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Excited state dynamics in Ni^{2+} doped $CsCdCl_3$: Excitation Avalanche

U. Oetliker, M. J. Riley, P. S. May and H. U. Güdel,

Department of Chemistry, University of Bern, Freiestrasse 3,
Bern 9, CH-3000, Switzerland.

Abstract

The excited state dynamics of Ni(II) doped $CsCdCl_3$ is studied in single crystals at low temperatures. The power dependence of the $^3A_{2g} \leftarrow {}^1T_{2g}$ luminescence can be interpreted in terms of an "excitation avalanche".

1. INTRODUCTION

Nonlinear excited state dynamics had been shown to occur in many rare earth doped crystals due to upconversion by nonradiative cross relaxation [1-4]. The phenomenon, which has been termed a "photon avalanche", was originally observed in Pr(III) doped $LaCl_3$ [1] and can be phenomenologically described as an ".. order of magnitude jump of fluorescence signal when the excitation light is increased from just below to just above a certain critical power" [3]. Others prefer to describe this phenomenon as "... upconversion by cross relaxation induced excited state absorption" [4]. Notwithstanding the terminology, many rare earth systems have subsequently been characterised and it has been experimentally found that the prerequisites for the effect are to have both the excitation laser resonant with a relatively strong excited state absorption in a region of low ground state absorption and for cross relaxation to provide a feedback effect for the population of the initial excited state.

Although it may seem unlikely for a transition metal complex to possess the necessary sharply resonant excited state absorption transition that exists in many rare earth ions, we undertook an investigation of the Ni(II)/$CsCdCl_3$ system because a) cross relaxation has been previously observed [5]; and b) the dynamics of this avalanche system is potentially more simple than for the rare earth systems as the process can be described essentially by three energy levels.

In this paper we show the existence of the necessary strong excited state absorption which populates the luminescent state involved in the cross relaxation process. The power dependence of this luminescence clearly displays a nonlinear behaviour due to the upconversion by cross relaxation. A three level model applied to this system can be used to *define* the onset of the avalanche and the rate processes which need to be optimised in order to enhance this effect.

2. UPCONVERSION BY CROSS RELAXATION AND THE AVALANCHE PHENOMENON

Nickel(II) is one of the few 3d ions that can exhibit luminescence from more than one excited state. In the Ni(II)/$CsCdCl_3$ system emission occurs from both the $^1T_{2g}$ and $^3T_{2g}$ states (O_h notation) and five different luminescence transitions occur, covering a spectral range from 4000 cm^{-1} to 18000 cm^{-1}. The two possible cross relaxation pathways that are known to occur [6] from a populated $^1T_{2g}$ excited state in highly doped samples are shown in Figure 1a. Together with fast radiationless relaxation, both these pathways result in the overall $^3A_{2g}{}^1T_{2g} \rightarrow {}^3T_{2g}{}^3T_{2g}$ (pair notation) process. The population of the $^1T_{2g}$ state can be monitored by the $^3A_{2g} \leftarrow {}^1T_{2g}$ luminescence which competes with the cross relaxation. The simplified three level model is shown in Figure 1b). All parameters are in units of s^{-1} and $F\sigma_1$ denotes the absorption rate constant where F is the photon density ($photons.cm^{-2}.s^{-1}$) and σ_1 is the absorption cross section ($photons.cm^{-2}$). It should be understood that the rate constants ω_1, ω_2 and ω_3 contain both radiative and nonradiative contributions, a full discussion of which can be found elsewhere [5]. X is the cross relaxation rate.

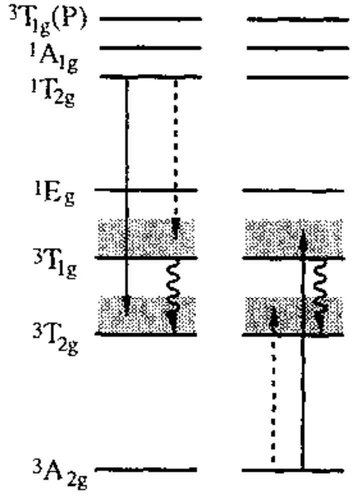

Figure 1a) $NiCl_6^{4-}$ energy levels.

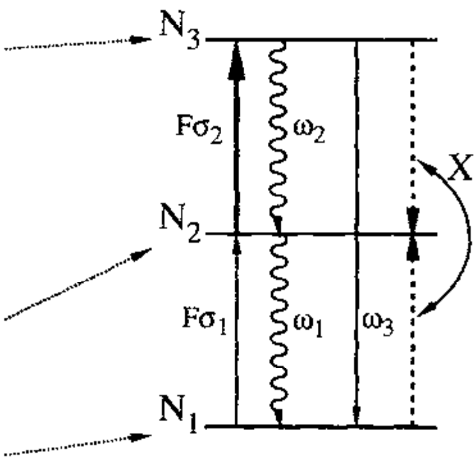

Figure 1b) Three level model.

The populations of these three levels are determined by the following three coupled nonlinear differential equations.

$$\begin{aligned}
\dot{N}_3 &= & & F\sigma_2 N_2 - (\omega_2+\omega_3) N_3 & & - X N_1N_3 \qquad (1)\\
\dot{N}_2 &= F\sigma_1 N_1 & - (F\sigma_2+\omega_1) N_2 & & + \omega_2 N_3 & + 2X N_1N_3\\
\dot{N}_1 &= - F\sigma_1 N_1 & + \omega_1 N_2 & & + \omega_3 N_3 & - X N_1N_3
\end{aligned}$$

These equations can be solved explicitly [7], but it is more constructive at this stage to make the substitution $X' = X.N_1$, making the equations linear. The solution of the linearized equations are:

$$N_3 = F\sigma_1F\sigma_2 / C \qquad (2)$$

$$N_2 = F\sigma_1(\omega_2 + \omega_3 + X') / C$$

$$N_1 = [F\sigma_2 + \omega_1(\omega_2 + \omega_3) - X'(\omega_1 - F\sigma_2)] / C$$

where $C = F\sigma_2(F\sigma_1 + \omega_3) + (F\sigma_1 + \omega_1)(\omega_2 + \omega_3) + X'(F\sigma_1 - F\sigma_2 + \omega_1)$.

These can be evaluated arbitrarily close to the exact solutions of (1) using the method of successive approximations [8], iterating $X' = X.N_1$. This is only true, however, up to a certain critical power where the denominator in equations (2) goes to zero. At this point the description of the nonlinear equations as an iteration of linear equations breaks down. These critical powers are shown as dashed lines in Figure 2 and are correlated with the abrupt jump in the population of N_3.

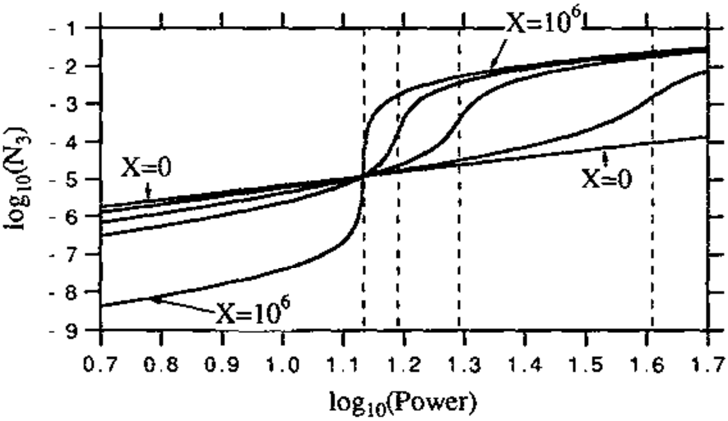

Figure 2. The population of N_3 as a function of power and cross relaxation rate (X). For the other parameters used see reference [5].

The model then gives a precise definition of the critical power (P_c) at which the avalanche occurs, and for high cross relaxation rates this critical power is given by

$$P_c \propto \omega_1 / (\sigma_2 - \sigma_1) \qquad (3)$$

The luminescence from N_3 ($^1T_{2g}$) is assumed proportional to its population, and a number of interesting features due to cross relaxation are shown in Figure 2. For zero cross relaxation ($X=0$), the luminescence intensity varies quadratically with the pump power as would be expected for a two photon process. With nonzero cross relaxation, however, two things are seen to occur. At low power the luminescence intensity is reduced as the cross relaxation competes directly with radiative relaxation. At high powers however, the cross relaxation process becomes so efficient at populating N_2 (and therefore the luminescent state N_3) compared to direct ground state absorption, that it outweighs the deactivation of the luminescence. At these high powers the luminescence intensity becomes greater than when cross relaxation is absent. At large cross relaxation rates there is an abrupt jump in the luminescence intensity for a small change in the pump power, exactly the behaviour that has been described as defining an "avalanche" effect.

There are two points worth pointing out at this stage. a) In our experiments the effect is observed indirectly as the emission intensity from N_3, this will be at all times less than the population of N_3, which in turn is much less than the population of N_2. b) The dynamics are different to that of Pr(III):$LaCl_3$ type systems where the luminescence that is monitored is from a higher fourth level which is not involved in the cross relaxation. The present three level model is essentially identical to that which describes the Nd(III):$YLiF_4$ upconversion system [4].

3. RESULTS

3.1. Excited state excitation.

Crucial to an avalanche process is the existence of an intense excited state absorption so that a laser can promote efficient excited state absorption. To this end we performed an excited state excitation spectrum using an IR lamp to populate the lowest excited state $^3T_{2g}$ (N_2) and monitoring the broad band $^3A_{2g}(N_1) \leftarrow {}^1T_{2g}(N_3)$ emission at 610 nm while scanning with an Ti:sapphire laser. Figure 3 shows this two color experiment. In this scanning range, the energy of the laser is less than that required for direct $^3A_{2g} \rightarrow {}^1T_{2g}$ excitation. This then represents $^1T_{2g}$ excitation from the $^3T_{2g}$ first excited state. A very intense and sharp (~5 cm^{-1}) transition assigned as $^3T_{2g} \rightarrow {}^1A_{1g}$ is observed at 14255 cm^{-1}. A short Franck-Condon progression appears in a

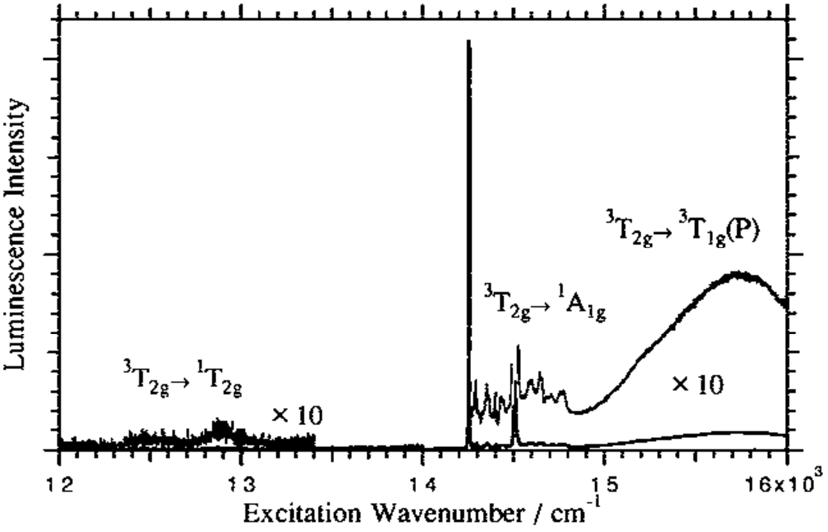

Figure 3. The two color excited state excitation spectrum of 5% Ni(II):$CsCdCl_3$ at 5K.

vibrational mode (~260 cm^{-1}) characteristic of the totally symmetric stretch of the $NiCl_6^{4-}$ complex. This excitation energy of the origin is then ideal to observe the avalanche effect as it is at a wavelength where there is very little ground state absorption.

3.2. Power dependence.

The dependence of the $^3A_{2g} \leftarrow {}^1T_{2g}$ luminescence intensity on the laser pump power, which is fixed at the energy of the $^3T_{2g} \rightarrow {}^1A_{1g}$ excited state transition (λ_{ex}=14255 cm^{-1}), is shown in Figure 4 for crystals with two doping concentrations. At low concentrations with two color excitation (with IR), the power dependence is linear as shown by a slope of 1 in the log-log plot of Figure 4a) corresponding simply to the effective one photon process. With only one color excitation (without IR), however, the effective two photon process occurs and the luminescence intensity is quadratic with pump power (slope of 2 in the log-log plot). The one color process is much weaker due to the low absorption probability of the first photon.

In samples of higher Ni(II) concentration a different power dependence is observed. At high powers the intensity of the luminescence of the one color experiment is increasing at a rate greater than quadratic over a range of half an order of magnitude of the pump power. This power dependence is a direct

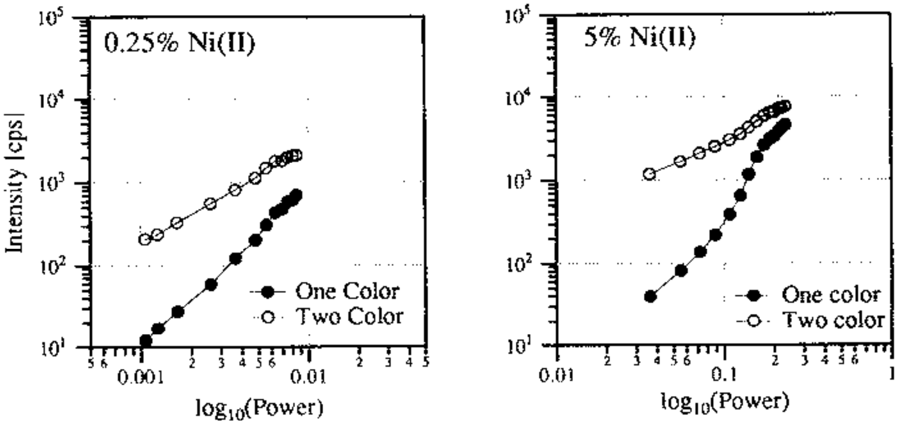

Figure 4. The power dependence of the ${}^3A_{2g} \leftarrow {}^1T_{2g}$ luminescence.

consequence of the dynamics represented by the rate processes given in equations (1) and qualitatively agrees with the results shown in Figure 2.

4. CONCLUSIONS

Evidence of efficient upconversion processes is presented for the 5% Ni(II):$CsCdCl_3$ system. The phenomenon is shown to be the same as has been described as a photon avalanche for rare earth systems [1-2]. To our knowledge this is the first time such effects have been observed in a transition metal ion system. Such systems are attractive as potential tunable laser materials which require both broad band luminescence and an efficient route to population inversion. Lasing action has already been achieved in some of the rare earth systems [4,9]. The time dependence of the luminescence build up of this system will be the subject of a future publication [7].

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