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Analog metal-to-nonmetal exciton transition: Effect of isotopic alloying on naphthalene triplet transport

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A low-temperature investigation of the rate of triplet exciton transport within the guest ($C_{10}H_8$) quasilattice of the $C_{10}D_8$-$C_{10}H_8$ crystal system has demonstrated a transition from bandlike to hoppinglike motion upon reduction of the guest-to-host concentration ratio. The analog metal and nonmetal regimes are characterized, respectively, by a negative and a positive transport temperature coefficient. In addition, reducing the naphthalene concentration by a factor of 5 reduces the transport rate by five orders of magnitude.

An experimental distinction between a metal and a nonmetal is whether the electron conductivity increases or decreases as the temperature goes to zero.[1] Exciton transport, like electron transport, has been described by both hopping and band models.[2–10] In most hopping models the transport rate is controlled by thermal activation energies, which lead to a positive temperature coefficient. In the band model, transport is adversely affected by temperature due to the scattering of wave packets by phonons, thus leading to a negative temperature coefficient. The relative magnitude of the exciton bandwidth and the exciton-phonon coupling determine whether a hopping or a band model is appropriate.

We report here the observation of a transition from band (metallic) transport to hopping (nonmetallic) transport with a change in alloy composition. We found that naphthalene triplet exciton transport is thermally inhibited in pure crystals, but becomes thermally enhanced with increased doping of naphthalene with its isotopic cognate, naphthalene-d_{10}. To our knowledge, this is the first time that experimental evidence for such a transition has been documented for excitons. In addition to this change in the sign of the temperature coefficient, the rate of exciton transport within the system is reduced by almost five orders of magnitude as the naphthalene concentration is reduced by a factor of 5.

METHOD

We measured the rate of triplet exciton transport by monitoring the time-resolved delayed fluorescence in a ternary crystal containing perdeuteronaphthalene ($C_{10}D_8$), naphthalene ($C_{10}H_8$), and a controlled trace amount of betamethylnaphthalene (BMN). The three components are referred to, respectively, as host, guest, and supertrap, based on their decreasing triplet transition energies. Alternatively, naphthalene and BMN excitons can be referred to as free and trapped excitons. The delayed fluorescence intensity originates from heterofusion at supertrap sites, and is controlled by the rate at which naphthalene excitons are able to find BMN molecules. This method of studying exciton transport is valuable in that it spans the time domain from 10^{-7} to 10^{-2} seconds. In addition, the relatively high concentration of the supertraps minimizes the effects of other natural impurities and defects which would otherwise complicate our results at low temperatures.

The kinetic rate equations which describe the experimental system at low temperature are as follows:

$$\dot{T}_g = -\gamma_1 T_g^2 - \tfrac{1}{2}\gamma_2 T_g T_s - \kappa T_g - \tau_g^{-1} T_g + \alpha \ ,$$

$$\dot{T}_s = -\tfrac{1}{2}\gamma_2 T_g T_s + \kappa T_g - \tau_s^{-1} T_s \ ,$$

where T_g and T_s are the $C_{10}H_8$ and BMN exciton densities. γ_1 and γ_2 define the exciton annihilation rates while κ gives the rate at which the free ($C_{10}H_8$) excitons are trapped at nonexcited BMN sites. The natural decay lifetimes are τ_g and τ_s. The laser excitation term is α.

When solving these equations we can make several simplifying assumptions. The time scale of our experiment is short enough to allow us to ignore the triplet natural decay. Our experimental conditions are such that the $C_{10}H_8$ exciton density is always much smaller than both excited and ground-state BMN densities, i.e., $T_g \ll T_s$ and $T_g \ll C_s^0$. Consequently (1) the homofusion term is negligible and (2) trapping and heterofusion will have a negligible effect on T_s during the course of a decay measurement. For the time duration of our decay measurements the equations simplify (for $\alpha = 0$) to

$$\dot{T}_g = -(\tfrac{1}{2}\gamma_2 T_s + \kappa) T_g ; \quad \dot{T}_s = 0 \ .$$

The delayed fluorescence intensity will be linear with T_g, which should decay exponentially with a rate constant $K = (\frac{1}{2}\gamma_2 T_s + \kappa)$, *i.e., decay at the rate at which free excitons are able to find either occupied or unoccupied BMN sites.* A full description of this kinetic model, as well as supporting evidence, will be given in a planned forthcoming paper.[11]

EXPERIMENTAL

The Bridgman crystals were grown from zone-refined BMN and from potassium-fused and zone-refined $C_{10}H_8$ and $C_{10}D_8$. We chose to study the $0.20 < C_g \leq 1.0$ mol fraction guest concentration range in order to avoid complications arising from homofusion and from nonnegligible triplet monomolecular decay, i.e., we stayed well above the triplet transport steady-state critical concentration.[12]

The excitation source was an argon ion laser pumped dye laser. The dye laser was set to directly excite either the $C_{10}D_8$ or $C_{10}H_8$ 0-0 first triplet transition. We inserted a Lasermetrics electro-optic modulator (EOM) between the two lasers in order to provide a fast shutter. The EOM was driven by an avalanche mode pulse driver system which was able to follow a transistor-transistor logic (TTL) signal from dc to 1 kHz with a rise time of 20 nsec. A square signal was typically used, with a pulse duration sufficient to allow the exciton population distribution to reach a steady-state value. The delayed fluorescence signal was filtered by using two Corning 7-54 filters which effectively eliminated any laser scatter and phosphorescence intensity. The signal was processed with either a PAR boxcar gated averager or a PAR signal averager, depending on the necessary instrumental time constant. The temperature of the Janis helium-flow cryostat was electronically monitored via a silicon diode Lake Shore Cryotronics temperature controller (±1.0 K).

RESULTS

Figure 1 shows the normalized rate constant K^R as a function of temperature for two different crystals. K^R is defined as $K^R = K/(C_s/C_g)$, where K is the delayed fluorescence exponential decay-rate constant. K^R can be interpreted as the rate of transfer within the guest quasilattice and is consequently proportional to the rate at which a free exciton samples new sites. The supertrap-to-guest concentration ratio C_s/C_g gives the probability that a newly sampled site is a supertrap rather than guest site.

Aside from the large change in relative magnitudes for the decay rates of the two crystals in Fig. 1, an important feature of this figure is the difference in the temperature dependence of the energy transport in the two crystals. Increasing the temperature in the $C_g \simeq 1.0$ crystal *inhibits* exciton transport while transport in the $C_g = 0.28$ crystal is thermally *enhanced.*

Figure 2 shows the temperature dependence of K^R for a number of crystals with various C_s and C_g values. The data were such that we were unable to differentiate between a power-law temperature dependence ($K^R = A_1 T^n$) and an exponential dependence $[K^R = A_2 \exp(-E_a/kT)]$. Both interpretations are presented in Fig. 2. All of these data were collected

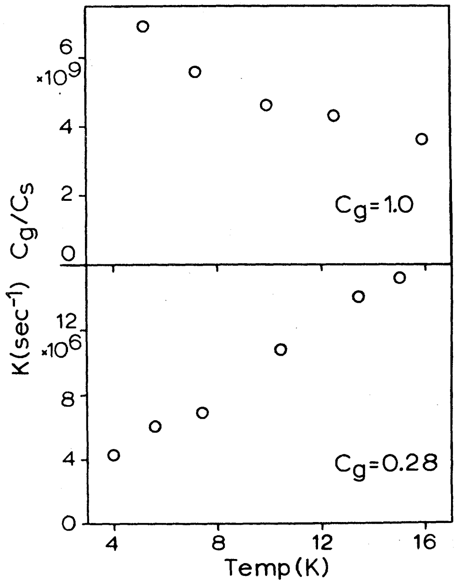

FIG. 1. Reduced delayed fluorescence decay-rate constant K^R as a function of temperature for two crystals. The lifetime of the $C_g = 1.0$ crystal (with $C_s = 2 \times 10^{-5}$) at 5 K was 8×10^{-6} sec. The lifetime of the $C_g = 0.28$ crystal (with $C_s = 1 \times 10^{-4}$) at 5 K was 5×10^{-3} sec.

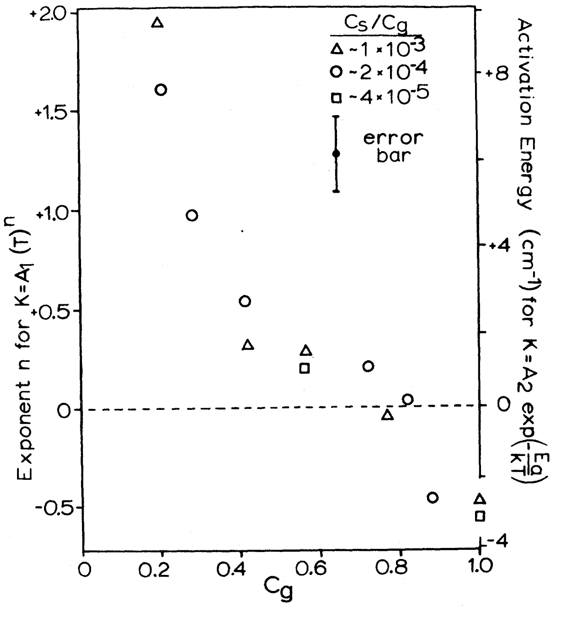

FIG. 2. Temperature dependence of K^R as a function of guest concentration. The temperature dependence is plotted both as a power-law exponent and as a Boltzmann activation energy. A positive power-law exponent, or a positive activation energy, corresponds to thermal enhancement of the exciton transport (nonmetallic behavior). A negative power-law exponent corresponds to thermal inhibition (metallic behavior). The temperaure range used in this experiment was $4.2 \leq T \leq 16$ K.

in the range of $4.2 \leqslant T \leqslant 16$ K. Above 16 K we began to see thermally enhanced detrapping out of the BMN traps. This was manifest as a sharp biexponential decay with the long time tail increasing with a rate constant controlled by an activation energy commensurate with the BMN trap depth.

Figure 2 does not supply any information about the dependence of the prefactor A_1 or A_2 on the guest and supertrap concentrations. Keeping the *temperature constant at $T = 1.8$ K,* we empirically found[11] that

$$K^R(C_g) = K^R(1.0)C_g^n, \quad n = 6.5 \pm 0.3 \ .$$

This relationship is followed across our entire concentration range, even though the delayed fluorescence lifetimes range from 230 nsec for a crystal with $C_g = 1.0$ and $C_s = 10^{-3}$ to 10 msec for a crystal with $C_g = 0.21$ and $C_s = 4 \times 10^{-5}$. In all cases, the transformation to the reduced rate constant K^R was able to compensate for the variations in the BMN concentration. Previous work[12] has shown that K^R continues to decrease sharply as the guest concentration is reduced in the region of $C_g < 0.20$.

DISCUSSION

There are a number of existing theories which address the temperature dependence of exciton diffusion in a pure crystal.[2-10] A common result[2-7] is that the diffusion coefficient can be expressed as two additive components. One is a band-model term with $D_b \propto \langle v_g^2 \rangle / \Gamma$, where $\langle v_g^2 \rangle$ is the thermally averaged square of the group velocity,

$$v_g(\vec{k}) = h^{-1}[\partial\epsilon(\vec{k})/\partial k] \ ,$$

and $\epsilon(\vec{k})$ is the energy dispersion of the exciton band. Γ is the total scattering rate from one $\vec{k}$ state to another. The second contribution to the diffusion coefficient is an incoherent hopping term $D_h \propto \gamma_1$. In the Haken-Strobl model,[6] γ_1 is due to the nearest-neighbor transfer matrix element fluctuations resulting from lattice vibrations and coupled molecular vibrations.

With respect to our experiments, D_b should decrease with temperature while D_h should increase with temperature. Consequently, the dominant term in the exciton transport expression for a pure $C_{10}H_8$ crystal at low temperatures is the coherent band-model term. It should be noted that while $\langle v_g^2 \rangle$ is temperature dependent since it is the square of the group velocity averaged over a Boltzmann population of exciton states, calculations of $\langle v_g^2 \rangle$ as a function of temperature show that there is very little change in the group velocity above 4.2 K for triplet naphthalene. (We used a technique similar to that used by Fayer and Harris in Ref. 8.)

It is interesting that our pure crystal inverse square-root temperature dependence of transport is the same as that seen for singlet naphthalene[13] and singlet anthracene[14] at higher temperatures. The singlet data was said to agree with the theory of Agranovich and Konobeev.[9] In our case, however, the large effective mass (small exciton bandwidth) of the naphthalene triplet exciton means that the experimental temperature is less than the Agronovich minimum temperature limit.

For $C_g < 1.0$ the role of isotropic impurities and the concomitant disorder becomes increasingly important. One significant effect of adding $C_{10}D_8$ is the formation of $C_{10}H_8$ nearest-neighbor finite clusters. Below about $C_g \simeq 0.70$ the number of guests belonging to finite clusters, rather than a maxicluster, begins to pick up at a fast rate.[15] The differences in cluster sizes and topologies lead to energy mismatches between guests on different clusters.[16,17] These mismatches act as activation energies, and are on the order of 1–5 cm^{-1} for triplet $C_{10}H_8$ in $C_{10}D_8$. At low C_g, where energy transport is very slow, there may be some contributions from shallow-trap to guest activation or from guest to host activation (100 cm^{-1}).[16]

A note of caution when discussing transport in an isotopically mixed crystal is that thermally enhanced transport does not rigorously eliminate quasicoherent band motion. Argyrakis and Kopelman[18] have used correlated walk simulations to show that above $C_g \simeq 0.80$ transport is indeed enhanced as the correlation length increases, i.e., as the phonon scattering length increases. Below $C_g \simeq 0.80$, however, transport becomes more efficient as the scattering length is reduced to one lattice spacing. These simulations are informative since they demonstrate that there can be a change in the sign of the transport temperature coefficient without resorting to any activation energies other than those inherent in the phonon scattering. These results have no bearing on quasicoherent transport in the case where the scattering length is on the order of one lattice spacing.

At this time we do not know how relevant our experimental $C_g \simeq 80\%$ thermal-dependence crossover concentration is. It is interesting, however, that in the case of the $T = 1.8$ K prefactor data nothing special seems to occur in the region of our transition concentration. This transition behavior between the two temperature effects warrants further theoretical study. One word of caution is that we have neglected any thermal influence on the trapping efficiency and on small polaron self-trapping.[10] We expect these effects to be small and independent of guest concentration.

CONCLUSIONS

We have presented experimental results based on low-temperature studies of the delayed fluorescence intensity decay in $C_{10}D_8$-$C_{10}H_8$-BMN ternary crystals. We analyzed the results by assuming that the decay in the delayed fluorescence intensity was a direct measurement of the decay in the free (naphthalene) exciton density.

The results indicate that the temperature dependence of exciton transport within the guest manifold shows a large dependence on the guest concentration. In a 1.0-mol fraction $C_{10}H_8$ crystal, the transport is thermally inhibited. This is commensurate with a band-model (metallic) picture, although the scattering length of the wave packet may be on the order of one lattice spacing. Reducing the guest concentration leads to a regime of continuously increasing thermal enhancement of the exciton transport (nonmetallic behavior). The crossover from thermal inhibition to thermal enhancement occurs at $C_g \simeq 0.80$. The results also show that concurrent with the change in the temperature effect, there is a large change in the magnitude of the transfer rate at a given temperature.

ACKNOWLEDGMENT

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