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## 1 Introduction

The luminescence properties of  $V^{3+}$  have received very little interest. The present work represents the first study of exactly octahedral  $VX_6^{3-}$  ( $X=Cl, Br$ ) units which were obtained by doping the elpasolite lattices  $Cs_2NaYCl_6$  with  $V^{3+}$  and growing single crystals by the Bridgman technique. Synthesis, crystal growth and the structure of the host lattices are described in the literature (Morss et al 1970; Mermant et al 1979).  $V^{3+}$  has a  $3d^2$  electron configuration and therefore  ${}^3T_{1g}$  as ground state in  $O_h$  symmetry. The lowest energy excited state is either  ${}^1T_{2g}$  or  ${}^3T_{2g}$ , depending on the ligand field strength. In both situations luminescence in the near infrared region is expected, either as sharp lines ( ${}^1T_{2g} \rightarrow {}^3T_{1g}$ ) or as a broad emission band ( ${}^3T_{2g} \rightarrow {}^3T_{1g}$ ). Such transition metal systems are investigated as possible solid state laser materials (Imbusch et al 1985).

In the title crystals we are in the crossover region between sharp-line singlet and broad-band triplet emission. This situation in the excited state makes the luminescence spectroscopy particularly interesting and informative. From studies of the temperature dependence of the luminescence and decay properties a rather detailed picture of the relevant excited states is obtained. In addition, the spin-orbit splitting of the ground state can be determined. In non-cubic crystals luminescence spectroscopy of  $d^2$  ions such as  $Ti^{2+}$  or  $V^{3+}$  is an excellent probe of the geometric distortions, because the low-symmetry splittings of  ${}^3T_{1g}$  can be resolved.  $Ti^{2+}$  in  $MgCl_2$  provides a nice example of this (Jacobson et al 1986).

## 2 Experimental results

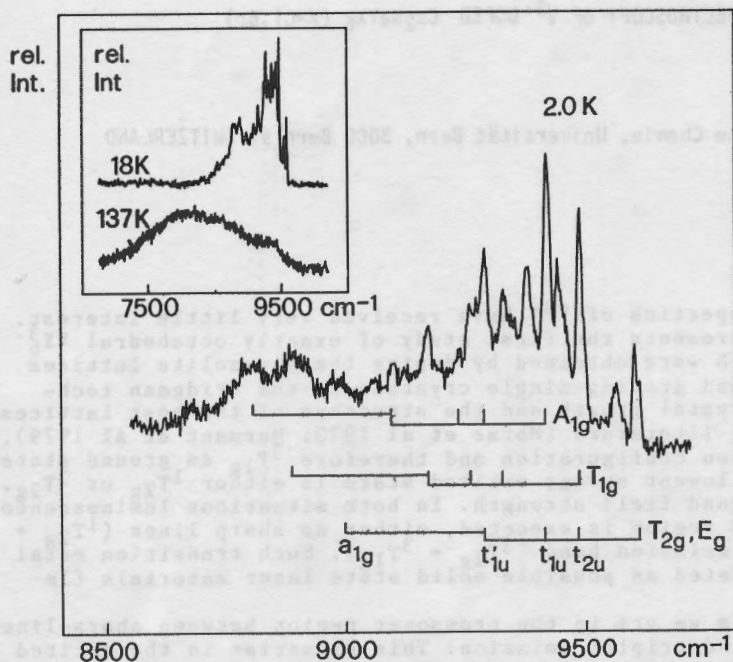
The luminescence spectrum of  $Cs_2NaYCl_6:V^{3+}$  is presented in Fig 1 at three temperatures. At 2K rich fine structure is observed. There is a pronounced change of the spectrum with temperature, above 100K a broad band becomes dominant. In contrast,  $Cs_2NaYBr_6:V^{3+}$  shows broadband luminescence already at the lowest temperatures (peak energy  $7500\text{cm}^{-1}$  at 4 K).

In Fig 2 the temperature dependence of the luminescence decay times is shown. All the decay curves are single exponentials. In the chloride host the decay time is 17.2msec at 21K, and it drops by nearly two orders of magnitude on increasing T to 270K. In contrast, the decay time in the bromide lattice is only 228µsec at 16K, similar to the chloride values at high temperatures, and it drops by only a factor of 3 on warming to 250K.

## 3 Discussion

### a) Low-temperature luminescence spectrum of $Cs_2NaYCl_6$

The rich fine structure in the luminescence spectrum of  $Cs_2NaYCl_6:V^{3+}$  at 2K (Fig 1) together with the narrow overall width of the spectrum clearly indicate a  ${}^1T_{2g} \rightarrow {}^3T_{1g}$  transition. The observed peaks can be assigned as electronic origins to the spin-orbit split components of the  ${}^3T_{1g}$  ground state and as vibronic  $t_{1u}$  and  $t_{2u}$  origins built on these



**Figure 1** Low-temperature single crystal luminescence spectra of  $\text{Cs}_2\text{NaYCl}_6:\text{V}^{3+}$  (0.05 mole%). The fine structure is assigned in terms of electronic transitions to the spin-orbit split ground state components and vibronic origins involving ungerade modes of the  $\text{VC1}_6^{3-}$  unit as indicated in the 2K spectrum. Built on the vibronic origins weak  $a_{1g}$  sidebands are indicated.

Although there is an overlap of electronic origins and vibronic sidebands an unambiguous assignment of the bands is possible by using all the observed transitions. The lowest-energy components of the  ${}^3\text{T}_{1g}$  ground state are the  $\text{T}_{2g}$  and  $\text{E}_g$  spinor states, which are degenerate in first order. Our spectra show that they are separated by  $9.3\text{cm}^{-1}$ , with  $\text{E}_g$  lower in energy, as could be shown with MCD (Neuenschwander 1981) and magnetic susceptibility measurements. The  $\text{T}_{1g}$  and  $\text{A}_{1g}$  origins lie at energies of  $132.6\text{cm}^{-1}$  and  $201.0\text{cm}^{-1}$ , respectively. From these splittings we determine a spin-orbit coupling parameter  $\zeta$  of  $130\text{cm}^{-1}$ . This is 62% of the free ion value, and we conclude that there is no Jahn-Teller effect in the ground state.

Three vibronic sidebands with energy displacements of  $318\text{cm}^{-1}$ ,  $186\text{cm}^{-1}$  and  $128\text{cm}^{-1}$  are observed on all the electronic origins. The ground state vibrational energies of  $t_{1u}$ ,  $t_{1u}$  and  $t_{2u}$  modes in the same host lattice doped with  $\text{Cr}^{3+}$  are  $322\text{cm}^{-1}$ ,  $187\text{cm}^{-1}$  and  $120\text{cm}^{-1}$ , respectively (Knochenmuss et al 1986). The vibronic sidebands in our spectrum can thus be assigned as  $t_{1u}$ ,  $t_{1u}$  and  $t_{2u}$  vibronic origins. These modes are internal  $\text{VC1}_6^{3-}$  modes (Lentz 1974). A group of relatively broad and weak bands, which is displaced by approximately  $300\text{cm}^{-1}$  from the intense group of vibronic origins, consists of  $a_{1g}$  sidebands.

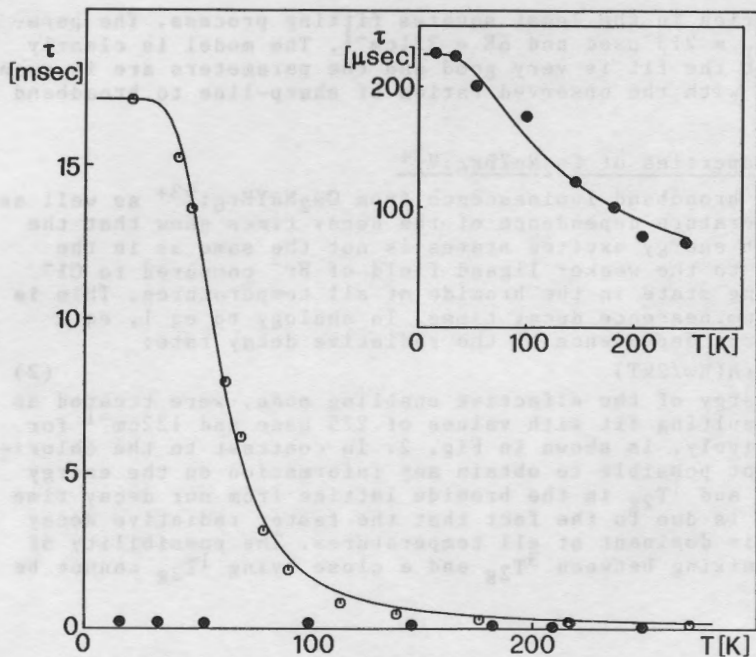


Figure 2 Temperature dependence of the luminescence decay times for  $\text{Cs}_2\text{NaYCl}_6:\text{V}^{3+}$  (0.1 mole%, open circles) and  $\text{Cs}_2\text{NaYBr}_6:\text{V}^{3+}$  (0.5 mole%, filled circles). The insert shows the bromide decay times on an expanded ordinate scale. The solid lines are fits to eq 1 and eq 2 for the chloride and bromide, respectively, as explained in the text.

#### b) Radiative relaxation in $\text{Cs}_2\text{NaYCl}_6:\text{V}^{3+}$

It is clear from the luminescence spectra in Fig. 1 that with increasing temperature the  ${}^3\text{T}_{2g}$  excited state becomes thermally populated and broadband luminescence is observed. This is confirmed by the luminescence decay times in Fig. 2 which can be considered as radiative below 200 K. The decay time of 17.2 msec at 21 K is typical for a spin-forbidden transition. The high temperature values of 100–200 μsec are in the typical range for spin-allowed vibronic transitions. In order to obtain a more quantitative picture a simple model was fitted to the decay times. We assume thermal equilibration within the  ${}^1\text{T}_{2g}$  and  ${}^3\text{T}_{2g}$  excited states to occur much faster than the luminescence transitions to the ground state. Neglecting the  ${}^1\text{E}_g$  excited state, whose energy is unknown, as well as spin-orbit coupling within and between  ${}^1\text{T}_{2g}$  and  ${}^3\text{T}_{2g}$ , we obtain equation 1 for the total radiative decay rate  $\tau^{-1}$ :

$$\tau^{-1} = \tau_s^{-1} P_s + \tau_t^{-1} \coth(\pi\omega/2kT) P_t \quad (1)$$

$$\text{with } P_s = 3/Z$$

$$P_t = 9 \exp(-\Delta E/kT)/Z$$

$$Z = 3 + 9 \exp(-\Delta E/kT)$$

where  $\tau_s$  and  $\tau_t$  are the intrinsic decay times of the  ${}^1\text{T}_{2g}$  and  ${}^3\text{T}_{2g}$  states, respectively, and  $\Delta E$  is their energy difference. The  $\coth$  term describes the temperature dependence of the  ${}^3\text{T}_{2g} \rightarrow {}^3\text{T}_{1g}$  radiative rate with an enabling mode frequency of  $179\text{cm}^{-1}$  which was determined from the temperature dependence of the  ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}$  absorption intensity.  $\tau_s$  was set to 17.2 msec, the observed low-temperature value, and  $\tau_t$  as

well as  $\Delta E$  were varied in the least squares fitting process. The parameter values are  $\tau_t = 213 \text{ usec}$  and  $\Delta E = 231 \text{ cm}^{-1}$ . The model is clearly oversimplified, but the fit is very good and the parameters are in quantitative agreement with the observed ratios of sharp-line to broadband emission.

### c) Luminescence properties of $\text{Cs}_2\text{NaYBr}_6:\text{V}^{3+}$

The observation of broadband luminescence from  $\text{Cs}_2\text{NaYBr}_6:\text{V}^{3+}$  as well as the different temperature dependence of the decay times show that the order of the lowest energy excited states is not the same as in the chloride host. Due to the weaker ligand field of  $\text{Br}^-$  compared to  $\text{Cl}^-$   $^3\text{T}_{2g}$  is the emitting state in the bromide at all temperatures. This is confirmed by the luminescence decay times. In analogy to eq 1, eq 2 gives the temperature dependence of the radiative decay rate:

$$\tau^{-1} = \tau_t^{-1} \coth(\hbar\omega/2kT) \quad (2)$$

$\tau_t$  and  $\hbar\omega$ , the energy of the effective enabling mode, were treated as parameters. The resulting fit with values of  $225 \text{ usec}$  and  $122 \text{ cm}^{-1}$  for  $\tau_t$  and  $\hbar\omega$ , respectively, is shown in Fig 2. In contrast to the chloride lattice it is not possible to obtain any information on the energy separation of  $^3\text{T}_{2g}$  and  $^1\text{T}_{2g}$  in the bromide lattice from our decay time measurements. This is due to the fact that the faster radiative decay channel from  $^3\text{T}_{2g}$  is dominant at all temperatures. The possibility of strong spin-orbit mixing between  $^3\text{T}_{2g}$  and a close lying  $^1\text{T}_{2g}$  cannot be excluded.

### 4 References

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