Exciton migration in quasi-one-dimensional crystals: Antiferromagnetic $CsMnCl_3 \cdot 2H_2O$

V. V. Eremenko, V. A. Karachevtsev, A. R. Kazachkov, V. V. Shapiro, and V. V. Slavin

Institute for Low Temperature Physics and Engineering, Ukrainian Academy of Sciences, 47 Lenin Avenue, Kharkov 310164, Ukraine

(Received 2 August 1993)

Pure and doped antiferromagnetic $CsMnCl_3 \cdot 2H_2O$ (CMC) crystals have been studied in the temperature range 4.2–300 K. With an increase in temperature the luminescence time and intensity of doped CMC crystals (1% and 0.1% Cu^{2+}) decrease. The exciton-emission quenching is associated with exciton migration and trapping. The emission decay kinetics is approximated by the calculated curves obtained using the Kenkre and Onipko, Malysheva, and Zozulenko theories. The exciton hopping (W) and trapping (U) rates have been defined. Exciton trapping by the Cu^{2+} traps in CMC is inefficient. The dependences $W(T)$ and $U(T)$ are given for two dopant concentrations in CMC obtained in the temperature range 77–237 K.

INTRODUCTION

Exciton migration in quasi-one-dimensional crystals is a matter of current interest. A good deal of effort undertaken in recent years[1-17] has resulted in some progress, owing mainly to investigations of the luminescence of quasi-one-dimensional excitons in the antiferromagnets (AFM's) $(CH_3)_4NMnCl_3$ (TMMC) and $(CH_3)_4NMnBr_3$ (TMMB).[3-8] These compounds proved to be fairly convenient model systems, with a high degree of exciton-migration one dimensionality (1D), a hoppinglike character of the exciton movement (this fact is important for processing the experimental results, since there is a quite complete mathematical description of an incoherent exciton walk along a 1D chain[11-17]), and exciton emission in a wide temperature range.

The above studies are concerned with exciton-migration properties which manifest themselves in exciton trapping. In this case 1D systems are characterized by deviation of the exciton-luminescence decay curves from the monoexponentional ones which are inherent to systems with isotropic exciton motion. An analysis of decay curves gives microscopic parameters characteristic of exciton transport in these crystals, namely, the exciton hopping rate (W), the rate of exciton trapping (U), and the degree of one dimensionality of exciton motion.

While describing migration processes it is a common practice to consider efficient ($U \geq W$) and inefficient ($U < W$) exciton trapping. Most theoretical papers have considered efficient exciton trapping.[11-15] Inefficient trapping has been treated by Onipko, Malysheva, and Zozulenko (OMZ).[17] These authors derived an expression which describes the emission decay kinetics for an arbitrary ratio of the trapping rate to the hopping rate. Inefficient trapping was also considered by Kenkre;[16] however, practical application of his theory to approximate the decay curves is complicated since the final formulas are written using Laplace variables.

It was assumed earlier that in TMMC (Ref. 3) and TMMB (Ref. 4) crystals doped with Cu^{2+} and Co^{2+} ions exciton trapping is efficient. However Knochenmuss and Güdel,[5] using the results of Kenkre's theory to approxi-

mate the exciton-emission decay curves, showed that in TMMC trapping is inefficient ($U/W = 10^{-4}$). The inverse Laplace transformation was calculated numerically. Recently, a simulation of the exciton random walk along a quasi-1D chain by the Monte Carlo method also led to the conclusion[6,7] that exciton trapping in TMMC was inefficient when doped with Cu^{2+}.

It should be noted that recent studies have been made on one compound (TMMC). In a sense, this is due to the fact that there are few AFM compounds with mainly 1D transport properties. The quasi-one-dimensional AFM $CsMnCl_3 \cdot 2H_2O$ (CMC) studied in the present work belongs to that small class of compounds.

CMC is a biaxial orthorhombic crystal with the space group $D_{2h}^8 (P_{ccq})$.[18] It has the following lattice parameters: $a = 9.06$ Å, $b = 7.295$ Å, $c = 11.445$ Å. Its chemical cell has four formula units. Experimentals showed that the AFM exchange interaction along the crystallographic direction a is a factor of 300 stronger than that along the c axis. The interaction along the b axis is weaker than that along the c axis by about an order of magnitude.[19,20] In the magnetically ordered phase ($T < T_N = 4.89$ K) the unit cell is doubled along the b direction, owing to the weak antiferromagnetic exchange along that axis. The fact that one of the exchange integrals much exceeds the others permits consideration of CMC as a quasi-one-dimensional AFM crystal.

It was assumed earlier that in CMC excitons were localized even at room temperature, due to the strong exciton-phonon interaction.[21] This assumption was based on the fact that at low temperatures the CMC luminescence spectrum consists mainly of a broad exciton-phonon sideband which changes only slightly, like the luminescence decay kinetics, with increase in temperature to 300 K.

In the present work experiments were carried out on pure and doped (0.1% and 1% Cu^{2+} ions) CMC crystals. The exciton-emission decay kinetics is studied over a wide temperature range (4.2–300 K). As a result, we could infer that exciton migration does exist in these crystals above 50 K. The observed exciton-emission decay curves can be approximated by those calculated using the OMZ (Ref. 17) and Kenkre theories.[16]

EXPERIMENTAL

The CMC crystals were grown from a saturated aqueous solution of $MnCl_2 \cdot 4H_2O$ with CsCl by slow evaporation at 30°C. CMC crystals doped with Cu^{2+} (0.1 and 1 mol% copper ions) were also obtained from the aqueous solution with the addition of $CuCl_2 \cdot 2H_2O$. The typical sizes of samples were about $10 \times 6 \times 2$ mm^3.

The dopant concentration in the CMC crystals was estimated from the loading ratio of CMC and $CuCl_2 \cdot 2H_2O$. Such an estimation was based on experiments where light absorption by copper ions in a solution with known loading ratio of the above components (1% Cu^{2+}) was compared with that of the doped CMC crystals dissolved in water. Those crystals were grown from a solution with the same ratio of initial components (1% Cu^{2+}). The dopant concentration in the crystal was in good agreement with that in the loading solutions.

Crystal luminescence was excited by a nitrogen laser (excitation wavelength 337 nm, maximum pulse power 30 kW) or by a mercury lamp using corresponding light filters to select separate lines. A double monochromator was used as a spectral device. The emission was recorded by a photomultiplier operating in a photon-counting mode. After emerging from an amplifier discriminator one-electron pulses entered a multichannel time analyzer (0.6 μs/channel, 4096 channels) which accumulated and averaged the emission decay curves. Experimental control and results processing were executed with a personal computer.

A sample was placed into an optical cryostat with gaseous helium. The temperature was varied from 4.2 to 300 K with an accuracy of 1 K.

EXPERIMENTAL RESULTS

The luminescence spectrum of CMC crystals at 1.5 K has been studied sufficiently well;[21,22] it consists of a weak exciton line [$v_e = 17\,064$ cm^{-1}, the transition $^4T_{1g}(^4G) \rightarrow {}^6A_{1g}(^6S)$] and a broad exciton-phonon band (full width at half maximum 1400 cm^{-1}, $v_{e\text{-ph}} = 15\,600$ cm^{-1}). Above 6 K the exciton line is, in fact, undistinguishable from the broadband. As the temperature rises to 300 K, the band broadens and shifts towards higher frequencies. It should be noted that similar changes are observed in TMMC and TMMB spectra with increasing temperature.[3,4]
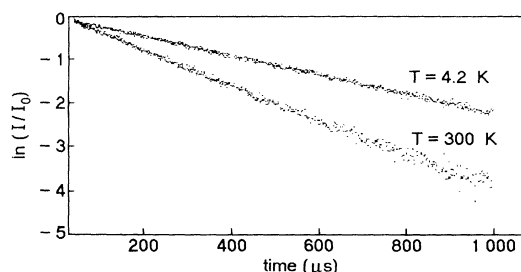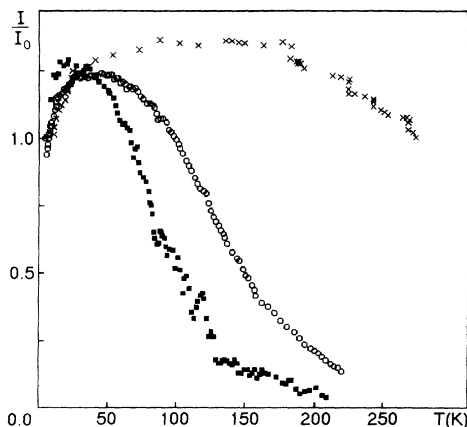

FIG. 2. Temperature dependences of the luminescence intensity of undoped (crosses) and doped (1 mol% of Cu^{2+}, solid squares, 0.1 mol% of Cu^{2+} open circles) CMC crystals.

The luminescence decay kinetics of a pure CMC crystal (registration wavelength $\lambda = 620$ nm) is shown in Fig. 1 at 4.2 K (the upper curve) and at 300 K (the lower curve). If the registration wavelength is varied within the emission band, the decay kinetics does not change. This confirms the earlier assumption[21] that the broadband is of exciton-phonon nature rather than from trapping. The decay curves are approximated quite well by a monoexponential dependence with lifetimes $\tau = 510$ μs ($T = 4.2$ K) and $\tau = 380$ μs ($T = 300$ K).

Figure 2 gives the temperature dependence of the emission intensity for undoped and doped CMC crystals in the range 4.2–300 K. In this temperature range the integral emission intensity (I) of the undoped crystal changes slightly. As the temperature increases from 4.2 to 30 K, I rises by about 30% due to an additional

FIG. 1. Exciton-emission decay kinetics of an undoped CMC crystal at 4.2 K ($\tau = 510$ μs) and 300 K ($\tau = 380$ μs).
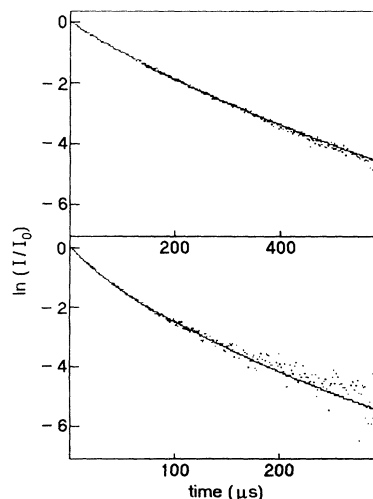

FIG. 3. Exciton-emission decay kinetics of doped CMC crystals (0.1 mol% of Cu^{2+}) at 169 K (upper part) and at 237 K (lower part). The approximating curves are calculated using the OMZ theory, Eq. (7) (upper curve) and Eq. (6) (lower curve).

thermally activated emission mechanism.[23] Further temperature increase leads to a decrease of I, which achieves its initial value at 270 K. At the same time, with the increase in temperature the emission intensity of the doped samples begins to decrease at $T > 50$ K. Moreover, the drop in luminescence intensity of a 1%-Cu^{2+}-doped crystal begins at much lower temperatures than that of 0.1%-Cu^{2+}-doped CMC. At room temperature emission from doped crystals, in fact, is not observed.

Figure 3 presents the luminescence decay kinetics of a 0.1%-Cu^{2+}-doped CMC crystal obtained at different temperatures. As the temperature rises, the emission time decreases, and the character of the decay curves changes appreciably. At higher temperatures the shape of the decay curves deviates more and more from the monoexponential time dependence. In a similar way, the luminescence decay kinetics of a 1%-Cu^{2+}-doped CMC crystal changes with temperature; however, those changes take place at much lower temperatures.

DISCUSSION

A. Exciton migration in CMC

As a test of the exciton mobility in crystals, a method is used to observe the luminescence from a sample doped with impurities forming excitation traps.[1–10,24] If in a crystal the energy is transferred by excitons, the exciton luminescence is quenched by traps even at fairly small dopant concentrations. The above phenomenon is observed in our investigations of doped CMC crystals. In AFM crystals copper ions are often used as dopants to form traps for excitons,[3–5,24] but emission from those traps is not observed.[24] It should be noted that the concentrations of dopants introduced into CMC (0.1% and 1%) are not very high, and the exchange interaction[19,20] along a chain is rather weak (2.48 cm^{-1}) to expect the appearance of other energy-transport mechanisms (e.g., percolation). Thus, the observed luminescence quenching by an impurity indicates the appearance of mobile excitations in CMC above 50 K.

As was mentioned above, in undoped CMC crystals the luminescence intensity at 4.2 and 300 K is, in fact, of the same magnitude (Fig. 2), and the decay kinetics is described by an exponential dependence at these temperatures (Fig. 1). Such an observation may seem unusual, since even after special purification some residual impurities are always present in a crystal. By distorting the crystal lattice they can form traps for excitons or can be traps themselves. In this case exciton-luminescence intensity should decrease with increase of exciton mobility (in CMC with increase in temperature) and the decay-curve shape should deviate from the exponential one, as this is inherent to crystals with quasi-1D exciton migration.[1–17] However, as has been shown in recent papers on computer simulation of the exciton migration along the quasi-1D lattice,[6,7] the deviation of exciton-luminescence decay curves from the monoexponential shape depends on the correlation between the exciton hopping rate, the degree of quasi-1D, the trapping efficiency, and the trap concentration, e.g., if the ex-

change interaction along one crystallographic axis is larger by a factor of 10^4–10^5 than along the others (as for TMMC and TMMB), the emission decay curves deviate from the monoexponential shape at fairly low impurity concentrations (less than 0.01%), comparable with those of residual undetected dopants. At lower ratios of exchange-integral values (3×10^2 in CMC), dopant concentrations should be increased to observe the above changes in the luminescence decay kinetics. In addition, trapping by residual dopants in antiferromagnets can be inefficient, e.g., the efficiency of trapping by Cu^{2+} ions in TMMC is 10^{-4}. Moreover, it is well known that in TMMC trapping of excitons by Co^{2+} and Ni^{2+} dopants is less effective than by Cu^{2+}.[24] It should be noted that in undoped TMMC and TMMB crystals the emission decay kinetics is nearly monoexponential at room temperature.[3,4]

Furthermore, the residual impurities do not always generate traps. It is well known[1,2,9,10] that some impurities are barriers for excitons, i.e., they have higher energy levels than the excitons, e.g., in TMMC and TMMB, Cd^{2+} ions are barriers for excitons.[3,4] In that case the luminescence intensity is defined by the ratio of concentrations of traps and barriers. When the barrier concentration is higher than that of traps, the excitons are screened from the traps in quasi-1D crystals. If the trap concentration increases, the role of the barriers will be reduced and the trapping of excitons becomes more important causing exciton-luminescence quenching. We assume that the situations discussed above (low concentration of residual impurities, inefficient trapping in AFM's and the important role of barriers in 1D systems) affect the low-temperature luminescence of undoped CMC crystals.

B. Exciton-luminescence decay kinetics in CMC

A choice of the exciton transport model which corresponds to the subject of investigation is an important matter when approximating decay curves. Two aspects of this question in the case of CMC should be noted: (i) the relatively high temperature range (for coherent excitons) of exciton-migration observation, 77–237 K, and (ii) the quite strong exciton-phonon interaction.[22,23] These circumstances allow us to consider exciton transport in CMC above 77 K to be incoherent. Since exciton trapping in most compounds studied was a priori assumed efficient (except in Ref. 25), and up to now inefficient trapping has been observed in one AFM (TMMC) only, it would be of interest to compare the degree of efficiency of exciton trapping in other AFM crystal with the same impurity (Cu^{2+} ions).

The theoretical results obtained by Kenkre[16] and OMZ[17] were used for approximation of the exciton-luminescence decay curves. In these works the same initial model was considered but different solution methods were used.[26] In this model exciton motion along the 1D chain is studied under different hopping and trapping rates. Carrying out the inverse Laplace transformation for the final expression describing the luminescence inten-

sity in Kenkre's theory, we have obtained analytical expressions for the luminescence decay kinetics. Using the results of the OMZ theory[17] we approximated the exciton-luminescence decay curves by those calculated in the limits of both efficient and inefficient trapping.

1. Trapping model of Kenkre

The decay of the luminescence intensity described in Laplace variables may be represented as follows:

$$\eta_H = \frac{1}{E'}\left[1 - \frac{CU}{E' + UE'\tilde{v}(E')}\right] , \tag{1}$$

where $\tilde{v} = C/E' + (1 - C)\Psi(E')$, $\Psi = [E'(E' + 4W)]^{-1/2}$, $E' = E + K_h$, C is the impurity concentration, and $(K_h)^{-1}$ is the radiation lifetime.

Substituting the expressions for $\tilde{v}$ and Ψ into $\eta_H(E')$, we obtain

$$\eta_H = \frac{1}{E'}\left\{1 - CU\sqrt{E' + 4W}\right.$$

$$\left. \times \frac{\sqrt{E' + 4W}\,(E' + UC) + U(C - 1)\sqrt{E'}}{F(E')}\right\} , \tag{2}$$

where $F(E') = (E' + 4W)(E' + UC)^2 - E'[(C - 1)U]^2$.
Let us introduce the parameter $\Lambda = U/CW$, which turned out to be convenient in this model. It should be noted that the same parameter was used in the OMZ theory[17] for describing the exciton trapping efficiency. Trapping was considered to be efficient while $\Lambda \gg 1$ and inefficient if $\Lambda \ll 1$.

Producing the inverse Laplace transformation of Eq. (2) (as in Ref. 27) we obtain the final expressions for decay of the luminescence intensity. This procedure is described in the Appendix in detail. An analysis given in the Appendix allows us to determine the limits of applicability of Kenkre's theory. As it turns out this theory may be used for inefficient trapping. Within the range $\Lambda < 16$ the intensity of the decay curve is described by the following expression:

$$\eta_H(t) = \exp(-K_h t)\left[1 + L_0 + U^2 C(1 - C)\frac{1}{\pi}\int_0^{4W}\left[\frac{4W - Y}{Y}\right]^{1/2}\exp(-Yt)F(-Y - K_h)dY\right]$$

$$+ L_1\exp(E_0 t) + \exp(at)UC[L_2\sin(bt) + L_3\cos(bt)] . \tag{3}$$

Parameters a, b, E_0, L_0, L_1, L_2, and L_3 are given in the Appendix.

Equation (3) is applicable for $\Lambda < 8$ while the correctness of this formula over the range $8 < \Lambda < 16$ is determined by the relation of the parameters U, W, C, and K_h [it was a surprise for us that over this range of Λ the applicability of Eq. (3) depends on the K_h value].

If $\Lambda > 16$, then the emission decay curve is described by another expression. We carried out a fitting between this dependence and the observed curves and obtained poor coincidence. Any attempt to improve the agreement led to breakdown (A9) because of a small K_h value in CMC (see Appendix) and, as a result, to the appearance of exponentially increasing solutions.

The approximation of experimental data by curves calculated using Eq. (3) shows that the best fit is for $\Lambda \ll 1$

TABLE I. Mn-Mn on-chain hopping and trapping rates in CMC from fits to the OMZ and Kenkre theories.

| Cu^{2+}	Temperature (K)	Hopping rate (s^{-1})	Trapping rate (s^{-1}) Kenkre Eq. (3)	OMZ Eq. (6)	OMZ Eq. (7)
	77	3.0×10^7	3.0×10^5		2.3×10^5
	99	8.0×10^7	7.3×10^5	3.8×10^5	6.3×10^5
1%	123	4.0×10^8	1.3×10^6	1.5×10^6	1.2×10^6
	145	3.5×10^9	2.0×10^6	2.3×10^6	1.7×10^6
	159	4.0×10^9	3.0×10^6	4.0×10^6	2.5×10^6
	150	8.0×10^{10}	5.0×10^6	4.3×10^6	3.5×10^6
	169	2.0×10^{11}	7.0×10^6	6.2×10^6	5.2×10^6
	179	3.0×10^{11}	1.1×10^7	9.4×10^6	7.7×10^6
0.1%	218	7.0×10^{11}	2.2×10^7	2.3×10^7	1.8×10^7
	225	7.0×10^{11}	1.9×10^7	1.8×10^7	2.0×10^7
	237	8.0×10^{11}	2.6×10^7	2.8×10^7	2.2×10^7
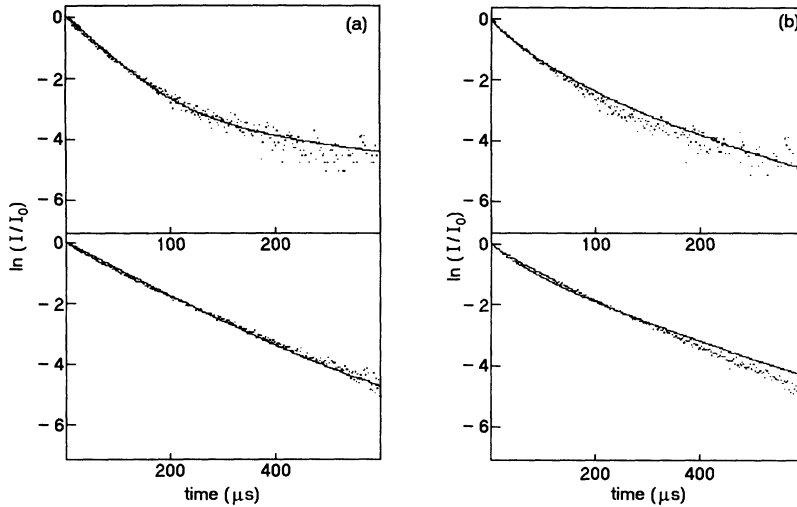
FIG. 4. Exciton-emission decay kinetics of doped CMC crystals: 1 mol % of Cu^{2+} at 159 K (upper parts) and 0.1 mol % of Cu^{2+} at 169 K (lower parts). The approximating curves are calculated using (a) Kenkre's theory [Eq. (2) for inefficient trapping], (b) the OMZ theory [Eq. (4) for efficient trapping].

(Fig. 4). Parameters U and W were varied. The results of this approximation (the least-squares method) are presented in Table I.

2. Trapping model of Onipko, Malysheva, and Zozulenko

This theory describes the exciton-emission decay kinetics using different asymptotic expressions for efficient and inefficient trapping.[17] However, for the case $U=W$ ($\Lambda \gg 1$, efficient trapping), the theory makes it possible to approximate experimental dependences without asymptotic formulas. In this case the calculated curves are obtained using a double summation taken on a computer. The calculation is performed in the form:

$$I(t)=I_0 C^2 \exp(-K_h t) \sum_{n=1}^{\infty} (1-C)p_n(t) , \qquad (4)$$

where

$$p_n(t)=\frac{1}{n+1} \sum_{i=1}^{n} [(-1)^{i+1}+1] \cot^2[\pi i/2(n+1)]$$

$$\times \exp\{-4Wt \sin^2[\pi i/2(n+1)]\} . \qquad (5)$$

When the emission decay kinetics was approximated using Eq. (4) only the parameter W was varied. The calculated curves gave a good fit to the experimental ones [Fig. 4(b)]. However, for all the temperatures the standard deviation of calculated dependences [Eq. (4)] from experimental curves obtained under the condition of the best fit appeared to be larger than that calculated by the approximation using calculated curves [Eq. (3)] in Kenkre's theory (inefficient trapping).

The exciton-luminescence decay kinetics with a different degree of efficiency of exciton trapping in the OMZ model can be approximated using an integral expression, viz.

$$I(t)=\frac{5}{6\Lambda^2} \exp(-K_h t) \int_0^{\infty} \frac{x(x+6)^2}{x^2+10x+30} \exp\left[-x/\Lambda - \frac{\Lambda^2(x+6)}{x^2+10x+30} \frac{10C^2 Wt}{x}\right] dx . \qquad (6)$$

This integral is obtained for small concentrations of traps ($C \ll 1$) and is applicable to approximate the decay curve beginning from the moment when the emission intensity has decreased by a factor of 2. The exciton emission kinetics of doped CMC crystals was approximated by the calculated curves obtained using Eq. (6) (Fig. 3, the lower curve). W and Λ are variable parameters in this fitting. As a result Λ values which made it possible to regard trapping in CMC as inefficient were obtained for all the dependences. To define W appeared to be complicated. The difficulties are associated with the fact that the calculated curve shapes change due to variation of Λ from 100 to 0.1. Beyond that interval of Λ values, the shapes of the calculated curves change only slightly. For more

efficient trapping ($\Lambda > 100$) the curve shapes change only as W varies (the diffusion-controlled regime), and for $\Lambda < 0.1$ only as U varies (the kinetic regime).[17] Since the best fit was obtained on the boundary of the above Λ range ($\Lambda \approx 0.1$), only U values for CMC were obtained (Table I).

The OMZ theory for inefficient exciton trapping ($\Lambda \ll 1$) gives an approximate analytical expression

$$I(t)=I_0 \sqrt{\pi \tau^{3/4}} \exp(-2\tau^{-1/2}-K_h t)[1+\tfrac{15}{16}\tau^{-1/2}] , \qquad (7)$$

which is applicable at $\tau \gg 1$, where $\tau=2CUt$.

The emission decay kinetics of doped CMC crystals were also approximated by curves calculated using Eq. (7)

(Fig. 3, the upper curve). The only variable parameter to fit the curves is U, while the hopping rate W is not included in the final expression. This is due to the fact that in the case of inefficient trapping ($\Lambda \ll 1$) in the $\tau \gg 1$ time interval the exciton-emission decay kinetics is mainly determined by trapping.

As a result, U values are obtained for different temperatures and dopant concentrations (Table I). The values of U obtained using the Kenkre and OMZ theories are in good agreement.

C. Temperature dependences of W and U

The temperature dependences of exciton hopping and trapping rates in CMC are associated with the peculiarities of exciton transport thermoactivation in quasi-1D AFM's. At low temperatures, exciton migration in these crystals is forbidden due to AFM ordering in the chains. As the temperature rises, the spin forbiddenness is lifted because of the breakdown of AFM ordering. It should be noted that exciton mobility in a CMC crystal is impeded also due to a fairly strong exciton-phonon interaction. In this case the exciton-migration process is jumping between nearest sites by overcoming some effective barrier.

Figure 5 shows the temperature dependence of the rate of exciton hopping between nearest sites. The barrier (Δ) was estimated using the Arrhenius relation $W = W_0 \exp(-\Delta/kT)$, and as a result the values of the effective barriers were obtained (Table II).

For different dopant concentrations the approximating lines have similar slopes, but they are shifted by some constant value. This shift may be due to an insufficiently exact determination of the dopant concentration in CMC. The shift between the two approximating sections almost disappears if the dopant concentration ratio is 1:6 in different crystals rather than the ratio 1:10 which was calculated from the loading proportions.
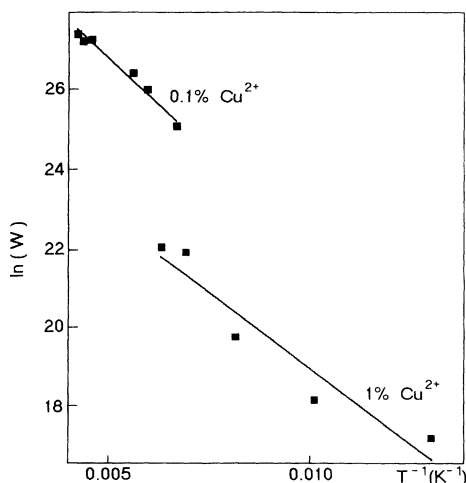
The temperature dependence of the exciton trapping

TABLE II. Effective barrier energy estimated from $W(T)$ and $U(T)$ dependences (Δ_W and Δ_U respectively). Units are cm^{-1}.

Cu^{2+}	Temperature range (K)	Kenkre theory Δ_W	Kenkre theory Δ_U	OMZ theory Δ_U Eq. (6)	OMZ theory Δ_U Eq. (7)
1%	77–159	550	240	250	310
0.1%	150–237	660	480	570	550

rate is presented in Fig. 6. The slopes of the approximating lines obtained from the Arrhenius relation also are different for the two dopant concentrations. It should be noted that barriers estimated from the temperature dependences of U obtained from different theories (Kenkre and OMZ) are in good agreement. In this case a barrier can have real physical meaning, since a dopant can distort the lattice so that a potential barrier can be formed between it and undistorted crystal ions.[28]

Different slopes of the approximating lines for $U(T)$ at two dopant concentrations are obtained in different temperature ranges and can be attributed to possible exciton tunneling through a barrier. In such a case the observed temperature dependence results from two processes, namely, tunneling and jumping over a barrier. It is clear that each mechanism has its own temperature dependence. Moreover, the contribution from tunneling increases at low temperatures. Thus, the obtained Δ values are effective. It should be noted also that the shift of the two approximating lines for different concentrations disappears if the concentration ratio is 1:6, as it does for W.

Unfortunately, we failed to detect and approximate the exciton-emission decay kinetics in one doped CMC crys-

FIG. 5. Temperature dependences of the exciton hopping rate for doped CMC crystals (Kenkre theory).
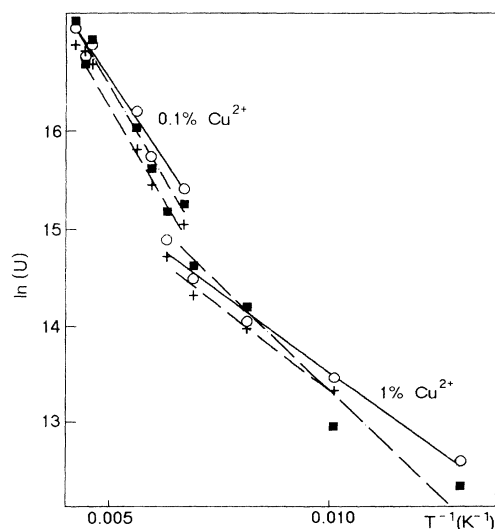

FIG. 6. Temperature dependences of the exciton trapping rate for doped CMC crystals. The approximating lines are calculated using the Arrhenius relation: open circles, Kenkre's theory (solid lines); crosses, OMZ theory, Eq. (6) (dashed lines); solid squares, OMZ theory, Eq. (7) (dot-dashed lines).

tal in such a temperature range that one could observe the deviation from the Arrhenius dependence for U. This is associated with the fact that, for example, at $T < 70$ K for 1%-Cu^{2+}-doped CMC crystals, the decay curve is quite well described by a monoexponential dependence and hence the approximation by calculated curves obtained using the Kenkre and OMZ theories fails. Above 160 K crystal emission is, in fact, not detected. The same difficulties arise in the case of 0.1%-Cu^{2+}-doped CMC crystals. The decay curves are of the monoexponential shape at $T < 150$ K (Fig. 3), and above 240 K strong quenching of this crystal luminescence is observed (Fig. 2).

CONCLUSION

Above 50 K in the quasi-1D antiferromagnet CMC exciton migration is detected. Earlier the excitons were considered to be localized in this crystal. Unlike in the undoped samples, the exciton-luminescence decay time and intensity in doped CMC crystals decrease appreciably with increase in temperature and increase of dopant concentration.

The exciton-emission decay kinetics of doped CMC crystals was approximated by calculated curves obtained using the Kenkre and OMZ theories. Application of these theories to describe the process of exciton trapping in CMC crystals proved to be successful. The Kenkre theory makes it possible to operate with the entire decay curve over the region of inefficient trapping ($\Lambda < 8$) and to define both W and U. The OMZ theory treats both efficient and inefficient exciton trapping; however, for $\Lambda \ll 1$ (exciton trapping in CMC by Cu^{2+}) this model gives an analytical expression describing the exciton-emission decay kinetics only for long times and permitting one to define only U. The exciton trapping rates obtained using both theories for different temperatures and dopant concentrations in CMC crystals are in good agreement. Traps for excitons formed by Cu^{2+} ions both in TMMC and in CMC crystals proved to be inefficient, e.g., at 230 K U/W for those traps in CMC is 10^{-4}–10^{-5} and the rate of hopping from site to site is 10^{11}–10^{12} s^{-1}. TMMC crystals show similar values of these parameters. Application of the above theories allows us to use analytic expressions to approximate the exciton-emission decay kinetics; this makes it possible to simplify the fitting appreciably as compared with Monte Carlo simulation of the exciton walk along a chain, which demands more computer time. Unfortunately, these theories do not take into account the quasi-1D migration character. However, this can be compensated to a certain degree by studying crystals with higher dopant concentrations (up to 10^{-2}), where the probability for an exciton to be trapped is greater than that of hopping to an adjacent chain. It should be noted that the decay curves are fairly well approximated by the calculated ones obtained also for efficient trapping; therefore in similar experiments the accumulation time of luminescence decay curves should be increased, so that the statistic error of measurements will be diminished.

The effective barrier was obtained from the temperature dependence of W, the overcoming of the barrier re-

sulting in thermoactivation of the exciton motion in CMC. Unlike the hopping rate, the temperature dependence of the exciton trapping rate shows different slopes of the approximation lines obtained using the Arrhenius dependence in different temperature ranges. This difference may be due to exciton tunneling through a barrier at trapping. The contribution from this process will increase with decreasing temperature.

ACKNOWLEDGMENTS

APPENDIX

Replacing in Eq. (2)

$$\alpha = 2UC + 4W;$$
$$\beta = U^2C^2 + 8UCW - U^2(C-1)^2 ; \qquad (A1)$$
$$\gamma = 4(UC)^2W ,$$

we obtain

$$F(E) = (E + K_h)^3 + \alpha(E + K_h)^2 + \beta(E + K_h) + \gamma$$
$$= (E - E_0)(E - E_1)(E - E_2) . \qquad (A2)$$

Then

$$\eta_H = \exp(-K_h t) - U^2C(1-C)\kappa_1 - UC\kappa_2 , \qquad (A3)$$

$$\kappa_1 = \frac{1}{2\pi i} \int_{R-i\infty}^{R+i\infty} dE \, \exp(Et) \frac{\sqrt{E + K_h + 4W}}{\sqrt{E + K_h}F(E)} , \qquad (A4)$$

$$\kappa_2 = \frac{1}{2\pi i} \int_{R=i\infty}^{R+i\infty} dE \, \exp(Et)$$
$$\times \frac{(E + K_h + UC)(W + K_h + 4W)}{(E + K_h)F(E)} . \qquad (A5)$$

If $\Lambda < \Lambda_r \approx 16$ then the discriminant $D(W,U,C) = (3\beta - \alpha^2)^3/729 + (\alpha^3/27 - \alpha\beta/6 - \gamma)^2$ of the cubic equation $F(E) = 0$ is positive and there is one real root E_0 and two other roots E_1 and E_2 are complex conjugate. In this case the roots E_0, E_1, E_2 are connected by the conditions:

$$E_0 + 2\,\mathrm{Re}(E_1) = -\alpha < 0 , \qquad (A6)$$

$$2E_0\,\mathrm{Re}(E_1) + |E_1|^2 = \beta , \qquad (A7)$$

$$E_0|E_1|^2 = -\gamma < 0 . \qquad (A8)$$

In order to avoid exponentially increasing solutions of Eq. (A3) it is necessary to require the real part of each root to be negative [see also Eq. (3)].

In accordance with (A8) $E_0 < 0$. Using (A7) we obtain the sufficient condition for $\mathrm{Re}(E_1)$ to be negative:

$$\beta = U^2C^2 + 8UCW - U^2(C-1)^2 > 0 ,$$

which is equivalent to $\Lambda < \Lambda_I$ where $\Lambda_I = 8(1-2C) \approx 8$.

Thus, within the range $0 < \Lambda < \Lambda_I$ Kenkre's theory is applicable independently of the K_h value. If $\Lambda > \Lambda_I$ it is necessary that

$$K_h > \sqrt{4W^2 + U^2 + U^2C^2 - 4UCW} - 2W - UC \ . \qquad (A9)$$

If $\Lambda > \Lambda_r$ then the discriminant $D(W,U,C)$ of the cubic equation $F(E)=0$ is negative and all three roots are real. The inequality (A9) imposes an additional restriction on W and U values. This condition turned out to be too strict for CMC (because of the small K_h value) and therefore this solution is not described in our paper.

In accordance with the Cauchy residue theorem,

$$\frac{1}{2\pi i} \left[\int_{R-i\infty}^{R+i\infty} + \int_{C_R} + \int_{-K_h+i0}^{-K_h-4W+i0} + \int_{-K_h-4W-i0}^{-K_h-i0} \right]$$

$$= \sum \text{res} \ , \qquad (A10)$$

where $\sum$res means the sum of residues inside the given contour. The final purpose is to express the first integral
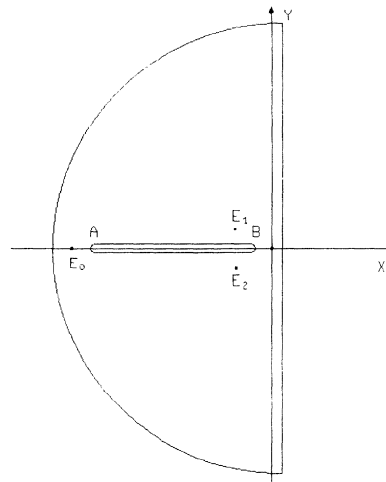

FIG. 7. Integration contour for Eq. (A10).

in the left-hand side of (A10) through the remaining terms. Let us limit our consideration to the case of $D > 0$. The integration contour is drawn in Fig. 7. In accordance with the Jordan lemma, the integral along the C_R arc is equal to zero. The sum of the last two integrals in the left-hand side of (A10) is equal to:

$$\int_{-K_h+i0}^{-K_h-4W+i0} \left[\frac{E+K_h+4W}{E+K_h} \right]^{1/2} \exp(Et)F^{-1}(E)dE + \int_{-K_h-4W-i0}^{-K_h-i0} \left[\frac{E+K_h+4W}{E+K_h} \right]^{1/2} \exp(Et)F^{-1}(E)dE$$

$$= [E+K_h = -Y] = -2i \exp(-K_h t) \int_0^{4W} \left[\frac{4W-Y}{Y} \right]^{1/2} \exp(-Yt)F^{-1}(-Y-K_h)dY \qquad (A11)$$

(variable substitution is shown in square brackets). Then

$$\kappa_1 = \frac{1}{\pi} \exp(-K_h t) \int_0^{4W} \left[\frac{4W-Y}{Y} \right]^{1/2} \exp(-Yt)F^{-1}(-Y-K_h)dY + \sum \text{res} \ , \qquad (A12)$$

where $\sum$res is the residue sum of the integrand inside the given contour.

Taking into account that $E_1 = E_2^*$, we obtain

$$\sum_{i=0}^{2} \text{res} \left[\exp(Et) \frac{\sqrt{E+K_h+4W}}{\sqrt{E+K_h}F(E)}, (E=E_i) \right]$$

$$= \exp(at) \frac{1}{\sqrt{g^2+b^2}\sqrt{h^2+b^2}} [\sin(bt)(hR_1+bI_i) + \cos(bt)(hI_1-bR_1)] + \left[\frac{E_0+K_h+UC}{E_0+K_h} \right]^{1/2} \ ,$$

$$(E_i = E_0, E_1, E_2) \ , \qquad (A13)$$

where

$$a = \frac{E_1+E_2}{2} = \frac{E_1+E_1^*}{2} = \text{Re}(E_1), \quad b = \frac{E_1-E_2}{2i} = \frac{E_1-E_1^*}{2i} = \text{Im}(E_1) \quad g = a+K_h, \quad h = a-E_0 \ .$$

Then

$$\kappa_2 = \sum_{i=0}^{3} \text{res} \left[\exp(Et) \frac{(E+K_h+UC)(E+K_h+4W)}{(E+K_h)F(E)}, (E=\varepsilon_i) \right] \qquad (A14)$$

where $\varepsilon_1 = (E_0, E_1, E_2, -K_h)$.

Analogous calculations give for κ_2:

$$\kappa_2 = \frac{4WUC}{(K_h+E_0)|K_h+E_1|^2}\exp(-K_ht) + \frac{(E_0+K_h+UC)(E_0+K_h+4W)}{(E_0+K_h)|E_0-E_1|^2}\exp(-E_0t)$$

$$+\exp(at)\frac{1}{b[(gh-b^2)^2+b^2(g+h)^2]}[R_2\sin(bt)+I_2\cos(bt)] \, , \tag{A15}$$

where

$$R_2 = (pf-b^2)(gh-b^2)+b^2(p+q)(g+h) \, ,$$

$$I_2 = b[(p+q)(gh-b^2)-(pq-b^2)(g+h)] \, ,$$

$$p=a+K_h+UC, \quad q=a+K_h+4W \, .$$

Using (A12), (A13), and (A15), we get the final expression (3) where

$$L_0 = \frac{WU^2C^2}{(E_0+K_h)([K_h+a]^2+b^2)} \, ,$$

$$L_1 = UC\frac{(E_0+K_h+UC)(E_0+K_h+4W)}{(E_0+K_h)|E_0-E_1|^2}$$

$$-UC(1-C)\left[\frac{E_0+K_h+UC}{E_0+K_h}\right]^{1/2} \, ,$$

$$L_2 = \frac{[ef-b^2][gh-b^2]+b^2[e+f][g+h]}{b[(gh-b^2)^2+b^2(g+h)^2]}R_2$$

$$-U(1-C)\frac{hR_1+bI_1}{\sqrt{g^2+b^2}\sqrt{h^2+b^2}} \, ,$$

$$L_3 = \frac{[e+f][gh-b^2]-[ef-b^2][g+h]}{(gh-b^2)+b^2(g+h)^2}I_2$$

$$-U(1-C)\frac{hI_1-bR_1}{\sqrt{g^2+b^2}\sqrt{h^2+b^2}} \, .$$

[1]D. D. Dlott, M. D. Fayer, and R. D. Wieting, J. Chem. Phys. **67**, 3808 (1977).

[2]R. D. Wieting, M. D. Fayer, and D. D. Dlott, J. Chem. Phys. **69**, 1996 (1978).

[3]R. A. Auerbach and G. McPherson, Phys. Rev. B **33**, 6815 (1986).

[4]W. J. Rodriguez, R. A. Auerbach, and G. McPherson, J. Chem. Phys. **85**, 6442 (1986).

[5]R. Knochenmuss and H. U. Güdel, J. Chem. Phys. **86**, 1104 (1987).

[6]M. F. Herman, W. J. Rodriguez, and G. McPherson, Chem. Phys. Lett. **144**, 541 (1988).

[7]W. J. Rodriguez, M. F. Herman, and G. McPherson, Phys. Rev. B **39**, 13 187 (1989).

[8]R. L. Blakley, C. E. Martinez, M. F. Herman, and G. McPherson, Chem. Phys. **146**, 373 (1990).

[9]R. M. Hochstrasser and I. D. Whiteman, J. Chem. Phys. **56**, 5945 (1972).

[10]A. A. Avdeenko, V. V. Eremenko, and V. A. Karachevtsev, Zh. Eksp. Teor. Fiz. **94**, 281 (1988) [Sov. Phys. JETP **67**, 1677 (1988)].

[11]B. Y. Balagurov and V. G. Vaks, Zh. Eksp. Teor. Fiz. **65**, 1939 (1973) [Sov. Phys. JETP **38**, 968 (1974)].

[12]G. Weiss and R. Rubin, Adv. Chem. Phys. **52**, 363 (1983).

[13]B. Movagher, G. W. Sauer, and D. Wurtz, J. Stat. Phys. **69**, 473 (1982).

[14]J. Klafter and R. Silbey, J. Chem. Phys. **72**, 849 (1980).

[15]G. Zumofen and A. Blumen, Chem. Phys. Lett. **88**, 63 (1982).

[16]V. M. Kenkre, in *Exciton Dynamics in Molecular Crystals and Aggregates*, edited by G. Hohler (Springer, Berlin, 1982), p. 1.

[17]A. I. Onipko, L. I. Malysheva, and I. V. Zozulenko, Chem. Phys. **121**, 99 (1988).

[18]S. J. Jensen and P. Andersen, Acta Chem. Scand. **16**, 1890 (1962).

[19]T. Smith and S. A. Friedberg, Phys. Rev. **176**, 660 (1962).

[20]H. Nashihara, W. J. M. de Jonge, and T. de Neef, Phys. Rev. B **12**, 5325 (1975).

[21]R. Ya. Bron, V. V. Eremenko, and E. V. Matyushkin, Fiz. Nizk. Temp. **5**, 659 (1979) [Sov. J. Low Temp. Phys. **5**, 314 (1979)].

[22]W. Jia, E. Strauss, and W. M. Yen, Phys. Rev. B **23**, 6075 (1981).

[23]V. V. Eremenko, V. A. Karachevtsev, A. R. Kazachkov, V. V. Shapiro, and V. V. Slavin, Solid State Commun. **87**, 1027 (1993).

[24]H. Yamamoto, D. S. McClure, Ch. Marzzacco, and M. Waldman, Chem. Phys. **22**, 79 (1977).

[25]W. Guttler, J. U. Von Schutz, and H. C. Wolf, Chem. Phys. **24**, 159 (1977).

[26]A. I. Onipko (private communication).

[27]Yu. P. Blagoy, I. A. Levitsky, Yu. V. Rubin, and V. V. Slavin, Chem. Phys. Lett. **203**, 265 (1993).

[28]A. I. Onipko and I. V. Zozulenko, J. Phys. Condens. Matter **1**, 9875 (1989).