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COMMENTS

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Comment on ''Energy transfer and upconversions in cubic Cs_2NaYCl_6:Er^{+3} and $Cs_2NaErCl_6$''

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Well-resolved luminescence from the crystal-field level $^2H(2)_{9/2}\, a\Gamma_8$ at 36236 cm^{-1} to 34 lower levels has been observed for $Cs_2NaErCl_6$ upon pulsed laser excitation at 273.9 nm. The assignments enable the location and identification of the upconversion luminescence state in the study of Hasan *et al.* [Phys. Rev. B **56**, 4518 (1997)] and support a two-photon vibronic excitation mechanism in the latter case. The experimentally determined energy for the $^2H(2)_{9/2}\, a\Gamma_8$ state differs considerably from the calculated value. The temporal behavior of blue upconverted luminescence from the $^2G_{9/2}$ state is reproduced from an analytical expression, and it is shown that the alternative fitting procedure does not enable the two-ion upconversion rate W to be well determined. [S0163-1829(99)13143-6]

Comments are given here concerning the upconversions and energy levels of $Cs_2NaErCl_6$ reported by Hasan *et al.*[1]

I. ULTRAVIOLET UPCONVERSION IN $Cs_2NaErCl_6$ FROM THE $^4S_{3/2}$ LEVEL TO $^2H(2)_{9/2}$

Pulsed laser excitation at $\sim 18\,270$ cm^{-1} was found to yield ultraviolet (uv) upconversion, with emission near 29 400 cm^{-1} at 15 K.[1] This poorly resolved emission was attributed to the $^2H(2)_{9/2}\, a\Gamma_8 \rightarrow {}^4I_{13/2}$ transition, from the absence of an emission rise time and the consideration of the (unreported) excitation spectrum. The highest $^2H(2)_{9/2}$ level, $b\Gamma_8$, was estimated to be at $36\,345\pm 25$ cm^{-1}, so that the excitation mechanism was attributed to the two-photon vibronic absorption, $^4I_{15/2}\rightarrow {}^2H(2)_{9/2}\, b\Gamma_8 + \nu_e$, where ν_e represents an even-parity mode of vibration of $Cs_2NaErCl_6$ with energy 195 cm^{-1}. However, no luminescence was reported from $^2H(2)_{9/2}$ to the ground state, $^4I_{15/2}$. Furthermore, the energy 195 cm^{-1} differs considerably from the energies of the $\nu_1\alpha_{1g}$ and $\nu_2\varepsilon_g$ modes of vibration, which are located at 296 and 236 cm^{-1}, respectively, in the 15-K Raman spectrum of $Cs_2NaErCl_6$. The mechanism, and the assignment of the luminescent state, therefore requires more consideration and proof, particularly since it is well known that trace rare-earth impurities can luminesce efficiently in elpasolite lattices (see, for example, Ref. 2). We therefore decided to employ direct ultraviolet excitation in order to ascertain if ultraviolet luminescence from the $^2H(2)_{9/2}$ multiplet term of Er^{3+} in $Cs_2NaErCl_6$ does in fact occur, and if so, to establish the energy of the luminescent level in order to elucidate the

upconversion mechanism of Hasan *et al.* According to the energy-level calculation of these authors the energy gap between $^2H(2)_{9/2}$ and the next lowest term, $^2D(1)_{5/2}$, is 1682 cm^{-1} (i.e., spanned by six or more vibrational quanta), so that our previous findings would support the possibility of observation of luminescence from this term.[2]

Many luminescence transitions were observed in the range from 36 236 to 11 450 cm^{-1} for $Cs_2NaErCl_6$ under 273.9 nm (36 499 cm^{-1}) excitation. In particular, well-resolved structure at 15 K could be assigned to the pure electronic transitions and associated vibronic sidebands of the transitions from $^2H(2)_{9/2}$ to 34 crystal-field levels from the $^4I_{15/2}\, a\Gamma_8$ crystal-field level up to the $^2G(2)_{9/2}\, b\Gamma_8$ level. The assignments of these spectra confirm our energy-level scheme for $Cs_2NaErCl_6$.[3] Figures 1(a)–(c) show the transitions which terminate upon the $^4I_{15/2}$, $^4I_{13/2}$, and $^2H(2)_{11/2}$ multiplet terms, with the positions of the highest energy zero-phonon lines marked. From the spectral analyses, the lowest $^2H(2)_{9/2}$ level, $a\Gamma_8$, is located at 36 236 cm^{-1}. Figure 1(b) is more clearly resolved, and at higher sensitivity than the uv-upconverted signal reported (Fig. 4 in Ref. 1), but clearly corresponds to the same emission transition. These results therefore enable both the identity and location to be made for the upconversion luminescent state, following the excitation by a pulsed laser at $\sim 18\,270$ cm^{-1} in the experiment of Hasan *et al.* We are unable to distinguish whether the excitation mechanism in the latter experiment is due to excited-state absorption from $^4S_{3/2}\, \Gamma_8$, or to two-photon absorption, but evidence from the upconversion excitation spectrum apparently supported the latter
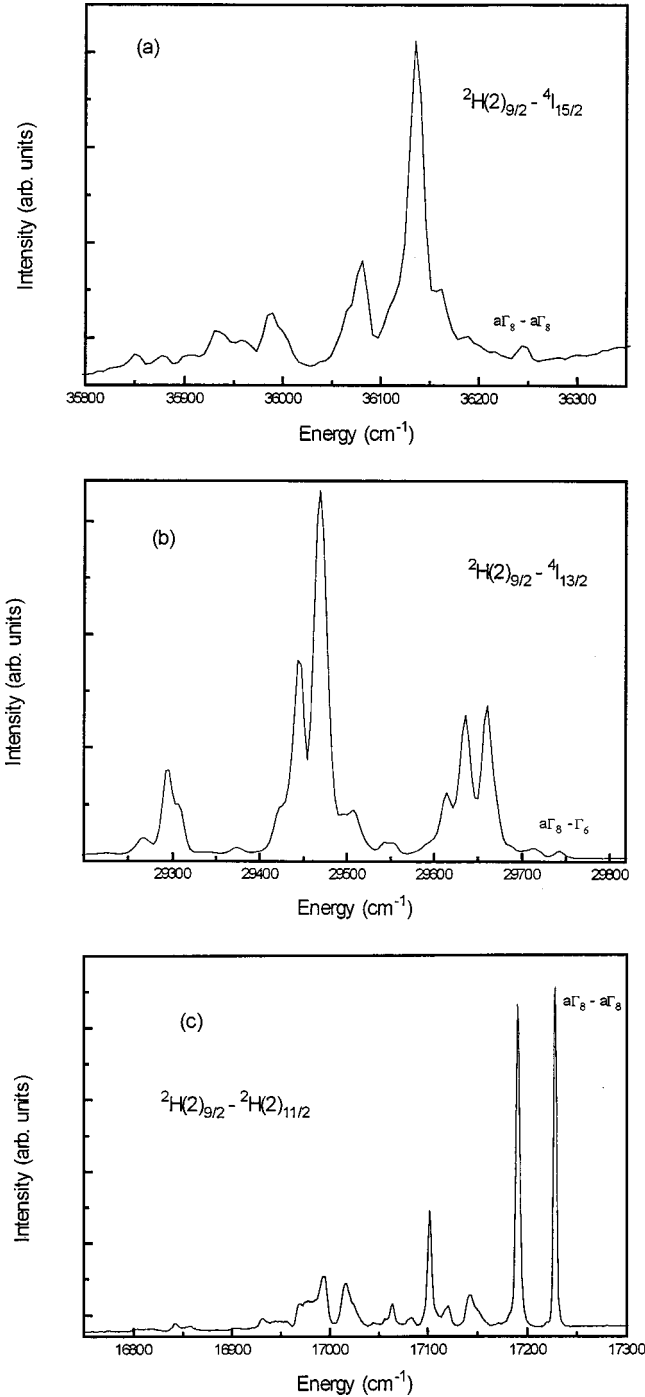
FIG. 1. 273.9-nm excited emission spectrum of $Cs_2NaErCl_6$ at 15 K: (a) $^2H(2)_{9/2}$-$^4I_{15/2}$ transition; (b) $^2H(2)_{9/2}$-$^4I_{13/2}$ transition; (c) $^2H(2)_{9/2}$-$^2H(2)_{11/2}$ transition. The sample was housed in an Oxford Instruments closed cycle cooler cryostat, and was excited by the Stokes H_2-shifted harmonics of a Nd-YAG pulsed laser. The emission was collected at 90° and passed through an Acton 0.5-m spectrometer, with a liquid-N_2-cooled SDS 9000 charge-coupled device (Photometrics). The spectral resolution was between 2 and 4 cm^{-1}. Spectral calibration was performed using various standard lamps and the wavelengths were corrected to vacuum.

mechanism.[1] Since the energy of the $^2H(2)_{9/2}$ $a\Gamma_8$ level determined herein is ~100 cm^{-1} higher than that postulated in Ref. 1, a more plausible two-photon absorption mechanism $^4I_{15/2}$ $a\Gamma_8 \rightarrow ^2H(2)_{9/2}$ $a\Gamma_8 + \nu_1$ is established be-

cause the derived energy of ν_1 is then ~300 cm^{-1}.

II. ENERGY-LEVEL PARAMETRIZATION OF $Cs_2NaErCl_6$

The accurate determination of the $^2H(2)_{9/2}$ $a\Gamma_8$ energy level permits a reassessment of the energy-level parameterization scheme of $Cs_2NaErCl_6$ in Ref. 1. It appears that 40 (two- or four-degenerate) levels of Er^{3+} in this lattice were fitted with mean deviation,

$$\delta = \sum_{i=1,N}(E_{i,\text{obs}} - E_{i,\text{calc}})^2/N)^{1/2} = 9.7 \,\text{cm}^{-1},$$

by varying various subsets of 23 parameters.[1] The energy levels were generally similar to those reported previously,[4] except for the $^4I_{9/2}$ levels, which all differed in energy by 12 cm^{-1}. These new assignments were made from the $^4I_{9/2}$ emission and excitation spectra, but these spectra had previously been reported at higher sensitivity[5] together with those of many other emissive transitions terminating upon $^4I_{9/2}$.[6–8] A previous fit of 41 levels of Er^{3+} in $Cs_2NaErCl_6$ by varying only seven parameters gave $\delta = 18.4$ cm^{-1}.[3] The major improvements in the fit of Hasan *et al.* were in the higher energy levels $^2G(2)_{9/2}$ and $^4G_{11/2}$ which were poorly fitted in Ref. 3. However, the extent to which the overparametrization has contributed to the better fit is questionable. The $^2H(2)_{9/2}$ $a\Gamma_8$ level was *calculated* to be at 36 156 cm^{-1} in Ref. 1, but our experimental study shows this energy to be inaccurate by 82 cm^{-1}, which is greater than eight times the mean deviation in Ref. 1. The ability to predict, rather than parametrize, upper $4f^n$ crystal-field level energies is thus questionable.

III. KINETICS OF THE BLUE UPCONVERSION PROCESS TO $^2G_{9/2}$ UPON EXCITATION INTO $^4F_{9/2}$

The rate equations involving blue upconversion process $[(^4I_{9/2}, {}^4I_{9/2}) \rightarrow (^4I_{15/2}, {}^2G_{9/2})]$ are given in Ref. 1. These equations can be solved either analytically or numerically. Analytically, the approximation has to be made that the effect of the upconversion process upon the population of the $^4I_{9/2}$ state is negligibly small compared with the linear terms in the rate equation describing the radiative decay and branching decay from the $^4F_{9/2}$ state. The time behavior of $^2G_{9/2}$ is then given as

$$\frac{1}{2}W\left(\frac{N\alpha k_1}{k_2-k_1}\right)^2\left(\frac{e^{-2k_1t}-e^{-k_3t}}{k_3-2k_1}+\frac{e^{-2k_2t}-e^{-k_3t}}{k_3-2k_2}\right.$$
$$\left.+\frac{2}{k_3-k_1-k_2}(e^{-k_3t}-e^{-k_1t-k_2t})\right),$$

where W is the two ion upconversion rate; N is the total number of active ions; α is the branching decay rate from $^4F_{9/2}$ to $^4I_{9/2}$; k_1, k_2, and k_3 are, respectively, the radiative decay rates of the $^4F_{9/2}$, $^4I_{9/2}$, and $^2G_{9/2}$ states. We find that using this expression, a line equivalent to the one shown in Fig. 5 of Ref. 1 can be plotted *without fitting W and N*.

On the other hand, the numerical solution of the differential equations, without taking any approximations, requires fitting of the parameters W and N. It is noted that the con-

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straint of N equal to the sum of the populations of the $^4F_{9/2}$, $^4I_{9/2}$, and $^2G_{9/2}$ states at time $t\neq0$, although correct for continuous excitation, is *incorrect* for pulsed excitation, because the total number of active ions will be smaller than N after $t=0$ due to the radiative decay of the various excited states. We have taken the initial conditions of the populations of $^4F_{9/2}=N$, $^4I_{9/2}$ and $^2G_{9/2}=0$, and α is found to be 35 s^{-1}.[6] Our fitting results show that the magnitudes of the W and N are anticorrelated, i.e., the larger the value of N, the lower the upconversion rate is required to obtain a good curve fitting. However, for a certain value of N, a broad range of values of W can yield a very good simulation of

temporal behavior of $^2G_{9/2}$ luminescence. This demonstrates the insensitivity of the fitting method for obtaining the upconversion rate W. As an alternative approach, we are now performing the direct calculation, employing a nondiagonal phonon-assisted energy-transfer model, to estimate the energy-transfer rate of this upconversion process.

[1] Z. Hasan, L. Biyikli, M. J. Sellars, G. A. Khodaparast, F. S. Richardson, and J. R. Quagliano, Phys. Rev. B **56**, 4518 (1997).
[2] P. A. Tanner, Chem. Phys. Lett. **145**, 134 (1988).
[3] P. A. Tanner, V. V. R. K. Kumar, C. K. Jayasankar, and M. F. Reid, J. Alloys Compd. **215**, 349 (1994).
[4] P. A. Tanner, A. DePiante, F. S. Richardson, and M. F. Reid, Mol. Phys. **60**, 1037 (1987).
[5] P. A. Tanner, Mol. Phys. **60**, 1037 (1987).
[6] P. A. Tanner, Mol. Phys. **63**, 365 (1988).
[7] Z. Hasan and F. S. Richardson, Mol. Phys. **45**, 1299 (1982).
[8] A. DePiante, F. S. Richardson, and Z. Hasan, J. Chem. Phys. **82**, 1102 (1985).