

# CHAPTER 1

## INTRODUCTION

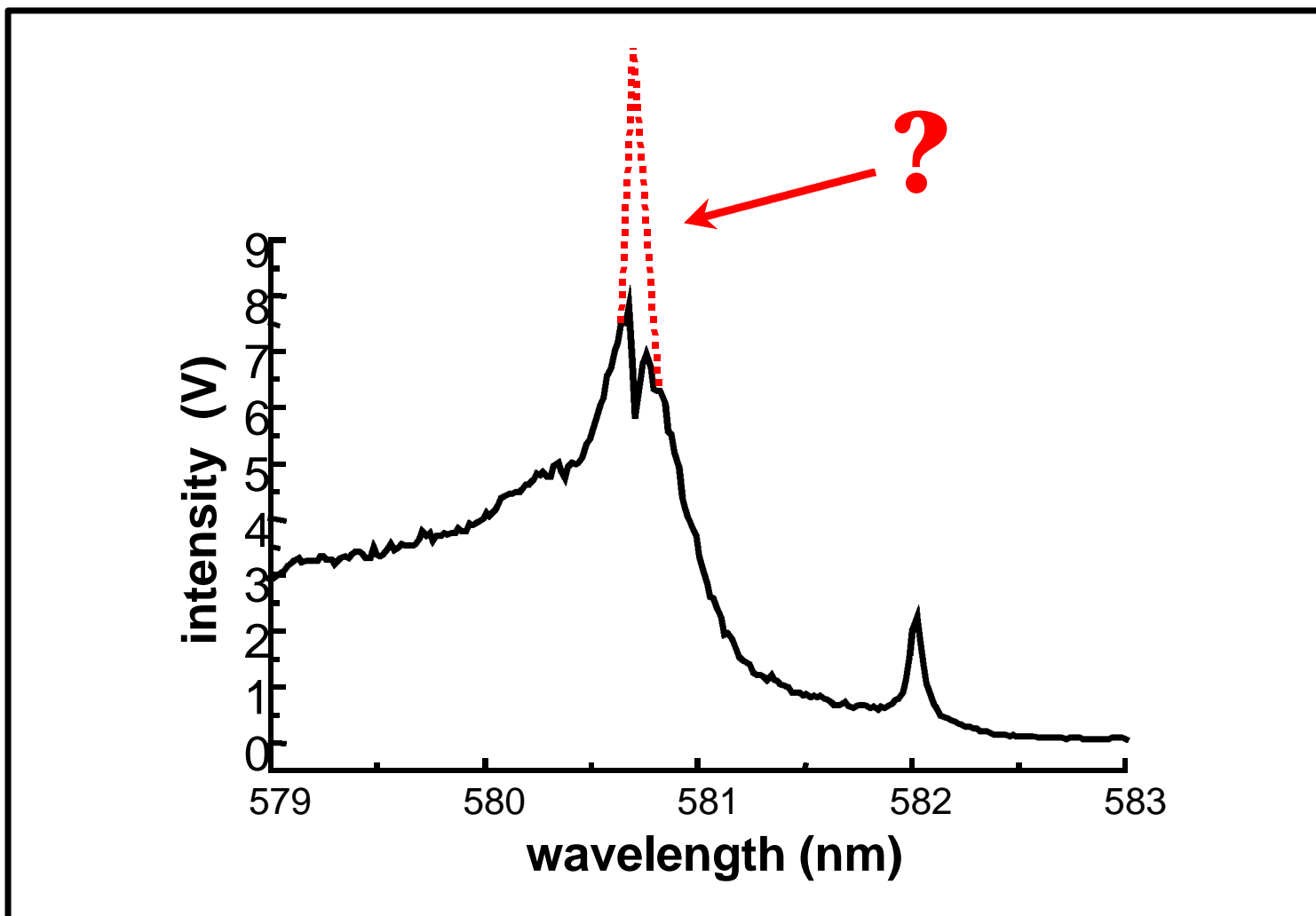
### 1.1 RESEARCH OBJECTIVE

During investigations into the spectra and dynamics of nano-sized  $\text{Eu}_2\text{O}_3$ , Bipin Bihari observed an apparent saturation dip in the excitation spectra of  $\text{Eu}_2\text{O}_3$  nanocrystals (refer to Figure 1). The cause of this apparent saturation dip was unknown. The goal of my research was to determine the nature of this saturation effect in  $\text{Eu}_2\text{O}_3$  and this thesis presents the results of this investigation.

The following is a list of the possible explanations that were investigated:

- (1) Experimental artifacts.
- (2) Direct energy transfer to luminescence traps.
- (3) Two-photon absorption, excited-state absorption, and second harmonic generation.
- (4) Cooperative luminescence and cooperative sensitization.
- (5) Superfluorescence and amplified spontaneous emission.
- (6) Localized heating.
- (7) Upconversion by energy transfer.

Each of these processes is described in more detail in the results & discussion chapter.



**Figure 1.** Fluorescence excitation spectrum of Eu<sub>2</sub>O<sub>3</sub> (cubic-phase, micron-sized crystals). Fluorescence measured at  $\lambda_{em} = 612\text{-nm}$ . The dashed line shows the excitation peak at low laser intensity.

## **1.2 SIGNIFICANCE OF OBJECTIVE**

$\text{Eu}_2\text{O}_3$  is a lanthanide oxide utilized for its luminescent and catalytic properties.<sup>[1]</sup> In  $\text{Eu}_2\text{O}_3$  the close proximity of  $\text{Eu}^{3+}$  ions makes energy transfer possible. Excitation energy can migrate to traps where it can be quenched nonradiatively. (For additional information regarding energy transfer refer to the Appendix.) This process of energy transfer to traps is called concentration quenching, and makes luminescence from  $\text{Eu}_2\text{O}_3$  too inefficient for use as a commercial phosphor. It is however commonly used as a source of  $\text{Eu}^{3+}$  ions in the production of other phosphors and laser materials. In these materials the  $\text{Eu}^{3+}$  ions are dispersed within an insulating host to eliminate energy transfer and concentration quenching.

Decades of research have focused on determining the mechanisms of energy transfer and excited-state interactions in the solid phase.<sup>[2-4]</sup> One recent example of the benefits of this research is the successful development of quantum dot lasers. A quantum dot is a nanometer-sized bit of semiconductor. For over ten years attempts to synthesize quantum dots that could be made to lase failed because of excited-state interactions. The interaction, known as Auger recombination in semiconductors, is identical to the process of upconversion by energy transfer in concentrated lanthanide systems. In both cases the excited-state interactions result in a loss of excitation energy by a nonradiative pathway. In order for lasing to take place in quantum dots,

stimulated emission must develop faster than Auger recombination. This was realized by packing the quantum dots into a small volume so that a photon emitted from a quantum dot can then stimulate emission from another quantum dot before the Auger process wins out.<sup>[5]</sup> It was not until the effects of nonlinear luminescence quenching were understood that quantum dot lasers became a reality, demonstrating the value of continued research into mechanisms of energy migration and excited-state interactions.<sup>[5]</sup>

Understanding nonlinear luminescence quenching is also important when developing mathematical models of energy transfer. One general assumption required for mathematical modeling is that the excited-state concentration is low enough that excited-state interactions do not occur. However, the excited-state concentration at which this is a safe assumption depends on the system. Often the influence of excited-state interactions on luminescence decay is ignored, which might explain why attempts to model energy migration in  $\text{Eu}_2\text{O}_3$  by Buijs had limited success.<sup>[6]</sup> The difficulties were assumed to be due to the complex nature of the energy migration, which is a reasonable assumption since energy transfer in  $\text{Eu}_2\text{O}_3$  is predicted to occur by multiple mechanisms.<sup>[6]</sup> However nonlinear luminescence quenching due to excited-state interactions may also be a factor. The possibility that nonlinear luminescence quenching occurs in  $\text{Eu}_2\text{O}_3$  was investigated as an explanation for the saturation dips observed by Bihari.

## **1.1 BACKGROUND ON Eu<sub>2</sub>O<sub>3</sub>**

Europium is a member of the lanthanide series of elements, characterized by a partially filled 4f-electron shell. Lanthanide ions have the fairly unique property of sharp spectral lines in the solid phase. Generally the optical spectra observed for ions in solids is continuous and broad. For the majority of inorganic solids, interactions between ions cause line broadening and overlapping of spectral lines resulting in continuous spectra of limited structure.<sup>[7]</sup> Sharp 4f→4f spectral lines are possible for lanthanides because their 4f electron orbitals lie within the shell of outer 5s and 5p electrons. The 4f electrons are largely shielded from the surrounding crystal field and are not involved in chemical bonding. However, some interaction with the crystal field does take place, because, depending on its symmetry, higher energy electronic states of opposite parity can be mixed with the 4f electronic states. It is this mixing of states which makes electronic dipole transitions possible.<sup>[8]</sup> Without mixing only magnetic dipole and quadrupole transitions could occur, and all optical transitions would be electric dipole forbidden (Laporte selection rule).<sup>[8]</sup> Ultimately any transition occurring within the lanthanide's 4f-orbitals is going to be only weakly coupled to crystal lattice vibrations, and the resulting spectra will appear free-ion-like in character.<sup>[1]</sup> The exceptions are higher energy transitions to levels above the 4f<sup>n</sup> electronic states, viz. 4f<sup>5</sup>→4f<sup>n+1</sup>5d transitions and/or charge-transfer transitions which are parity allowed. Unlike the 4f -electrons, the 5s and 5p shells do not

shield the 5d shell. These 4f→5d transitions are greatly influenced by their surroundings and result in the broadband structure more characteristic of solids.

Spin-orbit coupling splits the energy levels of the 4f-electronic states of  $\text{Eu}^{3+}$ . The magnitude of energy splitting caused by spin-orbit coupling results in the possibility of f→f transitions ranging from hundreds to tens of thousands of wavenumbers.<sup>[1]</sup> A partial energy level diagram for the  $\text{Eu}^{3+}$  ion is presented in Figure 2. The electronic states of the ion are labeled using Russell-Saunders coupling scheme notation. In describing the properties of a particular state, only the J total angular quantum number is required due to the strong spin-orbit-coupling characteristic of the lanthanides. The lower-energy states of the  $\text{Eu}^{3+}$  ion are derived from the  ${}^7F_J$  term. The ground state,  ${}^7F_0$ , is nondegenerate with J = 0. All other levels are 2J+1 fold degenerate. The first excited electronic configuration is derived from the  ${}^5D_J$  term. The  ${}^5D_0$  excited-state is nondegenerate and approximately  $17,200 \text{ cm}^{-1}$  higher in energy than  ${}^7F_0$ . The term splitting among the different J levels can be very large; for example the  ${}^5D_1$  excited-state is found  $1725 \text{ cm}^{-1}$  higher in energy than the  ${}^5D_0$ .<sup>[9]</sup>

Interaction with the crystal field can also cause the removal of a level's angular momentum degeneracy.<sup>[8]</sup> This is referred to as the Stark effect. Compared to spin-orbit coupling the Stark splitting will be small because of effective shielding of the 4f-electrons. However it is large enough to produce fine structure in the free-ion transitions <sup>[8]</sup>.

The absorption spectrum of  $\text{Eu}_2\text{O}_3$  consists of sharp lines in the  $18,000\text{-}34,000 \text{ cm}^{-1}$  range due to parity-forbidden transitions within the  $4f^6$  configuration.

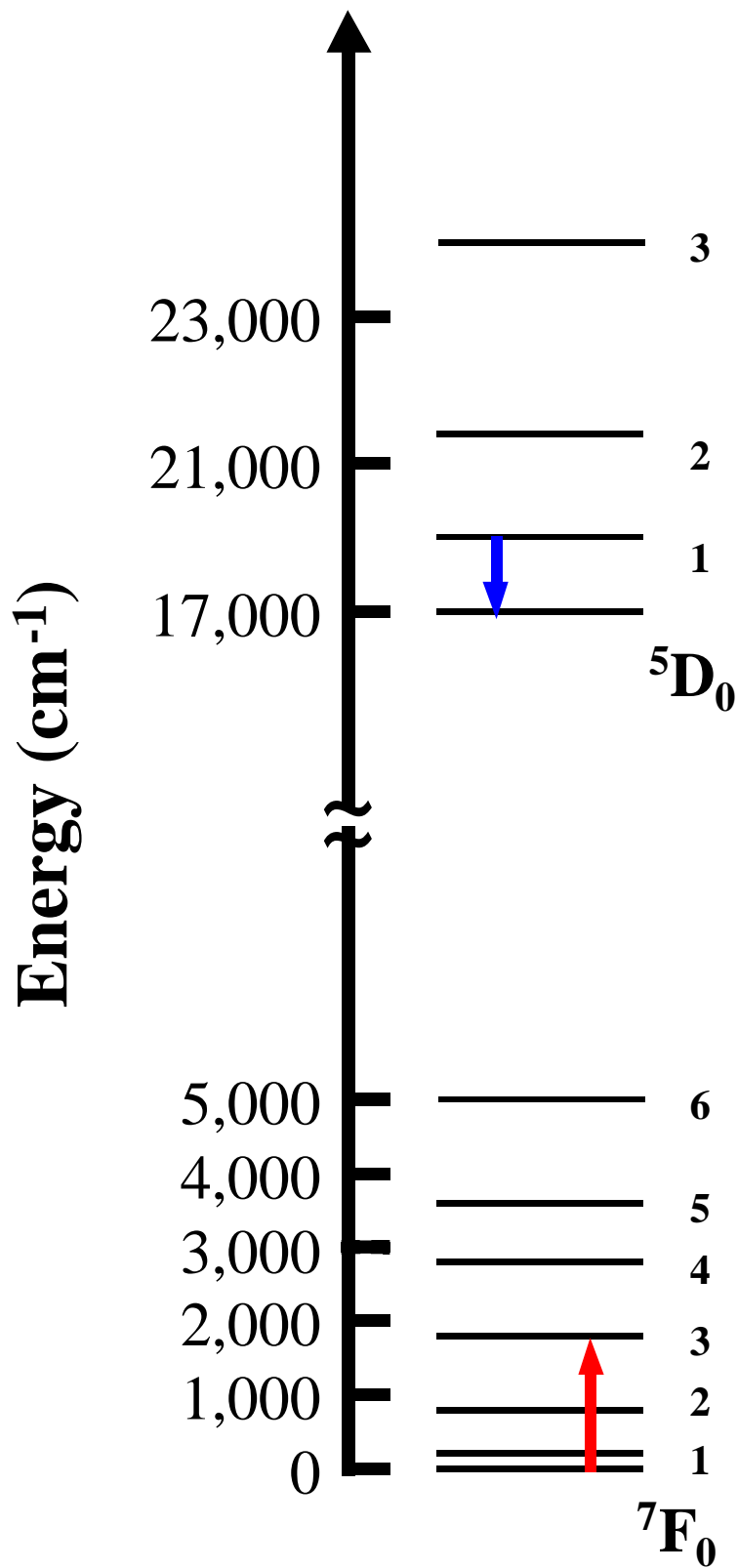
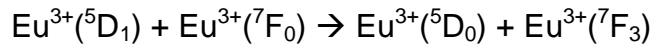


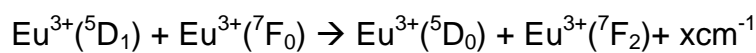
Figure 2. Partial Energy-Level Diagram of  $\text{Eu}_2\text{O}_3$ . The arrows represent cross-relaxation.

At energies above 34,000 cm<sup>-1</sup>, broad bands result from allowed charge-transfer transitions from 4f<sup>6</sup> to 4f<sup>5</sup>5d configurations [3]. The emission spectra of Eu<sub>2</sub>O<sub>3</sub> also consists of sharp lines due to transitions from the excited <sup>5</sup>D<sub>0</sub> level to lower <sup>7</sup>F<sub>J</sub> levels (J = 0, 1, 2, 3, 4, 5, and 6). Emission from higher energy excited-states such as <sup>5</sup>D<sub>1</sub> and <sup>5</sup>D<sub>2</sub>, does not occur in Eu<sub>2</sub>O<sub>3</sub> due to cross-relaxation.

The term cross-relaxation refers to a specific type of energy transfer in which only part of the excited-state energy is transferred. In the case of concentrated Eu<sup>3+</sup> systems cross-relaxation can occur between neighboring Eu<sup>3+</sup> ions [10].



The process is illustrated with the energy level diagram of Eu<sup>3+</sup> (refer to Figure 2). When cross relaxation occurs, the <sup>5</sup>D<sub>1</sub>-level emission of ion 1 is quenched in favor of <sup>5</sup>D<sub>0</sub> and ion 2 is excited to the <sup>7</sup>F<sub>3</sub> level. In this example the energy difference <sup>5</sup>D<sub>1</sub>-<sup>5</sup>D<sub>0</sub> of ion 1 is exactly equal to the energy difference <sup>7</sup>F<sub>3</sub>-<sup>7</sup>F<sub>0</sub> of ion 2, but this is not always the case. If the energy differences don't match exactly, the energy mismatch is compensated by phonon emission. For example, in monoclinic Eu<sub>2</sub>O<sub>3</sub>, cross-relaxation occurs via phonon-assisted energy transfer [11].





$\times$  (270 to 950  $\text{cm}^{-1}$ ) is the energy of phonon emission.

$\text{Eu}_2\text{O}_3$  can exist in either a cubic or a monoclinic crystalline phase. Both phases show saturation dips and are investigated in this thesis. In the cubic phase of  $\text{Eu}_2\text{O}_3$  the  $\text{Eu}^{3+}$  ion occupies two different crystallographic sites.<sup>[6]</sup> From work done on the lightly doped system of  $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ , it is known that the site symmetries are  $S_6$  and  $C_2$ .<sup>[8]</sup> Each  $\text{Eu}^{3+}$  ion is surrounded by six oxygen ions located at the corners of the cube. Two corners of the cube are vacant, and these can either be along a body or face diagonal of the cube (refer to Figure 3).<sup>[8]</sup> The structure of the crystal consists of  $\text{Eu}^{3+}$  ions arranged in two types of layers. One layer is simply composed of  $\text{Eu}^{3+}$  ions with  $C_2$  symmetry. The following layer consists of alternating  $S_6$  and  $C_2$  symmetry sites.<sup>[8]</sup> The  $S_6$  site has a  $^5D_0$  level 87  $\text{cm}^{-1}$  higher in energy than the  $^5D_0$  level of an  $\text{Eu}^{3+}$  ( $C_2$ ) ion.<sup>[6]</sup> The cubic packing structure of  $\text{Eu}_2\text{O}_3$  results in three times as many  $C_2$  sites as  $S_6$  sites.

The monoclinic phase of  $\text{Eu}_2\text{O}_3$  has three distinct crystallographic sites, each with sevenfold coordination. The symmetry of the three  $\text{Eu}^{3+}$  sites is low, each with  $C_s$  point group symmetry.<sup>[12]</sup> Although their point group symmetries are the same they each have a different crystal potential  $V$ .<sup>[12]</sup> Two of the sites are crystallographically similar, and can be described by six oxygen atoms at the apices of a trigonal prism with a seventh oxygen along the normal to a face.<sup>[13]</sup> The third site can be described as a distorted octahedron with the seventh oxygen at a long distance.<sup>[13]</sup>

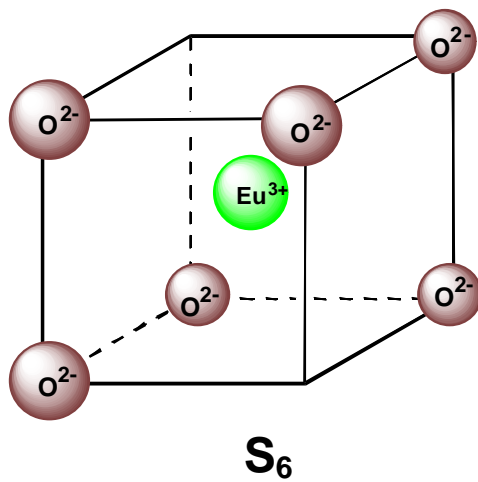
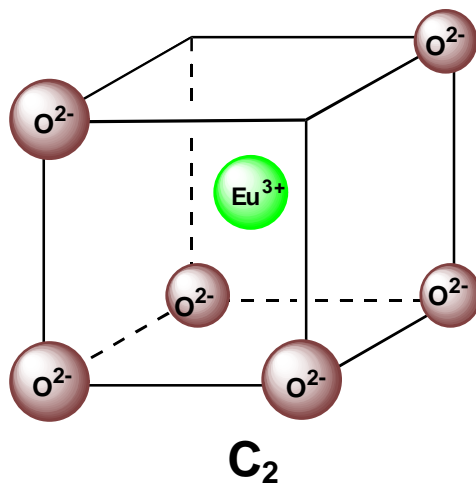


Figure 3. Symmetry Sites of Cubic-Phase  $Eu_2O_3$ .

## Chapter 1 References

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