Upconversion luminescence in Yb^{3+} doped CsMnCl₃: Spectroscopy, dynamics, and mechanisms

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(Received 5 November 2001; accepted 5 December 2001)

Single crystals of CsMnCl₃ doped with 0.9% Yb³⁺ were grown from the melt by the Bridgman technique and studied by means of variable temperature optical spectroscopy. At cryogenic temperatures, near-infrared Yb³⁺-excitation around 1 μ m leads to intense Mn²⁺ upconversion luminescence in the red spectral region. This very efficient upconversion process is possible because of magnetic Yb³⁺-Mn²⁺ exchange interactions, and a new type of upconversion mechanism is found to be active in this system. The upconversion properties of Yb³⁺:CsMnCl₃ are compared to those of Yb³⁺:RbMnCl₃ and Yb³⁺:CsMnBr₃. The upconversion efficiencies at cryogenic temperatures differ by many orders of magnitude. The bridging geometry between Yb³⁺ and Mn²⁺ is found to be a key factor for the efficiency of the process. The highest efficiency is observed for the title compound, and this is correlated with the most likely linear Yb³⁺-Cl⁻-Mn²⁺ arrangement in this crystal. At 15 K the dominant upconversion mechanism in the title compound involves an energy transfer step. By increasing the temperature to 100 K a new and very efficient mechanism involving a sequence of ground state and excited state absorption steps becomes dominant. © 2002 American Institute of Physics. [DOI: 10.1063/1.1446430]

I. INTRODUCTION

Photon upconversion processes are used to convert long wavelength radiation into shorter wavelength light.^{1,2} Upconversion is different from second harmonic generation in that it requires at least two metastable excited states with a finite lifetime.³ Systems which fulfill that criterion are most commonly found among the *f*-elements.^{4–7} It is thus not a surprise that over the past three decades upconversion research has largely focused on lanthanides and actinides. Only relatively recently it has been recognized that, in appropriate chemical and structural coordination, certain selected *d*-metal ions are capable to exhibit interesting upconversion phenomena.⁸ In our search for new upconversion materials and processes this has prompted us to combine rare earth (RE) and transition metal (TM) ions in the same host lattice.

Thus we have doped Yb³⁺ into several Mn²⁺ hosts. We have recently published the results of our upconversion studies on Yb³⁺:RbMnCl₃ and Yb³⁺:CsMnBr₃.⁹⁻¹¹ In these systems near-infrared (NIR) excitation of the Yb³⁺ ions leads to more or less intense visible (VIS) Mn²⁺ luminescence, and this has been interpreted as a result of exchange interactions between the Yb³⁺ and Mn²⁺ ions. Thus exchange-coupled RE-TM pairs are the chromophoric units in these systems, and this has no precedent in the field of upconversion. The relative upconversion efficiencies of Yb³⁺:RbMnCl₃ and Yb³⁺:CsMnBr₃ are very different, and this has been tentatively related to the different Yb³⁺ –Mn²⁺ bridging geometries in these two systems. However, which type of bridging arrangement is most effective for Yb³⁺-Mn²⁺ exchange and thus upconversion, is a question

^{a)}Permanent address: Departamento de Física Moderna, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain. that has not yet been answered unambiguously. With the present study on the structurally different Yb³⁺:CsMnCl₃ we want to shine more light on this issue. More generally, we are interested in the effects of structural and chemical variation on upconversion properties. Previous studies on upconversion materials involving TM ions have demonstrated that small chemical changes can alter their upconversion properties significantly.^{12–15} Thus, in Yb³⁺:CsMnCl₃, we expect significant differences in upconversion behavior to the previously investigated Yb³⁺:RbMnCl₃ and Yb³⁺:CsMnBr₃ systems.

II. EXPERIMENT

A. Crystal growth

Single crystals of Yb³⁺ doped CsMnCl₃ were grown from the melt by the Bridgman technique using stoichiometric amounts of CsCl and MnCl₂, as well as a nominal YbCl₃ amount close to 2.5% of the present Mn²⁺ ions. Crystals of millimeter dimensions were obtained with good optical quality. The actual ytterbium dopant concentration in the crystals was determined by inductively coupled plasma (ICP) measurements to be 0.9%. The crystals were selected and oriented with a polarizing microscope identifying the *c*-axis by the conoscopic image. They were cut along a plane containing the *c*-axis using a diamond saw and polished for the optical spectroscopic measurements. Due to the hygroscopic nature of the starting materials and the crystals, all the handling was carried out under N₂ or He inert atmosphere.

B. Spectroscopic measurements

Polarized absorption spectra were measured on a Cary 5e (Varian) spectrometer with $\mathbf{E} \perp c(\sigma)$ and $\mathbf{E} \parallel c(\pi)$, where c

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FIG. 1. Overview axial absorption spectrum of a 0.9% $\rm Yb^{3+}:CsMnCl_3$ single crystal at 12 K.

is the hexagonal optical axis of the CsMnCl₃ crystals. Yb³⁺ ² $F_{5/2}$ excitation occurred with an Ar⁺ laser (Spectra Physics 2060-10 SA) pumped tunable Ti³⁺:sapphire laser (Spectra Physics 3900 S). The luminescence was dispersed by a 0.85 m double monochromator (Spex 1402) using 500 nm blazed, 1200 grooves/mm gratings and detected by a cooled photomultiplier (RCA C31034 or Hamamatsu 3310-01) and a photon counting system (Stanford Research SR400). Direct Mn²⁺ excitation occurred with the 514.5 nm line of the Ar⁺ laser.

For excitation spectroscopy the Ti^{3+} :sapphire laser wavelength was scanned using an inchworm (Burleigh PZ501) controlled birefringent filter, and the wavelength was monitored with a wavemeter (Burleigh WA2100). For the two-color experiments, two Ti^{3+} :sapphire lasers were used.

Power dependent measurements were performed using neutral density filters (Baltzers) to attenuate the laser excitation power. The laser power was measured with a power meter (Coherent Labmaster-E). The Ti^{3+} :sapphire laser beam with a diameter of 1 mm was focused onto the crystal with a 80 mm focal length lens. Thus, excitation densities of up to 3.2 kW/cm² were obtained.⁴⁵

For time resolved experiments 10 ns pulses of the second harmonic of a Nd³⁺: YAG (Quanta Ray DCR-3) pumped dye laser (Lambda Physik FL3002; pyridine 1 in methanol) were Raman shifted (Quanta Ray, RS-1, H₂, 340 psi). The sample luminescence was dispersed by a 0.75 m single monochromator (Spex 1702) equipped with a 750 nm blazed 600 grooves/mm grating and detected with a photomultiplier (see above). Decay curves were recorded using a multichannel scaler (Stanford Research 430).

Sample cooling was achieved using a closed-cycle He cryostat (Air Products Displex) for absorption measurements and with a He gas flow technique for emission experiments.

III. RESULTS

In Fig. 1 the 12 K axial survey absorption spectrum of a 0.9% Yb³⁺ doped CsMnCl₃ crystal is shown. The Mn²⁺ absorptions between 17 000 and 34 000 are due to d-d transitions, and they are assigned according to the d^5 Tanabe-Sugano energy level diagram.¹⁶ Below 17 000 cm⁻¹ Mn²⁺ is



FIG. 2. (a) σ -polarized optical absorption spectrum of 0.9% Yb³⁺:CsMnCl₃ at 12 K. (b) 15 K σ excitation spectrum monitoring Yb³⁺ ${}^{2}F_{5/2}(0')$ $\rightarrow^{2}F_{7/2}$ (2) luminescence at 10 020 cm⁻¹. (c) 15 K σ excitation spectrum monitoring Mn²⁺ ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ upconversion luminescence at 14 925 cm⁻¹. Both excitation spectra are corrected for the wavelength dependence of the laser power. (d) Schematic f-f energy level diagram for Yb³⁺ in the C_{3v} site symmetry.

spectroscopically innocent. The sharp and relatively weak features between 10 200 and 10 700 cm⁻¹ are due to Yb³⁺ ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transitions, and they are shown on an enlarged scale in the inset of Fig. 1. The broad absorption band at about 25 100 cm⁻¹ is assigned to an f-d transition of a Yb²⁺ impurity.^{17,18}

Figure 2(a) shows a high resolution $Yb^{3+2}F_{7/2} \rightarrow {}^2F_{5/2}$ absorption spectrum (σ -polarized) of 0.9% Yb³⁺:CsMnCl₃ at 12 K. The three peaks at 10 200, 10 245, and 10 685 cm^{-1} are assigned to electronic transitions to the three Stark components 0', 1', 2' of ${}^{2}F_{5/2}$, as illustrated in the scheme of Fig. 2(d). As a consequence of the internal magnetic field in the CsMnCl₃ host below the magnetic ordering temperature $T_N = 67$ K,¹⁹ the bands show some additional fine structure. Figure 2(b) is a 15 K excitation spectrum monitoring Yb³⁺ ${}^{2}F_{5/2}(0') \rightarrow {}^{2}F_{7/2}$ (2) luminescence at 10020 cm⁻¹. This spectrum is essentially identical with Fig. 2(a), however, the higher signal to noise ratio in the excitation spectrum allows us to observe some vibrational side bands. As emphasized by the brackets, they appear 103, 135, 235, and 275 cm^{-1} to higher energies than their associated electronic origins. Figure 2(c) is a 15 K upconversion excitation spectrum of 0.9% Yb³⁺:CsMnCl₃ monitoring Mn^{2+ 4} $T_1 \rightarrow {}^6A_1$ luminescence at 14925 cm⁻¹. This spectrum shows peaks at the same energies as Figs. 2(a) and 2(b), but with different relative intensities.

In Fig. 3 the 10 K Yb³⁺ ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ luminescence spectrum obtained after excitation of Yb³⁺:CsMnCl₃ into the most intense absorption line at 10 685 cm⁻¹ is presented. The assignment of the individual luminescence bands was made according to that given in Ref. 20 for Yb³⁺:CsCdBr₃, whose Yb³⁺ ${}^{2}F_{7/2} \leftrightarrow {}^{2}F_{5/2}$ absorption and luminescence spectra are very similar to those of Yb³⁺:CsMnCl₃. We extract the ${}^{2}F_{7/2}$ and ${}^{2}F_{5/2}$ crystal field splittings given in Table



FIG. 3. 10 K unpolarized Yb³⁺ ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ luminescence spectrum of 0.9% Yb³⁺:CsMnCl₃ excited at 10 685 cm⁻¹. The inset shows a Yb³ energy level scheme and indicates the observed 15 K luminescence transitions.

I from Figs. 2 and 3. As illustrated by the brackets, analogous vibrational side band features as in Fig. 2(b) are observed in emission. As in other Yb³⁺ systems the $0 \leftrightarrow 0'$ transition carries most of the side band intensity.

Figure 4 shows the 10 K Mn^{2+ 4} $T_1 \rightarrow {}^{6}A_1$ upconversion luminescence spectrum obtained after Yb³⁺ excitation at 10 685 cm⁻¹ (full line). The dashed line is the 10 K Mn²⁺ ${}^{4}T_1 \rightarrow {}^{6}A_1$ luminescence spectrum obtained after direct Mn²⁺ excitation at 19 436 cm⁻¹. It is essentially identical with the upconversion luminescence spectrum except for a small blueshift by about 60 cm⁻¹.

Figure 5(a) shows the temporal evolution of the 15 K $\text{Mn}^{2+} {}^{4}T_{1} \rightarrow {}^{6}A_{1}$ luminescence after excitation pulses of 10 ns duration at 18 797 cm⁻¹, i.e., after direct Mn^{2+} excitation (faint line), and at 10 685 cm⁻¹, i.e., after Yb³⁺ excitation (strong line). The inset shows the same upconversion transient on a extended time scale. After 10 685 cm⁻¹ excitation most of the $\text{Mn}^{2+} {}^{4}T_{1}$ population builds up slowly and reaches a maximum about 220 μ s after the laser pulse. At this temperature only about 15% of the $\text{Mn}^{2+} {}^{4}T_{1}$ population occurs within the laser pulse. Figure 5(b) shows the same data on a semilogarithmic scale. This representation illustrates that the decay time of the Mn^{2+} and after Yb³⁺ excitation illustion.

TABLE I. Energies of the crystal field levels of Yb^{3+} in CsMnCl₃ derived from absorption, excitation, and emission spectroscopy at 15 K. All energies are given in cm⁻¹ relative to the lowest energetic Stark level.

Multiplet	Crystal-field level	Energy (cm^{-1})
² <i>F</i> _{7/2}	0	0
	1	135
	2	180
	3	540
² <i>F</i> _{5/2}	0'	10200
	1'	10245
	2'	10685



FIG. 4. 10 K $Mn^{2+} {}^{4}T_{1} \rightarrow {}^{6}A_{1}$ luminescence spectra of 0.9% Yb³⁺:CsMnCl₃ obtained after excitation at 10 685 cm⁻¹ (full line) and at 19 436 cm⁻¹ (dashed line).

Figures 6(a) and 6(b) show the upconversion luminescence transients at 15 K and 75 K, respectively. As emphasized by the shaded areas, in this pulsed experiment at 15 K about 15% of the total upconversion luminescence is due to $Mn^{2+4}T_1$ excitation within the laser pulse, whereas the remaining 85% are due to $Mn^{2+4}T_1$ population after the ex-



FIG. 5. (a) Temporal evolution of the 15 K $\text{Mn}^{2^+ 4} T_1 \rightarrow {}^6A_1$ luminescence excited at 10 685 cm⁻¹ (strong line) and at 19 436 cm⁻¹ (faint line) with pulses of 10 ns width. The inset shows the first 500 μ s of the upconversion transient in more detail. (b) The same transients as in (a), but in a semilogarithmic representation.

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FIG. 6. Upconversion luminescence transients obtained after 10 ns pulsed excitation at 10 685 cm⁻¹ at (a) 15 K and (b) 75 K. The shaded areas indicate the GSA/ESA upconversion contributions. (c) Dots: ETU part of the transient from (a). Solid line: Fit with Eq. (1) to the experimental data. The fit parameters are $k_1 = 740 \text{ s}^{-1}$, $k_2 = 960 \text{ s}^{-1}$, and $\omega_{\text{ETU}} = 8720 \text{ s}^{-1}$.

citation pulse. At 75 K the respective percentages have changed to 60% and 40%, respectively.

The spectrum in Fig. 7(a) is the result of a two-color pump and probe experiment with 0.9% Yb³⁺:CsMnCl₃ at 15 K. The pump laser with a power of 200 mW was kept fixed at 13700 cm^{-1} . At this energy there is neither Mn^{2+} nor Yb³⁺ ground state absorption, but there is the peak of the Yb³⁺ ${}^{2}F_{5/2} \rightarrow Mn^{2+} {}^{4}E, {}^{4}A_{1}$ excited state absorption (ESA).¹⁰ The probe laser with an excitation power below 200 μ W was scanned through the Yb³⁺ ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ excitation region while the Mn^{2+ ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ luminescence intensity at} 14925 cm⁻¹ was monitored. The spectrum obtained from this experiment is very similar to the 12 K Yb^{3+ 2} $F_{7/2}$ $\rightarrow {}^{2}F_{5/2}$ absorption spectrum which is shown for comparison in Fig. 7(b). Figure 7(c) shows the spectrum obtained with the probe beam alone. The absence of any excitation peaks in this trace proves that the probe laser excitation density was low enough to avoid upconversion by this light source alone, and we conclude that ESA contributes to the upconversion process.



FIG. 7. (a) 15 K two-color upconversion excitation spectrum monitoring $Mn^{2+} {}^{4}T_{1} \rightarrow {}^{6}A_{1}$ luminescence at 14 925 cm⁻¹. Pump laser energy and power: 13 700 cm⁻¹, 200 mW. Probe laser scanned with a power of $< 200 \ \mu$ W. (b) 12 K Yb³⁺ ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ absorption spectrum. (c) Spectrum obtained under identical conditions as (a), but without pump beam.

Figure 8 displays the normalized integrated $Mn^{2+} {}^{4}T_{1} \rightarrow {}^{6}A_{1}$ luminescence intensity of 0.9% Yb³⁺:CsMnCl₃ as a function of temperature for direct Mn²⁺ excitation at 19 436 cm⁻¹ (circle markers) and Yb³⁺ excitation at 10 685 cm⁻¹ (cross markers). Both data sets are corrected for the temperature dependence of the absorption cross-section at the laser excitation wavelength. After direct Mn²⁺ excitation the luminescence intensity increases by about 25% between 10 and 65 K. Above 70 K it steeply decreases and at

FIG. 8. Temperature dependence of the normalized integrated $\text{Mn}^{2+4}T_1 \rightarrow {}^{6}A_1$ luminescence intensity after direct Mn^{2+} excitation at 19 436 cm⁻¹ (circle markers) and after Yb³⁺ excitation at 10 685 cm⁻¹ (cross markers). Both data sets are normalized to one at their respective maximum value.

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FIG. 9. Upconversion efficiency η_{UC} of 0.9% Yb³⁺:CsMnCl₃ at 75 K after 10 685 cm⁻¹ excitation, as a function of the laser power. For an estimate of the highest excitation power density achieved in this experiment see Sec. II B. For the definition of η_{UC} , see Eq. (3).

room temperature the luminescence is almost completely quenched. After Yb^{3+} excitation the temperature dependence of the Mn^{2+} upconversion luminescence intensity is even more pronounced: Between 40 and 90 K it increases by a factor of 5. This is followed by a similar reduction at higher temperatures as after direct Mn^{2+} excitation.

In Fig. 9 we plot the upconversion luminescence quantum efficiency $\eta_{\rm UC}$ at 75 K as defined in Eq. (3) (see Sec. IV D) as a function of the near-infrared laser excitation power. We note that at the highest excitation power of 263 mW used in our experiments, we reach an $\eta_{\rm UC}$ of 8%. This means that 16 out of 100 absorbed NIR photons are used to create VIS photons in the upconversion process.

IV. DISCUSSION

A. Crystal structure of CsMnCl₃ and Yb³⁺ dopant sites: Analysis of the Yb³⁺ ${}^{2}F_{7/2} \leftrightarrow {}^{2}F_{5/2}$ transitions

CsMnCl₃ crystallizes in the space group $R\overline{3}m$.^{21,22} The crystal structure is illustrated in Fig. 10. It consists of trimers of face-sharing $MnCl_6^{4-}$ octahedra which are linked to six other trimers in a corner-sharing arrangement. Consequently, there are two crystallographically distinct sites for the Mn²⁺ ions: one site with C_{3v} and one site with D_{3d} point symmetry. Thus the CsMnCl₃ crystal structure can be considered as an intermediate between the CsNiCl₃ and the KNiF₃ structure types. Numerous studies of RE³⁺ doped crystals with the CsNiCl₃ structure have demonstrated that already at RE^{3+} dopant concentrations as low as 0.1% more than 90% of the trivalent dopant ions cluster in RE³⁺-vacancy-RE³⁺ trimer units in these crystals.^{23–25} The vacancy at the central M²⁺ site ensures charge compensation. This dopant scheme can also occur in Yb³⁺:CsMnCl₃, see the upper part of Fig. 10, and we consider this the most likely way of incorporating Yb^{3+} into the CsMnCl₃ structure. This is in contrast to the



FIG. 10. Relevant elements of the CsMnCl₃ crystal structure illustrating the two distinct Mn^{2+} sites, D_{3d} and C_{3v} , as well as the bridging geometries. The most probable $Yb^{3+} - Yb^{3+}$ pair arrangement is also shown.

system Yb^{3+} :RbMnCl₃ which has recently been studied by us.¹⁰ The RbMnCl₃ does not provide the possibility of a face-sharing Yb^{3+} -vacancy- Yb^{3+} unit, and this will significantly effect the upconversion behavior, as will be discussed in Sec. IV C.

The low temperature $Yb^{3+2}F_{7/2} \leftrightarrow^2 F_{5/2}$ absorption and emission spectra of 0.9% Yb^{3+} : CsMnCl₃ in Figs. 2(a) and 3 are consistent with a Yb³⁺-vacancy-Yb³⁺ arrangement. These spectra exhibit a striking similarity to the corresponding spectra of Yb³⁺:CsCdBr₃,^{20,28} for which the above RE³⁺ dopant arrangement has been confirmed by EPR experiments.²⁵ Most of the intensity in the ${}^{2}F_{7/2} \leftrightarrow {}^{2}F_{5/2}$ transitions, both in absorption (Fig. 2) and in emission (Fig. 3) is located in the electronic origins rather than in vibrational side bands, confirming that the Yb³⁺ ions are situated in noncentrosymmetric sites with a large odd-parity crystalfield contribution, such as the C_{3v} sites in Fig. 10. In this trigonal crystal field the ${}^2F_{7/2}$ and ${}^2F_{5/2}$ states split into 4 and 3 Stark components, respectively. These crystal-field levels are labeled in Fig. 2(d), and their energies are summarized in Table 1. The crystal field splitting in Yb^{3+} :CsMnCl₃ is somewhat larger than in Yb³⁺:CsCdBr₃, and this is attributed to the stronger crystal field in the chloride compared to the bromide.

Finally, the splitting of the ${}^{2}F_{7/2}(0) \rightarrow {}^{2}F_{5/2}(0')$ transi-

tion in the absorption and excitation spectra of Figs. 2(a) and 2(b) appears noteworthy. Below $T_N = 67$ K the CsMnCl₃ host is magnetically ordered,¹⁹ and consequently we attribute this splitting to an effect of an internal magnetic field, created by the magnetically ordered Mn²⁺ ions, on the Yb³⁺ ions. This leads to a Zeeman splitting of the Yb³⁺ ² F_J levels. Similar effects have been observed in other RE³⁺ doped manganese lattices.^{26,27}

B. $Mn^{2+4}T_1 \rightarrow {}^6A_1$ luminescence and its temperature dependence

At cryogenic temperatures excitation into the Mn^{2+} absorption bands above 17 000 cm⁻¹ leads to intense Mn^{2+} luminescence from its lowest excited ${}^{4}T_{1}$ state. This is illustrated by the dashed trace in Fig. 4. The luminescence band is very broad because the ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ luminescence transition involves an electron promotion from a weakly antibonding t_{2} to a strongly antibonding e orbital. Consequently, the $MnCl_{6}^{4-}$ complex undergoes an overall expansion after the light emission process, and this causes the luminescence band to be broad.²⁹

As shown in Fig. 8, the integrated Mn^{2+} luminescence intensity after excitation at 19 436 cm⁻¹ slightly increases between 10 and 70 K (circle markers). Above 70 K there is a steep decrease which is attributed to the onset of efficient energy migration to killer traps. Below $T_N=67$ K CsMnCl₃ is antiferromagnetically ordered,¹⁹ and there is a spin-barrier which impedes efficient energy migration.³⁰ The killer traps are present as nonintentional impurities such as Mn^{3+} ,³¹ and they act as very efficient luminescence quenchers. This is a well known phenomenon in concentrated Mn^{2+} systems, and it prevents most compounds of this type from being efficient luminescent materials at room temperature.

Trace amounts of Mn^{3+} are usually reduced by addition of some Mn metal to the melt.³¹ In the case of Yb³⁺ doped Mn²⁺ hosts, however, this approach has proven to be unfeasible because it leads to a reduction of Yb³⁺ to Yb²⁺.¹⁰ The spectroscopic evidence for this is given by the broad Yb²⁺ f-d absorption feature around 25 100 cm⁻¹ in Fig. 1.

C. Upconversion mechanisms

At T < 200 K, excitation into the Yb^{3+ 2} $F_{5/2}$ absorption bands around 10 200-10 700 cm⁻¹ [Fig. 2(a)] leads not only to $Yb^{3+2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ NIR luminescence (Fig. 3) but also to VIS $Mn^{2+4}T_1 \rightarrow {}^{6}A_1$ upconversion luminescence; see the full trace in Fig. 4. There is a redshift at 15 K of the upconversion luminescence band relative to the ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ luminescence band obtained after direct Mn2+ excitation at 19436 cm^{-1} (dashed trace) by roughly 60 cm^{-1} . Similar redshifts have previously been observed at 15 K in and Yb³⁺:CsMnBr₃ Yb^{3+} : RbMnCl₃ (200 cm⁻¹) and Yb^{3+} : CsMnBr₃ (130 cm⁻¹).^{10,11} They are attributed to the fact that at 15 K the normal Mn²⁺ luminescence occurs from the bulk of Mn^{2+} ions, whereas the upconversion luminescence is emitted from the subset of Mn^{2+} ions in the neighborhood of a Yb³⁺ ion. This trivalent impurity leads to a distortion of the neighboring $MnCl_6^{4-}$ unit, in particular to a squeezing, since Yb^{3+} is somewhat bigger than Mn^{2+} .³² Therefore the



FIG. 11. Schematic illustration of three potential upconversion mechanisms in Yb³⁺:CsMnCl₃. The solid upward arrows represent the radiative processes of GSA and ESA. The solid downward arrows stand for luminescence and the dashed arrows represent nonradiative energy transfer processes.

crystal-field strength is increased and thus the $Mn^{2+4}T_1 \rightarrow {}^{6}A_1$ upconversion luminescence transition is slightly red-shifted.

Since the first report of upconversion processes in 1966,³³ several upconversion mechanisms have been described in the literature. By far the most important in lanthanide systems are the following: (i) Ground state absorption (GSA) to the intermediate state followed by an excited state absorption (ESA) to an upper excited state on a single ion.³⁴ (ii) GSA to an intermediate state on two neighboring ions, followed by an energy transfer (ET) step to promote one ion to the upper state and the other one to the ground state. These GSA/ESA and GSA/ETU mechanisms account for most of the upconversion processes observed in lanthanide systems. They can experimentally be distinguished by their upconversion excitation spectra and by their time evolution after an excitation pulse.³⁴ The excitation spectrum for a GSA/ESA upconversion sequence corresponds to the product of the GSA and ESA spectra,^{14,35} whereas for a GSA/ETU mechanism it corresponds to the square of the GSA spectrum.³⁶ For a GSA/ESA mechanism the upconversion luminescence shows an immediate decay after a sharp laser pulse, because both steps have to occur during the pulse. In contrast, the transients for a GSA/ETU mechanism after a short excitation pulse show a rise followed by a decay part.³⁴ Both these mechanisms in their pure form can be ruled out in our system. But they are nevertheless a good guide to understand the processes in Yb³⁺:CsMnCl₃. Since excitation is into ${}^{2}F_{5/2}$ of Yb³⁺ and emission occurs from ${}^{4}T_{1}$ of Mn²⁺ the active mechanism in our system must be cooperative, with participation of both Yb³⁺ and Mn²⁺. It is also clear that the role of Yb³⁺ is not that of a sensitizer, as it is in many lanthanide upconversion systems because Mn²⁺ has no energy levels around 1 μ m. Yb³⁺ is an active participant, and we use the most simple model of an exchangecoupled Yb³⁺-Mn²⁺ dimer to discuss the observed behavior. We are aware that this is rather simplistic, in view of the fact that the host lattice CsMnCl₃ is magnetically ordered below 67 K. But nearest neighbor interactions are by far the most important ones in a magnetic lattice, and a dimer model thus contains the principal interaction. With the Yb³⁺-Mn²⁺ dimer as the relevant chromophore the GSA/ ESA sequence can now be represented as shown in Fig.

11(a). The ESA step, which is very mysterious in a single-ion picture, because it takes the system from an excited Yb^{3+} level to an excited Mn^{2+} level, is now a normal transition between two excited states of the dimer. Similarly we can draw Fig. 11(b) for a GSA/ETU process involving two neighboring $Yb^{3+}-Mn^{2+}$ dimers. We have used the mechanism in Fig. 11(a) to account for the upconversion in Yb^{3+} doped RbMnCl₃ and CsMnBr₃. In the title compound the situation is more complicated, and both Figs. 11(a) and 11(b) will be relevant. In order to identify the relevant mechanisms in Yb^{3+} :CsMnCl₃ we analyze the experimental data.

Yb^{3+ 2} $F_{5/2}$ excitation at 10 685 cm⁻¹ into the intense 2' absorption line (Fig. 2) with 10 ns excitation pulses at 15 K yields the Mn^{2+ 4} $T_1 \rightarrow {}^{6}A_1$ upconversion luminescence transient presented in Fig. 5 (strong line). There is a relatively slow rise preceding the luminescence decay. However, the inset in Fig. 5(a) shows that already at t=0, immediately after the excitation pulse there is a nonzero population in the Mn^{2+ 4} T_1 state. This is attributed to a GSA/ESA upconversion mechanism as illustrated in Fig. 11(a). This conclusion is supported by the result of the two-color pump and probe experiment in Fig. 7; see description of this experiment in Sec. III.

We now return to the upconversion transient in Fig. 5(a). Its quantitative evaluation shows that 15% of the total intensity is due to the GSA/ESA mechanism discussed above (shaded area) and 85% of the total Mn²⁺ upconversion luminescence builds up slowly after the excitation pulse. It is thus tempting to attribute this dominant part to a GSA/ETU mechanism. However, we first have to rule out an alternative possibility, namely that not the upconversion process itself is slow, but a process which occurs *after* the upconversion step. A possible scenario of this type for Yb³⁺:CsMnCl₃ is schematically depicted in Fig. 11(c). In this scenario upconversion occurs instantaneously by GSA/ESA in a Yb³⁺-Mn²⁺ pair. A slow energy transfer process to a neighboring Mn²⁺ trap could then account for the observed slow rise in the transient. However, a detailed previous study of the pure CsMnCl₃ system has demonstrated that at 10 K luminescence exclusively occurs from the Mn^{2+} (D_{3d}) site,²⁹ because there is efficient $Mn^{2+}(C_{3v}) \rightarrow Mn^{2+}(D_{3d})$ energy transfer between nearest neighbors down to the lowest temperatures. If this step was slow, it should also be observable after direct $Mn^{2+4}T_1$ excitation, since this predominantly excites $Mn^{2+}(C_{3v})$ ions. Short pulsed excitation into ${}^{4}T_{1}$ at 18797 cm⁻¹ leads to an immediate decay of the 10 K Mn²⁺ luminescence; see faint curves in Fig. 5. There is no indication for a slow energy transfer step. On that basis we rule out scheme 11(c) and conclude that in 0.9% Yb³⁺: CsMnCl₃ the dominant upconversion mechanism at 15 K is indeed GSA/ ETU, as schematically illustrated in Fig. 11(b).

This is the first $Yb^{3+}-Mn^{2+}$ system for which evidence for this GSA/ETU mechanism is found. In order to understand the kinetics governing the ETU process, we attempt to model the upconversion transient in Fig. 5(a). For that purpose the GSA/ESA contribution was subtracted, see Fig. 6(a), and the new transient obtained in this way is presented in Fig. 6(c) (dots). We use a simple dimer model, which has first been used by Vial *et al.*,³⁷ to simulate our experimental transient. In our specific case, a dimer consists of two $Yb^{3+}-Mn^{2+}$ chromophoric units. The basic assumptions of the Vial model are described in detail in Refs. 38 and 4. Its most relevant simplification is that it considers the dimers as isolated units, and consequently neglects interdimer energy transfer. Figure 10 shows that for Yb^{3+} -CsMnCl₃ this is quite a reasonable assumption: $Yb^{3+}-Mn^{2+}$ chromophoric units do indeed occur as dimers in this systems, electrostatically held together by the vacancy. The beauty of the Vial model lies in its mathematical simplicity: the temporal behavior of the upconversion luminescence intensity I_{UC} is given by³⁷

$$I_{\rm UC}(t) \propto e^{-(\omega_{\rm ETU}+2\cdot k_1)\cdot t} - e^{-k_2\cdot t},\tag{1}$$

where k_1 , k_2 are the decay rate constants of the intermediate and upper emitting states, respectively. In our case $k_1 = 1/\tau (Yb^{3+2}F_{5/2}) = 740 \text{ s}^{-1}$ and $k_2 = 1/\tau (Mn^{2+4}T_1)$ = 960 s⁻¹, and these values were determined by independent 15 K lifetime measurements. ω_{ETU} is the ETU rate constant we are interested in. From the best fit with Eq. (1) to the experimental data in Fig. 6(c) (solid line), we obtain ω_{ETU} = 8720 s⁻¹. This compares to ETU rate constants for Er³⁺:CsCdBr₃ ranging from 128 to 1942 s⁻¹, depending on the Er³⁺ dopant concentration.³⁹ Er³⁺ is known to be a very efficient upconversion ion, and thus this comparison underlines the efficiency of the GSA/ETU mechanism in 0.9% Yb³⁺:CsMnCl₃.

Figure 2(c) shows the 15 K upconversion luminescence excitation spectrum. At this temperature upconversion occurs 85% via GSA/ETU and 15% via GSA/ESA. We thus expect this spectrum to correspond to the appropriately weighted sum of GSA² (85%) and GSA · ESA (15%) line shape functions. The 15 K Yb³⁺ ${}^{2}F_{5/2}$ GSA spectrum is given in Fig. 2(a). The intensity ratio of the 0, 1, 2 absorption peaks is roughly 3:2:4. We have no direct information about the ESA cross sections at the respective energies. We estimate them on the basis of the Mn^{2+} GSA spectrum shown in Fig. 1. After baseline correction we find a ratio of roughly 1:1:100 for the ESA cross sections at 10200, 10245, and $10\,685\,\mathrm{cm}^{-1}$. The excitations at $10\,200+10\,200/$ $10\,245 \text{ cm}^{-1}$ fall essentially into the window between the $Mn^{2+4}T_1$ and 4T_2 absorptions, whereas the excitation at $10\,200+10\,685$ cm⁻¹ occurs into the lower energy tail of the $Mn^{2+4}T_2$ band. Thus we calculate a ratio of 2:1:20, respectively, for these three main upconversion excitation peak maxima. Considering the experimental uncertainty, particularly in the involved ESA cross sections, this is in good agreement with the experimental intensity ratio of 3:1:45 in the upconversion excitation spectrum of Fig. 2(c).

In Fig. 8 (cross-markers) the integrated upconversion luminescence intensity is plotted as a function of temperature. It increases by roughly a factor of 5 between 40 and 90 K, before it steeply drops and becomes essentially undetectable at temperatures above 200 K. The drop above 90 K parallels the drop of the Mn²⁺ ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ luminescence observed after direct Mn²⁺ excitation; see Fig. 8 (circle markers). It is thus explained by the same luminescence quenching mechanism as described in Sec. IV B. Here, we focus on the increase between 40 and 90 K.

As demonstrated above, after $10\,685\,\mathrm{cm}^{-1}$ excitation at 15 K the dominant upconversion mechanism is GSA/ETU. Because of the small ESA cross section GSA/ESA contributes only 15% at 15 K [Fig. 6(a)]. With increasing temperature this changes dramatically. From the 75 K upconversion transient in Fig. 6(b) we obtain a 40%:60% ratio for the relative contributions of the GSA/ETU and GSA/ESA mechanisms, respectively, to the total upconversion luminescence intensity. Assuming a constant efficiency of the GSA/ ETU mechanism between 15 and 75 K, the efficiency of the GSA/ESA upconversion mechanism thus increases by about a factor of 13 in this temperature range. On the basis of temperature dependent Mn²⁺ absorption spectra (data not shown), we estimate that the GSA cross section at 10200 $+10\,685 \text{ cm}^{-1}$ increases by a factor of about 6 between 15 and 75 K. We can thus expect an increase of the relevant ESA cross section at 10658 cm⁻¹ of about an order of magnitude between 15 and 75 K. In conclusion, we attribute the increase of the upconversion luminescence intensity between 40 and 90 K [Fig. 8(b)] to the onset of an efficient GSA/ESA upconversion mechanism [Fig. 11(a)] in this temperature regime.

D. Upconversion efficiency and structure

Figure 9 shows a plot of the upconversion efficiency $\eta_{\rm UC}$ as a function of the NIR laser excitation power at 75 K. Luminescence quantum efficiencies η are usually defined as the ratio of the number of emitted photons per number of absorbed photons.⁴⁰ In practice, direct measurement of these quantum efficiencies is a very difficult task. In our case non-radiative relaxation from the ${}^{2}F_{5/2}$ excited state of Yb³⁺ to the ground state can in good approximation be neglected. Thus all ${}^{2}F_{5/2}$ excitations are either used for upconversion or emitted in the NIR. Since two NIR excitations are used to produce one VIS excitation, we get

$$NIR_{abs} \simeq NIR_{em} + 2 \cdot VIS_{em}, \qquad (2)$$

where VIS and NIR denote the numbers of visible and nearinfrared photons, respectively, and the subscripts abs and em stand for absorbed and emitted, respectively. In Eq. (2) we have also assumed that emission to the ground state is the main depopulation mechanism for the ${}^{4}T_{1}$ state of Mn^{2+} . Previous studies on $\text{Yb}^{3+}-\text{Mn}^{2+}$ systems indicate that this is a reasonable assumption at low temperatures.^{10,11} This then leads to the following definition for the upconversion efficiency:

$$\eta_{\rm UC} = \frac{\rm VIS_{em}}{\rm NIR_{abs}} \simeq \frac{\rm VIS_{em}}{\rm NIR_{em} + 2 \cdot \rm VIS_{em}}.$$
(3)

Using Eq. (3), $\eta_{\rm UC}$ is now experimentally accessible via measurement of the ratio of VIS Mn²⁺ ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ versus NIR Yb³⁺ ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ emitted photons at low temperatures. In the low-power limit, i.e., roughly below 30 mW, $\eta_{\rm UC}$ has an approximately linear dependence on the excitation density. This is the limiting case in which upconversion is a negligible depopulation pathway for the intermediate level.^{34,41} As shown in Fig. 9, there is a distinct leveling off of the power dependence of $\eta_{\rm UC}$ at high excitation powers.

The theoretical limit for $\eta_{\rm UC}$ is 0.5, and this is because two near-infrared photons are required to yield one visible photon. In this limit each NIR photon would be used for upconversion. As seen in Fig. 9, we reach a value at 75 K of $\eta_{\rm UC} = 0.08$ for an excitation power of 263 mW.

It is interesting to compare the upconversion efficiency of this system with those of the previously investigated Yb³⁺:RbMnCl₃ and Yb³⁺:CsMnBr₃ systems. Under comparable NIR excitation densities the upconversion efficiency of 0.9% Yb3+:CsMnCl3 is almost one order of magnitude higher than in 0.1% Yb³⁺:RbMnCl₃ and more than two orders of magnitude higher than in 0.2% Yb³⁺:CsMnBr₃.^{10,11} In all these systems and according to our model, the basis for their upconversion ability is an exchange coupling between neighboring Yb^{3+} and Mn^{2+} ions. We conclude that this type of upconversion is efficient, whenever there are efficient Yb³⁺-Mn²⁺ exchange pathways. In Yb³⁺:CsMnBr₃ neighboring Yb³⁺ and Mn²⁺ ions are connected all by facesharing octahedra.11 In Yb3+:RbMnCl3 both face- and corner-sharing Yb³⁺-Mn²⁺ bridging geometries are possible. Experimentally two crystallographically distinct Yb³⁺ dopant sites are found. However, only excitation into one of the two Yb³⁺ sites yields efficient upconversion.¹⁰ This suggests that the two sites correspond to corner- and facesharing $Yb^{3+}-Mn^{2+}$ connections, respectively, and that corner-sharing leads to more efficient upconversion. The most plausible Yb³⁺ substitution is that shown in Fig. 10 with a Yb³⁺-vacancy-Yb³⁺ face-sharing trimer unit. This leads to a dominance of linear $Yb^{3+}-Cl^{-}-Mn^{2+}$ bridges, in agreement with the presence of one dominant Mn^{2+} site. This indicates that Yb³⁺-Mn²⁺ exchange interactions are stronger for corner-sharing than face-sharing bridging geometries. This is supported by the results of a recent study on the system Yb³⁺:Rb₂MnCl₄,⁴² in which only corner-sharing bridging occurs.⁴³ The upconversion efficiency of this system is even higher than in Yb3+:CsMnCl3. At the moment this is a purely empirical correlation, based on a number of studies on Yb³⁺ doped Mn²⁺ halide lattices with different bridging geometries between neighboring Mn²⁺ ions. We are in the process to put this correlation on a firm quantitative basis and to attempt a theoretical calculation of the relative strengths of exchange interactions for various Yb³⁺-Mn²⁺ bridging geometries. The $Yb^{3+}-Mn^{2+}$ distance is larger for a corner-sharing $Yb^{3+}-Cl^{-}-Mn^{2+}$ than for a face-sharing $Yb^{3+}(Cl^{-})_{3}-Mn^{2+}$ arrangement. And yet the upconversion efficiency is at least two orders of magnitude higher in the corner-sharing case. This is also a direct proof that it is an exchange mechanism and not a multipole-multipole mechanism such as the mechanism suggested in Ref. 44 to account for an unusual upconversion in a Yb^{3+}/Tb^{3+} system, which is responsible for upconversion in our system.

V. CONCLUSIONS

In the course of our systematic study of $Yb^{3+}-Mn^{2+}$ upconversion systems we have found that in Yb^{3+} :CsMnCl₃ at 15 K an upconversion mechanism is dominant which has not been observed in previous $Yb^{3+}-Mn^{2+}$ systems. This mechanism involves energy transfer between dimers of exchange-coupled $Yb^{3+}-Mn^{2+}$ pairs, the formation of which is favored by the CsMnCl₃ crystal structure. An upconversion mechanism based on a sequence of radiative GSA and ESA steps, as previously observed in Yb³⁺:RbMnCl₃ and Yb³⁺:CsMnBr₃, is thermally activated in the title system. Thus the upconversion efficiency of Yb³⁺:CsMnCl₃ is highest around liquid-nitrogen temperature, and it is higher by orders of magnitude than in Yb³⁺:CsMnBr₃. This is ascribed to the possible presence of corner-sharing Yb³⁺-Mn²⁺ octahedra in Yb³⁺:CsMnCl₃, opening a more efficient exchange pathway than face-sharing octahedra.

For decades upconversion research has focused on rare earth based materials. The results of our study are encouraging for an alternative approach in the search for new upconversion materials. This paper demonstrates that the combination of rare earth and transition metal ions may lead to the discovery of new exciting and potentially very efficient upconversion processes.

ACKNOWLEDGMENTS

The authors thank D. R. Gamelin, G. M. Salley, and M. Wermuth for valuable discussions. This work was financially supported by the Swiss National Science Foundation.

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