Emission dynamics from doped crystals of $(CH_3)_4NMnCl_3$ (TMMC): Exciton trapping in a one-dimensional lattice

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(Received 1 November 1985)

The emission decay curves from $(CH_3)_4NMnCl_3$ [tetramethylammonium manganese chloride (TMMC)] crystals doped with small amounts of Cu^{2+} deviate dramatically from simple exponential form. Consistent with the linear chain structure of TMMC, the curves are adequately described by decay expressions derived for exciton trapping in one-dimensional systems. Analysis of the data indicates that exciton migration in TMMC is nearly one-dimensional with an intrachain hopping frequency at room temperature of 10^{11} to 10^{12} sec^{-1} and an interchain hopping frequency of only 10^2 to 10^4 sec^{-1}. The presence of small concentrations of Cd^{2+}, a scattering impurity, greatly reduces the rate of exciton trapping. The temperature dependence of the decay curves suggests an energy barrier of 800 to 1000 cm^{-1} for migration along the chains in TMMC.

I. INTRODUCTION

Tetramethylammonium manganese chloride (TMMC), like many AMX_3 salts, adopts a hexagonal lattice in which the MX_6^{4-} octahedra share opposite faces to form infinite linear $[MX_3^-]_n$ chains.[1] The bulky $(CH_3)N^+$ ions which occupy positions between the chains tend to diminish the interchain interactions. As a result TMMC behaves as a near-perfect one-dimensional antiferromagnet where the intrachain exchange energy of about 4 cm^{-1} exceeds the interchain interaction by 4 orders of magnitude.[2-4] The three-dimensional ordering temperature for TMMC is less than 1 K.[5,6] Because of the strongly one-dimensional coupling, the magnetic properties of TMMC have been the subject of considerable theoretical as well as experimental interest for the past fifteen years.

In 1977, Yamamoto, McClure, Marzzacco, and Waldman investigated the luminescence from doped and undoped crystals of TMMC.[7] Undoped crystals exhibit an intense red emission when photoexcited which is observed even at room temperature. The emission lifetime of approximately 0.8 msec is nearly independent of temperature. The red emission is efficiently quenched in crystals doped with small concentrations of transition-metal impurities such as Cu^{2+}. From the dependence of the quenching on temperature and impurity concentration it was concluded that exciton migration in TMMC is thermally activated and confined to individual $[MnCl_3^-]_n$ chains (one dimensional). It was noted that the emission decay curves from certain doped samples were not simple exponentials; however, the time-dependent behavior was not analyzed in detail. From theoretical considerations of the properties of random walks it is clear that exciton migration on a one-dimensional lattice containing traps should lead to distinctly nonexponential decays.[8] This paper presents the results of time-resolved studies of the emissions from doped TMMC crystals under pulsed laser excitation. In addition to crystals doped with varying concentrations of trapping impurity (Cu^{2+}), double-doped samples containing scattering (Cd^{2+}) as well as trapping impurities were characterized. The choice of trapping impurity was based on the analysis of Yamamoto *et al.*, which indicates that Cu^{2+} is an extremely effective trap with a near unit probability of exciton capture at each close encounter. Divalent cadmium was selected as the scattering impurity because it is diamagnetic and has no low-lying electronic excited states. In addition, $(CH_3)_4NCdCl_3$ (TMCC) is known to be isostructural with TMMC,[9] indicating that Cd^{2+} should easily substitute for Mn^{2+} in doped TMMC crystals. The double-doped samples are of particular significance since the exciton migration in a system that is perfectly one dimensional is dramatically impeded by the presence of even small concentrations of scattering centers. The analysis of the observed decay curves leads to several important conclusions regarding the exciton motion in TMMC.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

TMMC was crystalized by slow evaporation from aqueous solutions containing equimolar quantities of $(CH_3)_4NCl$ and hydrated $MnCl_2$. Doped crystals were grown by dissolving approximately 15-g samples of TMMC in dilute aqueous HCl and adding small amounts ($\sim$0.3 g) of $CdCl_2$ and/or ($\sim$0.05 g) $CuCl_2$. The resulting solutions were allowed to evaporate slowly in a desiccator over $CaCl_2$. The Cd^{2+} and Cu^{2+} contents of the doped crystals were determined analytically by Galbraith Laboratories, Knoxville, Tenn. It is interesting to note that even small concentrations of Cu^{2+} produce a noticeable color change in crystals of TMMC.

B. Emission decay curves

Excitation was accomplished with a PRA LN100 nitrogen laser or with a NRG dye laser tuned to about 520 nm and pumped by a Lambda Physik model No. EMG 52MSC excimer laser. The latter laser combination proved more useful because of its higher intensity and, in

cases of Cu^{+2} doping, its ability to selectively excite the manganese. Emission was collected at right angles through a McPherson model No. EU700 monochromator with a Hamamatsu model No. R777 phototube with a base wired for long-pulse emissions. Data were collected using either an 8 bit, 5 MHz Biomation 805 transient digitizer or a 10 bit, 60 MHz Tektronix/Sony 390AD transient digitizer. Data were transferred to a Hewlett-Packard series 200 HP 9826 microcomputer for averaging, storage, and analysis. Typical data sets consisted of averages of 100 to 500 transients. Since data analysis required fits to both exponential and nonexponential terms, care was taken to test and insure the fidelity of data. It was found that satisfactory results were obtainable using either digitizer, but the Tektronix with its superior precision gave less scatter to the analyzed results. Decays known to be exponential can be collected with this system to better than eight e-folds maintaining a single exponential decay.

III. RESULTS AND DISCUSSION

A. Emission decay curves

Laser excitation of TMMC at 520 nm or 337 nm produces the red luminescence associated with the $^4T_1 \rightarrow {}^6A_1$ ligand-field transition of the octahedrally coordinated Mn^{2+} ions. The emission is broad and featureless with its peak at approximately 650 nm. Undoped samples showed emission lifetimes at room temperature of about 680 μsec. The decay curve shows a small but noticeable deviation from exponential behavior which will be discussed in subsequent sections. Upon doping with Cu^{+2}, the luminescence is visibly less intense in the TMMC crystals. There also appears to be a uv absorption associated with the Cu^{2+} ion, possibly a charge transfer transition, which interferes with Mn^{+2} excitation by light at 337 nm. Time-resolved experiments show that the Mn^{2+} luminescence decays more rapidly as the concentration of Cu^{2+} (exciton trap) in the doped TMMC crystal increases. Consistent with a thermally activated process, the emissions from the doped crystals decay more slowly when the temperature is lowered. The most striking feature of the time-resolved emissions is the actual shapes of the decay curves which are clearly not simple exponentials. As shown in Fig. 1, the deviations from linearity of ln (intensity) versus time plots are quite dramatic. At the laser power levels used, no intensity dependence is observed for the emission decay.

Relatively small concentrations of Cd^{2+} ($X_{Cd} \sim 0.02$) have a profound effect on the migration of excitons in TMMC crystals. Even with substantial Cu^{2+} concentrations, the luminescence from the double-doped crystals decays at a rate which approaches that of undoped TMMC. Exciton trapping at the Cu^{2+} impurities is greatly reduced in these double-doped samples.

B. Theoretical expressions for emission decay

The temperature dependence of the exciton trapping in TMMC indicates incoherent motion in which excitons hop between neighboring lattice sites at random. The

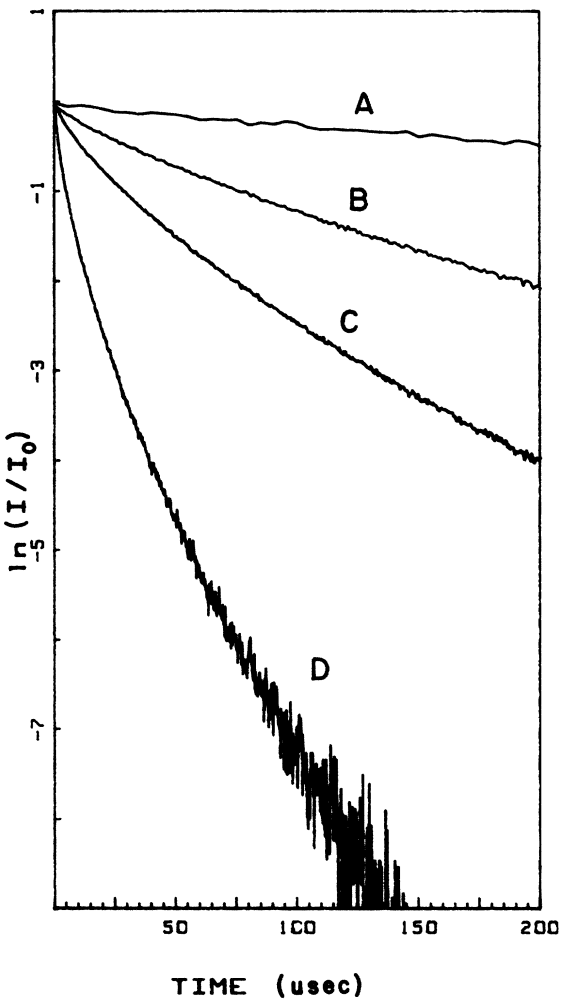


FIG. 1. Normalized log plot of the emission decay curves from several TMMC crystals recorded at room temperature. Curve A corresponds to undoped TMMC while curves B, C, and D correspond to doped crystals containing Cu^{2+} mole fractions of 7.0×10^{-5}, 2.7×10^{-4}, 1.0×10^{-3}, respectively.

behavior of a random walker moving on a lattice containing traps has been a problem of mathematical interest for many years. It was recognized by Montroll and Weiss that the average number of lattice sites visited after n hops on a one-dimensional lattice is proportional to $n^{1/2}$.[10] Thus, the probability that the walker on the next hop will enter a site that has not already been visited steadily decreases with the number of hops. Therefore, the decay of an exciton population due to trapping at impurity centers will not follow a simple exponential. Approximate and exact decay laws have been derived for a number of specific cases. Unfortunately, each theoretical model requires a number of assumptions regarding the distribution of trap sites and the exciton capture process which are very difficult to characterize for any real system. The decay curves from the doped TMMC crystals were analyzed in terms of two theoretical models. The first, proposed by Wieting, Fayer, and Dlott (WFD) was

derived explicitly to treat a linear chain lattice which contains scattering as well as trapping centers.[11] The distribution of impurities in the lattice is taken to be ordered (a superlattice). It is recognized that hops between chains may contribute to the decay curve even though the interchain hopping rate may be very small relative to the intrachain rate. Under these conditions the decay law is approximated by the rather simple analytical expression given below:

$$I(t)=I_0\exp(-k_e t-k_1 t^{1/2}) .$$

In this equation k_1 is the rate constant for exciton trapping due to migration along the chain while k_e is a cumulative exponential decay constant for processes such as spontaneous emission and three-dimensional migration. The second theoretical model is based on an expression derived by Balagurov and Vaks (BV) to treat a one-dimensional lattice which contains traps distributed according to a poisson distribution.[12] The equation for emission decay given below does not have a simple analytical form and must be solved by numerical integration. The quantity within large parentheses represents the

$$I(t)=I_0\exp(-k_e' t)\left[(4/\pi^2)\int_0^\infty \exp(-k_1' t/\xi^2)\frac{\xi}{\sinh\xi}d\xi\right]$$

exciton trapping resulting from the intrachain (one-dimensional) migration, while the effects resulting in exponential decay are incorporated into the term outside the large parentheses.

Each model presents us with strengths and weaknesses. Since the impurities are likely to be distributed in a random or nearly random manner, the basic construction of the second model is more rigorously correct. The first model, however, has the advantage of considering the unavoidable effects of interchain transfer and of explicitly considering the effects of scattering centers as well as traps. It should be noted that the deviation between the two models is greatest at long times, when the number of intrachain hops greatly exceeds the average trap separation.[13,14] Under these conditions the BV expression asymptotically approaches the analytical form given below:

$$I(t)=I_0\frac{16}{\pi}\left[\frac{k_1' t}{3\pi}\right]^{1/2}\exp\left[-k_e t-3\left[\frac{k_1 t}{4}\right]^{1/3}\right] .$$

Thus, the term in the exponential that reflects one-dimensional trapping depends on $t^{1/3}$ while the corresponding term in the WFD model depends on $t^{1/2}$. Log-log plots of the intensity data with the simple exponential component factored out were studied to establish the asymptotic behavior. Unfortunately, the data taken from the very weak tails of the decay curves ($I<0.01I_0$) are not precise enough to give a conclusive indication of the long-time behavior.

In our analysis the kinetic parameters and the value of I_0 in the two decay expressions were adjusted by computer to give the best least-squares fit to each set of experimental data. Both models give calculated curves which by visual comparison are in excellent agreement with the observed decay curves. The standard deviations are typically less than 0.3% of the I_0 value. There is some indication that the expression based on the exact treatment of BV gives better fits to some of the data sets, but the differences are quite small. A careful consideration of the residuals from the least-squares fits indicates a small but noticeable systematic deviation between the observed and calculated decay curves with some of the data sets, particularly those recorded at the high end of the temperature range. It is not clear if this results from an inadequacy of the theoretical expressions, a failure of the experimental apparatus to precisely reproduce the decay curves, or a pathological feature of some of the doped crystals. The best-fit kinetic parameters for the room-temperature emission decay curves of several doped crystals as well as an undoped sample of TMMC are given in Table I. Even in undoped TMMC, exciton trapping resulting from intrachain migration appears to make a small but observable contribution to the emission decay. The TMMC used in this study may contain a small background concentration of impurity or defect sites which behave as exciton traps. The effect of relatively small concentrations of a scattering center (Cd^{2+}) is clearly evident from the parameters presented in Table I. Samples *D* and *F* contain nearly the same trap (Cu^{2+}) concentration, but the rate parameters for exciton trapping in one dimension are dramatically smaller in sample *F* which has a 0.04 mole fraction of Cd^{2+}.

C. Physical interpretation of the best-fit parameters

The least-squares refinement of the decay curves from Cu^{2+}-doped TMMC indicates features consistent with

TABLE I. Best-fit parameters for emission decay curves at room temperature.

Sample	X_{Cu}	X_{Cd}	k_e (sec^{-1})	k_1 ($sec^{-1/2}$)	k_e' (sec^{-1})	k_1' (sec^{-1})
A	0	0	1.5×10^3	1.5×10	1.6×10^3	1.9×10^2
B	7.0×10^{-5}	0	5.0×10^3	8.7×10	4.5×10^3	2.0×10^4
C	2.7×10^{-4}	0	8.0×10^3	2.0×10^2	1.0×10^4	6.9×10^4
D	1.0×10^{-3}	0	2.0×10^4	6.0×10^2	3.2×10^4	6.7×10^5
E	2.0×10^{-3}	1.9×10^{-2}	2.0×10^3	4.4×10	2.2×10^3	3.3×10^3
F	9.8×10^{-4}	4.6×10^{-2}	1.2×10^3	1.9×10	1.3×10^3	2.6×10^2

one-dimensional exciton migration. The parameters provide considerable insight into the exciton dynamics in TMMC. The hopping frequency for migration along the chain can be calculated from the observed rate constants using expressions derived by BV if it is assumed that the Cu^{2+} impurities do not trap excitons over an extended region of the TMMC lattice but that every direct encounter between exciton and impurity results in capture. Thus,

$$k_1=\left[\frac{8(X_{Cu})^2\nu_1}{\pi}\right]^{1/2},$$

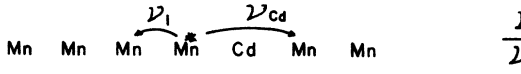
$$k_1'=\frac{(X_{Cu})^2\pi^2\nu_1}{2}.$$

In these expressions X_{Cu} corresponds to the mole fraction of Cu^{2+} (trapping sites) to Mn^{2+} and ν_1 represents the intrachain hopping frequency. WFD have considered the effects of scattering impurities such as Cd^{2+} as well as traps in the following way. Each chain is cut into "cages" whose length is defined by end scatterers. Since the exciton migration through a scattering center is certain to be much slower than the normal intrachain migration, it is assumed that an exciton samples all the sites within a cage long before a hop to another cage takes place. If the concentration of scattering centers is significantly greater than the concentration of traps, most of the cages will not contain a trapping impurity so that the time-dependent behavior will be determined largely by the relatively slow migration between cages. An approximate between-cage hopping frequency can be calculated from the observed rate constants by incorporating this central concept of the WFD paper in the BV-derived theory. The expressions are modified to reflect the fact that each hop to a new cage allows an exciton to visit not just a single site but all of the enclosed lattice sites. For the double-doped TMMC crystals the average number of lattice sites per cage is $X_{Cd}^{-1}-1$, where X_{Cd} is the mole fraction of Cd^{2+} (scattering center). The modified expressions are given below:

$$k_1=\left[\frac{8[X_{Cu}(X_{Cd}^{-1}-1)]^2\nu_1'}{\pi(1-X_{Cd})^2}\right]^{1/2},$$

$$k_1'=\frac{[X_{Cu}(X_{Cd}^{-1}-1)]^2\pi^2\nu_1'}{2(1-X_{Cd})^2}.$$

In these equations ν_1' represents the intercage hopping frequency along the linear chain. The calculated frequencies for the TMMC crystals doped with Cu^{2+} and double doped with Cu^{2+} and Cd^{2+} are given in Table II. The values for the intrachain hopping rate which fall between 10^{11} and 10^{12} sec^{-1} are quite compatible with the value of 10^{12} sec^{-1} given by Yamamoto *et al.*[7] The frequency of hopping between cages is more than 6 orders of magnitude smaller than that between adjacent Mn^{2+} ions within the same chain which indicates that a Cd^{2+} impurity represents an extremely effective barrier to excitons migrating along a $[MnCl_3^-]_n$ chain. If an exciton rapidly visits all the sites within a cage, the probability of occupying a given site is $1/m$, where m is the number of enclosed sites. The hopping frequency for a single Mn^{2+} ion caged by two Cd^{2+} ions (ν_{Cd}) is then equal to the product of the calculated intercage frequency, ν_1', and the number of enclosed sites, $(X_{Cd}^{-1}-1)$. From the data in Table II, ν_{Cd} is approximately 3×10^6 sec^{-1}, which indicates that exciton migration across a Cd^{2+} ion (between next-nearest Mn^{2+} ions) is 5 orders of magnitude slower than migration between nearest-neighbor Mn^{2+} ions:



An additional insight provided by the WFD model deals with the roll of hops between chains. Such interchain hops contribute to the exponential component of the exciton decay so that the observed rate constant (k_e or k_e') represents the sum of two processes:

$$k_e=k_c+k_3.$$

The rate constant k_c corresponds to the normal radiative and nonradiative relaxation associated with the $^4T_1$ excited state localized on a Mn^{2+} ion in the TMMC lattice while k_3 represents exciton trapping due to cross-chain (three-dimensional) migration. The measurements on undoped TMMC reported by Yamamoto *et al.* indicate that the normal relaxation of the $^4T_1$ state is nearly independent of temperature and has a rate constant of approximately 1.2×10^3 sec^{-1} ($k_c=1/\tau$). If this is taken to be a reasonable estimate for k_c in the doped crystals, the value of k_3 can be found by the difference. Theoretical expressions for k_3 are given below from WFD:

$$k_3=\frac{X_{Cu}(X_{Cd}^{-1}-1)\nu_{tot}}{\mu_0},\quad \nu_{tot}=\nu_1'+\nu_3$$

and with no Cd^{2+} present,

$$k_3=\frac{X_{Cu}\nu_{tot}}{\mu_0},\quad \nu_{tot}=\nu_1+\nu_3.$$

ν_{tot} represents the total hopping frequency while the μ_0 parameter is dependent on the sample topology as well as the relative rates of interchain, ν_3, and intrachain hopping. The intrachain hopping frequency, and the total hopping frequency, have different meanings in the above two expressions for k_3. With scatterers present they refer to the cage hopping frequency and without scatterers they refer to the Mn^{+2} hopping frequency. In a strongly one-dimensional system the total hopping frequency is essentially equal to the intrachain frequency:

$$\nu_{tot}\sim\nu_1.$$

TABLE II. Intrachain hopping frequencies.

Sample	X_{Cu}	$X_{Cd}^{-1}-1$	ν_1 (sec^{-1}) from k_1	from k_1'
B	7.0×10^{-5}		6.1×10^{11}	8.2×10^{11}
C	2.7×10^{-4}		2.2×10^{11}	1.9×10^{11}
D	1.0×10^{-3}		1.4×10^{11}	1.4×10^{11}
E	2.0×10^{-3}	52	7.0×10^{4} [a]	6.2×10^{4} [a]
F	9.8×10^{-4}	21	3.3×10^{5} [a]	1.2×10^{5} [a]

[a]These values correspond to ν_1'.

TABLE III. Parameters for interchain hopping.

Sample	k_3 (sec^{-1})	μ_0	ν_{tot}/ν_3	ν_3 (sec^{-1})
B	3.5×10^3	1.4×10^4	1.6×10^8	4.4×10^3
C	7.5×10^3	7.2×10^3	4.1×10^7	4.9×10^3
D	2.5×10^4	5.6×10^3	2.5×10^7	5.6×10^3
E	9.0×10^2	7.6	4.7×10	1.4×10^3
F	1.0×10^2	4.1×10	1.4×10^3	1.4×10^2

Although the case of a hexagonal lattice is not treated explicitly, a comparison of a number of different topologies shows that μ_0 can be approximated as

$$\mu_0 \sim 0.9 \left[\frac{\nu_{tot}}{\nu_3} \right]^{1/2} .$$

The values for k_3, μ_0, ν_{tot}/ν_3, and ν_3 for the doped TMMC crystals are given in Table III. The really striking feature of these calculated values is how close the exciton migration in TMMC apparently comes to being perfectly one dimensional. The intrachain hopping rate seems to be more than 8 orders of magnitude greater than the interchain hopping rate. Even in the double-doped crystals, the hopping frequency between cages on the same chain appears to be significantly faster than the interchain hopping.

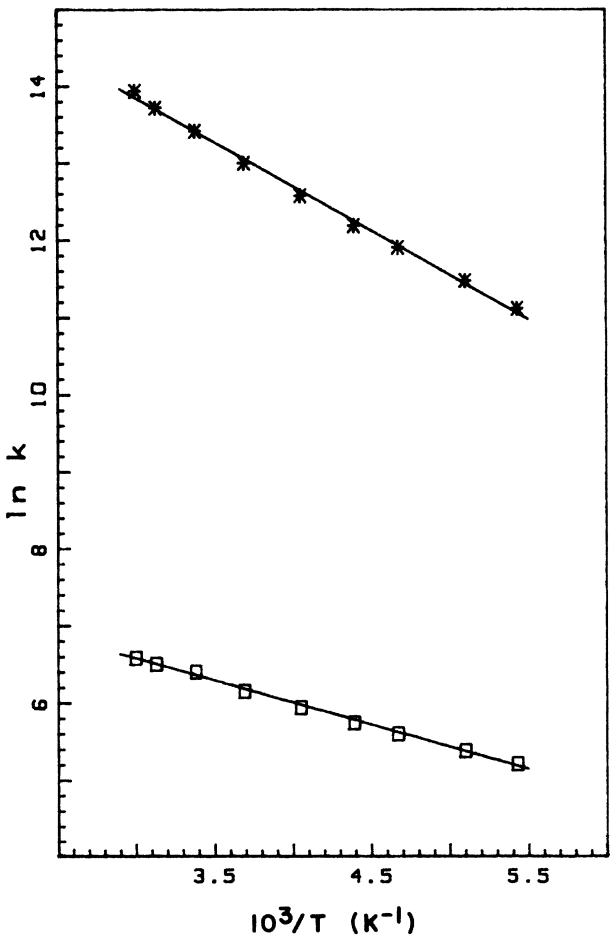


FIG. 2. Plots of $\ln k_1$ (open squares) and $\ln k_1'$ (asterisks) versus reciprocal temperature for sample *D*. The slope of the least-squares line through the $\ln k_1$ data corresponds to an energy of 398 cm^{-1} while the slope of the line through the $\ln k_1'$ data corresponds to an energy of 798 cm^{-1}.

The temperature dependence of the emission decay curves reflects the thermal activation required for exciton migration. An estimate of the energy barrier to intrachain hopping can be obtained from an activation plot of the rate constants for one-dimensional trapping, k_1 or k_1'. Figure 2 shows plots of $\ln k_1$ and $\ln k_1'$ versus reciprocal temperature for sample *D* (TMMC doped with Cu^{2+}). The data show the slope of the line based on $\ln k_1$ to be almost exactly half as large as that of the line based on k_1'. This is expected since the value of k_1 is proportional to the square root of the hopping frequency, while the value of k_1' is proportional to the hopping frequency. Both sets of data are quite linear and are consistent with a barrier of 800 cm^{-1} for migration along the $[MnCl_3^-]_n$ chains. The data from the other Cu^{2+}-doped TMMC samples also give linear activation plots, but there is some variation in the activation energies that are determined. Sample *B*, for example, indicates a barrier of 1000 cm^{-1} for intrachain migration. Considering the data from all of the Cu^{2+}-doped samples, it appears that the actual activation energy is somewhere between 800 to 1000 cm^{-1}. This is in disagreement with the value of 430 cm^{-1} reported by Yamamoto and co-workers for the barrier in TMMC.

IV. CONCLUSIONS

Our analysis of the emission decay curves provides a reasonable and self-consistent description of the exciton dynamics of TMMC. Although some of the results, the hopping frequencies in particular, are dependent on assumptions that have no experimental verification, a number of significant features appear to be unambiguously established. The important conclusions are listed below.

(1) The emission decay curves from Cu^{2+}-doped TMMC crystals deviate from exponentiality in a manner consistent with exciton trapping in one dimension.

(2) Exciton migration in TMMC is very nearly one dimensional. Regardless of the theoretical model it is clear that the intrachain hopping frequency is greater than the

interchain frequency by many orders of magnitude.

(3) Scattering impurities such as Cd^{2+} dramatically reduce the rate of exciton trapping. This is a reflection of the one-dimensional character of TMMC.

(4) There is a significant energy barrier, 800 to 1000 cm^{-1}, to exciton hopping between adjacent Mn^{2+} sites in TMMC.

The failure to establish the asymptotic behavior of the decay curves and differentiate the two theoretical models is the only disappointing aspect of this study. The problem of defining the asymptotic form of the one-dimensional trapping component is experimentally difficult because the simple exponential processes (k_e) tend to dominate the observed decay curves at long times. It is interesting to note that preliminary studies on doped crystals of the analogous bromide salt, TMMB, indicate that the material is even more one dimensional than TMMC. It appears that it will be possible to establish the long-time behavior of the one-dimensional trapping in this TMMB.

ACKNOWLEDGMENTS

One of us (G.L.M.) wishes to acknowledge helpful discussions with G. Zumofen on trapping in one-dimensional systems. This work was partially supported by grants (R.A.A.) from Research Corporation and from the Petroleum Research Fund administered by the American Chemical Society.

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