Computer simulation of exciton trapping in Cu^{2+}-doped crystals of $(CH_3)_4NMnCl_3$ and $(CH_3)_4NMnBr_3$: Significance of trap efficiency in one-dimensional systems

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Computer simulations of exciton trapping in Cu^{2+}-doped crystals of the highly-one-dimensional salts, tetramethylammonium manganese chloride (TMMC) and tetramethylammonium manganese bromide (TMMB), have been performed. The model, which assumes a slow interchain (three-dimensional) hopping process in conjunction with very rapid intrachain (one-dimensional) migration, treats inefficient as well as efficient trapping. The agreement between the simulated survival probabilities and the experimental decay curves is excellent. The results indicate that at room temperature in TMMC the intrachain exciton hopping frequency is on the order of 10^{12} s^{-1}, the interchain hopping frequency on the order of 2×10^{3} s^{-1}, and the absolute efficiency of the Cu^{2+} traps between 10^{-3} and 10^{-4}. The results for TMMB are qualitatively similar, but are not as definitive. The effect of a small three-dimensional component in a fast one-dimensional hopping process has been examined in the general case. In order for a decay curve to deviate from simple exponential form, the exciton migration has to be extremely anisotropic.

I. INTRODUCTION

Energy transport in solids is a topic of considerable interest both in terms of theory and experiment. In photoexcited crystals energy transport occurs by motion of wave packets known as excitons. Excitonic motion can be treated from the perspective of two limiting cases: coherent motion where the exciton propagates throughout the solid as a wave and incoherent or diffusive motion where the exciton moves by random steps. This study focuses on the latter case, where the phenomenon is mathematically describable in terms of a random walk.[1] The behavior of crystals containing impurities (exciton traps) is often used to study the excited-state motion since the presence of traps changes the rate of exciton depopulation, altering the observable kinetics. Motion in one dimension has been given special consideration since it is a mathematically simpler problem and the rate of depopulation in a lattice with traps deviates dramatically from a simple exponential form.[1] Many models of one-dimensional exciton trapping have been derived and some have been used to fit experimental data to give kinetic parameters.[2–9]

The manganese salts, $(CH_3)_4NMnCl_3$ (TMMC) and $(CH_3)_4NMnBr_3$ (TMMB), adopt a hexagonal structure where the MnX_6^{4-} octahedra share opposite faces, forming an infinite chain of manganese ions separated by a distance of ~3.3 Å.[10,11] The bulky $(CH_3)_4N^+$ groups separate the chains by ~9.3 Å, making the interaction between Mn^{2+} ions in the lattice strongly one dimensional. Yamamoto, McClure, Marzzacco, and Waldman studied the red luminescence of undoped and doped TMMC, where they concluded that the exciton motion was a thermally activated incoherent process largely restricted to the $[MnCl_3^-]_n$ chains (one dimensional).[2] Detailed studies of the time-resolved luminescence from Cu^{2+}-doped TMMC and TMMB performed in our laboratories support the conclusion that exciton migration is highly one dimensional.[3,4] The luminescence-decay curves were fitted to trapping expressions for one-dimensional systems given by Weiting, Fayer, and Dlott[5] (WFD) and Balagurov and Vaks[6] (BV). It was possible to obtain estimates of the important kinetic parameters such as the intrachain and interchain hopping rates. Knochenmuss and Güdel also examined the luminescence decay from Cu^{2+}-doped TMMC.[7] Using a model developed by Kenkre and Parris[8] (KP), they concluded that the Cu^{2+} ion was a relatively inefficient exciton trap.

Even though these models can be made to fit the experimental data, they contain assumptions and limitations which may not be realistic or appropriate for the TMMC or TMMB systems. The WFD model was developed for organic one-dimensional lattices with a known natural abundance of an isotopic scattering impurity (e.g., 1, 2, 4, 5-tetrachlorobenzene with the 0.03% abundance of monodeuterated scattering impurity). It assumes one-dimensional cages of molecules defined by uniformly distributed scattering impurities (supersites) where migration can be thought as hops between cages, in a lattice of cages (superlattice).[5] Our systems are clearly very different since the isotopic scattering impurities are not present and the migration occurs as hops between nearest-neighbor Mn^{2+} ions. In addition, the WFD model is incorrect in the long-time limit where the exponential decay has been shown to be dependent on $t^{1/3}$ rather than $t^{1/2}$.[4,8,9] The BV model is developed from an exact expression, but does not explicitly include three-dimensional motion (interchain hopping) and is restricted to a Poisson (random) distribution of traps. Both the WFD and BV models assume perfectly efficient trapping. The Kenkre model does allow for inefficient trapping, but the application of the model to TMMC by Knochenmuss

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and Güdel did not include interchain hopping.[7] In addition, the KP model is derived in Laplace space, so the application is computationally difficult.

A Monte Carlo method for the simulation of a fast one-dimensional random walk with a slow three-dimensional component in a lattice with efficient or inefficient traps has been developed to model the exciton migration in materials such as TMMC and TMMB. This method treats the fast one-dimensional process by the continuous diffusion equation, while sampling for the slower three-dimensional process as discrete hops from a Poisson time distribution. This model allows the study of the effect of various physical parameters on the decay curves such as interchain hopping, trap efficiency, trap distribution, and the presence of scattering as well as trapping impurities.

This article is the second of a series in which the Herman-Rodriguez-McPherson (HRM) model is shown to be useful in understanding exciton dynamics. In the first article the role of trap efficiency in decay curves is discussed for the general case.[12] This work applies the HRM model to the time-resolved luminescence data from Cu^{2+}-doped TMMC and TMMB crystals. The role of interchain hopping as well as trap efficiency is investigated. The results provide significant insight into the exciton migration and trapping processes which occur in these one-dimensional inorganic crystals.

II. EXPERIMENT

A. Sample preparation

Undoped TMMC was prepared by slow evaporation of tetramethylammonium chloride $[(CH_3)_4NCl_3]$, a 10% excess of the stoichiometric amount of manganous dichloride ($MNCl_2 \cdot 4H_2O$) in hydrochloric acid (HCl) solution. The TMMB salt was prepared with tetramethylammonium bromide $[(CH_3)_4NBr_3]$ and manganous carbonate ($MnCO_3$) ($\sim 10\%$ excess) in hydrobromic acid (HBr) solution. The solutions were placed in a desiccator over a $CaSO_4$ drying agent for evaporation. Since these materials, particularly TMMB, are hygroscopic, the samples were manipulated and stored under dry nitrogen. Spectroscopic samples were dealt in 4-mm-diam tubes under dry nitrogen.

B. Luminescence-decay curves

The crystals were irradiated with a NRG dye laser tuned to 520 or 460 nm, which was pumped by a 308-nm XeCl Lambda Physik model EMG 52MSC excimer laser. The emission was collected at right angles through a McPherson model EU700 monochromator with a Hamamatsu model R777 phototube with a base wired for long-pulse emissions. The signal was collected by a 10-bit 60-MHz Tektronix/Sony 390 AD transient digitizer driven by a Hewlett-Packard series 200 HP9826 microcomputer, where the data are averaged and stored for subsequent analysis. An average of 300 transients were collected for each data set.

Data were recorded under conditions chosen to give the most accurate reproduction of the actual decay curve. To avoid over driving the phototube, the monochromator slits were adjusted to give a maximum voltage pulse (at $t=0$) of 20 mV (200 counts) or less. The signal from the phototube was terminated into 50 Ω at the digitizer to ensure a short instrumental time constant (<20 ns). The decay curves were examined over various time ranges between 33.3 and 2000 μs to ensure accurate definition of both early- and long-time behavior.

C. Computer simulations

Monte Carlo simulations were performed on an IBM 3081 HX mainframe. A typical simulation of 10 000 walks takes from 15 to 70 min, depending on the fitting parameters.

III. THEORY

Numerical difficulties are posed by the large number of one-dimensional steps in the time frame of interest. These difficulties were overcome by treating the fast one-dimensional random walk by the continuous diffusion equation with the appropriate boundary conditions, while sampling for the slower three-dimensional process as discrete steps from a Poisson time distribution. The solutions of the problem of a one-dimensional random walk in a lattice with efficient and inefficient traps as well as a description of the algorithm of our computer-simulation approach are presented in this section.

The one-dimensional random walk is described by the master equation,

$$\frac{dP_j}{dt} = -2KP_j + KP_{j+1} + KP_{j-1} , \tag{1}$$

for the interior of the chain, and

$$\frac{dP_1}{dt} = -KP_1 + KP_2 - K_1P_1 \tag{2}$$

and

$$\frac{dP_N}{dt} = -KP_N + KP_{N-1} - K_NP_N \tag{3}$$

for sites adjacent to traps or scatterers. In (1)–(3), P_j is a lattice site, P_{j+1} and P_{j-1} are the nearest neighbors at distance l, K is the hopping rate between neighboring sites in the chain, and K_N and K_l are hopping rates from the end sites in the chain to the neighboring trap or scatterer. On the right-hand side of (1) the first term describes the depopulation of site j to the nearest neighbors $j+1$ and $j-1$, while the second and third terms account for populating the site j from $j+1$ and $j-1$. At the limit where l goes to zero, keeping the chain length $L=Nl$, the diffusion coefficient $D=Kl^2$, and the hopping constants $K_0=lK_1$ and $K_L=lK_N$ constant, Eq. (1) transforms to the continuous diffusion equation

$$\frac{\partial \rho(L,x,t)}{\partial t} = D\frac{\partial^2 \rho(L,x,t)}{\partial x^2} , \tag{4}$$

and the boundary conditions become

$$D\frac{d\rho(L,x,t)}{dx}\bigg|_{x=x_0} = -K_L\rho(L,x_0,t) \tag{5}$$

and

$$D\frac{d\rho(0,x,t)}{dx}\bigg|_{x=x_0} = K_0\rho(0,x_0,t)\ , \tag{6}$$

where $\rho = \lim_{l\to 0}(P_j/l)$ is the particle density at position x, x_0 is the initial particle position, and t is time. For efficient absorbing walls the limit where K_T ($K_T = K_0 = K_L$) goes to infinity is used for the boundary conditions. The initial condition is $\rho(x,x_0,0)=\delta(x-x_0)$.

As stated by Agmon,[13] the solution of this problem with efficient absorbing walls (traps) is given by

$$\rho(x,x_0,t)=\frac{2}{L}\sum_{n=1}^{\infty}\sin\left[\frac{n\pi x}{L}\right]\sin\left[\frac{n\pi x_0}{L}\right] \times \exp(-\pi^2 n^2 Dt/L^2)\ , \tag{7}$$

or by

$$\rho(x,x_0,t)=\frac{1}{2(\pi Dt)^{1/2}}\sum_{m=-\infty}^{\infty}\{\exp[-(x-x_0+2mL)^2/4Dt]-\exp[-(x+x_0+2mL)^2/4Dt]\}\ . \tag{8}$$

In the case of inefficient traps, the solution is given by

$$\rho(x,x_0,t)=\sum_{n=1}^{\infty}a_n^2[\cos(\alpha_n x)+\gamma_n\sin(\alpha_n x)][\cos(\alpha_n x_0)+\gamma_n\sin(\alpha_n x_0)]\exp(-\epsilon_n t)\ , \tag{9}$$

where $\varepsilon_n = D\alpha_n^2$, $\gamma_n = K_T/D\alpha_n$, and a_n is the normalization factor. The substitution of Eq. (9) into (4), together with the boundary conditions (5) and (6), gives a transcendental equation for α_n which is solved numerically (details in Ref. 12).

The integration over x from 0 to L of Eqs. (7) and (8) or (9), and averaging these results over an x_0 uniform distribution, gives the survival probability at time t of a particle in a chain with two efficient [Eqs. (7) and (8)] or inefficient [Eq. (9)] absorbing walls. A Poisson distribution serves as the sampling function of the slower interchain hopping process, which is simulated in a discrete fashion. For the efficient case, the eigenvalue expansion (7) converges rapidly at long times, while the image approximation (8) converges quickly at short times.

The distributions of traps in the crystals were taken to be Poisson (random). The spontaneous decay of the exciton is included by multiplication of the survival probability by an exponential decay term where the spontaneous decay rate k_s is obtained from the experimental data of the undoped salts.[3,4]

The algorithm developed is briefly explained as follows.

(a) The chain length L, interchain hopping time $\tau_{\rm hop}$, and the initial particle position within the chain x_0 are chosen from appropriate distributions.

(b) The survival probability $q_s(t)$ for the chain is calculated from the integrated (over x) result of Eqs. (7), (8), or (9) for times up to the sampled interchain hopping time $\tau_{\rm hop}$.

(c) The particle hops to a new chain at $\tau_{\rm hop}$ and steps (a)–(c) are repeated until maximum observation time is reached.

(d) The survival probability for several thousand walks are averaged, multiplied by the exponential factor $S(t)$ for spontaneous decay, and plotted [$Q_s(t)$] versus time.

The algorithm presented above neglects the history of the walks (i.e., the probability of the exciton to return to the chain just excited) since it is not expected to have a significant effect on the results.

We have monitored the statistical error during the numerical simulations and they appear to be small. In 10 000 walks the percent errors of the survival probability curves range from a tenth of a percent at early times to about 3% at long times.

The experimental data were fitted by trial and error since a least-squares analysis is computationally prohibitive. The fits are obtained by varying the rates for intrachain and interchain hopping and the rate for absorption by traps. The best fits were selected by visual examination. The effects of the parameters on the decay curves became clear after a few trial simulations. An increase in the one-dimensional hopping rate primarily causes an overall more rapid decay, and an increase in trap

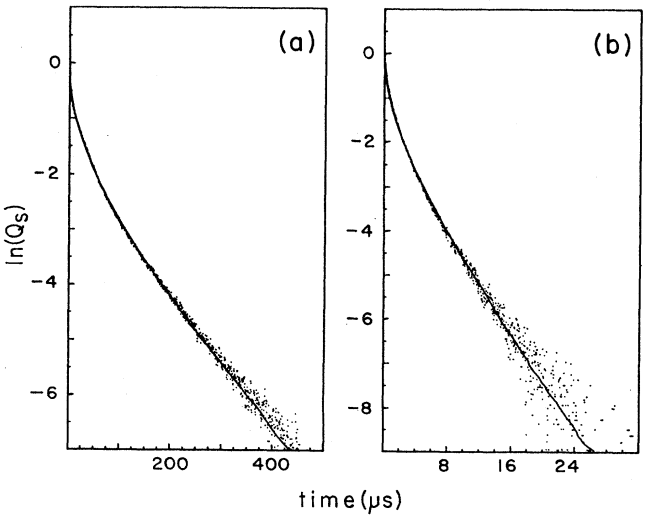

FIG. 1. Decay curves of TMMC crystals containing 2.7×10^{-4} (left) and 4.5×10^{-3} (right) mole fractions of Cu^{2+}. The solid-line fits were simulated assuming efficient trapping.

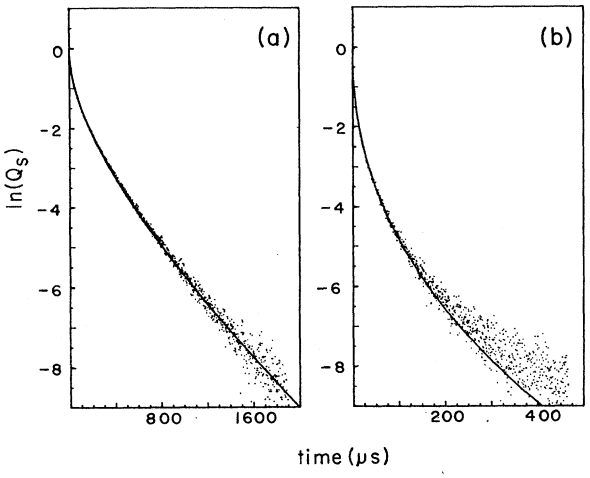

FIG. 2. Decay curves of TMMB crystals containing 1.5×10^{-4} (left) and 3.3×10^{-4} (right) mole fractions of Cu^{2+}. The solid-line fits were simulated assuming efficient trapping.

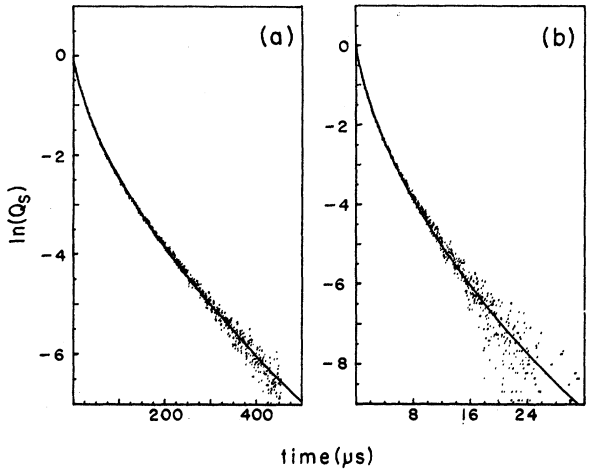

FIG. 3. Decay curves of TMMC crystals containing 2.7×10^{-4} (left) and 4.5×10^{-3} (right) mole fractions of Cu^{2+}. The solid-line fits were simulated assuming inefficient trapping: $\Theta_T=2.7\times10^{-4}$.

efficiency causes a quicker decay at short times, while an increase in the three-dimensional hopping rate has the same effect at long times.

IV. RESULTS

By varying the intrachain diffusion rate and the interchain hopping time, it is possible to obtain excellent fits of the decay curves from Cu^{2+}-doped TMMC and TMMB crystals under the assumption of efficient trapping (see Figs. 1 and 2). According to Chandrasekhar,[14] the one-dimensional diffusion coefficient, D, in our model relates to the intrachain hopping frequency by

$$D=\frac{\ell^2\nu_1}{2}\ , \tag{10}$$

where ν_1 is the hopping frequency and ℓ is the distance between sites. The three-dimensional hopping rate ν_3 is obtained from the reciprocal of the average interchain hopping time, $\tau_{\rm hop}$,

$$\nu_3=1/\tau_{\rm hop}\ . \tag{11}$$

The values for ν_1 and ν_3 obtained from the simulations for Cu^{2+}-doped TMMC and TMMB are given in Tables I and II.

The values for intrachain hopping, ν_1, and interchain hopping, ν_3, are in general agreement with those obtained in the earlier studies.[2–4,7] For the TMMC data, there is a rather noticeable variation in the ν_1 and ν_3 values depending on the concentration of traps (Cu^{2+}). Such a systematic variation indicates an inadequacy in the model, most likely the assumption of efficient trapping. Initially, the decay curve from the most heavily doped sample (D) was examined to explore this possibility, since the effects of inefficient trapping are most apparent when the trap concentrations are high.[12] From earlier estimates, it was determined that the intrachain diffusion rate, ν_1, in TMMC must be at least 10^{12} s^{-1}. By reducing the trapping rate, K_T, it was possible to obtain good fits of the decay curve from sample D with hopping rates on the order of 10^{12} s^{-1}. This indicates a trapping efficiency, Θ_T (defined below), between 10^{-3} and 10^{-4},

$$\Theta_T=\frac{K_T}{K_T+D/\ell}\ . \tag{12}$$

A Θ_T value of 2.7×10^{-4} was taken to be constant and used in fitting the decay curves from the other samples. As before, it was possible to obtain excellent agreement between observed and calculated curves (see Fig. 3). The ν_1 and ν_3 values obtained in this manner are given in Table III. The assumption of inefficient trapping clearly leads to a much more consistent set of kinetic parame-

TABLE I. Kinetic parameters for TMMC: efficient trapping.

Sample	$X_{\rm Cu}$	k_s (s^{-1})	ν_1 (s^{-1})	ν_3 (s^{-1})
A	7.0×10^{-5}	1.2×10^{3}	1.2×10^{12}	4.0×10^{3}
B	2.7×10^{-4}	1.2×10^{3}	3.8×10^{11}	5.0×10^{3}
C	1.0×10^{-3}	1.2×10^{3}	1.6×10^{11}	3.3×10^{4}
D	4.5×10^{-3}	1.2×10^{3}	2.8×10^{10}	1.7×10^{5}

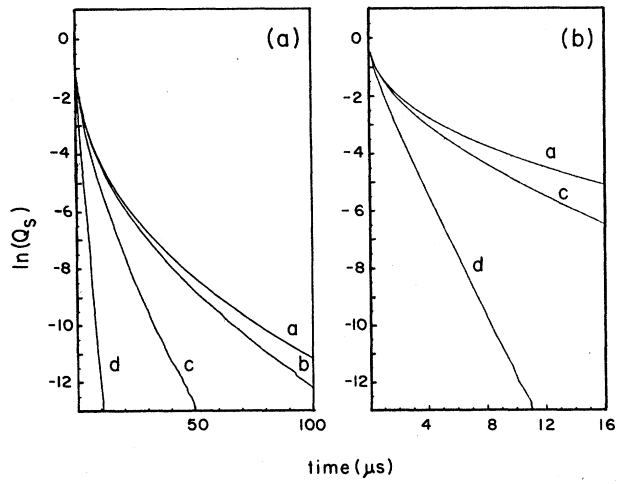

FIG. 4. Simulated decay curves of exciton trapping (mole fraction of efficient traps is 10^{-3}; $\nu_1 = 10^{12}$ s^{-1}) with different rates of three-dimensional hopping. In the left-hand panel curves *a*, *b*, *c*, and *d* correspond to ν_3 values of 10^3, 10^4, 10^5, and 10^6 s^{-1}, respectively. The right-hand panel figure shows the same data on a 5-times-shorter time scale.

ters. The value 2.7×10^{-4} chosen for Θ_T probably does not represent a precise evaluation of the trapping efficiency since no attempt was made to optimize Θ_T with respect to the internal consistency of the calculated ν_1 and ν_3 values. It seems certain, however, that the optimum efficiency falls between 10^{-3} and 10^{-4}.

The situation for Cu^{2+}-doped TMMB is not as clear-cut. Although there are significant variations in the ν_1 and ν_3 values obtained under the assumption of efficient trapping (see Table II), the variations do not appear to be systematic with respect to trap concentration. Unfortunately, the doped TMMB samples do not span as great a range in Cu^{2+} concentration as the doped TMMC samples. In addition, it has been noted that chemical analysis may not provide a reliable indication of the actual Cu^{2+} concentration in a doped TMMB crystal.[4] With the present data it is difficult to make even a crude estimate of the trapping efficiency of Cu^{2+} in TMMB.

The simulations clearly demonstrate the impact that even a very small three-dimensional component (interchain) of the migration has on the trapping dynamics of one-dimensional systems. As evidenced by the data from Cu^{2+}-doped TMMC, an interchain hopping process almost 9 orders of magnitude slower than the intrachain migration is sufficient to have a noticeable effect on the decay curves. Although this is not unexpected in view of earlier analyses,[5] the calculated decay curves presented in Fig. 4 make the point in dramatic fashion. As the interchain hopping rate reaches 1×10^6 s^{-1}, still 6 orders of magnitude slower than the intrachain rate, the decay becomes very rapid and appears to be nearly a single exponential.

As with the trapping efficiency, the importance of interchain hopping to the exciton dynamics of TMMB is not well established by the simulations. The decay curves from three of the four Cu^{2+}-doped TMMB samples indicate an interchain hopping rate too small to be measured (less than 5×10^2 sec^{-1}); however, one curve (from sample C) requires an interchain rate similar to that of TMMC to give a reasonable fit. The explanation for this discrepancy is not clear at this point.

V. CONCLUSIONS

This study demonstrates that the computer-simulation approach (HRM model) can be utilized to fit actual luminescence-decay curves from doped one-dimensional systems. The agreement between observed and simulated decay curves for the Cu^{2+}-doped TMMC and TMMB crystals is excellent. Because the HRM model explicitly treats both interchain hopping and inefficient trapping, it represents a more accurate overall reflection of the physical situation in the manganese salts than do any of the previously applied models. The successful simulations provide detailed insight into the exciton dynamics of TMMC. At room temperature the migration rate along the $[MnCl_3^-]_n$ chain appears to be a little greater than 10^{12} s^{-1}, with an interchain hopping rate on the order of 2×10^3 s^{-1}. It also seems almost certain that Cu^{2+} is an inefficient exciton trap with capture occurring only once in every 10^3–10^4 encounters. These results indicate that the intrachain hopping in TMMC is somewhat faster (by a factor of 2 or 3) than was determined in our previous study, which was based on fits of the data to the WFD and BV models.[3] The conclusion of inefficient trapping is clearly consistent with the earlier analysis of Knochenmuss and Güdel;[7] however, the kinetic parameters obtained in our computer simulations show much less variation. In addition, the agreement between the observed and calculated decay curves in this study is noticeably better than that shown by Knochenmuss and Güdel. The exciton dynamics in TMMB are not as well defined, but appear to be very similar to those of TMMC. The contradictory results in terms of interchain hopping casts an element of doubt on the earlier conclusion that exciton

TABLE II. Kinetic parameters for TMMB: efficient trapping.

Sample	X_{Cu}	k_s (s^{-1})	ν_1 (s^{-1})	ν_3 (s^{-1})
A	5.8×10^{-5}	2.0×10^3	7.0×10^{11}	
B	1.5×10^{-4}	2.0×10^3	3.5×10^{11}	
C	1.9×10^{-4}	2.0×10^3	1.7×10^{12}	3.3×10^3
D	3.3×10^{-4}	2.0×10^3	1.0×10^{12}	

TABLE III. Kinetic parameters for TMMC: inefficient trapping.

Sample	X_{Cu}	k_s (s^{-1})	ν_1 (s^{-1})	ν_3 (s^{-1})	Θ_T
A	7.0×10^{-5}	1.2×10^{3}	2.6×10^{12}	2.0×10^{3}	2.7×10^{-4}
B	2.7×10^{-4}	1.2×10^{3}	1.0×10^{12}	2.0×10^{3}	2.7×10^{-4}
C	1.0×10^{-3}	1.2×10^{3}	1.3×10^{12}	2.9×10^{3}	2.7×10^{-4}
D	4.5×10^{-3}	1.2×10^{3}	1.1×10^{12}	2.9×10^{3}	2.7×10^{-4}

migration in TMMB is more one dimensional than in TMMC.[6] In any event, it is certain that the migration in both salts is extremely one dimensional.

For any lattice the actual energy-transfer process resulting in exciton capture depends on the nature of the coupling between the trap and neighboring host chromophores, as well as on the overlap of the trap and host energy levels. These factors may be very difficult to establish by experiment or first-principles computations. The assumption of unit efficiency is often made in the absence of a direct determination. This assumption may not be unreasonable for one-dimensional systems where efficiency often does not affect trapping dynamics, particularly at low trap concentrations.[12] Our analysis indicates that Cu^{2+}, which was judged to be a particularly effective exciton trap in earlier studies,[4] is actually quite inefficient. Inefficient trapping may, in fact, be the general rule for metal-ion impurities in ionic crystals. For two- and three-dimensional lattices trap efficiency has a significant impact on trapping dynamics regardless of the trap concentration.[15] Thus, the exciton-migration rates inferred from the luminescence dynamics under the assumption of unit efficiency for doped two- and three-dimensional crystals may be in error, possibly by orders of magnitude.

The significance of the trap distribution to the trapping dynamics is an aspect of the problem which has not been addressed in this study. While a random (Poisson) distribution is certainly a logical choice, the correctness of the assumption in this case is not verified by experiment. In doped TMMC and TMMB crystals where an impurity ion enters an ionic host lattice, one can easily imagine a thermodynamic stability associated with some type of nonrandom distribution. Preliminary experiments indicate that calculated decay curves are strongly influenced by the choice of trap distribution, and that this may be significant for the luminescence decay in Co^{2+}-doped TMMC. This possibility is now being investigated in detail.

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