, for the crystal of Figure 2, the phosphorescence intensities of BMN and N-h are about equal. Thus the critical concentration at ambient pressure is 13%, which agrees with the findings of Ahlgren.[12]

We also measured the ratio of BMN (0,0) phosphorescence intensity to the total of the (0,0) phosphorescence intensities of N-h and BMN in crystals of other concentrations. These results are shown by the solid dots in Figure 3, for crystals of 6.6, 8.0, 9.5, 12, 13, 16 and 25% N-h. Again, the smooth curve rises sharply as the N-h concentration is increased, and the apparent critical concentration is 13%.

When *pressure* is applied to the 13% N-h crystal, the N-h peak and all the defect trap peaks become much weaker compared to the BMN phosphorescence peak at 4769 Å (Figure 2, bottom curve). If crystals of other concentrations are studied (Figure 3), the BMN phosphorescence is also enhanced relative to N-h; the open squares represent the phosphorescence ratios of these crystals. The dashed curve drawn through these points indicates that the apparent critical concentration at 4 kbar is 11% N-h, vs. 13% at ambient pressure.

b) Defect traps and phosphorescence linewidths

As is common in mixed crystal studies, we observed emission from defect of "X-traps," which were not intentionally added to the crystal melt. These X-traps can arise from either minute chemical impurities or structural imperfections.

Although our crystals were similar to those of Ahlgren's "series B" samples, in that the relative (BMN to N-h) concentration was 10^{-3}, we did not purify our starting materials by potassium fusion, as was done in Ahlgren's work.[12] Thus our samples contained more defect traps due to chemical impurities (see below). Nevertheless, it is worth noting that the critical concentration, as determined by the BMN/N-h phosphorescence ratios (Figure 3) was not affected.

The top spectrum of Figure 2 shows prominent trap emissions at 4721, 4737 and 4751 Å. These additional traps have all been observed by Ahlgren[12] in his "series A" samples, which he did not subject to purification by potassium fusion. The trap at 4721 Å is attributed to "environmental effects" in perdeuterated naphthalene, presumably a structural defect. The 4737 Å trap is attributed to a chemical impurity in perprotonated naphthalene, while the trap at 4751 Å is assigned to perdeuterated BMN, present in the starting material. We would have expected the trap phosphorescence intensities to behave differently as the N-h concentration is increased; specifically, one might expect that the intensity of emission from the 4737 Å trap would increase more rapidly, since this is assigned to an impurity in perprotonated naphthalene. In contrast to this expectation, these trap intensities remained roughly comparable *to each other* through the concentration range studied.

As the N-h concentration was varied at ambient pressure, the intensities of the defect phosphorescence, relative to N-h and BMN, changed. Below the critical concentration, the average of the defect trap phosphorescence intensities at 4721, 4737 and 4751 Å was comparable to BMN, while above this concentration, it became comparable to N-h. As is evident from Figure 2 (top spectrum), the phosphorescence of the defects, BMN and N-h are all of roughly equal intensity *at* the critical concentration.

One would expect *pressure* to alter the relative phosphorescence intensities of the defect traps, since pressure should increase the number of structural defects, but would not increase the number of impurities. In the 8% and 9.5% crystals, the intensity of the "environmental" defect at 4721 Å does become significantly larger than the impurity defect traps at 4737 and 4751 Å.[14] This is consistent with the previous assignment of this emission to a structural defect.[12]

Also, the apparent *linewidth* of the N-h emission in the 8% and 9.5% crystals increases by at least a factor of two or three at 4 kbar pressure.[14] This statement must be qualified by noting that, owing to our illumination and detection geometry, signal optimization was a tedious process, and we had to use wide slits (ca. 300–400 μm) in most cases to obtain satisfactory signal to noise from crystals mounted in the pressure cell. Thus the measurement of linewidth is only approximate. Nevertheless, the FWHM of the N-h emission in these crystals increased from ca. 5 Å at ambient pressure to ca. 14 Å at 4 kbar. The apparent broadening of the N-h phosphorescence line can be at least partially attributed to pressure induced enhancement of other X-traps within 6 Å of the N-h (0,0) which have been observed in $C_{10}D_8$ at higher resolution.[12] Part of this broadening is likely to be due to *increased inhomogeneous broadening* of the N-h emission, however, since the additional grouping of $C_{10}D_8$ X-traps occurs to the red of the N-h phosphorescence peak, and the pressure induced broadening appears to be symmetric. An estimate of the effect of pressure on the inhomogeneous broadening of the N-h triplet state is important in the assessment of the validity of the Anderson-Mott description (see below).

2. Consideration of theoretical models

a) *Anderson-Mott transition* Klafter and Jortner[7] derive the following relation which must be satisfied by the critical concentration $\overline{C}$ in systems where the exciton interactions are important only in two dimensions:

$$\overline{C}\exp(-\pi\overline{C}) = (W/2\pi\eta\beta)\ln^2(\Delta/\beta) \qquad (1)$$

In the above, W is the inhomogeneous site energy broadening of the species forming the "impurity band" which gives rise to long range energy transport, η is a parameter of the theory which ranges between 6 and 28, β is the nearest neighbor exchange interaction (1.16 cm^{-1})[17] and Δ is the triplet trap depth for N-h in N-d (88 cm^{-1}).[3] This relation is obtained by equating the lattice-averaged superexchange interaction (see Equation (2) below), in a quasi-continuum approximation, to the inhomogeneous broadening parameter W/η.

As we have no direct measure of the value of W/η, we can use the ambient pressure results to fit this parameter. At ambient pressure, $\overline{C} = 0.13$, so that Equation (1) yields $W/\eta = 0.0336$. Taking η to be between 6 and 28 gives a W value between 0.20 and 0.94 cm^{-1}. The lower end of the range is certainly the right magnitude for the expected degree of inhomogeneous broadening in an isotopically mixed crystal.[1,18]

If we assume that at 4 kbar, the exchange interaction is increased by 20% to 1.392 cm^{-1}, in analogy to anthracene,[10] then we may calculate from Equation (1) above that the critical concentration would be reduced to $\overline{C} = 0.087$, which is a much larger change than was actually observed. To obtain a lowering of $\overline{C}$ from 13% to the observed value of 11% requires only a 7.3% increase in β. However, these calculations make the severe assumption that W, the inhomogeneous broadening, is unaffected by the pressure. From Equation (1) one can see that an increase in W of only 11% would be sufficient to override the effects of a 7% increase in β, and thus leave the critical concentration unaffected. A 31% increase in W would wash out the effect of a 20% increase in β.

As we mentioned above, the N-h phosphorescence linebroadening observed in samples below the critical concentration is certainly consistent with at least a 30% increase in W. Other evidence for increased inhomogeneity of molecular environment with pressure comes from the observations[11,14] that, near the critical concentration, the pressure induced changes in luminescence yields remained even after the crystal was warmed to room temperature, removed from the pressure cell, and then re-examined at liquid helium temperatures at ambient pressure. As mentioned above, this is probably due to plastic deformation of the sample, which relaxes incompletely when the pressure is released. This "irreversible" pressure effect occurs only in crystals near the critical concentration, and does not take place in the 6.6%, 8%, 16% and 25% crystals. It indicates that, near the critical concentration, the energy transfer pathways are very sensitive to small changes in structure. The effect also suggests an increase in non-uniformity of environment with pressure.

Thus although we do not have sufficient information to make a definitive conclusion regarding this model, we believe that the applicability of the Anderson description to our results is unlikely, in view of the probably large increase in inhomogeneous broadening with pressure. A more conclusive statement will await improvements in our optical configuration which will allow us to measure emission and, hopefully, absorbance linewidths more accurately.

b) Dynamic exciton percolation

In this model, used extensively by Kopelman and co-workers, the relative intensity of BMN to N-h phosphorescence depends upon the ability of a triplet exciton, migrating among N-h traps connected by the superexchange interaction (which allows for tunnelling between non-nearest neighbor N-h traps) to find a BMN supertrap within the triplet lifetime (2.7 sec).[19] It should be mentioned at the outset that the Klafter-Jortner application of the Anderson model also assumed that the superexchange interaction

$$J_n = \beta\ (\beta/\Delta)^{n-1} \tag{2}$$

where n is the number of steps or "bonds" between sites in the lattice separating the two N-h dopant molecules, and β and Δ have been defined above, is also the mechanism which gives rise to N-h trap to trap energy transfer. (The term "bond," which is not meant to imply a chemical bond, arises from classical percolation theory, in which a walker is permitted to step between two sites on a lattice only if there exists a bond between them.) Whereas the Anderson model relates $\langle J \rangle$ to the inhomogeneous broadening W, the dynamic percolation model considers the growth of clusters in the N-d lattice with increasing mole fraction of N-h. Relevant parameters are the triplet lifetime and the supertrap concentration relative to N-h.

The most complete expositions of the dynamic percolation model can be found in articles by Hoshen *et al.*[20] and Monberg *et al.*[21] The model is applied to samples similar to ours by Ahlgren,[12] and we use his notation for the most part. There are three key relationships:

$$\overline{C} = 4/[n^2 + (n+1)^2] \tag{3}$$

$$t = \Delta^{n-1}/\Gamma_n\beta^n c \tag{4}$$

$$t\xi/S = \tau_0 \tag{5}$$

The first equation is a semi-empirical relation, based on simulations, between the critical concentration for percolation in a two dimensional square lattice (reflecting the topology of the dominant, translationally inequivalent nearest neighbor exciton interaction in naphthalene[3,22]), and the maximum number of "bonds" in the lattice which can be spanned by a naphthalene triplet exciton in its lifetime. The second equation expresses the time t needed to transfer through n "bonds" in the lattice in terms of the superexchange interaction. The speed of light c is included in this equation because β and Δ are usually expressed in cm^{-1}. The n which is used here is the maximum number of lattice "bonds" through which the exciton can transfer, consistent with the apparent critical concentration [Equation

(3)]. The term Γ_n is intended to account for the multiple zig-zag pathways connecting two sites on the square planar lattice, which will accelerate the transfer. Values of Γ_n for integer n have been given by Kopelman *et al.*.[3] Since the time determines the maximum range of a naphthalene triplet exciton through Equations (4) and (5), the value of n need not be an integer; values of Γ_n for non-integer n can be interpolated graphically.[12]

The last equation, Equation (5), states merely that the exciton must traverse enough N-h sites within its lifetime τ_0 to have an even chance of finding a supertrap. The parameter S is the relative supertrap concentration, i.e. the ratio of the BMN and N-h concentrations. If this factor is, for example, 1000, then, assuming that each jump visits a new site, the exciton must make at least 1000 jumps within its lifetime, with the average time between jumps given by the t of Equation (4), to visit the supertrap site at least once. Since not all jumps will occur to distinct sites, a "jump efficiency factor" ξ, whose value is in fact *inversely* related to the efficiency of finding a supertrap, is introduced. This factor ξ is thus intended to incorporate trap site revisitation, supertrap capture efficiency (an exciton may have a less than unit probability of being captured by a supertrap once it has encountered one), and phonon assistance.

We now try to see if the dynamic percolation mechanism can account for our pressure results, assuming that β is increased by 20% by 4 kbar pressure. Starting with the ambient pressure value of $\bar{C}$ as 0.13, we calculate from Equation (3) that n should be 3.39. The appropriate value of Γ_n is then 2.55.[12] The apparent value of the jump efficiency factor is determined by Equation (5). Since $S = 10^{-3}$ for our samples, and τ_0, the naphthalene triplet lifetime is 2.7 sec,[19] we find that the apparent value of ξ is 7.69×10^3. That is, the exciton must make about $\xi/S \sim 8 \times 10^6$ jumps of duration t during its lifetime to have an even chance of finding a supertrap.

We now calculate the apparent increase in β implied by the decrease of $\bar{C}$ to 0.11 at 4 kbar pressure. The corresponding value of n is 3.73, for which $\Gamma_n = 3.08$. Using Equation (4), and assuming that the jump efficiency factor is unchanged, we find that β must increase by 41%. This is about twice the increase in β (20–22%) reported for anthracene at 4 kbar.[10]

Before discussing the possible reasons for this apparent discrepancy, we note that for a given increase in β, the change in critical concentration is certainly much larger in the Anderson description than in the case of dynamic percolation. As we have seen, only a 7% increase in β is needed to lower $\bar{C}$ from 0.13 to 0.11 in the case of the Anderson description, while a 41% increase in β is needed in the dynamic percolation case.

We have just noted that the increase in β which is required by the dynamic percolation model is larger than what was reported for anthracene at similar pressures. It is however possible that a pressure of 4 kbar could produce an increase in β which is larger than 20% in naphthalene. In the anthracene work,[10] it was the Davydov splitting which was actually measured; it increased by 16% at a pressure of 5.4 kbar. This splitting was considered to be the resultant of exchange and charge-transfer contributions, and the individual terms were calculated from measured changes in lattice parameters and approximate molecular wavefunctions, using quantum chemical methods.[23,24] The calculated change in Davydov splitting was in fairly good agreement with the experimentally observed value, but it is clear that there could easily be large uncertainties in the calculated changes in the exchange interaction. The enhancement in the Davydov splitting itself was stated to be uncertain by ±30%. Thus it would not be surprising if, in naphthalene, the exchange interaction β might be increased by 30%, rather than 22% at 4 kbar. The compressibility of naphthalene is a few percent larger than that of anthracene.[25]

Also, it is quite possible that the jump efficiency factor ξ changes with pressure. At a particular temperature, ξ is associated with the number of exciton hops needed to find, and to be captured by a supertrap. Once a supertrap is found, the capture probability may be less than unity, and ξ also incorporates this factor. It is known that "energy funnels," i.e. distorted host molecules of slightly lower energy surrounding a chemical impurity trap, exist in naphthalene,[26] and it is likely that pressure would enhance the intermolecular interactions which lead to such funnel states, thus lowering their energy. For example, if we retain the assumption that β increases by only 20% at 4 kbar, then a 45% decrease in ξ would be consistent with the observed lowering in critical concentration (*decreases in ξ are associated with increased supertrapping efficiency*). If one allows for the possibility of a 30% increase in β at 4 kbar, then only a 26% decrease in ξ with pressure is needed.

Thus we conclude that our observed lowering of the critical concentration from 13% to 11% at high pressure is consistent with the dynamic percolation model, if one allows for a 20%–30% increase in the exchange interaction, along with a 45%–25% increase in supertrapping capture efficiency with pressure. Other, independent recent evidence for percolation-like behavior of exciton migration in this system will be discussed below, when we describe our phosphorescence decay measurements.

In our initial report of our pressure results,[11] we noted that our observed lowering of the critical concentration (then assumed to be 3%) was larger than would be predicted by the dynamic percolation model for a 20% increase in β with pressure (keeping ξ constant). We also noted that this model assumed a linear dependence of the trap to trap jump rate on the superexchange interaction. A quite reasonable alternative would be to assume that phonon scattering is fast enough so that incoherent or diffusive transport would occur. The phonon induced scattering rate between the $|+\rangle$ and $|-\rangle$ dimer states in isotopically mixed naphthalene has been determined by electron spin echo methods to lie in the range of 10^8 sec^{-1},[27] and it is entirely reasonable to expect that exciton transport between two N-h molecules separated by three bonds ($J_n \sim 2.5 \times 10^{-4}$ cm^{-1}) in the N-d lattice would be incoherent. This would lead to a quadratic dependence of the transfer rate on the superexchange interaction.

More recent time-resolved delayed fluorescence measurements by Gentry and Kopelman, in which the rate of supertrap capture was monitored in the N-h concentration range of 20% to 100%, have indicated that trap to trap transport in this range is *diffusive*, i.e. the rate of exciton transport does depend on the square of the superexchange interaction.[28] We suggested in our earlier report that this model might have closer agreement with our results, because a given increase in β and hence J_n would lead to a larger increase in the transfer rate. However, it should also be kept in mind, that with a quadratic dependence, the transfer rate would also fall off faster with distance, and the effect on the size of the clusters needed for percolation at criticality might not be affected, in a "diffusive," dynamic exciton percolation description.

One may simply modify Equations (3)–(5) above, to include a quadratic dependence of t on the superexchange interaction by writing:

$$t = k\,(\Delta^{n-1}/\Gamma_n \beta^n c)^2 \tag{6}$$

where k is a proportionality constant. One may then ask what increase in β is required to produce the observed change in $\overline{C}$ from 0.13 to 0.11, in this modified model. The values of n are determined by Equation (3) from the observed critical concentrations, so these are unchanged. Also, the values of S and τ_0 in Equation (5) are not changed, and for the purposes of this calculation, we assume that the jump efficiency factor ξ is also unchanged. It is clear then that we have the condition $t' = t$, or

$$k(\Delta^{n'-1}/\Gamma_{n'} \beta^{n'} c)^2 = k(\Delta^{n-1}/\Gamma_n \beta^n c)^2 \tag{7}$$

where the prime refers to high pressure conditions. It is apparent that, in terms of the model as presently formulated, the power to which the superexchange interaction is raised has no effect on the apparent increase in β; one simply takes the square root in Equation (7) and obtains the same required change in β as obtained above.

It is in fact *likely* that the exciton transfer between isolated N-h monomers in these crystals at 1.7 K is diffusive, as argued above. However, this assumption does not affect our ability to fit our high pressure results with the percolation model.

B. Phosphorescence decay measurements

Previous work of Ahlgren *et al.*[12,29] has shown that the phosphorescence decay time of N-h traps in a perdeuterated naphthalene host, decreases dramatically near the critical concentration. For example, Ahlgren[12] has found that in a crystal with a relative BMN concentration of 10^{-3}, at 1.7 K, the first 1/e time decreases from 2.6 sec for 1% N-h to 0.45 sec at 11% N-h. This decrease is attributed to a combination of increased energy transfer to supertraps[29] and increased triplet-triplet annihilation or fusion.[4,19]

Based on previous results, it is clear that both these processes contribute to the acceleration of the decay. Klymko and Kopelman[19] have shown that, in crystals grown from naphthalene which had been subjected to potassium fusion so as to remove BMN, and excited with a 1600 W Xe lamp, the phosphorescence lifetime decreases sharply from a low concentration (0.1%) limiting value of 2.7 sec, as the N-h concentration increases, and the probability of annihilation also increases. Also, as would be expected, in crystals of fixed concentration, the phosphorescence decay was accelerated and the yield of delayed fluorescence increased with increasing excitation intensity, as the xenon lamp excitation intensity was varied with neutral density filters. However, no quantitative measurements of excitation photon flux were reported.[19]

In ternary mixed crystals studied by Ahlgren,[4,12,29] supertrapping takes place in addition to the triplet fusion seen in crystals lacking BMN. This channel is *also* enhanced as the N-h concentration is increased, as seen from the steady state phosphorescence measurements reported previously[3,4,12] and in the present work, and measurements of the time evolution of BMN phosphorescence after the excitation is shuttered.[12] The BMN phosphorescence shows a rise time, on the time scale of seconds, which can only result from the feeding of BMN supertraps by excited N-h traps after the excitation is extinguished. This rise time shortens as the N-h concentration increases toward the critical concentration.

We have obtained decay data which is also qualitatively consistent with the increase of supertrapping and annihilation near the critical concentration. For a 13% N-h in N-d crystal, we obtained a first 1/e time of 1.16 ± 0.10 sec, much shorter than the 2.7 sec monomolecular decay time observed for naphthalene in the limit of low concentration.[19] Our decays were highly non-exponential, and the apparent 1/e time depended on the interval of the decay curve which was fit. Table I displays these 1/e times for different time intervals of the decay, and shows that the effective lifetime increases sharply as the decay proceeds. In the tail of the decay, the lifetime approaches the value for monomolecular decay.

To investigate the effect of pressure, we examined a 13% N-h crystal which had been previously exposed to 4 kbar pressure, and retained the pressure-induced changes in phosphorescence intensities after the pressure had been released. This pre-pressurized crystal showed a first 1/e time of 0.46 ± 0.05 sec, much shorter than the crystal studied at ambient pressure. The effective 1/e times, determined over intervals chosen from the first second of the decay profile, also decrease with exposure to high pressure (Table I). This is consistent with enhanced supertrapping and triplet fusion at high pressure; both of these effects are consistent with an increase in the exchange interaction β. An increase in supertrapping efficiency would also be consistent with the decrease in ξ under pressure which was proposed above to explain the change in steady state phosphorescence intensity ratios with

TABLE I

Apparent 1/e decay times for naphthalene-h_8 phosphorescence at 1.7 K in a 13% N-h crystal at ambient pressure and in a 13% N-h crystal previously exposed to 4 kbar pressure. Decay times were obtained by fitting a monoexponential decay function to data recorded during specified time intervals after the closing of the shutter.

Time Interval (sec)	Apparent 1/e Time Ambient Pressure	Apparent 1/e Time Pre-Pressurized Sample
.04–.10	.50 ± .06	.17 ± .05
.12–.20	.66 ± .01	.44 ± .02
.22–.40	.88 ± .11	.59 ± .08
.42–1.00	1.46 ± .10	1.05 ± .11
1.02–2.00	1.88 ± .04	2.13 ± .04
2.02–8.00	2.36 ± .06	2.61 ± .16

pressure. The problem with this latter interpretation, tempting as it is, is that it is difficult to assess quantitatively the separate contributions of an enhanced exchange interaction and an enhanced supertrapping efficiency to the observed increase in decay rates.

Interestingly, the N-h phosphorescence lifetime in the tail (2–8 sec) of the decay is longer in the pre-pressurized crystal than in the crystal at ambient pressure. This can also be understood in terms of the increase in β with pressure in the following way. Exciton interactions in the isotopically mixed naphthalene crystal give rise to a range of triplet energies which correspond to N-h monomers, dimers, trimers, etc. which occur in the randomly doped host lattice. For example, the dimer $|+\rangle - |-\rangle$ splitting has been determined to be about 1.2 cm^{-1},[17,27] and it is reasonable to assume that energy mismatches of ca. 1 cm^{-1} between the lowest states in the various N-h clusters exist in heavily doped crystals. These mismatches need to be overcome in order to achieve long range energy transport to BMN sites, and this factor accounts for the observed lowering of the critical concentration when the temperature is raised from 1.7 to 4.2 K.[21] The lowering of the critical concentration with increase in temperature demonstrates the importance of phonon assistance in overcoming the energy mismatches among clusters. In terms of our decay experiments, after the illumination is shuttered, naphthalene triplet species either decay to the ground singlet state, self-annihilate, or are captured by supertraps. The tail of the curve reflects those N-h excitons that are unable to reach a BMN site within their lifetime, either because they are topologically unconnected to a cluster containing a BMN molecule, or because they are energetically detuned from such clusters. Pressure, by increasing the exchange interaction, increases the energy mismatches so that these N-h species are unable to reach BMN sites within their lifetime and so decay with the naphthalene monomolecular lifetimes. Since in steady state, pressure enhances the BMN phosphorescence, it is clear that the apparent enhancement of N-h to BMN transfer in the initial portion of the decay curve affects more N-h sites than the inhibition of transfer in the tail.

Recently, studies of luminescence decays in naphthalene crystals have demonstrated the utility of fractals, or structures of fractional dimension, in interpreting the dynamics of energy migration in these crystals, and similar substitutionally disordered materials.[30–32] This has been demonstrated through measurements of the decay of delayed fluorescence, produced from the annihilation of two naphthalene triplet excitons, and studied vs. N-h concentration. In a classical homogeneous medium, the ratio of the intensity of the delayed fluorescence to the squared intensity of the phosphorescence should be a constant with time. However, if the excitons are migrating on structures of fractional dimension, this ratio will be time dependent. Klymko and Kopelman[30] have deduced the relation

$$DF/P^2 \propto t^{-h}$$

for annihilating excitons migrating on a fractal structure, where h is the "heterogeneity exponent." Experimentally, for isotopically mixed naphthalene they observe a value of $h = 0.35$, for a crystal at the critical concentration[31]; above the critical concentration, the plot of DF vs. P^2 is horizontal, i.e. $h = 0$, the result expected for classical kinetics. Evesque and Duran[32] have obtained similar results by studying the decay of the delayed fluorescence over short time intervals after a laser flash, during which time the naphthalene triplet concentration did not change appreciably.

The value of h has been shown[30] to be equal to $1 - d_s/2$, where d_s is the "spectral dimension," which itself is related to the number of distinct sites $N(t)$ visited by a random walker on a fractal structure,[33-35]

$$N(t) = t^{d_s/2}$$

For classical migration $d_s = 2$, so that h would be expected to be zero. Alexander and Orbach[35] have shown that for a *percolating cluster* at the critical threshold, $d_s = 4/3$, so that h would equal 0.33, very close to the experimental value found by Kopelman for an isotopically mixed naphthalene crystal at the critical concentration.

Since the heterogeneity exponent has a value which is consistent with the value expected for an exciton walking randomly on a percolating cluster, this implies, or is at least consistent with the idea that energy transfer in this system should be viewed as a percolation phenomenon, in which the connectivity of the N-h sites in the lattice is the crucial factor in determining the yield of long-range energy transport. This body of recent experiments[19,30-32,36] constitutes another line of evidence in favor of the percolation description in these naphthalene crystals. To investigate how the spectral dimension changes with pressure, we are planning to make measurements of delayed fluorescence and phosphorescence in highly purified isotopically mixed naphthalene crystals. Large changes in d_s are expected for a crystal which is below the critical concentration at ambient pressure but is above it at high pressure. Such experiments will provide additional evidence regarding the validity of the percolation model in describing our pressure results.

SUMMARY AND CONCLUSIONS

By studying the pressure effect on the phosphorescence intensities of betamethylnaphthalene and naphthalene-h_8 in crystals of varying N-h concentration in a naphthalene-d_8 host, we have determined that the critical concentration is lowered from 13% (ambient) to 11% (4 kbar) in our samples. Using theoretical relationships which predict the critical concentration from values of the exchange interaction β and other relevant parameters, we have shown that, for a given increase in β there is a much larger effect on the critical concentration in the Anderson-Mott description than in the case of dynamic percolation. This conclusion holds even if we allow for diffusive hopping in the percolation model. Thus, even though the superexchange interaction permits non-nearest neighbor tunnelling between N-h sites, the predicted effect of pressure in increasing β is much smaller in the percolation model than in the Anderson description, reinforcing our original view as to the greater importance of connectivity between neighbors in the percolation model, and the likely smaller effect of pressure.

The applicability of the Anderson description to our results is not ruled out by our experiments, which have provided no direct measure of *W*, the inhomogeneous broadening. However, it is likely that there are large increases in *W* under pressure, as inferred from observed increases in emission linewidths and persistent pressure-induced changes, which imply the role of plastic deformation of the crystals. Fairly modest increases in *W* would be sufficient to wash out the effect of the increased β. By contrast, the observed change in critical concentration is consistent with dynamic percolation, if one allows for reasonable increases in the exchange interaction and superexchange capture efficiency with pressure. Other recent work which has demonstrated the fractal nature of the kinetics of exciton fusion in these crystals provides strong evidence for a percolation process.

Based on our work, we would conclude that the probable mechanism for the critical concentration effect in these BMN/N-h/N-d crystals is diffusive, dynamic percolation, but additional confirmatory work is needed to measure directly the changes in β and *W* with pressure, and to determine the changes in spectral dimension with pressure.

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