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1993 J. Phys.: Condens. Matter 5 1143

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Time-resolved luminescence spectroscopy of the nearly one-dimensional crystal $[(\text{CH}_3)_3\text{NH}]\text{MnCl}_3 \cdot 2\text{H}_2\text{O}$

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Received 31 July 1992, in final form 19 October 1992

Abstract. Absorption and luminescence were investigated in a nearly one-dimensional antiferromagnetic crystal $[(\text{CH}_3)_3\text{NH}]\text{MnCl}_3 \cdot 2\text{H}_2\text{O}$. The luminescence decay process was studied by time-resolved spectroscopy using a streak camera. An intrinsic emission band with a peak at 661 nm was observed by the excitation in the Mn^{2+} absorption band at 15 K. This emission shifts towards a higher energy as the temperature is increased. Transfer of electronic excitation energy was found to occur in the high-temperature range above 90 K where short-range order becomes ineffective. An emission from Mn^{2+} traps, which is caused by the energy transfer from the bulk Mn^{2+} ions, was observed spectrally separately from the Mn^{2+} intrinsic emission.

1. Introduction

The crystal structure of $[(\text{CH}_3)_3\text{NH}]\text{MnCl}_3 \cdot 2\text{H}_2\text{O}$ (TMAMnC) is orthorhombic and belongs to the space group $Pnma$ (or D_{2h}^{16}) (Iio *et al* 1975). The structure is the same as that of $[(\text{CH}_3)_3\text{NH}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$ (Losee *et al* 1973). The lattice constants are $a = 16.733 \text{ \AA}$, $b = 7.422 \text{ \AA}$ and $c = 8.198 \text{ \AA}$. This compound contains polymetric $-\text{MnCl}_2-$ chains which are in relative isolation from one another. The $-\text{MnCl}_2-$ chains are parallel to the b axis as shown in figure 1. The distance between nearest Mn ions along the b axis is 3.711 \AA . The ratio of the intra-chain Mn–Mn distance to the inter-chain distance is 1:2.2, which is compared with the ratios 1:2.8 and 1:1.3 for the linear chain compounds $[(\text{CH}_3)_4\text{N}]\text{MnCl}_3$ (TMMC) and $\text{CsMnCl}_3 \cdot 2\text{H}_2\text{O}$ (CMC). Therefore, if we take into account that the exchange interaction perpendicular to the b -axis chain is considerably weaker than that along the chain, TMAMnC is suggested to be a one-dimensional (1D) antiferromagnet with the spin $S = \frac{5}{2}$ and the Néel temperature $T_N = 0.98 \text{ K}$ (Chikazawa *et al* 1980).

The electronic excitation energy in magnetic insulators travels a considerable distance rapidly from the site at which the excited state is initially formed. McPherson *et al* (1990) have established the occurrence of exciton migration in pseudo-1D antiferromagnetic CsMnBr_3 (CMB) crystals doped with metal impurities using a time-resolved luminescence technique. Yamamoto *et al* (1977) concluded, from the temperature dependence of the luminescence of crystals of a nearly 1D antiferromagnetic material TMMC, that the energy migration takes place by a random hopping process which requires thermal activation. They have observed non-exponential decay and suggested the presence of two decay components in the decay.

It is interesting to investigate the origin of the two decay components if the fact that there are two components is true. In the present paper we examine the

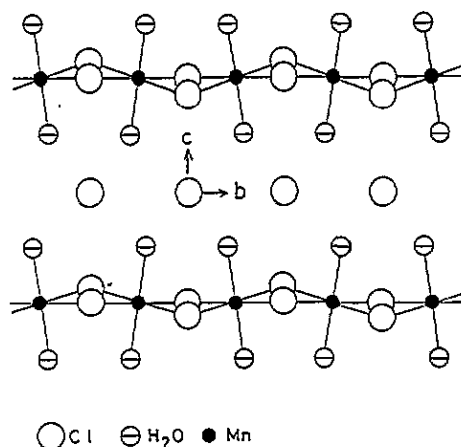


Figure 1. Schematic structure of a TMAMnCl crystal (by courtesy of Professor K Iio).

luminescence of a 1D antiferromagnet TMAMnCl using a time-resolved spectroscopy technique. The reason why we choose this material is that although the absorption and luminescence of 1D materials such as CMC, CMB, TMMC and $[(\text{CH}_3)_4\text{N}]\text{MnBr}_3$ (TMMB) have been studied so far (Day and Dubicki 1973, Kambli and Gudel 1984, Talluto *et al* 1984, Jia *et al* 1981, McPherson *et al* 1990), few studies have been made on the optical properties of TMAMnCl.

2. Experimental procedure and results

Single crystals of TMAMnCl were excited by a Moletron UV14 N_2 laser in the temperature range 15–300 K. The pulse width of the laser is 10 ns, and its peak power is 425 kW. The crystal luminescence was collimated, from the direction perpendicular to the exciting light, to an entrance slit of a Jobin–Yvon HR 320 polychromator where a ruled grating (size, 68 mm \times 68 mm) with a groove density of 100 g mm^{-1} and a blaze wavelength of 450 nm is installed. The exit slit width was fixed to be 15 mm. The luminescence intensity was detected by a Hamamatsu Photonics C2830 streak camera attached to a Peltier-element-cooled charge-coupled device photodetector. It was possible to synchronize the laser pulse with the streak sweep within a jitter of less than 2 ns. The luminescence decay and time-resolved luminescence spectrum were obtained using a Hamamatsu Photonics Temporal Analysis computer system. Absorption spectra were measured using a Shimadzu spectrophotometer UV-3100.

TMAMnCl has several absorption bands associated with electronic transitions in Mn^{2+} ions, called A, B, C, D, E, F, α , β , γ and δ bands in order of increasing energy, in the visible–UV region as shown in figure 2. The α – δ bands are stronger than the A–F bands. The whole spectrum is similar to those obtained for various Mn^{2+} compounds such as MnF_2 , TMMC and CMC (Day and Dubicki 1973, Marzzacco and McClure 1970). Thus the A, B, C, D, E and F bands are attributable to the transition from the ${}^6\text{A}_{1g}$ ground state to the ${}^4\text{T}_{1g}(\text{I})$, ${}^4\text{T}_{2g}(\text{I})$, (${}^4\text{A}_{1g}$ or ${}^4\text{E}_g(\text{I})$), ${}^4\text{T}_{2g}(\text{II})$, ${}^4\text{E}_g(\text{II})$ and ${}^4\text{T}_{1g}(\text{II})$ excited states, respectively, in Mn^{2+} ions. The temperature dependences of the intensity of the α – δ bands are different from those of the single-exciton A–F bands. An example of the temperature dependence is shown in figure 3. It is similar

to the cases of the double-exciton bands observed in various magnetic insulators (Petit *et al* 1977, Tsuboi and Kleemann 1983, Stokowski *et al* 1971, Fujiwara *et al* 1972). Thus the α - δ bands are attributable to the double-exciton bands which are due to the coupling of two Mn^{2+} ions. From the energies of the α , β , γ and δ bands, their excited states are assigned to the ${}^4\text{T}_{2g}(\text{I}) + {}^4\text{T}_{2g}(\text{I})$, ${}^4\text{T}_{2g}(\text{I}) + ({}^4\text{A}_{1g} \text{ or } {}^4\text{E}_g(\text{I}))$, $({}^4\text{A}_{1g} \text{ or } {}^4\text{E}_g(\text{I})) + ({}^4\text{A}_{1g} \text{ or } {}^4\text{E}_g(\text{I}))$ and $({}^4\text{A}_{1g} \text{ or } {}^4\text{E}_g(\text{I})) + {}^4\text{T}_{2g}(\text{II})$, respectively.

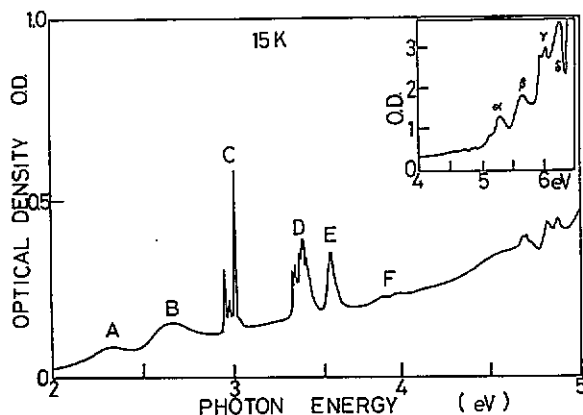


Figure 2. Absorption spectrum of a TMAMnC crystal at 15 K which was measured using unpolarized light. The inset shows the higher-energy spectrum.

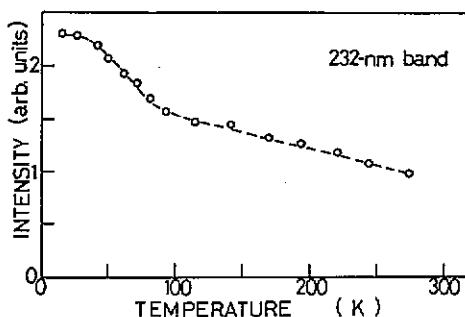


Figure 3. Temperature dependence of the integrated intensity of the α band. The broken line is a guide to the eyes.

The E band appears in the 352–336 nm region. Therefore the N_2 laser emitting 337.1 nm wavelength light excites the high-energy tail of the E band. A single emission band with a peak at around 661 nm is produced by the excitation at 15 K. The 661 nm emission is ascribed to the electronic transition ${}^4\text{T}_{1g}(\text{I}) \rightarrow {}^6\text{A}_{1g}$ in Mn^{2+} ions. The peak position does not change below 90 K but, as in the case of TMMC, it shifts toward a higher energy as the temperature is further increased from 90 K (figures 4 and 5). The shift of the emission peak is about 500 cm^{-1} in the range 15–300 K, which is compared with the amount of the blue shift, 510 cm^{-1} , in TMMC.

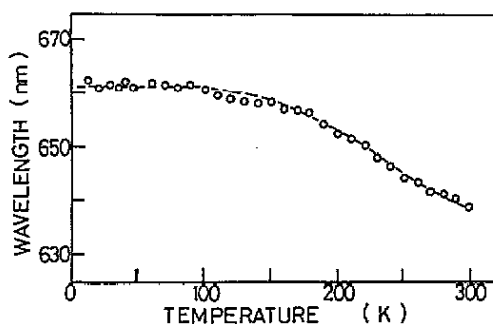


Figure 4. Peak shift of the emission band.

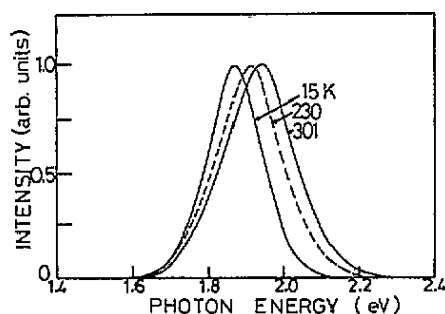


Figure 5. Emission spectra at various temperatures, which are obtained 0–0.1 ms after the laser pulse excitation. The peak heights are normalized.

The 661 nm emission shows a single-exponential decay curve in the temperature range 15–90 K. The decay curve, however, deviates from the simple exponential form as the temperature is increased from 90 K, as shown in figure 6. The non-simple exponential curve seems to be expressed approximately as a sum of two exponentials. The presence of the two decay components (fast- and slow-decay components) is found at temperatures above about 90 K. It was found that the emission band appearing in the fast-decay process is not the same as the emission band appearing in the slow decay; the former band is shifted to a slightly higher energy than the latter band as shown in figure 7. The high-energy emission band has a shorter lifetime than the low-energy emission band has; for example, at 110 K, the high-energy band has a lifetime of 0.33 ms, while the low-energy band has a lifetime of 0.57 ms. The lifetime of the high-energy band decreases with increasing temperature as also does the low-energy band.

TMAMnC has a luminescence lifetime of 0.66 ms at 15 K which is the same order as those of other 1D Mn compounds (e.g. 0.85 ms for TMMC (Yamamoto *et al* 1977) and 0.35 ms for CMB (Kambli and Gudel 1984)). The 3D materials MnF_2 and RbMnF_3 , however, have longer lifetimes of 39 ms (Tsuboi and Silfsten 1991) and 55 ms (Di Bartolo *et al* 1987), respectively, at the same temperature. The lifetime of TMAMnC decreases from about 0.66 ms to about 0.15 ms upon heating from 15 to 300 K (figure 8). The luminescence lifetime of the 3D antiferromagnetic Mn compounds MnF_2 (Di Bartolo *et al* 1987, Tsuboi and Silfsten 1991), RbMnF_3 (Di Bartolo *et al*

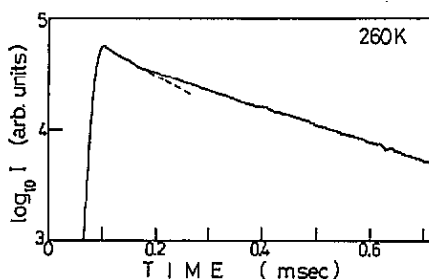


Figure 6. Decay curve of the red emission band at 260 K.

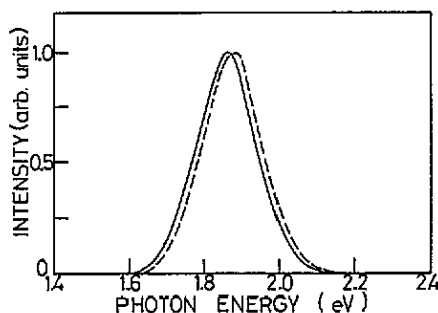


Figure 7. Emission bands produced at 110 K 0-0.1 ms (---) and 0.2-0.5 ms (—) after the laser pulse excitation. The peak heights are normalized.

1987) and CsMnF_3 (Moncorge *et al* 1982) and of the 2D antiferromagnets Rb_2MnCl_4 (Vanoy *et al* 1988, Tsuboi *et al* 1992) and BaMnF_4 (Tsuboi and Silfsten 1990) decreases by orders of magnitude in the same temperature region. Contrary to these 3D and 2D magnets, a very weak temperature dependence of the lifetime is expected in 1D materials (Jia *et al* 1981). The present result is consistent with the cases of other 1D materials: TMMC, TMMB and CMC (Yamamoto *et al* 1977, Blakley *et al* 1990).

3. Discussion

We observed different behaviours below and above 90 K in the decay curve. Below 90 K, only a single emission band is produced while, above 90 K, two emission bands occur. The luminescence decay data are not sufficiently precise to establish unambiguously that the high-temperature curves represent exactly the sum of two exponentials. The data could be described by an expression of the type $I(t) = I(0) \exp(-k_1 t - k_2 t^{1/2})$, which has been used to describe exciton trapping in 1D systems such as TMMC and CMB (Weiting *et al* 1978, Auerbach and McPherson 1986, McPherson *et al* 1990).

Yamamoto *et al* (1977) suggest, from the non-exponential decay of Mn^{2+} luminescence, that two kinds of luminescent Mn^{2+} centre are involved: one arises from Mn^{2+} ions in close proximity to the impurities (called Mn^{2+} traps) and the other from the unperturbed Mn^{2+} ions of the bulk lattice which have no impurity

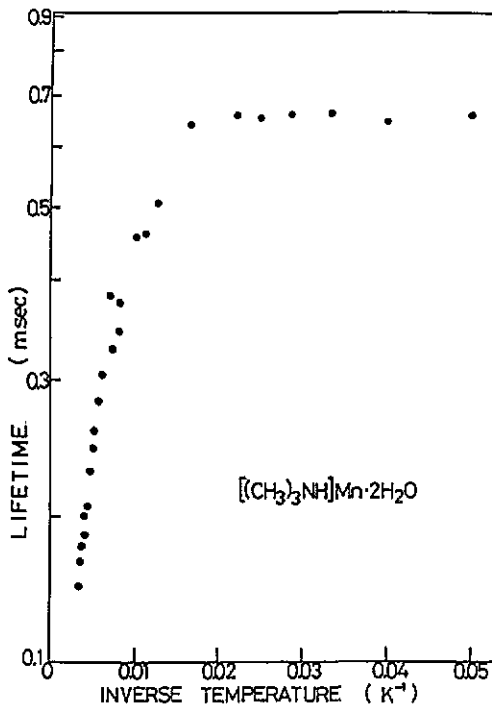


Figure 8. Temperature dependence of the lifetimes of the intrinsic Mn^{2+} emission of TMAMnCl .

ions as their nearest neighbours (called chain Mn^{2+} ions). The Mn^{2+} traps must radiate differently from the chain Mn^{2+} ions, giving rise to the result that the decay curve consists of two components whose weights would be in the ratio of the trap population to the chain population (Yamamoto *et al* 1977). If this suggestion is correct, the emission band due to the Mn^{2+} traps has a different peak position from the emission due to the chain Mn^{2+} ions. As shown in figure 7, we observed two emission bands depending on the time evolution after the excitation. Shortly after excitation the emission band is at a higher energy than after a longer time after excitation.

The Mn^{2+} ion in the Mn^{2+} trap is perturbed by the nearby impurity ions, but the energy levels are expected to be similar to those of the unperturbed Mn^{2+} ion. Therefore we can understand why the peak positions of the two emission bands are quite close to each other. It is reasonable to suggest that the perturbed ions give rise to an emission of lower energy than the unperturbed ions do because the perturbed ions act as traps. Therefore the fast component of the decay curve in figure 7 is attributed to the chain Mn^{2+} ions, while the slow component is attributed to the Mn^{2+} traps. In this way, our observation of the two decay components is understood by the presence of these two kinds of Mn^{2+} luminescence centre.

In antiferromagnetically ordered Mn^{2+} compounds, exciton transfer between the Mn^{2+} nearest neighbours on opposite sublattices is spin forbidden since it requires a change in spin projection. As a result of the 1D character, no long-range order occurs above T_N , but short-range order is present over a large range of temperatures in the 1D antiferromagnetic materials (e.g. up to about 100 K in TMMC (Ebara and

Tanabe 1974)). Therefore, in the low-temperature region where the short-range order is effective, the emission caused by energy transfer never appears, and only the intrinsic Mn^{2+} emission (i.e. emission from the chain Mn^{2+} ions) is observed. At high temperatures where the nearest-neighbour Mn^{2+} spins are not strictly antiparallel to each other, exciton migration is allowed and consequently the energy transfer from chain Mn^{2+} ions to Mn^{2+} traps occurs, giving rise to the Mn^{2+} trap emission. Our observation of the two emission bands above 90 K is understood to be due to the appearance of the Mn^{2+} trap emission and the intrinsic Mn^{2+} emission.

4. Conclusion

An intrinsic emission from the chain Mn^{2+} ions is observed at 661 nm at 15 K in TMAMnC. This emission is shifted towards a higher energy with increasing temperature as in the case of TMMC. At temperatures above 90 K where the spin short-range order becomes ineffective and the nearest-neighbour Mn^{2+} spins are not strictly antiparallel to each other, an emission from the Mn^{2+} traps is observed in addition to the intrinsic emission since the energy transfer from chain Mn^{2+} ions into Mn^{2+} traps becomes allowed. The trapping occurs at perturbed Mn^{2+} ions with energies lower than that of the bulk Mn^{2+} lattice, and subsequently the perturbed Mn^{2+} ions give rise to an emission with a lower energy than the intrinsic emission.

Acknowledgments

We thank Professor K Iio for kindly providing the single crystals of TMAMnC and the figure of the crystal structure of TMAMnC. We also thank Mr P Ahmet for his assistance with the measurements at the early stage of the present study. The present work was supported by a Grant-in-Aid from the Japanese Ministry of Education and Science.

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