Unusual Luminescence from Crystals Containing Eu^{2+}

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Luminescence at 368 nm from crystals containing Eu^{2+} exhibits the small spectral shifts from host to host typical of a parity-forbidden rare-earth transition, and yet has the emission oscillator strength ($f \gtrsim 1$) of a highly allowed transition. It is improbable that this anomaly can be trivially resolved, e.g., in terms of measurement errors, stimulated emission, or impurity involvement.

We report evidence of unusual properties for a luminescence emitted by europium chalcogenides[1] and cubic fluorites (CaF_2, SrF_2, BaF_2) dilutely doped with Eu^{2+} (Fig. 1). Although the emission exhibits the small spectral shifts from host to host typical of a forbidden inner-shell rare-earth transition,[2] the emission oscillator strength is anomalously large ($f \geqslant 1.3 \pm 0.7$). In addition, the luminescence occurs with high quantum efficiency ($\varphi \approx 0.14$) only from small ($\sim 2 \times 10 \times 10$ μm^3) crystals or localized regions of larger crystals.[3]

A lower limit on f can be obtained from φ and the luminescence delay τ_d. (Here τ_d is defined as the delay by which the luminescence pulse maximum lags the laser-pulse maximum, see Fig. 2.) The measurement of φ was made by comparing the luminescence signal with that of the laser pump beam scattered from a MgO surface. This technique was in turn crosschecked by measuring φ for a well-known standard, 9,10-diphenylanthracene (DPA) in benzene. The argon ion laser was operated at 3638 Å and 640 W/cm^2 for these measurements.

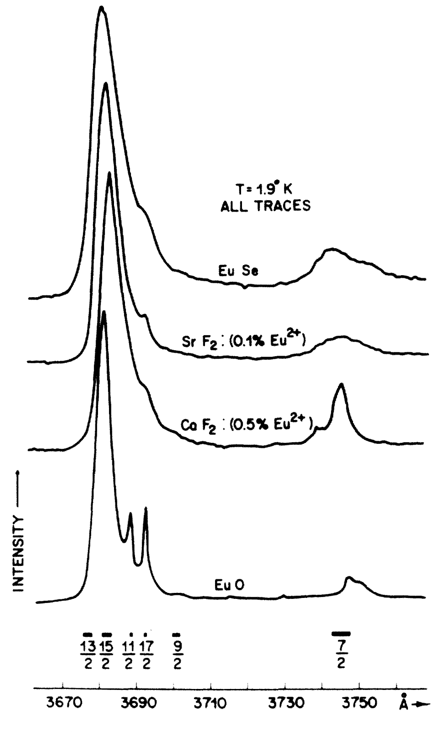

FIG. 1. Eu^{2+} uv luminescence versus wavelength for various hosts.

The expression for φ using conventional corrections[4] is

$$\varphi = \eta \int I_L(\omega)\,d\omega \Big/ \int I_P(\omega)\,d\omega,$$

$$\eta = 8n[n^2 - \sin^2(\varphi_L)]^{1/2} R_m \cos(\varphi_P)/T^4 \cos(\varphi_L).$$

$I_L(\omega)$ and $I_P(\omega)$ are the luminescence and pump intensities, respectively, as a function of frequency ω, n (1.66 ± 0.06) the refractive index of the luminescing medium, φ_L ($>0°$) the angle of observation of the luminescing sample measured with respect to the normal to the surface,[5] φ_P ($45 \pm 4°$) the angle of observation of the scattered laser radiation measured with respect to the normal to the MgO surface, T (0.92 ± 0.02) the transmissivity of the Dewar windows at 364 nm including reflection losses, and R_m (0.96 ± 0.02) the diffuse reflectivity of MgO at 364 nm, giving $\eta_{\min} = 21.6 \pm 2.8$. Note that $\eta_{\min}$ is a *lower limit* on η.[5] The probable error in η has been obtained by taking the square root of the sum of the squares of the probable errors in the factors comprising $\eta_{\min}$. The assumption that the laser radiation scattered off MgO obeys Lambert's law was checked experimentally and found to be valid within $\sim 5\%$ of the measured value. The values of the integrals were obtained by measuring the areas of the spectral traces with a pla-

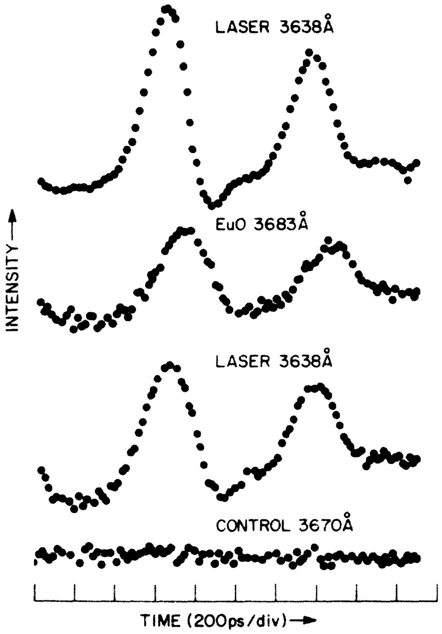

FIG. 2. Luminescence and laser pump versus time. Traces were taken sequentially in time with the order proceeding from top to bottom.

nimeter and found to be reproducible to ± 3% of the measured values. A factor of 2.0 ± 0.1 enters as a correction for reabsorption.[6] For the well-known standard DPA at $3 \times 10^{-3} M$ in benzene we have $n = 1.5 \pm 0.01$, $\varphi_L = 45 \pm 5^\circ$, and T^{-4} is replaced by T^{-2} since only two quartz windows were involved. We obtain $\varphi = 0.95$ which is within the expected probable error (± 12%) of the generally accepted value (0.84) for DPA.[7]

As evidence against errors caused by involvement of stimulated emission, measurements of φ were made at 640 W/cm^2 which is below the intensity for onset of nonlinear processes in these materials (typically 10^4 W/cm^2). Also, φ was *unchanged* with decreasing pump intensity over 6 *orders of magnitude*, 640 W/cm^2 to 0.64 mW/cm^2 (detection threshold). Furthermore, the spectrum does not change with decreasing pump intensity (640 W/cm^2 to 0.64 mW/cm^2) and no evidence of stimulated emission in the form of directionality of emission, line narrowing, or sharp thresholds is observed in this entire intensity regime.

The measurement of the luminescence delay τ_d (80 ± 40 psec, see Fig. 2) was also made at 640 W/cm^2 and at lower intensities, 160 W/cm^2. No intensity dependence was observed. This luminescence was examined for a delayed component trailing the primary pulse; however, none was found to within experimental accuracy (~12% of peak intensity). Traces of the laser pulse were taken before and after the luminescence trace to demonstrate system stability in time (Fig. 2). In addition a trace at 3670 Å was run to show that no laser radiation passed through the spectrometer at the luminescence wavelength (3683 Å). The optical paths for the scattered laser light and luminescence were identical except for a negligible difference of the order of ~100 μm (for grating rotation), ruling out errors due to path differences.

A *lower limit* on f in emission can now be calculated. First, even if the entire departure of φ from unity is due to nonradiative shortening of the excited-state lifetime τ_e, the actual radiative lifetime τ_r can be no longer than τ_e/φ. Furthermore, τ_e can be no longer than τ_d. Hence we can state with assurance that $\tau_r \leq \tau_d/\varphi$. Replacing τ_r by this limit in the formula for f in emission[8] gives the lower limit on f of $f_{\min} = 1.5\varphi(g_u/g_l)\lambda^2/\tau_d$. Here λ is the optical wavelength in centimeters, g_u and g_l are the statistical weights of the upper and lower states, respectively, and τ_d is in seconds. To obtain g_u/g_l we use as a tentative assignment of the transition the ${}^6I$-${}^8S_{7/2}$ in Eu^{2+}.[9] (See Fig. 1 for J-value assignments.) The dominant feature is assigned as ${}^6I_{15/2}$-${}^8S_{7/2}$, giving $g_u/g_l = 2$. For the case shown in Fig. 2, $\varphi = 0.14 \pm 0.02$, giving $f_{\min} = 7.1 \pm 3.6$. This is a very large f, exceeding that expected classically for a single electron. To estimate the smallest possible f consistent with our measurements, we take the point of view that our excited-state assignment could be in error and let g_u/g_l have the smallest value consistent with typical solid-state selection rules. That is, given a ground-state ${}^8S_{7/2}$ level and $\Delta J_{\max} = 6$, the smallest value for g_u/g_l would be $\frac{8}{21}$, giving $f_{\min} = 1.3 \pm 0.7$. This is a worst-case estimate and yet exceeds the typical f for transitions exhibiting such small shifts by a least 4 orders of magnitude.

A remaining trivial explanation which must be considered is that some impurity with large f is common to all these hosts as a surface contaminant. An impurity incorporated in the host would not provide a trivial explanation since strong impurity lines shift markedly from host to host.[2] Contaminants from the Dewar or sample mount are unlikely since changing sample mounts (copper, aluminum, and silver) as well as Dewars did not remove the signal. Surface contaminants on the samples are unlikely since freshly cleaved surfaces contain microcrystals giving this luminescence as do surfaces which have had the original surface layer removed by sandblasting or by polishing with polishing agents which do not emit this luminescence. In addition, the obvious surface contaminants such as those produced by interaction of europium with the atmosphere, Eu_2O_3, do not yield this signal. Finally, the impurity picture requires the coincidence that the impurity mimic the $Eu^{2+}\,{}^6I$-${}^8S_{7/2}$ multiplet transition as to number of components, relative intensities, component spacing, and spectral position. While this is possible it seems unlikely.

We note in closing that a large oscillator strength in emission is not necessarily inconsistent with a low oscillator strength per ion. That is, if the *single-quantum* excited state involves a large number of ions oscillating in phase, as in a zero-wave-vector exciton, the oscillator strength for this phased array can become very large even if the oscillator strength per ion is small.[10] While we do not claim to have proved the existence of such a state we do point out that such an occurrence would resolve the above anomaly.

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[1] D. Hulin, C. Benoît à la Guillaume, and J. Hanus, C. R. Acad. Sci., Ser. B 272, 1207 (1971). This paper attributes the emission to magnon sidebands, an interpretation which we regard as unlikely given the occurrence of the emission from nonmagnetic hosts.

[2] Small spectral shifts from host to host are uncommon except for rare-earth transitions in which both initial and final states belong to the well-shielded $4f$ configurations. These transitions are necessarily parity forbidden and rarely have $f > 10^{-4}$. In particular, the analogous transitions in Gd^{3+}, the isoelectronic analog of Eu^{2+}, have $f \leq 10^{-6}$ to 10^{-7}. B. G. Wybourne, Phys. Rev. 148, 317 (1966).

[3] We are indebted to Mme. Hulin for informing us that this emission occurred preferentially from localized regions of their EuO crystals. Examination of these regions in our crystals revealed them always to contain microcrystals or surface projections, and we subsequently prepared our samples as arrays of such microcrystals. Sizes were determined by electron microscopy.

[4] J. N. Demas and G. A. Crosby, J. Phys. Chem. 75, 991 (1971).

[5] With our small samples it is difficult to measure φ_L with much precision. Hence, we take φ_L as zero, making the expression for η a lower limit since φ is a monotonically increasing function of φ_L.

[6] It is difficult to assign a probable error for this correction; however, the major source of error is usually re-emission following reabsorption. In our case this amounts to less than 5% of the absorbed luminescence. Hence, we assign a probable error of this order.

[7] J. B. Birks, Chem. Phys. Lett. 17, 370 (1972).

[8] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge Univ. Press, Cambridge, England, 1961), p. 97.

[9] Considerable absorption and luminescence data on Eu^{2+} $4f^7$-$4f^7$ transitions taken by us as well as a theoretical calculation by H. M. Crosswhite suggest this assignment.

[10] Oscillator-strength enhancement in the case of zero-wave-vector excitons is discussed, e.g., by E. I. Rashba and G. E. Gurgenishvili, Fiz. Tverd. Tela 4, 1029 (1962) [Sov. Phys. Solid State 4, 759 (1962)]. While our case must be necessarily different since the emission occurs from both pure and dilute samples, and zero-wave-vector excitons have been observed only in dilute systems, a theoretical calculation by one of us (R.L.F.) suggests that such enhancements are possible in crystals containing Eu^{2+} and could be extremely large. In this model, as in the case of zero-wave-vector excitons, the excited state involves a single excitation quantum and does not depend on stimulated emission or nonlinear processes for its occurrence. Also, the small volume of the state would cause diffraction to destroy directional emission caused by the common phasing.