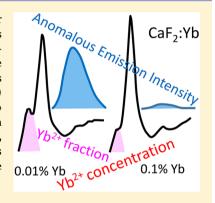


# Evidence That the Anomalous Emission from CaF<sub>2</sub>:Yb<sup>2+</sup> Is Not Described by the Impurity Trapped Exciton Model

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ABSTRACT: Yb-substituted CaF2 exhibits an anomalous red-shifted luminescence after UV excitation, attributed to the relaxation of impurity trapped excitons (ITE). CaF<sub>2</sub>:Yb is the archetype system for this model, in which the Yb2+ ions can be excited into a longlived (ms) exciton state. Upon de-excitation, the emission intensity should be proportional to the Yb2+ concentration, but that could not be checked when this model was first proposed. Using the X-ray absorption near edge structure (XANES) technique, we determine the fractions of Yb<sup>2+</sup> and Yb<sup>3+</sup> for low Yb concentrations, 0.01% to 0.1%, and thus determine the net concentration of Yb2+. A comparison with luminescence data shows that the intensity is not proportional to the Yb<sup>2+</sup> concentration, and only a fraction of Yb2+ ions contributes to the anomalous luminescence. This is inconsistent with the ITE model and illustrates the importance of checking the dependence of the emission intensity on the Yb<sup>2+</sup> concentration.



n a large number of lanthanide-doped crystals there is a large Stokes shift of the luminescence emission upon UV excitation, particularly for Yb2+ and Eu2+ ions. The optical properties of CaF<sub>2</sub>:Yb<sup>2+</sup> were first reported about 50 years ago, 2,3 and the unusually large red-shift and bandwidth of the luminescence emission were considered anomalous. A model to describe such systems was developed in the 1980s by McClure and others, 1,4,5 in which the optical center is called an impurity trapped exciton (ITE). Dorenbos1 provides a long list of potential ITE systems with anomalous emissions, mostly with Yb and Eu dopants.

Upon UV excitation (within this model), one of the 4f14 electrons of Yb<sup>2+</sup> is excited to the 4f<sup>13</sup>5d state; this state decays to the exciton state in which the excited electron forms a delocalized extended state on neighboring metal atoms.<sup>5</sup> The resulting Yb3+ ion plus the delocalized electron state forms the transient ITE state-a bound electron-hole pair. While in the ITE state, the cube of surrounding F<sup>-</sup> atoms should collapse slightly (again a transient effect), leading to a decreased Yb-F bond distance, by  $\sim$ 0.2 Å, 4 which explains the bandwidth of the emission. The ITE model has been accepted in the literature for over 30 years 1,4-8 and continues to be used in the current literature. 9,10

Recently, however, Barandiarán and Seijo<sup>11</sup> have examined the ITE hypothesis by means of ab initio relativistic quantum chemical calculations. The results for Yb2+ in CaF2 allow the authors to conclude that none of the electronic states of the Yb<sup>2+</sup> active centers can be considered responsible for the anomalous emission; hence the need of direct experimental scrutiny of the ITE model.

Yb substitutes for Ca in CaF<sub>2</sub>:Yb and forms several defects. Clusters form at higher concentrations, 12,13 while the anomalous emission centers form at much lower concentrations. In the ITE model, the number of excitons excited by UV should be proportional to the number of Yb<sup>2+</sup> ions present. At the time the ITE model was first developed, there was no way to measure the Yb<sup>2+</sup> concentration in order to check for a linear dependence of anomalous luminescence intensity. In fact only recently has this been possible for very low defect concentrations down to 0.01% Yb. Here we provide direct experimental evidence that the ITE model cannot explain anomalous luminescence in CaF2:Yb; first the anomalous luminescence intensity is not proportional to the Yb<sup>2+</sup> concentration, and second, only a small fraction of Yb2+ ions are involved in anomalous emission.

Normalized Yb L<sub>III</sub> absorption edges are plotted in Figure 1 for three concentrations: 0.01, 0.05, and 0.1% Yb; the plots are normalized well above the edge. The  $L_{III}$  edge has two peaks separated by about 7 eV: the lower one (8942 eV) is associated with Yb2+, while the upper one (8949 eV) is for Yb3+. For the

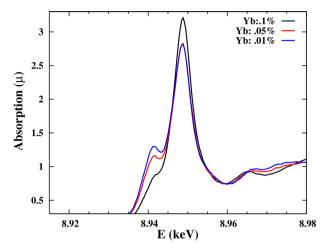
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**Figure 1.** Normalized Yb  $L_{\rm III}$  edge absorption coefficient,  $\mu$ , as a function of total Yb concentration (0.01, 0.05, and 0.1% Yb) for fresh samples at 10 K. The Yb<sup>2+</sup> peak is at 8942 eV, while the Yb<sup>3+</sup> peak is at 8949 eV. The Yb<sup>3+</sup> peak still dominates even at the lowest concentration, 0.01% Yb.

higher concentration samples the  $Yb^{3+}$  peak dominates, and only below  $\sim\!0.05\%$  is there a separate, well-defined  $Yb^{2+}$  peak; this peak is largest for the 0.01% Yb sample. Hughes-Currie et al. recently showed for higher Yb concentrations that the  $Yb^{2+}$  peak grows as the Yb concentration is decreased. Here we extend such measurements down to lower concentrations.

A fit of the  $L_{\text{III}}$  edge for the 0.01% Yb sample is shown in Figure 2. The XANES spectrum is fit to a sum of two pseudo-

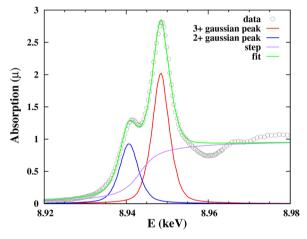
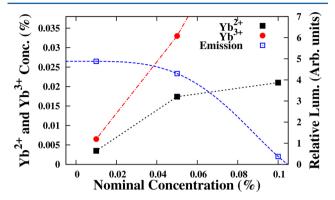


Figure 2. Fit of the  $L_{\rm III}$  edge for the 0.01% Yb sample. The normalized data are shown as circles while the fit is shown as a green line. The blue and red pseudo-Voigt peaks show the contributions for Yb<sup>2+</sup> and Yb<sup>3+</sup> respectively; the main step function is shown as a purple line.

Voigt peaks plus a step function; these are plotted below the data. Similar fits were done for the other samples. In converting to fractional concentrations, one needs the relative matrix elements for the 2+ and 3+ transitions; often these are assumed equal. However, Hughes-Currie et al. 4 used the ratio  $M^{2+}/M^{3+}$  = 0.656 from Eu solutions. In a separate experiment (unpublished), we have determined this ratio for Yb to be 0.93 in CaF<sub>2</sub>, and that value is used here. Once the fractions f(2+) and f(3+) of Yb<sup>2+</sup> and Yb<sup>3+</sup> are known, the estimated concentrations of the two valence states are approximately given by  $f(2+)n_o$  and  $f(3+)n_o$ , where  $n_o$  is the nominal

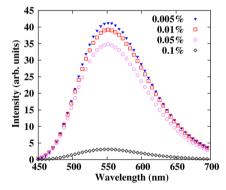
concentration. The concentrations of Yb<sup>2+</sup> and Yb<sup>3+</sup> are plotted in Figure 3 as a function of  $n_o$ . The Yb<sup>2+</sup> concentration tends to saturate even near 0.05% Yb.



**Figure 3.** Estimated Yb<sup>2+</sup> and Yb<sup>3+</sup> concentrations and the relative emission intensity (see Figure 4) as a function of the nominal concentration  $n_o$  (0.01–0.1% Yb) for fresh samples. It is clear that the emission intensity is not directly proportional to the concentration of Yb<sup>2+</sup> ions.

In Figure 3, we have used the nominal concentration  $n_0$  instead of the actual concentration  $n_1$ ; however,  $n_1$  usually scales with  $n_0$  and typically  $n < n_0$ . In addition, the ratio  $S = n/n_0$  is nearly constant at low concentrations (S is often called the segregation coefficient), and small variations in S will slightly shift the points on the Yb<sup>2+</sup> concentration scale. However, as long as this ratio does not vary by more than 10-20%, the order of the points will not change, and the overall result remains; i.e., the anomalous emission decreases as the concentration of Yb<sup>2+</sup> increases.

The anomalous emission spectra for these samples are plotted in Figure 4. In order to obtain relative intensities, the



**Figure 4.** Anomalous emission spectra are plotted for the samples studied using XANES, keeping the geometry the same and the incident UV power level constant.

geometry was kept the same (same orientation and sample thickness), and the incident UV power level was constant. The relative intensities extracted from these data are also plotted in Figure 3; in contrast to the variation of the Yb<sup>2+</sup> concentration, the anomalous emission intensity decreases as the nominal concentration increases.

The results presented above are inconsistent with the accepted ITE model for anomalous luminescence from Yb centers in  $CaF_2$ . As the Yb concentration is reduced, from 0.1 to 0.01% (Figure 3), the number of Yb<sup>2+</sup> ions decreases but the

anomalous emission increases dramatically instead of decreasing; the inconsistency from 0.1 to 0.01% Yb is nearly a factor of 90. Thus, only a small fraction of the Yb<sup>2+</sup> ions are involved in this concentration range.

A possible new model to describe the anomalous emission in CaF<sub>2</sub>:Yb is that proposed by Barandiarán and Seijo, <sup>11</sup> according to which the anomalous emission is an intervalence charge transfer (IVCT) between Yb2+ and Yb3+ impurities. The same interpretation has been used to understand that X-ray excitation triggers the anomalous emission of Yb in CaF2 but not in SrF<sub>2</sub>. According to the mechanism proposed for the UV excited anomalous emission, 11 only a fraction of the initially excited Yb2+ would ultimately lead to IVCT luminescence because the nonradiative transitions (step II of model) branch along several pathways, several of which go either directly to the ground state or indirectly via Yb3+ emissions. Such pathways do not lead to luminescence emission near 550 nm. Also, it has been suggested from experiments that it is only the nonlocally compensated (cubic) trivalent ions which participate in the charge transfer from divalent to trivalent lanthanide ions (e.g., from Eu<sup>2+</sup> to Sm<sup>3+</sup> in CaF<sub>2</sub>).<sup>17</sup> In oxygen-free CaF<sub>2</sub>:Yb samples, charge compensation is attained by fluoride ions occupying nearby or distant interstitial sites leading to local or nonlocal compensation and mostly  $C_{4\nu}$  or cubic Yb<sup>3+</sup> centers, respectively (cf. ref 18 and references therein). It is reasonable to expect that these cubic nonlocally compensated Yb3+ ions are more probable as the concentration is lowered and hence the IVCT between cubic Yb2+ and Yb3+ centers appears to be in qualitative agreement with the large observed increase in anomalous emission for low Yb concentrations.

These results also raise questions about the many other centers with anomalous emissions that are usually assumed to be described by the ITE model. The above results do not invalidate the ITE model but rather point out the importance of measuring the concentration of the +2 ions in each sample and determining whether the anomalous emission intensity varies linearly with it. It may be that many of these systems, currently assumed to be described by the ITE model, do not have a linear relationship between emission intensity and Yb2+ concentration; such cases may be better described by the IVCT model. Recent advances at synchrotrons in the past decade (higher Xray intensity and better fluorescence detectors) now make it relatively straightforward to determine 2+/3+ ratios for rare earths at very low impurity concentrations. In addition, since only a fraction of Yb2+ ions are involved for CaF2:Yb, a new challenge arises in finding ways to probe different types of Yb sites and thus better test the IVCT model.

# **EXPERIMENTAL METHODS**

The CaF<sub>2</sub>:Yb samples were grown as described in ref 14. For the 0.1 and 0.05% Yb samples, a small piece was powdered and mounted on scotch tape as described in ref 19; the XANES data were collected in fluorescence mode on beamline 4–1 at the Stanford Synchrotron Radiation Lightsource (SSRL) using a small Ge fluorescence detector (16 elements). For 0.01% Yb, a thin, polished, single crystal was used, together with a 100 element fluorescence detector on the high X-ray intensity beamline 11–2 at SSRL. Because of Bragg reflections from the single crystal, some detector channels had large (Bragg) spikes at some energies in a scan, and these channels had to be removed. Since Bragg peaks are sensitive to the orientation of the single crystal, the appropriate channels had to be determined each time a sample was mounted. Typically 50–

70 channels had no Bragg spikes and were used for the XANES data collection. The package RSXAP<sup>20</sup> was used for data reduction and analysis, and follows standard procedures. The anomalous emission experiments (Figure 4) were carried out at the University of Canterbury NZ, and the methods and apparatus are described in refs 8 and 10. The UV excitation was at 364 nm.

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Notes

The authors declare no competing financial interest.

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