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LUMINESCENCE UPCONVERSION UNDER HIGH PRESSURE IN Ni^{2+} DOPED $CsCdCl_3$

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The near-infrared to visible upconversion properties of Ni^{2+} doped $CsCdCl_3$ are studied as a function of hydrostatic pressure. At 15 K and ambient pressure, near-infrared excitation of Ni^{2+} around 810 nm leads to upconversion luminescence centered around 610 nm. Due to the increase of the ligand field strength with increasing pressure, the emission band moves to higher energies with a rate of 19 cm^{-1}/kbar, and at 46 kbar it is centered around 585 nm. Thus the upconversion luminescence undergoes a color change from red to yellow in the 1 bar–46 kbar pressure range. The 15 K pressure-dependent upconversion excitation spectra reveal a slight red-shift of $-4\,cm^{-1}$/kbar of the upconversion relevant $^3T_{2g} \rightarrow {}^1T_{2g}$ excited state absorption (ESA) transition, and this is related to a reduction of the Racah B and C parameters, caused by an increasing degree of covalency in the Ni^{2+}–Cl^- interaction towards higher pressures. Thus, with upconversion luminescence excitation spectroscopy we can obtain information about the pressure-dependence of an ESA transition. The pressure-induced intensity redistributions within this excitation spectrum are indicative of an increasing spectral overlap of $^3T_{2g} \rightarrow {}^1T_{2g}$ ESA with $^3A_{2g} \rightarrow {}^3T_{1g}(^3F)$ ground state absorption, potentially leading to more efficient upconversion at higher pressures than at ambient pressure.

Keywords: High pressure; Upconversion; Luminescence; Optical Spectroscopy; Ni^{2+}

1 INTRODUCTION

In the field of optical spectroscopy, the Ni^{2+} ion is one of the most thoroughly studied systems. Numerous research efforts devoted to Ni^{2+} and its optical properties have ultimately led to its implementation in solid state laser systems [1]. In appropriate host lattices and at cryogenic temperatures, aside from its lasing abilities, the Ni^{2+} ion exhibits another remarkable phenomenon, namely luminescence from two excited states. This is very unusual for transition metal ions: Upto now, only a handful of octahedrally coordinated transition metal ions is known to luminesce from more than one excited state. This is due to the generally stronger electron-phonon coupling in transition metal ions when compared to the rare earths, where multiple emitting states are common. Thus, when doped into oxide,

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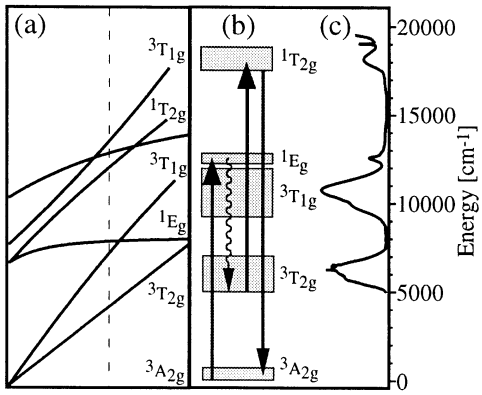

FIGURE 1 (a) d^8 Tanabe–Sugano diagram. The vertical dashed line represents the ligand field strength in Ni^{2+}:$CsCdCl_3$ at ambient pressure. (b) Energy level scheme illustrating the upconversion process in Ni^{2+}:$CsCdCl_3$. The solid arrows represent the radiative processes of GSA, ESA and luminescence, and the wavy arrow indicates nonradiative relaxation. (c) 15 K ambient pressure survey absorption spectrum of 5% Ni^{2+}:$CsCdCl_3$.

fluoride, chloride or bromide host lattices [2–4], Ni^{2+} fulfills the basic conditions for upconversion processes. In these, long wavelength excitation energy is absorbed and stored in an intermediate metastable excited state with a typical lifetime on the order of milliseconds. From there, the absorption of a second quantum of long wavelength radiation can lead to upconversion to a higher excited state, from where short wavelength luminescence can occur. Numerous upconversion mechanisms have been established over the past 30 years [5]. The upconversion mechanism which is active in Ni^{2+} is schematically shown in Figure 1b and comprises of a sequence of ground state absorption (GSA) and excited state absorption (ESA) steps, involving $^3T_{2g}$ and $^1T_{2g}$ as intermediate and upper emitting states, respectively. On the example of Ni^{2+}:$CsCdCl_3$, this paper represents the first study of the pressure-dependent upconversion properties of an upconversion system.

2 EXPERIMENTAL

The 5% Ni^{2+}:$CsCdCl_3$ crystal used in this study was grown by the Bridgman technique. Ambient pressure absorption spectra were measured on a Cary 5e spectrometer, and the sample was cooled in a closed-cycle He cryostat.

For the pressure-dependent luminescence and excitation measurements the sample was enclosed in a sapphire anvil cell and an appropriate He gas flow cryostat as described in Ref. [6]. Paraffin oil was used as the pressure transmitting medium and ruby chips were used to calibrate the applied pressure [7].

An Ar^+ laser pumped Ti^{3+}:sapphire laser (Spectra Physics) served as near-infrared excitation source for the upconversion experiments. The detection system consisted of a 3/4 m single monochromator (Spex 1702), a SR400 photon counting system and a RCA C31034 photomultiplier tube.

3 RESULTS

Figure 1c shows the 15 K ambient pressure survey absorption spectrum of 5% Ni^{2+} : $CsCdCl_3$ on a vertical energy axis. The assignment of the individual absorption bands is straightforward according to the d^8 Tanabe–Sugano diagram in Figure 1a. The vertical dashed line

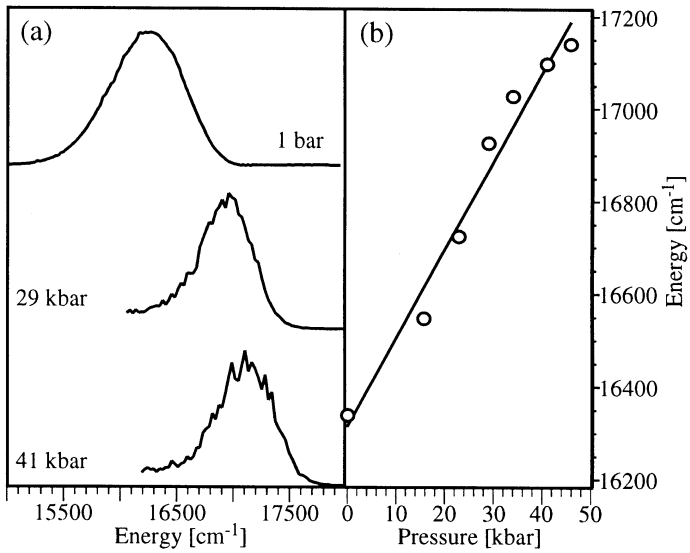

FIGURE 2 (a) 15 K Ni^{2+} $^1T_{2g} \rightarrow {}^3A_{2g}$ upconversion luminescence excited around 12350 cm^{-1} at ambient pressure (top), 29 kbar (middle) and 41 kbar (bottom). (b) Energy of the 15 K $^1T_{2g} \rightarrow {}^3A_{2g}$ upconversion luminescence band maximum as a function of pressure. The solid line represents a linear fit to the experimental data. Slope: 19 cm^{-1}/kbar.

in 1a represents the ligand field strength in Ni^{2+}:$CsCdCl_3$ at ambient pressure. Note the large ($\approx$ 4500–5000 cm^{-1}) energy gaps below the $^3T_{2g}$ and $^1T_{2g}$ excited states: Those are responsible for the occurrence of luminescence from these two states. Figure 2a presents the 15 K $^1T_{2g} \rightarrow {}^3A_{2g}$ upconversion luminescence at ambient pressure, 29 kbar and 41 kbar, excited around 12350 cm^{-1}. Upon increasing pressure this transition undergoes a blue-shift with

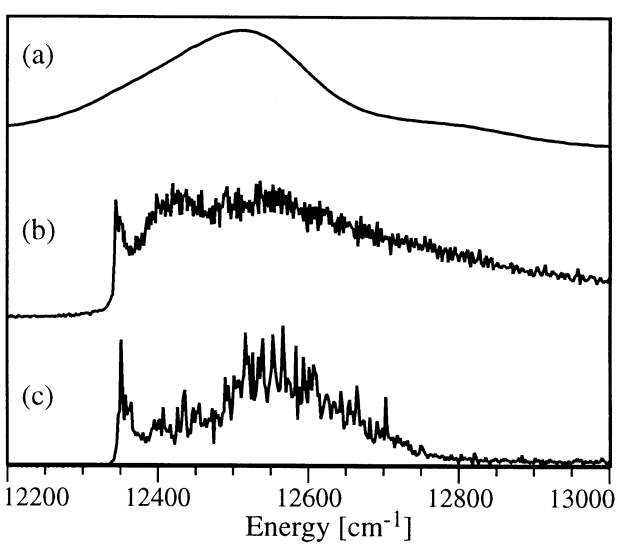

FIGURE 3 15 K ambient pressure spectra of 5% Ni^{2+}:$CsCdCl_3$ showing (a) $^3A_{2g} \rightarrow {}^1E_g$ GSA, (b) $^3T_{2g} \rightarrow {}^1T_{2g}$ ESE, (c) upconversion excitation (detected at 16400 cm^{-1}).

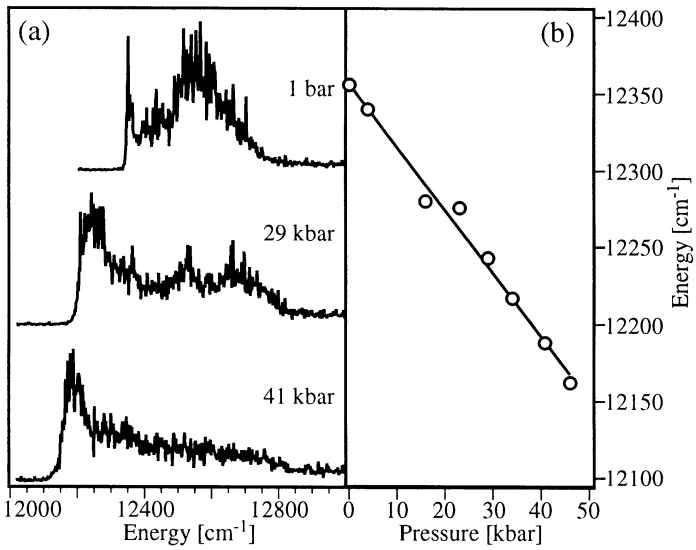

FIGURE 4 (a) 15 K excitation spectra of Ni^{2+} $^1T_{2g} \rightarrow {}^3A_{2g}$ upconversion luminescence at ambient pressure (top), 29 kbar (middle), 41 kbar (bottom). (b) Energy of the sharp $^3T_{2g} \rightarrow {}^1T_{2g}$ ESA features (see text) as a function of pressure. The solid line is a linear fit to the experimental data with a slope of $-4\,cm^{-1}$/kbar.

$19\,cm^{-1}$/kbar as illustrated by the pressure-dependence of the emission band maximum in Figure 2b. At ambient pressure the emission band maximum is in the red (610 nm) and at 46 kbar it is in the yellow (585 nm) spectral region.

Figure 3 shows the 15 K ambient pressure (a) $^3A_{2g} \rightarrow {}^1E_g$ GSA spectrum, (b) the $^3T_{2g} \rightarrow {}^1T_{2g}$ excited state excitation (ESE) spectrum and (c) the upconversion excitation spectrum. The ESE experiment (b) is a pump and probe (two-color) experiment and it is described in detail in [8]. The upconversion excitation spectrum only uses one excitation color. As expected for a so-called GSA/ESA upconversion mechanism, [5] the upconversion excitation spectrum (c) is essentially given by the product of the GSA (a) and ESA (b) lineshape functions. Note that the sharp features on the low-energy side of (c) are due to $^3T_{2g} \rightarrow {}^1T_{2g}$ ESA.

Figure 4a presents the 15 K upconversion excitation spectra of 5% Ni^{2+}:$CsCdCl_3$ at ambient pressure, 29 kbar and 41 kbar. Upon increasing pressure this spectrum undergoes a red-shift and a redistribution of intensity. The sharp features at the low energy tail in particular, identified above as due to $^3T_{2g} \rightarrow {}^1T_{2g}$ ESA, shift with $-4\,cm^{-1}$/kbar, as illustrated by the circles in Figure 4b.

4. DISCUSSION

$CsCdCl_3$ crystallizes in the hexagonal space group R3m [9]. There exist two crystallographically distinct Cd^{2+} sites in this lattices for which divalent dopant ions can substitute. It has been previously demonstrated that at low dopant concentrations Ni^{2+} substitutes only for the smaller C_{3v} rather than the larger D_{3d} site [10, 11]. The trigonal distortion of the $NiCl_6^{4-}$ unit in this lattice is relatively small, and thus we neglect it in our study.

Photo-excitation into the Ni^{2+} $^3A_{2g} \rightarrow {}^1E_g$ GSA transition around $12300\,cm^{-1}$ (Fig. 1c) leads to fast multiphonon relaxation to the $^3T_{2g}$ first excited state around $5000\,cm^{-1}$ (wavy

arrow in Fig. 1b). Absorption of a second $12300\,cm^{-1}$ photon excites the system to $\approx 5000 + 12300\,cm^{-1} = 17300\,cm^{-1}$ into the $^1T_{2g}$ state. From there, emission to all lower lying states occurs. Shown in Figure 2a is the $^1T_{2g} \rightarrow {}^3A_{2g}$ luminescence transition. The reverse transition, $^3A_{2g} \rightarrow {}^1T_{2g}$ GSA, involves an electron promotion from the formally non-bonding t_{2g}-set of d-orbitals to the formally anti-bonding e_g-set, and as such depends on the octahedral ligand field splitting 10 Dq. This is represented by the slope of 1 of the $^1T_{2g}$ state versus the $^3A_{2g}$ ground state in the strong-field limit of the Tanabe–Sugano diagram in Figure 1a. Upon increasing pressure, the $NiCl_6^{4-}$ unit is compressed, resulting in an increase of 10 Dq. According to Figure 1a this should result in a blue-shift of the $^3A_{2g} \rightarrow {}^1T_{2g}$ absorption and also its reverse luminescence transition. As shown in Figure 2, this is exactly what we observe experimentally. In the 1 bar–46 kbar pressure range, this luminescence transition moves linearly with a rate of $19\,cm^{-1}$/kbar. This compares to shift rates of around 10–12 cm^{-1}/kbar for the ligand field dependent $^4T_{2g} \rightarrow {}^4A_{2g}$ luminescence transition in Cr^{3+} doped oxide and fluoride lattices [12, 13]. The slightly higher value obtained here is mainly due to the higher compressibility of the chloride lattice relative to the oxides and fluorides.

The bandwidth (full width at half maximum, FWHM) of the 15 K $^1T_{2g} \rightarrow {}^3A_{2g}$ luminescence band decreases from $750\,cm^{-1}$ at ambient pressure to $550\,cm^{-1}$ at 41 kbar (Fig. 2a). This is a manifestation of the fact that with increasing pressure the expansion of the $NiCl_6^{4-}$ unit in the $^1T_{2g}$ excited state with respect to the ground state becomes smaller. Obviously, in this specific case, this effect dominates over the effect of increasing vibrational frequencies with increasing pressure, because the latter would lead to a broadening of the emission and absorption band shapes.

In order to be able to understand the pressure-dependence of the upconversion excitation spectrum, we first analyze the 15 K ambient pressure spectrum shown in Figure 3c. As discussed above, this spectrum is essentially the product of the $^3A_{2g} \rightarrow {}^1E_g$ GSA (Fig. 3a) and $^3T_{2g} \rightarrow {}^1T_{2g}$ ESA spectra (Fig. 3b). Knowing the individual spectra of these two absorption transitions, we can identify which features in the upconversion excitation spectrum are predominantly caused by GSA or alternatively by ESA. Thus, we are able to obtain information about the pressure dependence of both individual transitions by simply studying the pressure dependence of the upconversion excitation spectrum. From Figure 3 we conclude that the sharp bands around $12350\,cm^{-1}$ are mainly due to $^3T_{2g} \rightarrow {}^1T_{2g}$ ESA, whereas the broad feature around $12500\,cm^{-1}$ is due to both, GSA and ESA.

In the pressure dependent upconversion excitation spectra of Figure 4a we observe a red-shift of the sharp $^3T_{2g} \rightarrow {}^1T_{2g}$ ESA bands with increasing pressure of $-4\,cm^{-1}$/kbar. This is a transition between states with parallel slopes in the strong field limit of the Tanabe–Sugano diagram (Fig. 1a), *i.e.* an intra-configurational transition which is, in first-order approximation, ligand field independent. Therefore the pressure dependence of this transition is almost a factor of 5 smaller than for the $^1T_{2g} \rightarrow {}^3A_{2g}$ transition. The slight red-shift is caused by a decrease of the Racah parameters B and C at higher pressures. A ligand field calculation shows that a decrease of only about 4% in B and C can account for the observation of the decreasing $^3T_{2g} \rightarrow {}^1T_{2g}$ energy separation between 1 bar and 46 kbar. This is in line with previous studies on $Cr^{3+}:Al_2O_3$ (ruby), where in a comparable pressure range a similar reduction of B and C has been observed [14]. The physical significance of this reduction is an increase in the metal-ligand bonding covalency with increasing pressure and thus a decrease in inter-electronic repulsion.

Finally, we note that there is an intensity redistribution in the series of upconversion excitation spectra in Figure 4a. The higher the pressure, the more efficient upconversion excitation into the lower energy tail of the GSA/ESA overlap band becomes relative to excitation into the rest of this band. This is very likely due to the pressure-induced

blue-shift of the spin-allowed and $^3A_{2g} \rightarrow {}^3T_{1g}(^3F)$ GSA transition and its increasing overlap with $^3T_{2g} \rightarrow {}^1T_{2g}$ ESA. This is a very important and promising situation, because it shows that upconversion properties can be tuned by external pressure, giving us an experimental handle. At ambient pressure the Ni^{2+} upconversion mechanism involves two spin-forbidden and therefore weak absorption transitions. As a consequence, the whole Ni^{2+} upconversion process is relatively inefficient. At elevated pressures, upconversion can also be induced upon excitation into a spin-allowed and therefore more intense GSA transition. This is expected to lead to more efficient upconversion with respect to the ambient pressure situation. We are currently engaged in further experiments to quantify this process.

5 CONCLUSIONS

We have demonstrated the feasibility of upconversion experiments in pressure cells. The example of $Ni^{2+}:CsCdCl_3$ has demonstrated that high pressure is a useful tool to tune upconversion properties, and may potentially become an important technique to study photophysical properties such as spectral overlaps, competition between radiative and nonradiative relaxation processes and energy level sequences in many further upconversion systems.

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