

Energy Transfer by Ion-Ion Cross-Relaxation in Cs₂NaTmCl₆

P. A. TANNER,* T. K. CHOI, and K. HOFFMAN[†]

Department of Applied Science, City Polytechnic of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong (P.A.T., T.K.C); and Department of Physics and Astronomy, University of Georgia, Athens, Georgia 30605, U.S.A. (K.H.)

Index Headings: Luminescence; Absorption; Concentration quenching; Lanthanide ion; Spectroscopic techniques.

INTRODUCTION

In this study we present experimental results from absorption, excitation, and luminescence spectroscopy which enable us to account for the concentration quenching of near-ultraviolet emission in $Cs_2NaTmCl_6$. The thulium ions are situated at sites of octahedral symmetry¹ in this compound, forming a model system for the investigation of energy transfer phenomena.²

EXPERIMENTAL

Neat $Cs_2NaTmCl_6$ and $TmCl_6^{3-}$, doped (0.01-10 mol %) into the colorless, cubic-host Cs₂NaGdCl₆, were prepared as single crystals by the Morss method.³ Absorption spectra of polished single crystals were recorded between 300 and 10 K with the use of a Bio-Rad FTS-60A wide-range spectrometer equipped with DTGS, InSb, PbSe, Si, blue and solar-blind photomultiplier detectors. Spectral calibrations with neon, cadmium, and mercury lamps indicate that the wavenumber error in the assignment of the energy levels is similar to the resolution employed $(1-2 \text{ cm}^{-1})$. The sample was held in an Oxford Instruments closed-cycle-cooler cryostat. Excitation spectra were recorded at 300-85 K with an SLM 4800C spectrofluorometer. Selective excitation was provided by a xenon lamp. The luminescence and emission decay measurements (between 300 and 2 K) utilized the 476.5nm excitation (into the vibronic sideband of the ${}^{1}G_{4}$ level of Tm³⁺) from an argon-ion laser, the emission being dispersed by a 0.25-m Jobin-Yvon monochromator and detected by a photomultiplier. Decay measurements were made by chopping the beam and also involved the use of a waveform digitizer, a Digital Pro 300 computer, and an X-Y plotter.

RESULTS AND DISCUSSION

Excitation Spectra. With the use of selective excitation into the ${}^{1}G_{4}$ vibronic sideband, for *dilute* Cs₂NaGdCl₆: TmCl₆³⁻, emission is observed from the ${}^{1}G_{4}$ level (near 20,850 cm⁻¹) to the ground-state term (${}^{3}H_{6}$) and the first excited terms (${}^{3}F_{4}$ and ${}^{3}H_{5}$), within the spectral region of our detectors. However, for *neat* Cs₂NaTmCl₆, no emission is observed from the ${}^{1}G_{4}$ level, but instead, emission is observed from the ${}^{3}H_{4}$ level, situated near 12,500 cm⁻¹. The excitation spectrum of the ${}^{3}H_{4}$ emission in the neat compound shows that this level is populated directly from ${}^{1}G_{4}$, and that the intermediate levels ${}^{3}F_{2}$ and ${}^{3}F_{3}$ are bypassed. The concentration quenching of the ${}^{1}G_{4}$ emission is therefore due to an ion-ion cross-relaxation between Tm³⁺ neighbors at sites A and B, of the form:

$$G_4 \text{ (site A/B)} + {}^{3}H_6 \text{ (site B/A)} \rightarrow {}^{3}H_4 \text{ (site A/B)} + X(\text{site B/A}).$$

Absorption Spectra. The energy levels of Tm^{3+} in $TmCl_6^{3-}$ are labeled according to representations of octahedral point group symmetry. From previous studies,⁴ the locations of the crystal field components of the 1G_4 , 3H_4 , and 3H_6 levels have been determined, and the relevant energy levels are shown in Fig. 1. The term multiplet X is therefore situated near 8000 cm⁻¹ and thus corresponds to 3H_5 . We have investigated the crystal field energy levels of this term by absorption spectroscopy (Fig. 2). Most of the intensity of the ${}^3H_5 \leftarrow {}^3H_6$ transition arises from the magnetic dipole (MD) mechanism. The oscillator strengths, P(calc), of the individual transitions $j \leftarrow i$ between crystal field components were calculated with the use of the eigenvectors⁴ from a six-parameter crystal field model:⁵

$$P(ext{calc}) = rac{8\pi^2 mc}{3he^2 g_i} \, ar{
u}_{ij} n_{ij} S_{ij}$$

where g_i is the degeneracy of level *i*; $\bar{\nu}_{ij}$ and n_{ij} are the transition wavenumber and the refractive index, respectively; and S_{ij} is the transition line strength. The *calculated* oscillator strengths are in good agreement with

1

Received 10 December 1992; revision received 10 February 1993.

^{*} Author to whom correspondence should be sent.

[†] Present address: Division of Basic Sciences and Mathematics, Whitman College, Walla Walla, WA 99362.



FIG. 1. Possible cross-relaxation processes responsible for quenching the ${}^{1}G_{4}$ emission in Cs₂NaTmCl₆. (Note: The processes A-F may account for the quenching of the blue emission in Cs₂NaTmCl₆. v denotes a transition involving phonon emission. The site 2 transitions A and E, terminate at the $({}^{3}H_{4})E_{g}$ and $({}^{3}H_{4})T_{2g}$ levels, respectively, with a ν_{6} phonon being emitted in process E. The locations of the ${}^{3}F_{2}$, ${}^{3}F_{3}$, and ${}^{3}F_{4}$ levels (between 15,133 and 14,959, 14,457 and 14,381, and 5938 and 5547 cm⁻¹, respectively⁴) and the other ${}^{3}H_{6}$ levels are not shown in the diagram (which is not to scale) for the sake of clarity.

the experimentally measured oscillator strengths determined by software integrations of the single crystal absorption spectra:⁶

$$P(\text{expt}) = \frac{4mc\epsilon_0}{\text{Le}^2} \ln 10 \int \epsilon(\nu) \, d\nu$$

where $\epsilon(\nu)$ is the molar absorptivity, and the integration is over frequency/Hz. For the room-temperature spectrum, the bands were deconvoluted, and the locations of the resultant features were checked from the derivative spectra. All the observed spectral features, at the different temperatures of measurement, have been assigned either to magnetic-dipole-allowed origins or to vibronic structure based upon these origins. The detailed assignments are not included here, and the vibronic sideband structure of the TmCl₆³⁻ moiety has been discussed previously.⁷ The derived energy levels of the ${}^{3}H_{5}$ crystal field components are shown in Fig. 1.

Luminescence Decay Measurements. The emission lifetimes of elpasolites are sensitive to the moisture content of the crystals, the presence of trace amounts of other lanthanide ion impurities, and the quality of the crystals. Due to these factors, the emission parameters varied somewhat from one batch of crystals to another,



FIG. 2. ${}^{3}H_{5} \leftarrow {}^{3}H_{6}$ absorption spectrum of Cs₂NaTmCl₆ between 300 and 20 K.

but the same conclusions were formulated from the results from different batches. From the integration of the emission spectra, and the calculated MD line strengths, the radiative lifetime of ${}^{1}G_{4}$ is calculated to be <11 ms, since the vibronic structure of the ${}^{1}G_{4} \rightarrow {}^{3}F_{2}$, ${}^{3}F_{3}$ transitions has not been observed and is not included in the calculations. The lowest ${}^{1}G_{4}$ level is situated at 19 quanta of the highest energy mode of vibration of TmCl₆³⁻ above the next lowest level, ${}^{3}F_{2}$, so that multiphonon relaxation from ${}^{1}G_{4}$ is expected to be slow. Consistent with this, the measured lifetime in dilute $Cs_2NaGdCl_6:TmCl_6^{3-}$ is up to 6 ms. In our preliminary emission decay study, we have monitored the nonexponential decay of ${}^{1}G_{4}$ in 1.3 and 9.8 mol % Tm-doped samples of Cs₂NaGdCl₆ at 2 K and 10 K, by observing the ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$ emission between 14,900 and $15,300 \text{ cm}^{-1}$. The luminescence intensity as a function of time, I(t), was analyzed in terms of the multipole interaction between Tm³⁺ ions, according to the model of Inokuti and Hirayama⁸ (I&H):

$$[I(t)/I(0)] = \exp[-t/t_0 - \Gamma(1 - 3/s) (c/c_0)(t/t_0)^{3/s}]$$

where t_0 is the lifetime in the absence of quenching (taken from measurements on 0.08 mol % Cs₂NaGdCl₆: TmCl₆³⁻ as 4.53 ms; c_0 is the critical concentration, calculated as 3.3 mol %; and s is a parameter which describes the type of multipole interaction. The results indicate that s = 6, which corresponds to energy transfer between Tm³⁺ ions by a dipole transition occurring at each ion. The efficiency of energy transfer⁸ from ¹G₄ is ~40% in the 1.3 mol %-doped sample, and greater than 90% in the 9.8 mol % sample.

CONCLUSIONS

The excitation spectra of $Cs_2NaTmCl_6$ indicate that the quenching of near-ultraviolet luminescence is due to an ion-ion cross-relaxation between an excited ion and its ground-state neighbor, in which one Tm^{3+} ion transfers to the ${}^{3}H_{4}$ term multiplet. The assignments of representations to the energy levels from the absorption spectra, and the understanding of the vibrational behavior of the crystal, enable certain conclusions to be drawn, concerning the energy transfer process(es) in

Cs₂NaTmCl₆. For Tm³⁺ at an octahedral site at 2–10 K, there are only two resonant transfer processes possible (A and **B**, Fig. 1). The mechanisms of these processes are electric quadrupole (EQ) and/or magnetic dipole (MD)-EQ transfer (process A); and EQ and/or MD-MD transfer (process **B**). First-order selection rules exclude nonresonant mechanisms involving even parity vibrational modes. Furthermore, the intensity of lattice modes in the optical spectra is relatively small.7 Thus mechanisms C and D, with ED-ED phonon-assisted transfer, involve sparsely populated regions of the phonon density of states spectrum. (The representation of these processes in Fig. 1 differs from that given elsewhere.⁹) Process \mathbf{C} , for example could involve the emission of a phonon at site 1 with simultaneous (virtual) photon emission, leaving site 1 in the $aT_{1g}({}^{3}H_{5})$ state, and then (virtual) photon absorption and phonon emission at site 2, changing it to $({}^{3}H_{4})T_{2g}$. Other mechanisms, involving the emission of only one phonon are possible (E and F), the phonon energy corresponding to the $\nu_6 t_{2\mu}$ internal mode. The resonant process \mathbf{B} and the nonresonant processes C and D therefore correspond to the mechanism predicted by the I&H model.

One further mechanism which we have discounted, due to the low intensity of extrinsic emission from Tm³⁺ at noncentrosymmetric defect sites,⁷ is transfer involving trap sites. We are, however, cautious in accepting the validity of the I&H model for the system studied. First, the model assumes that the donor-donor transfer rate is negligible. Second, the model neglects the angular dependence of the transfer. Third, the fit of the data is rather insensitive to the parameter s. The fits to the experimental data are not as good if the I&H exchange interaction model is parametrized. We are carrying out a theoretical analysis of the energy transfer rates by the processes A-F and other mechanisms, and a more detailed experimental investigation of the temperature dependence of the quenching in order to understand the energy transfer mechanism in more detail.

It is interesting to compare the two-ion process studied here with the proposed population mechanism of the $Eu^{3+5}D_0$ level in $EuCl_3$.¹⁰ The thermal equilibrium between ${}^{5}D_{0}$ and ${}^{5}D_{1}$ (at ~1760 cm⁻¹ to higher energy) would seem to be a more reasonable explanation of the temperature dependence of the ${}^{5}D_{0}$ lifetime than the postulation of a virtual level. We note that the data¹⁰ may be satisfactorily parametrized with this model and a fast ⁵ D_1 lifetime (near 0.04 μ s) is calculated, which would explain the failure to distinguish a risetime for the ${}^{5}D_{0}$ emission. The transfer from ${}^{5}D_{0}$ to a Eu³⁺ ion at a defect site (with a water molecule neighbor), and nonradiative relaxation through the excitation of four quanta of the O-H stretching vibration, may be a competing nonradiative process in the relaxation from ${}^{5}D_{0}$ in hygroscopic EuCl₃.

ACKNOWLEDGMENTS

This research was funded by the Research Grants Council of the HK UPGC under project Number 904022. We thank Professor W. M. Yen for making his laboratory available for performing the luminescence decay measurements.

- 1. G. Meyer, Progr. Solid St. Chem. 14, 141 (1982).
- 2. M. Bettinelli and C. D. Flint, J. Phys. Cond. Matt. 3, 7053 (1991).
- L. R. Morss, M. Siegal, L. Stenger, and N. Edelstein, Inorg. Chem. 9, 1771 (1970).
- 4. P. A. Tanner, Mol. Phys. 54, 883 (1985).
- 5. D. R. Foster, M. F. Reid, and F. S. Richardson, J. Chem. Phys. 83, 3225 (1985).
- P. W. Atkins, *Physical Chemistry* (Oxford University Press, Oxford, U.K., 1978), p. 586.
- 7. P. A. Tanner, Mol. Phys. 53, 813 (1984).
- 8. M. Inokuti and F. Hirayama, J. Chem. Phys. 43, 1978 (1965).
- Laser Spectroscopy of Solids, W. M. Yen and P. M. Selzer, Eds. Topics in Applied Physics, Vol. 49, (Springer-Verlag, New York, 1981), p. 64.
- G. Chen, N. A. Stump, R. G. Haire, and J. R. Peterson, Appl. Spectrosc. 46, 1198 (1992).