A Study of the Luminescence of Organic-Sensitised Europium Ions in Lanthanum Trifluoride Nanocrystals towards Optical Amplification

Gavin Gordon George King

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Abstract

The luminescence of europium ions in lanthanum trifluoride nanocrystals are measured, with and without thenoyltrifluoroacetate (TTA) sensitisers. It is found that the luminescence from the Eu$^{3+}$ is constant in intensity and frequency without TTA; with the TTA the intensity is seen to degrade significantly with exposure to pump light. A number of possibilities for this are explored.

It was intended to include the nanocrystals in polymer films to measure the gain possible; this is explored theoretically. The losses that might be expected using scattering theory are calculated, and using this the gain requirements for nett optical transparency are calculated.
ABSTRACT
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# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>v</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2 The Rare Earths</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Chemistry</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Optical Properties</td>
<td>6</td>
</tr>
<tr>
<td>2.3 Luminescence with Ligands</td>
<td>10</td>
</tr>
<tr>
<td>3 Optical Amplification</td>
<td>13</td>
</tr>
<tr>
<td>3.1 Different Methods</td>
<td>13</td>
</tr>
<tr>
<td>3.2 Side-pumping</td>
<td>15</td>
</tr>
<tr>
<td>3.3 Thin Film Coupling</td>
<td>16</td>
</tr>
<tr>
<td>3.4 Amplifier Theory</td>
<td>17</td>
</tr>
<tr>
<td>4 Nanoparticles</td>
<td>23</td>
</tr>
<tr>
<td>4.1 History and Uses</td>
<td>23</td>
</tr>
<tr>
<td>4.2 Nomenclature</td>
<td>24</td>
</tr>
<tr>
<td>4.3 Production</td>
<td>27</td>
</tr>
<tr>
<td>4.4 Refractive Index of Nanoparticles</td>
<td>28</td>
</tr>
<tr>
<td>4.5 Our Nanoparticles</td>
<td>30</td>
</tr>
<tr>
<td>5 Luminescence</td>
<td>31</td>
</tr>
<tr>
<td>5.1 Methods and Apparatus</td>
<td>31</td>
</tr>
<tr>
<td>5.2 Luminescence in Trivalent Europium</td>
<td>36</td>
</tr>
<tr>
<td>5.3 Europium Trifluoride Nano-crystals</td>
<td>41</td>
</tr>
<tr>
<td>5.4 Europium-TTA Complexes</td>
<td>55</td>
</tr>
<tr>
<td>5.5 TTA-capped Nanocrystals</td>
<td>58</td>
</tr>
<tr>
<td>5.6 Conclusions</td>
<td>70</td>
</tr>
</tbody>
</table>
## CONTENTS

6 Scattering and Gain ........................................... 73
   6.1 Measurements ........................................... 73
   6.2 Theoretical Scattering ................................... 78
   6.3 Gain Calculations ......................................... 81
   6.4 Conclusions ............................................... 88

7 Conclusions ..................................................... 89

A History, Uses and Occurrence ................................. 91
   A.1 History ................................................... 91
   A.2 Uses ...................................................... 96
   A.3 Occurrence ............................................... 97

B Mie Calculations ............................................... 99

C Scattering Calculations ...................................... 109
List of Figures

2.1 Radial function of rare earth ions ............................. 7
2.2 Splittings ...................................................... 8
2.3 Dieke energy-level diagram .................................... 9
2.4 Ligand—rare-earth energy transfer .......................... 11
3.1 Film coupling scheme ......................................... 18
3.2 Transitions in general .......................................... 18
4.1 Surface fraction of nanoparticles ............................. 26
5.1 Apparatus Mk. I ................................................ 33
5.2 Long-pass filter spectrum ...................................... 33
5.3 Apparatus Mk. II ............................................... 35
5.4 Spectrometer temperature dependence ....................... 37
5.5 Eu$^{3+}$:LaF$_3$ energy levels ................................. 39
5.6 Eu$^{3+}$:LaF$_3$ lifetime ....................................... 43
5.7 Intensity parts .................................................. 44
5.8 Nanoparticle lifetimes .......................................... 45
5.9 Nanoparticle lifetime proportions ............................ 46
5.10 Eu$^{3+}$:LaF$_3$ spectra ........................................ 48
5.11 Nanoparticle amplitudes ...................................... 49
5.12 Transition intensity ratio ...................................... 50
5.13 Eu$^{3+}$:LaF$_3$ system ......................................... 51
5.14 Average lifetimes .............................................. 52
5.15 (Eu(tta)$_3$:1%) : PMMA lifetime ............................. 56
5.16 (Eu(tta)$_3$:1%) : PMMA spectra ............................. 57
5.17 (Eu$^{3+}$:LaF$_3$)$_{1\%}$ lifetimes ............................... 59
5.18 Nanoparticle lifetimes ........................................ 60
5.19 Nanoparticle lifetime proportions ............................ 61
5.20 Average lifetimes .............................................. 62
5.21 (Eu$^{3+}$:LaF$_3$)$_{1\%}$ spectra ................................. 63
LIST OF FIGURES

5.22 Nanoparticle amplitudes ........................................ 64
5.23 Transition ratio .................................................... 65
5.24 (Eu$^{3+}$:LaF$_3$)$_n$ system ........................................ 66
5.25 Sample reflectance .................................................. 69

6.1 Coupling arrangement .............................................. 74
6.2 Coupling to film with rare-earths ................................. 75
6.3 Coupling to general films .......................................... 76
6.4 Bubbles in the films ................................................ 77
6.5 Appearance of films ............................................... 77
6.6 Scatter-o-meter ...................................................... 78
6.7 Refractive index determination ..................................... 79
6.8 Theoretical Mie scattering ........................................ 82
6.9 Experimental lineshape ............................................. 84
6.10 Four-level Scheme ................................................ 86

A.1 Derivation of Cerite elements ..................................... 92
A.2 Derivation of Gadolinite elements ................................. 93
List of Tables

6.1 Eu$^{3+}$ parameters .............................................. 84
6.2 Transparency parameters ......................................... 86
6.3 Maximum gain ......................................................... 87
LIST OF TABLES
Chapter 1

Introduction

“Aber neue Phaenomena zu erklären, dieses macht meine Sorgen aus, und wie froh ist der Forscher, wenn er das so fleissig Gesuchte findet, eine Ergötzung wobei das Herz lacht.”

“To explain new phenomena, that is my task; and how happy is the scientist when he finds what is so diligently sought, a pleasure that gladdens the heart.”

— Carl Wilhelm Scheele

Fibre optic communications are of great importance for their high bandwidth. However, for long distances, attenuation can be significant, requiring amplification of the signals passed along it. It is possible to decode the data, amplify it, and to re-encode it into light, reminiscent of the earliest telegraph amplifiers, but this is inefficient and slow. All-optical amplification is ideal, as it means that the data doesn’t have to be decoded for amplification to occur. While it is possible to use wavelength-division multiplexing, the bandwidth of electronics is much less than the possible bandwidth of the optical system.

Likewise, amplification is the basis of all lasers; all-optical amplification is useful in the creation of fibre lasers. High powered fibre lasers have supplanted many other forms of high powered laser in industry, for example in welding and cutting steel, because they are reliable, and don’t require any form of sensitive alignment, since the entirety of the active medium is encased.

One of the better ways to perform amplification is to use in-fibre amplification. Of the all-optical methods for this, here are broadly two ways to

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1To a colleague explaining his decision to remain in his own research pharmacy rather than entering an academic career. The pharmacies of his day were quiet centres of original research, compared to the busy and metropolitan academic world in the Universities. [JS p.101]
do this; co-axial (end) pumping of a gain medium in the fibre, which has the complications of requiring an injector for the pump light, and having the fibre suitable for propagation of the pump light; and side-pumping which avoids some of the problems with materials and obviates the need for the injection of pump light, although the size of single mode fibres makes this difficult to realise in practice.

Rare-earth ions for fibre optics have great potential due to their narrow spectral lines and the wavelengths at which they can emit. This is shown by the wide-spread adoption of erbium-doped fibre amplifiers, which act at a wavelength in the “telecommunications window” at 1.5 \( \mu \text{m} \). Erbium-doped fibre amplifiers have somewhat broad-band gain due to a large number of over-lapping bands in the relevant multiplets of the transition used. One of the motivations for this research was to use praseodymium ions to create gain in the first optical window at 1.3 \( \mu \text{m} \) as present amplifiers in this band have restrictions on the materials that can be used; another was to use samarium for gain at 650 nm, which corresponds to a transparency window in plastic fibres. We however began initial investigations using europium, as it emits and is pumped in the visible, and also has a dramatic enhancement in the luminescence with the addition of an organic ligand. When these measurements were taken, there was found to be unexpected changes in the luminescence. The study of these changes became the basis of this work.

There are two problems with the rare-earths: they have small absorption cross-sections, and they are rather insoluble in polymers. Both of these can be addressed with the use of nano-crystals. The nanocrystal increases the doping rate in the polymer, and can be “capped” with an organic ligand that has a large absorption cross-section to improve the pumping efficiency. In addition to this, the use of nanocrystals preserves the crystalline environment of the rare-earth ions, which means that the desirable narrow spectral line-widths are preserved.

This research investigated the use of ligand-capped rare-earth-ion-doped rare-earth nanocrystals made by Industrial Research Ltd (IRL)\(^{2}\) for amplification in polymer waveguides, with the view of making lasers out of the nanoparticles supplied. The materials were specifically oleic acid capped and oleic acid/thenoyltrifluoroacetone capped europium ion doped lanthanum trifluoride in polymer films. Films were used rather than fibres, because films are simpler to construct in small runs for research purposes.

It was found that there are two serious factors that need to be considered: scattering losses in the polymer films, and a great decrease in the intensity of luminescence from the organic-ligand-capped nanocrystals when exposed

\(^{2}\)In early 2013, IRL was restructured to form Callaghan Innovation.
to the UV light used to pump them. While there have been studies of the luminescent behaviour of these nanocrystals before\cite{49, 47, 48}, studies of the gain from neodymium-, erbium- and ytterbium-doped lanthanum trifluoride nanoparticles in polymers\cite{22, 110, 63} and some studies of the stability of rare-earth ions in complexes and in polymers (e.g \cite{111}), to the author’s knowledge there has not been a study of the stability of ligand-capped nanoparticles. Likewise, the scattering properties of the nanoparticles when inserted into the polymers have not been investigated.

The structure of this thesis is as follows:

Chapter 2 presents a number of the properties of the rare-earth elements which are used here.

Chapter 3 gives details of optical amplifiers: what they are, how they are made, and the current state of the art.

Chapter 4 gives details of nanocrystals, both in general and specific to those nanocrystals investigated by us: how they are made, special properties and problems, and how they can be used.

Chapter 5 presents what was seen regarding luminescent stability, or a lack thereof, in the nanocrystals. For nanocrystals without a sensitising agent, the luminescence lifetime and spectra were recorded, and from these a number of properties found. These measurements and analyses were repeated for nanocrystal samples with organic sensitising agents, whence significant decreases were seen in the luminescence. To investigate this, further measurements of the same sort were made of a rare-earth in complex with the sensitising ligand.

Chapter 6 shows the measurements made pertaining to scattering losses in our systems. This includes finding the refractive index of the nanocrystals used, the theory of scattering, suitable models quantifying the scattering, and what can be done to minimise it.

Appendix A provides a brief history of the discovery and past uses for the rare-earth elements which was discovered in the researches for this work.

Appendices B and C show the theory of Mie scattering and the computations performed for these.
Chapter 2

The Rare Earths

“These elements perplex us in our researches, baffle us in our speculations and haunt us in our very dreams. They stretch like an unknown sea before us, mocking, mystifying and murmuring strange revelations and possibilities.” — Sir William Crookes, quoted in [6]

This chapter will introduce the rare-earths, give a background of the chemistry and physics of rare earths, and show some of their special properties. A brief history of the rare earths, their occurrence and their historical uses is given in appendix A.

The “rare-earths”, are the elements with atomic numbers 21 (scandium), 39 (yttrium), and 57 (lanthanum) to 71 (lutetium). The elements scandium and yttrium are included with the broader rare-earths, because of their similar history and chemistry. The “lanthanides” are a subset of these, the elements from lanthanum to lutetium. In this thesis, these terms are used exactly as defined here.

2.1 Chemistry

All of the rare-earths have very similar chemical properties, which led to the historic difficulty in separating the different elements. The rare earths generally have a $\text{Ln}^{3+}$ valency, and this is where much of the research has taken place. The $\text{Ln}^{2+}$ and $\text{Ln}^{4+}$ states are known to exist [20]; however these are generally considered of little interest, and sometimes as a nuisance; for example, the Eu$^{2+}$ ion has a broad, relatively uninteresting band of emission.

$^1$Ln is used to denote the lanthanides in general. Another symbol used is M, and in older and European literature Me, although with the rise of organic chemistry this last leads to possible confusion with the organic “methyl” group.
and absorption that obscures much of the more interesting \( \text{Eu}^{3+} \) structure of sharply resonant lines\[23\].

Because of the electronic structure of the ions, which is explained in the next section, the lanthanides show a monotonic decrease in ionic radii with increasing atomic number, the \textit{lanthanide contraction}. Despite this, the consecutive ions are all of a similar size, which means the ions readily substitute for other lanthanide ions in crystal hosts; this is especially so for lanthanide hosts. Lanthanide fluorides and chlorides are common hosts\[23, 55, 24\], as is yttrium-aluminium-garnet (YAG)\[40, 90\]. Up to 5% is a common doping rate, but for certain combinations of elements up to 20% is heard of\[48\].

### 2.2 Optical Properties

In the rare-earths, the 4\(f\) electron shell is partially full, within the full 5\(s\) and 5\(d\) shells, as shown in figure 2.1. This means the electronic transitions between the 4\(f\) levels are shielded from the surrounding electromagnetic fields somewhat. These electronic transitions give rise to \textit{luminescence}, the process whereby the relaxation of the ion from an excited state emits a photon of the corresponding wavelength.

The partially filled shells mean that in a solid host, the ions can be very well modelled as free-ions in a frozen gas; that is, can be modelled as gas ions, but with fixed spatial co-ordinates\[68, 61\]. These free-ions have degenerate states depending on the total angular momentum, with quantum number \(J\). In solids, there are Coulombic potentials; we therefore see splitting of the levels, as shown in figure 2.2. The crystal field splitting comes from the varying field the ion is exposed to; hyperfine splitting from the nuclear and electronic spin; and Zeeman splitting from the application of a magnetic field.

At room temperature, the phonon assisted dephasing broadening is large enough that the free-ion and crystal field splittings are the only effects visible, the others being present but washed out by the broadening. The crystal field splits the free-ion levels into at most \(2J + 1\) states.

Because the energy of the levels for the rare-earths remain similar in many hosts, we can use the results from any one host as a reference; the archetypal form is the \textit{Dieke Diagram}, of the energy levels of rare-earths in \(\text{LaCl}_3\), which is shown in figure 2.3. In this diagram, the splitting of the levels is shown by the width of the lines.

Since the total angular momentum \(J\) is approximately a “good” quantum number, the multiplets are labelled in the Russell-Saunders notation for
2.2. OPTICAL PROPERTIES

Figure 2.1: The radial probability function $P_2(r)$ of Gd$^+$. The radial functions of all the rare earths are similar. Reproduced from [36] with the kind permission of the publisher.
Figure 2.2: The various degrees of splitting seen in the rare-earth ions, where each column is the splitting seen in a single level of one level in the column to the right. The magnitude of separation between the levels is shown. After [68]
2.2. OPTICAL PROPERTIES

Figure 2.3: The Dieke Diagram, showing the energy levels of the rare earths doped into lanthanum trifluoride. From [26].
the free-ion $^{2S+1}L_J$, where $S$ is the total spin quantum number and $L$ is a letter referring to the orbital angular momentum quantum number, where $S, P, D, F, G, H, I, K, L, \ldots$ correspond to 1, 2, 3, 4, 5, \ldots using a notation from the 19th century. Using this notation, the primary transitions studied in this work are the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions in Eu$^{3+}$, which are at ca. 592 nm and ca. 613 nm respectively.

### 2.3 Luminescence with Ligands

The rare-earths have $4f^n \rightarrow 4f^n$ electronic transitions, which are partially allowed in solids because overlapping wavefunctions of opposite parity reduce this restriction. This causes the oscillator strength, which is directly proportional to the absorption cross-section\[^44\], to be weak; this means the absorption efficiency of the ions is low.

It has been known for some time that ligands can increase the luminescent intensity of the rare-earths\[^73\]. The accepted process is in general terms as follows\[^101\]. The organic ligand has an excited singlet level $S_1$, which is populated by absorption of pump light, usually in the UV. This singlet level rapidly transfers energy to a slightly lower energy set of triplet states $T_{1,2}$, which in turn rapidly decay to the lowest energy $T_1$ state. Note that from both $S_1$ and $T_1$ it is possible for the ligand to radiatively decay, a process called ligand fluorescence or ligand phosphorescence, respectively\[^9\]. Naturally, it is desirable to minimise this; this is done through appropriate combination of ligand and ion.

With a suitable combination of ligand and rare earth, the $T_1$ level is slightly above an excited emitting state of the rare-earth, and it is energetically favourable to transfer energy from the $T_1$ state to the rare-earth. This is shown in figure 2.4. This transfer results in the selective pumping of the rare-earth ion, effectively increasing the absorption cross-section, while not increasing the emission cross-section, and so preserving the long lifetimes of the rare-earth excited states. This increase of the absorption cross-section can be referred to as the “antenna effect.”

\[^2\] $S$ refers to “sharp,” $P$ to “principle,” $D$ to “diffuse,” and $F$ to “fundamental;” why there is no $J$ is unknown, but may be typographical, as handwritten “$i$” and “$j$” are similar in form.\[^41\]
Figure 2.4: Schematic of energy transfer of a rare-earth ion with organic ligands present. The pump raises the ligand to the singlet level, which transfers energy to the triplet levels, from which it is transferred to the rare-earth ion in a somewhat resonant process. As shown, it is also possible for ligand fluorescence to return the ligand to the ground state directly. After [73, 9] and [48].
Chapter 3
Optical Amplification

Optical amplifiers are needed for many things. Not least among these are the gain media of lasers, the amplifiers used to counteract attenuation in long optical fibres, and to compensate for the loss of power in a distribution network where the signal is split.

In optic fibres, dispersion causes pulses to broaden, and thus to increase the error rate of the signal, while attenuation limits the distance over which a signal can be transmitted\[19\]. While dispersion can be easily compensated for by a device with dispersion characteristics opposite to the fibre, attenuation is harder and more pressing to deal with, involving as it does loss of information.

3.1 Different Methods

There are any number of methods to regenerate an optical signal that has been degraded. One simple method is referred to as “3R” (Reshaping-Regeneration-Retransmission)\[19\]. This takes the signal, converts it to an electrical signal, re-times and reshapes it, and then converts the signal back to an optical signal. Although this has the advantage of potentially including error correction, it is complicated and can be considered inelegant, requiring as it does breaking the optical link and a number of discrete steps. Optical amplification can replace the large amount of electronics required for this with a smaller (and cheaper) optical device, especially when there is a large bandwidth to be amplified over.

Therefore an optical method should be preferred, where possible. There are several of these, which can broadly be split into semiconductor optical amplification and fibre amplification\[94\].

Semiconductor optical amplification (SOA) uses electron-hole recombination in a semiconductor material to achieve gain\[106\]. Compared to fibre
amplification, the use of semiconductors gives lesser gain, slightly more noise, and there can be significant non-linearities, but there is the advantage that they are monolithic, and they can be used to easily for signal processing with this.[19]

There is also optical fibre amplification. This is amplification in the fibre itself, compared to in a separate device. There are two types I will mention here; the erbium-doped fibre amplifier (EDFA) and the Raman fibre amplifier (RFA).

The Raman fibre amplifier uses the fibre itself as a medium for the gain. Stokes shifting in Raman scattering causes the emission of photons that have a lower frequency, and thus longer wavelength, than the pump. For an appropriate pump then, amplification can be seen in a signal that is co-axial with the pump[93]. Raman fibre amplification often has only a modest rate of amplification per unit length, but this is offset by using long lengths of fibre — in certain cases, a maximum in gain at 1550 μm is seen in fibres approximately 50 km long.[94]

Raman fibre amplifiers have a noise level that is close to the quantum limit, the amplification is done in the fibre itself, and have gain over a broad band of frequencies, compared to many other amplifiers, but not to the erbium-doped fibre amplifier. However, reasonably high power pumps are required, as well as a means of inserting the pump into the fibre.

Another type of amplification is the Erbium-doped fibre amplifier. There are a number of “transmission windows” in silica glass fibres, where the attenuation is at a minimum. The lowest loss these is at 1.55 μm. The rare-earth ion erbium (Z = 68) has a radiant transition at this wavelength ($^4I_{15/2} \rightarrow ^4I_{13/2}$). As is suggested by the name, this fibre is doped with erbium ions, which can be done in a number of ways. Refer to reference [27] for more details of this.

In both of these fibre amplifiers, the pump has to propagate with the signal; this can be done with double-clad fibres, which enable the propagation of the signal and pump through different but overlapping mode volumes.

All of these methods of amplification require population inversion. There are many ways for this to be achieved, some much easier and much more common than others. Some reasonably rare methods include creating the products of chemical reactions in the excited state so that they can decay and emit (chemical lasers)[38], nuclear pumping using the products of nuclear fission[65] to excite the gain medium, and gas dynamic lasers where population inversion is a result of changing the temperature and pressure of the gaseous gain medium adiabatically, and so changing the thermal equilibrium populations of the relevant energy levels.[38] [107]. More common however are
methods using electricity: either directly — via electrical discharge, or via current causing recombination of electrons and holes in semiconductors — or indirectly using coherent or incoherent sources of electromagnetic radiation. The electrical discharge method is especially common, as it is the easiest (but not only) method to pump semi-conductor lasers, using a current density to effect holes and electrons moving in the material. Furthermore, not requiring a solid medium, it is used to pump gaseous gain media; this is most common in the helium-neon, argon-ion and carbon dioxide lasers.

The final method we mention is also the method used on the original ruby laser: electromagnetic excitation. Using a flashlamp, the chromium ions in a ruby rod were excited, and a population inversion induced to emit at 694 nm. This is an example of using a broad-band incoherent source; by necessity the efficiency of a broad-band source is limited, as there is a great deal of emission that cannot excite the appropriate energy levels, in ruby in the blue and green regions of the spectrum. A way to the efficiency is to use a narrow-band source, such as another laser or an LED; chosen appropriately these can directly excite only the desired levels and no others. Furthermore, using another laser can make coupling the pump to the gain medium easy, as in fibre amplifiers.

3.2 Side-pumping

Polymers have some excellent properties for laser amplification, including ease of construction and the properties of organic materials that can be included in them. It is also possible that polymers could be electrically rather than optically pumped.

However, because the majority of polymers have melting temperatures that are low (compared to crystals and glasses) there are drawbacks. One of these is the inability to withstand high optical power densities. This is a problem with end-pumped methods because the intensity of the pump may be sufficient to melt the fibre.

A side-pumped amplifier is one where the energy source (the pump light) is not co-axial with the signal beam but comes in from the side of it.

There are a number of ways to side-pump a fibre; one is to use bar diodes to illuminate all sides, another is to use a prismatic cell to pump from all sides from a point source. It is also possible to pump from one side alone; this has the disadvantage of increasing the power density required at the interface, which could cause damage to the surface and fibre.

Having to choose fibre carefully is one reason to want to side pump a gain medium: with a side pumped amplifier the pump light only has to
travel through the width of the fibre, not the length, and it also does not have to remain in the fibre; it can pass through and perhaps be reflected from the outside of the fibre. Another reason is to simplify construction: because the pump light doesn’t have to couple to the film, there is one fewer alignment step to perform, as well as not requiring a collimated source, since non-collimated sources are much simpler and cheaper to maintain and build.

However, with side-pumping the pump intensity is uniformly low; this means that the fibre has to be doped to a much higher level than for co-axial pumping, or that materials with a higher gain are required. Increasing the weighting of dopant has its own drawbacks, such as adversely affecting the transmission of the fibre, which in turn requires more amplification; as well, at high levels it can affect the structural integrity of the fibre. Also, it can be impossible to find materials with a higher gain.

### 3.3 Thin Film Coupling

The initial aim of this project was to use nano-particle-doped organic thin-films for laser gain. This would be useful in a number of ways, including ease of fabrication and the ability to side-pump the beam.

Side-pumping is putting the pump light into the gain medium perpendicular to the amplified beam, rather than co- or contra-axially\(^1\), as is often done. This would make the manufacture of such things much easier as there is not the same need to align the beams as there is for co-axial pumping.

The propagation of light through a film is very similar to the propagation of light to an optical fibre; it uses total internal reflection to keep the light enclosed, and allows the guiding of light through curves. The coupling into the films is the slightly more difficult part.

The principles of coupling into thin films have been known since the 1970s\[^95^]\(,\) although at that time it was not organics/plastics but sputtered ZnO, and other metals and metal oxides.

The simplest conceptually is to focus the light to a point smaller than the edge thickness of the film, and to align it into the edge. This has a number of difficulties in practice, not least maintaining alignment, and ensuring the edge of the film is “sharp” enough to catch the light.

Therefore, a method of coupling with prisms was used\[^95^]\(]. This involved bringing a prism with a refractive index much higher than both the film and the substrate it is on into contact with the film.

It is desirable to have as large refractive index in the prisms as possible, to permit coupling and ensure the angles are easy to deal with. Diamond and

\(^1\)Or forward- and back-pumped.
cubic zirconia are two possibilities for this; from such prisms as we had at
hand, this gave us two choices: gadolinium-gallium-garnet (GGG, $n \approx 1.95$)
and the birefringent rutile ($\text{TiO}_2$, $n_o \approx 2.5$, $n_e \approx 2.8$). Although it has the
higher refractive index, rutile is birefringent which could cause difficulties in
coupling; therefore the GGG prism was used.

To mount the prism, an apparatus (shown in figure 3.1) was designed to
bring the prism into intimate contact with the film.

To couple to the film, the optimal and minimum angles needed to be
known. To do this, we apply Snell’s Law to the angles shown in the figure 3.1.

For pumping, the light used has to have greater quantum energy than
the signal; it also depends on the absorption in the gain material. In our
films, the pump was in the UV. It was found that the GGG turns brown
under UV light. This means that it is not particularly suitable for coupling
in this system. The formation of colour centres is a reasonably well known
phenomenon, in other crystals \cite{39, 8} and in GGG in particular \cite{72, 103, 81}. It was found, though, that allowing the prisms to “rest” under darkness or
even room light would restore the optical clarity of the prisms. It was feared
that it would be necessary to bake the prisms in order to allow the colour
centres to relax, but this turned out to be unnecessary.

3.4 Amplifier Theory

There are a number of ways of calculating and quantifying gain. We present a
theory of calculating optical amplification with the method of Einstein, using
the $A_{21}$ and $B_{21}$ coefficients. This theory considers pairs of energy levels in
an atom or ion, as shown in figure 3.2. We use the conventional notation
with “1” for the lower level of the transition and “2” for the upper excited
level. These are not to be confused with the terms in the Russell-Saunders
notation, for example $^5\text{D}_2$, which are widely used with the rare-earths.

We consider that level 1 has population density $N_1$, and level 2 has pop-
ulation density $N_2$. The coefficient $A_{21}$ is the rate of spontaneous emission
from the upper level to the lower,

$$\left. \frac{dN_2}{dt} \right|_{\text{spontaneous emission}} = -A_{21} N_2.$$  (3.1)

$B_{12}$ is the absorption coefficient, the rate at which the system absorbs a

\footnote{This is predominantly a précis of §7.3 and §7.10 in Verneyen\cite{96}}
Figure 3.1: In-coupling and out-coupling, in the ray-optics scheme, showing the path of the light rays, and the incident angle $\theta$. Pressure is indicated by the arrows. In theory, the pressure required is negligible, so long as the surface of the film and prism are sufficiently flat. In our case, the pressure was used to ensure the film surface was in sufficiently intimate contact. The process can also be understood in terms of evanescent fields; for our purposes this is unnecessary. Note thicknesses are not to scale.

Figure 3.2: The upper and lower states of a transition 2 and 1, and the three types of transitions between them. $a$ shows spontaneous emission from the excited upper state, $b$ absorption from ground to the upper state, and $c$ stimulated emission, where an incident photon is emitted with a second identical photon.
3.4. AMPLIFIER THEORY

photon from the field to excite the ion to a higher level, so that

$$\frac{dN_2}{dt} \bigg|_{\text{absorption}} = +B_{12}N_1\rho(\nu) = -\frac{dN_1}{dt} \bigg|_{\text{absorption}}, \quad (3.2)$$

where $\rho(\nu)$ is the energy density of the field as a function of the frequency $\nu$ (in Hz), and the final term logically arises from the conservation of ions.

$B_{21}$ is the stimulated emission cross-section; the process whereby an ion gives up energy $h\nu$ to the field coherently, *viz.* with the same phase, polarisation, and direction to the stimulating photon. This is

$$\frac{dN_2}{dt} \bigg|_{\text{stimulated emission}} = -B_{21}N_2\rho(\nu) = -\frac{dN_1}{dt} \bigg|_{\text{stimulated emission}}, \quad (3.3)$$

At thermodynamic equilibrium, we can relate the populations of each state with Boltzmann statistics, so that

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{\frac{h\nu}{kT}} = \frac{B_{12}\rho(\nu)}{A_{21} + B_{21}\rho(\nu)}, \quad (3.4)$$

where $g_J = 2J + 1$ is the degeneracy factor of the level, for the total angular momentum quantum number $J$.

We also introduce the lineshape function $g(\nu)$ which can be defined in three equivalent ways:

- as the probability density of spontaneous photon emission at frequency $\nu$;
- the relative absorption strength of radiation at frequency $\nu$;
- the relative strength of stimulated emission at frequency $\nu$.

This is introduced as a parameter in order to take into account the non-zero width of each transition, which can be for a number of reasons: Doppler shifts, lifetime broadening, collision (or pressure) broadening, isotope broadening, or as in our case phonon-assisted dephasing. *Phonons* are the quanta of energy in a crystal lattice vibrations, analogous to how photons are the quanta of electromagnetic radiation. Thus, phonon modes are the allowed frequencies of oscillation in a crystal lattice, and depend on the reciprocal lattice vectors of the crystal.

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3It is an unfortunate result of convention that the degeneracy factor and line-shape are both called “$g$”. Here, I will always use $g_J$ for the former, and $g(\nu)$ as the latter.
When dealing with (what is essentially monochromatic) laser light, the energy density $\rho(\nu)$ is, to a good approximation, a $\delta$-function, to give $\rho(\nu) = \rho_0 \delta(\nu_0 - \nu)$.

With a bit of mathematics we can find that the rate of radiative decay from 2 is

$$\frac{dN_2}{dt} \bigg|_{\text{radiative emission}} = -A_{21} N_2 \frac{\sigma_a(\nu)}{h\nu} \left[ N_2 - \frac{g_2}{g_1} N_1 \right],$$

where $\sigma(\nu)$ is the stimulated emission cross-section, which can be considered, for example in scattering measurements, as the cross-sectional area the ion exposes to the incident radiation, such that

$$\sigma_a(\nu) = A_{21} \frac{\lambda^2}{8\pi n^2} g(\nu).$$

There are the three processes of stimulated emission, spontaneous emission and absorption occurring in the ions that are used for amplification. Taking these into account, we can obtain an expression for the net gain per unit length of material in terms of the Einstein coefficients, the population densities and the lineshape function,

$$\frac{dI_\nu}{dz} = \left[ \frac{h\nu}{c/n_g} (B_{21} N_2 - B_{12} N_1) g(\nu) \right] I_\nu + \left[ h\nu A_{21} N_2 g(\nu) \frac{d\Omega}{4\pi} \right],$$

where $n_g$ is the group velocity of the photons, $h$ is Planck’s constant, $c$ is the speed of light in the vacuum, and $\frac{d\Omega}{4\pi}$ is the solid angle subtended by our beam of interest. This last angular dependence arises because the spontaneous emission occurs over all directions, but our beam only has finite angular spread; any light outside of this solid angle is of no interest to us, except perhaps in practical terms of heating of the gain material.

The two terms relate to the stimulated emission and spontaneous emission as shown. The spontaneous emission corresponds, in amplifier terms, to noise, as it is (for a given pumping power) a constant, regardless of whether there is a signal or not. As it is over the entire solid angle, however, the portion that effects our signal is often negligible. We therefore ignore this constant “zero off-set” for the purposes of gain.

For $n$ the refractive index of the medium the ion is in and $n_g$ the group velocity, we can say

$$\frac{B_{21}}{B_{12}} = \frac{g_2}{g_1} \quad \text{and} \quad \frac{A_{21}}{B_{21}} = \frac{8\pi n^2 n_g h\nu^2}{c^2},$$
and so we can write
\[ \frac{dI_\nu}{dz} \equiv \gamma(\nu)I_\nu, \] (3.8)
where
\[ \gamma(\nu) = \left[ A_21 \frac{\lambda^2}{8\pi n^2} g(\nu) \right] \left[ N_2 - \frac{g_2}{g_1} N_1 \right] \] (3.9)
is the small-signal gain coefficient. Small-signal means that the populations of the upper and lower levels are un-affected by the intensity of the incident light. This is true for amplifiers; laser gain however relies on this not being true.

From the Boltzmann statistics of equation (3.4), we can see the population inversion required for gain \( N_2 > \frac{g_2}{g_1} N_1 \) would, at thermodynamic equilibrium, require a negative temperature; hence the system requires an external source of energy, and does not violate the second law of thermodynamics.

By integrating equation (3.8) over a path length \( z \) we can obtain an expression of the form
\[ I_f = I_i e^{\gamma(\nu)z}, \] (3.10)
where \( I_f \) is the final intensity and \( I_i \) is the initial intensity. This is a form of the Beer-Lambert Law, and becomes important when discussing scattering and losses.
Chapter 4

Nanoparticles

It has always seemed to me extreme presumptuousness on the part of those who want to make human ability the measure of what nature can and knows how to do, since, when one comes down to it, there is not one effect in nature, no matter how small, that even the most speculative minds can fully understand. —Galileo Galilei

Nanoparticles are an area of intense research and popular interest due to their interesting and unusual properties, especially compared to materials in large quantities; our use however tends away from this, as it seeks to capture some of the properties of the rare-earth ions that are seen when they are in bulk crystals. In particular our nanocrystals have the same similar lifetimes, and therefore similar low non-radiative decay rates, as bulk LaF$_3$.$^{[49]}$

4.1 History and Uses

Nanoparticles have been used naively for centuries, for the mundane and the beautiful. The use of lamp black (carbon soot collected from oil lamps and candles) as a pigment is an example of the former; the creation of colours for artistic and devotional purposes is an example of the latter. A specific example of artistic use is the Lycurgus Cup held by the British Museum, which shows pale green from reflected light, but red from transmitted light.$^{[29]}$ from the inclusion of gold and silver nanoparticles; as an example of devotional use any one of a large number of stained glass church windows from the Middle Ages are fine samples.$^{[29]}$

Although the ancients had applications for nanoparticles, they had no knowledge as to why they had these properties. Scientific investigations

$^{1}$The Victoria and Albert Museum holds a number of fine examples of this.
of the properties of nanoparticles, especially their behaviour as scattering agents began in the 19th century with the investigations of Lord Rayleigh [85] and Clausius [18], not that they were called thus until much later. Although much was learned about the particles, it was not until the scanning electron microscope was developed in 1982 that there were instruments capable of directly studying and even building them.

Since that time, nanoparticles have become important in many fields, and in popular culture as well: there are any number of products that tout the advantages of their “nano” construction, from the (perhaps useful) “iPod nano” to the to the splendidly named “Philips TRESemmé HP4669/17 Salon Shine Diamond Digital Slim Straightener,” which has “nano-diamond ultragliss ceramic plates” [86].

Although these uses have perhaps some validity from the origin of the word “nano”, which came from the Greek “νανος” (“nanos”) meaning dwarf, in science the word properly refers to the SI prefix denoting $10^{-9}$; often it relates to length.

In the sciences, there is still a multitude of interests in the usages of nanoparticles. Although carbon black was long used in rubber manufacture [87] and printing, the first modern uses for carbon nanoparticles occurred after the discovery of carbon-60 (buckminsterfullerene, or bucky-balls) and carbon nanotubes. Applications for the latter range from the fanciful — space elevator cables [82] — to the more practical — utilising the large surface area for a given mass of nanomaterial to increase the storage capacity of gases [70].

Because of their size, nanoparticles are easily able to access the body. This causes medical concerns [87], but also allows the use of these as novel methods to treat diseases. This can be through mechanically interacting with the undesired microbes [99], which reduces the development of drug resistance, and for the targeted delivery of drugs to those parts that require treatment, for example by only allowing the toxic drug to be released when interacting with (undesired) cancer cells [100]. A further method is to coat the nanoparticles with organics such that they only bond with cancer cells, and then dose the area with non-ionising radiation tuned to the nanoparticle resonant frequency to cause “thermal ablation” of the cancerous cells [14].

There are also applications in bioanalysis [79]; food production [25]; foaming materials [112]; as well as surface coatings, cleaning and cosmetics [87].

### 4.2 Nomenclature

What many of these uses have in common is that they use the surface of the material. In bulk materials, the number of ions affected by the surface
discontinuities of the material as a proportion of the whole is negligible, and so is usually neglected.

When we refer to bulk here, we mean a particle with at least one dimension greater than $10^{-5} \text{m}$, usually all dimensions. Nanoparticles are those with dimensions of less than $10^{-8} \text{m}$, although in some sources it can be used to mean any particle of less than 1000 nm. Although we don’t deal with them here, particles between $10^{-5}$ and $10^{-8} \text{m}$ could be called microparticles using this scheme.

In the past, these microparticles were called “fine” particles; when the smaller nanoparticles were studied, they were thus called “ultra-fine” particles to distinguish them. This has not been current usage since the 1980s, however, and the term “nanoparticles” along with the related “nanotechnology,” nanoscience” and “nanofluorides” have become accepted usage.

Nanoparticles behave somewhat differently than bulk samples; this is a result of many things, but a major reason is that they have a very large surface area compared to their volume. In a bulk crystal, the ions are arranged in a very regular lattice (the substrate); at the edge of the crystal the structure has to be much less regular. This irregularity causes the ions near the surface to have a somewhat different environment than the substrate ions. In a bulk sample the vast majority of the sample is in the substrate, causing the surface irregularities to be insignificant. In nanoparticles, this is not the case. There are a number of ways to consider this; two possibilities looked at here are a spherical approximation, and a method that counts the ions in the crystal, small as it is.

In the spherical approximation, we treat the nanoparticles as a sphere of radius $R$. The depth to which surface effects are significant can depend on the properties measured, but are generally considered to be around three ions deep. In the rare earths this is approximately 0.6 nm. If we consider a layered sphere with a “surface” shell of thickness $r$ around a core of radius $R - r$, the proportion of ions in the surface as a proportion of the total number of ions is approximately

$$\frac{V_s}{V} = \frac{R^3 - (R - r)^3}{R^3}. \quad (4.1)$$

This is plotted in figure 4.1.

From this it can be found that a 1 μm sphere will have ca. 2 parts in $10^{10}$ on the surface, a 10 nm sphere will have ca. 1 in 10 on the surface. This approximation is only valid for large numbers of particles where the shape can be well approximated as a sphere; this fails for small ($N < 1000$) particles.
Figure 4.1: The proportion of particles in a surface layer 6 nm thick as a function of (spherical) particle size.

The other method is to cut out the object from the lattice with the required number of ions, and then count the number on the surface\textsuperscript{11}. This can be done with a scanning electron microscope, for example, or as a thought experiment. This is accurate for any size particle; it does not however easily account for effects further into the lattice, or how these change with distance from the “surface.” Using this method it is found that for 300 atoms in a face-centred-cubic arrangement that approximately one half are on the surface; the proportion does not get below 10% until there are $\sim 80000$ atoms\textsuperscript{11}.

This method does show however the “edge” atoms as well as the “vertex” atoms that are not apparent in the spherical approximation. In a crystal lattice there is discrete rotational symmetry; this results in a finite number of faces on the crystal, regardless of size. This forms a polyhedron which has a certain number of faces, edges and vertices. An ion in each of these will have a different amount of symmetry, with the face ions having the most, the vertex ions the least, and the edge ions somewhere in between.

The number of vertex ions does not change with increasing “radius,” by which I mean the radius of the sphere containing the vertices of the polyhedron; for a given polyhedron, the number of edge ions increases approximately linearly; the number of face ions increases approximately quadratically, while the total number of ions increases approximately cubically. This renders the
edges and vertices of a single perfect crystal insignificant past a certain number of ions or volume of particle.

A detailed analysis of this sort was not deemed necessary for our work, but this is included as it does have a slight effect and is worth remembering qualitatively.

Considering only the faces, by assuming that the particles is “large” and has no edges/vertices, a property \( X \) could then be naively expected to scale with the number of ions \( N \) in it as
\[
X(N) = \alpha N + \beta N^{2/3},
\]
(4.2)

where the first term relates to the “bulk” behaviour, and the second refers to the surface. This approach only is valid in a certain regime; specifically, it is not valid with very few ions, when quantum mechanical effects become significant and (implicit) classical approximations fail.

4.3 Production

There are a number of ways to make nanoparticles, which can be separated into two rough approaches: the “top-down” approach and the “bottom-up” approach.

The “top-down” approach could be likened to Rodin’s approach to sculpture: “I chose a block of marble and chop off what I don’t need.” This begins with a bulk sample of the substance required which is reduced in size until the desired particle is produced. This can be done photo-lithographically, or through focused ion beam milling. The current state of the art is such that it is possible to very precisely control the size and shape of the resultant particles, but they are limited to particles greater than approximately 20 nm.

“Bottom-up” methods start with ions singly and build them together to form the desired particle. This can be performed in the gas phase, where supersaturated metal vapour is condensed into nanoparticles, which allows control of the size, mass and location of formation; through the deposition and self-assembly of shapes on a surface, often gold, which can form useful shapes; and with wet chemistry.

It was with wet chemistry that the nanoparticles used in this work were formed. The method used is described in section 4.5.

When creating nanoparticles, they are often “capped” with organic ligands. There are a number of reasons for this, although on a practical level this is required to decrease their reaction with each other. Because there
are many incompletely bonded ions, there is a strong attraction between
the particles. To prevent the formation of clumps of what might be called “mac-
roparticles” it is necessary to coat the particles with a layer of materi".54.
Commonly long-chain organic molecules are used to do this, although other
organic substances can be used. These have the additional benefit of increas-
ing the “solubility” of the nanoparticle into other organic materials97.

As mentioned in section 2.3 above, it is also possible to use organic lig-
ands on rare earth ions as sensitising agents. This works by increasing the
absorption (and thus emission) cross-section of the ion. The effect however is
a short-range dipole-dipole interaction that thus falls off with distance from
the ion as $R^{-6}$. The rare-earth ion can be directly incorporated into a lig-
and complex, which greatly increases the absorption, but at the expense of
greater line-width and reduced quantum efficiency89, which is a result of
the great distortion the ligand causes in the ion.

As we shall see, it is possible to use the ligand on nanoparticles as both
coating and sensitiser, which provides a compromise between a pure crystal
environment with the narrow emission line that it entails but with small
absorption cross-section, and the broad line but large cross-section that can
be obtained from a complex. The increased absorption and energy transfer to
the rare-earth ions is called the “antenna effect” in allusion to the properties
of an electromagnetic antenna46.

4.4 Refractive Index of Nanoparticles

It is often necessary to know the refractive index of the nanoparticles, es-
specially for effectively embedding these into waveguides. The refractive in-
dex also has an effect on the ions embedded in it, whether directly or in
nanoparticles. Nanoparticles are affected similarly to single ions since the
wavelength of the electromagnetic radiation involved is larger than the ex-
tent of the particle. This can lead to changes in the electronic transitions
in the ions, such as increasing the oscillator strength (and hence decreasing
the luminescent lifetime)71. The refractive index is a predominantly macro-
scopic parameter: it can be considered the ratio of the speed of propagation
of electromagnetic waves in a vacuum to the speed in the material, i.e.

$$n = \frac{c}{v},$$

(4.3)
4.4. **REFRACTIVE INDEX OF NANOPARTICLES**

or following from Maxwell’s equations as

\[ n = \sqrt{\varepsilon_r \mu_r} = \sqrt{\frac{\varepsilon \mu}{\varepsilon_0 \mu_0}}, \quad (4.4) \]

where \( \varepsilon \) is the dielectric constant (or permittivity) and \( \mu \) is the magnetic permeability of the material. The subscript \( r \) denotes “relative”; the subscript \( 0 \), per convention, denotes the vacuum parameters.

The definition of the above does not take into account absorption by the material; it is possible to generalise the refractive index to account for this by introducing the complex refractive index

\[ \tilde{n} = n + ik = n(1 + i\kappa), \quad (4.5) \]

where \( i \) is the unit complex number, \( k \) is the *absorption coefficient* and \( \kappa \) is the *attenuation index*. \( n \) remains the standard refractive index. In classical materials, Maxwell’s equations relate the refractive index and the attenuation index to the charge density and conductivity of the material, as well as the permittivity and permeability.

These parameters are, however, calculated over a homogeneous medium; this homogeneity is defined by taking a spatial average over a volume characterised by a volume \( d \). This \( d \) has to be large compared to the lattice parameters \( a \), and small compared to the wavelength \( \lambda \). There is some debate as to the precise requirements; this varies from \( d \sim \frac{1}{\lambda^4} \) to \( d \sim 1–2 \text{nm} \)\[60\]. To effectively average over the volume characterised by \( d \) it must then be smaller than the size of the particle, which we will denote as \( a \), not to be confused with the lattice constant.

Taking this into consideration, we will have two definitions of the refractive index, for different purposes. For the purposes of the environment of an ion within a crystal lattice, we will use the classical refractive index of the bulk material, with certain adjustments where the size of the particles is known\[60\]. For the purposes of optical continuity (scattering, reflection and transmission) a more practical definition will be used, relating to the amount of scattering seen from a suspension of the nanoparticles. The refractive index of the nanoparticles will be considered to be the refractive index of the liquid that causes the least amount of scattering (i.e. using refractive index oil to match). In theory the scattering could be zero, but in practice will be finite but small, owing to scattering from inhomogeneities in the liquid.
4.5 Our Nanoparticles

Our samples were prepared by Dr David Clarke at Industrial Research Ltd, following a procedure modified from the literature\cite{48,97,47}. There are two types of sample considered here: powdered samples and polymer-mounted samples. The initial production methods are the same for both, with the differences occurring toward the end of manufacture. We recount the procedure here to explain the differences in the in the samples we have.

High purity solutions of LaCl$_3$, LnCl$_3$ (Ln $\equiv$ Eu$^{3+}$,Pr$^{3+}$,Sm$^{3+}$, as appropriate), NaF and Oleic Acid were obtained. NaF was diluted in a mixture of de-ionised water, ethanol and oleic acid, and the mixture heated under an argon atmosphere. A solution of LaCl$_3$ and the appropriate LnCl$_3$ in proportion to match the desired dopant level was then added drop-wise and stirred at 75$^\circ$C for 5 hours. This was then cooled and put into a large excess of ethanol to precipitate the nanoparticles; this mixture was then centrifuged at 3000 rpm to remove excess oleic acid before being dispersed into toluene for storage.

Partial ligand exchange was achieved by mixing a solution of the nanoparticles and of the $\beta$-diketonate (thenoyltrifluoroacetate, TTA, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione overnight. The resulting ligand-exchanged nanoparticles were precipitated by addition of ethanol, then were centrifuged and stored in toluene. This is a particularly successful ligand for use with Eu$^{3+}$\cite{10}.

To prepare solid powder samples, the solvent was then evaporated off. This caused the nanocrystals to clump together in quite irregular-sized lumps. To ensure consistency, and to reduce the size of the samples, these were roller-milled in Nalgene bottles with isopropyl alcohol and zirconium beads for two days. At this, the samples were dried and put through a 150$\mu$m mesh. This gave a satisfactory consistency to the size of the resultant clumps of nanoparticles\cite{16}. These clumps have been shown to be clusters of much smaller nanocrystals, of ca. 10 nm diameter\cite{18}. This is presumably from the organic ligands — oleic acid and TTA — bonding to each other; note that the crystal LaF$_3$ structures do not appear to bond together.

To prepare the nano-crystal containing films, a known mass of nanocrystal stored in toluene was added to a known mass of amorphous polycarbonate (APC) dissolved in toluene and 1,1,2-trichloroethane. These were put under a vacuum and dried overnight, at room temperature or heated to 80$^\circ$C. The trichloroethane was added as a secondary solvent after it was seen that the toluene alone caused phase separation and bubbling\cite{16}.

\footnote{Bayer APEC-9389; measured refractive index of $n = 1.557.$}
Chapter 5

Luminescence

While performing a set of preliminary measurements of the luminescence of rare-earth nanocrystals in films, it was found that the intensity of the luminescence was changing significantly with exposure to the pump light used. The amount of this change was unexpected, and so was investigated in some depth, becoming a major part of this work.

In this chapter, we investigate a number of luminescence properties of Eu$^{3+}$:LaF$_3$ nanocrystals. The fluorescence lifetimes of the rare-earths are important to obtain gain from the ions, and are analysed in terms of the amount of non-radiative decay that is present. Similarly, the spectral response of the rare-earths are interesting; we investigate the initial response and how it changes over time and with exposure to the light used to pump it. We begin by describing the apparatus and the methods used, and then the process of luminescence in the rare-earth ions, specifically of the Eu$^{3+}$ ion. How this is affected by using nanoparticles is explained, as is the use of organic ligands to improve the absorption of Eu$^{3+}$, specifically thenoyltrifluoroacetone (TTA).

We then present the results seen with three different classes of sample. The first is Eu$^{3+}$:LaF$_3$ nanocrystals capped with oleic acid. The lifetime and spectra of this are analysed for changes. To provide a reference to the behaviour of TTA with the ions, we look at a non-crystalline complex of Eu$^{3+}$ with TTA, mounted in poly(methyl-methacrylate) (PMMA). Finally, we look at TTA-capped nanocrystals, where the greatest changes are seen.

5.1 Methods and Apparatus

The method and apparatus used for the three classes of measurement are the same, and so are described here.
The preliminary measurements that cause this investigation were made using nanocrystal samples in thin amorphous polycarbonate (APC) and PMMA films. A schematic of the apparatus used is shown in figure 5.1.

Light from a 365 nm UV-LED\textsuperscript{1} was collimated and focussed onto a thin film. Using aspheric glass lenses, the optical power at the film was measured to be 72 ± 2 mW. To maintain power and wavelength, and improve the LED lifetime, the LED was mounted on a thermo-electrically controlled stage and temperature controlled with a commercial PID system\textsuperscript{2} to be at ca. 12°C. To switch the LED, a MOSFET control was built. This had a fall time of 250 μs, much less than the lifetime of the samples.

The fluorescence was measured with a photomultiplier\textsuperscript{3} attached to a monochromator\textsuperscript{4}. This enabled one part of the spectrum to be concentrated on at a time, in this case the sensitive transition at ca. 613 nm. In order to eliminate any stray UV from the monochromator, a glass absorptive long-pass filter with cut-off at 532 nm was used. The transmission spectra of this filter is shown in Figure 5.2.

The voltage across the PMT was measured and recorded with a digital oscilloscope, and read into a computer for analysis.

A schematic of the apparatus is shown in Figure 5.1. The lab lights are fluorescent tubes\textsuperscript{5}. As with many fluorescent tubes, these have an europium phosphor\textsuperscript{69, 80}. Since we are investigating transitions in europium, this could cause incorrect measurements. To avoid the room lighting affecting the spectral measurements, the entire apparatus was enclosed in black-out cloth.

Our initial measurements were made with this; these were difficult to replicate as the intensity of the transition monitored rapidly decreased. Not knowing if it was only the one transition or all of them, we introduced a spectrometer to monitor all of the transitions in the rare-earth ion.

The apparatus was supplemented with a spectrometer\textsuperscript{6} to see if the spectrum changed. This device returned an intensity as a function of “counts”; a measure of the number of electrons displaced from the CCD at its heart. This is greatest at approximately 600 nm (with ca. 41 photons/count) falling with increasing (ca. 203 photons/count at 800 nm) and decreasing (ca. 90

\begin{enumerate}
\item Nichia NCSU033B(T); nominally 350 mW; spectral half width 9 nm.
\item Newport 325 controller; Jaycar ZP9104 peltier unit; homebuilt mounting; 10 kΩ thermistor.
\item EMI 9781RA; predecessor to the ET Enterprises 9781. Biased at ca. 825 V and voltage measured across 100 kΩ.
\item Spex Micromate; in-line Cassegrain type; set to wavelength 613 nm, slit width of 7 nm.
\item Philips TL-D Alto 36W/840.
\item Ocean Optics USB2000 Fibre-coupled USB spectrometer.
\end{enumerate}
5.1. METHODS AND APPARATUS

Figure 5.1: Schematic of the apparatus used for preliminary measurements of the decay of fluorescence.

Figure 5.2: The transmission spectrum of the long-pass filter used.
photons/count at 400 nm) wavelengths\textsuperscript[77]. Because there is not any precise documentation for this, and our area of interest is in the middle of the “band,” our results are presented in terms of “counts.” The spectrometer is of the “small-well” type, that achieves accurate measurements by averaging over a number of cycles. Here, it was set up to integrate incident photons over 0.5 s averaged 10 times.

The modified apparatus is shown in Figure \textbf{5.3}.

The amount of fluorescence from the films was low. It was difficult to capture enough to raise the signal above the noise floor of the spectrometer. Therefore instead of the films, with a low density of nano-crystals, small amounts of powdered nano-crystals were used.

To remove some of the higher-frequency noise in the PMT signal, whilst still using the high sensitivity\textsuperscript[96, p.700] amplification of the PMT, a low-pass filter\textsuperscript[7] was designed, that could handle signals of up to \textit{ca.} 12 V. This was inserted between the PMT and the oscilloscope.

A series of LaF\textsubscript{3} nano-particles of different Eu\textsuperscript{3+} concentrations were made up and roller-milled to approximately 100\textmu m, as described in section \textbf{4.5}. A small sample (approximately 30 mg) was then put into a 2 mL vial and illuminated with UV. A special mount was built to increase the repeatability of the measurements between samples; this was measured to be no more than 15\%. To avoid spurious data, Raman spectroscopy vials\textsuperscript[8] were used; these are manufactured to ensure as little contamination from luminescent materials as possible.

Further, it was decided to see what the long-term effects of the exposure to UV were. This involved illuminating the sample for a number of days. A computer script was written to control the process for this time. In brief, this took note of the starting time, from which all times were referenced, and took a “dark” spectrum with the spectrometer, to account for the electrical noise and room lighting. Then, it started the UV-LED flashing at a rate of 2.185 Hz, allowing the lifetime to be measured. It then stopped the UV-LED flashing, measured the spectrum, and re-started the flashing. After 40 s, the lifetime and spectrum were measured again. All of this was recorded, along with the time of each, for a total of approximately 63 hours.

The recorded spectra from the spectrometer had to be corrected for three flaws: a) an intrinsic dark count from the nature of the CCD used; b) an extrinsic count from stray room lights; and c) changes in dark levels from temperature fluctuations.

The first two of these were dealt with by recording a “dark” spectrum

\footnotetext[7]{3 kHz, 12dB/octave roll-off.}
\footnotetext[8]{J.G. Finneran R.A.M. large opening 2.0 mL clear vial model number 32009-1232.}
Figure 5.3: Schematic of the apparatus used for measurements of the decay of fluorescence. The mirror was used to aid alignment coupling to the fibre.
and subtracting this from the recorded spectra; the last took more though, both to discover and to correct.

A drift of approximately ten counts was seen in the data recorded, recurring diurnally. There was another experiment recording the room temperature in the lab, which varied by up to 2.4°C. This was used to show the co-incidence between the change in baseline and room temperature, as shown in figure 5.4. The spectrometer had no specification regarding the temperature stability of it; the manufacturer’s data sheet for the CCD did not suggest such a great variation in counts with such small temperature variations[92]. Knowing this, and that the spectrum of Eu$^{3+}$ above 800 nm has nothing of interest, the variation was easy to adjust for. The mean of the counts from 800 nm to the end (ca. 1100 nm) was subtracted from the entire spectrum, after the dark counts had been subtracted. This gave a series of spectra that have “zero” related to zero photons measured[9].

5.2 Luminescence in Trivalent Europium

We will first describe the well known properties of luminescence in Eu$^{3+}$, then describe the changes that nano-particles have on this, then the effect of TTA.

5.2.1 Europium Alone

When we refer to bulk here, we mean a particle with at least one dimension greater than $10^{-5}$ m, usually all dimensions. These are particles where edge effects are negligible. Nano-particles are those where the dimensions are less than approximately $10^{-7}$ m (100 nm), where surface and edge effects are significant. Although not dealt with here, using this same scheme, particles with dimensions between $10^{-8}$ m and $10^{-5}$ m would be referred to as micro-particles.

The luminescence of Eu$^{3+}$ has been investigated since before the turn of the 20th century[7], and in specific detail with the rise of quantum mechanical theory in the 1920s and ’30s. Generally, the rare-earths are considered good spectroscopic samples, because their electronic structure in a crystal is similar to that of a free ion, as explained in chapter 2.2. LaF$_3$ is used as a host because it has a low phonon energy, which means that non-radiative decay is

\footnote{The temperature coefficient for the photomultiplier is 0.5%/°C; as there was only a variation of approximately 2.4°C the 1.2% variation was not significant and was not compensated for.}
5.2. LUMINESCENCE IN TRIVALENT EUROPIUM

Figure 5.4: Relationship between room temperature and spectrometer drift, during five of the recorded datasets. There is a slight delay in the zero level and the temperature which comes about because the temperature was recorded in a cryostat, inactive at the time, which is very well insulated and thus slightly delayed in responding.
minimised from the upper $^5D_0$ level, while the non-radiative decay from the lower $^7F_1$ and $^7F_2$ levels is large.

The interaction between the LaF$_3$ and the Eu$^{3+}$ is relatively straightforward. The energy is incident on the particle; if absorbed, this excites the Eu$^{3+}$. From the excited ion there are two routes of decay: through luminescence, primarily from the $^5D_0 \rightarrow ^7F_J$ transitions; and through the creation of phonons in the crystal lattice. The crystal LaF$_3$ has phonon modes with energy between approximately 200 cm$^{-1}$ and 400 cm$^{-1}$ [48, p.94], which corresponds to a photon of wavelength 50000 nm to 22000 nm. Because this phonon energy is so much lower than the transitions in the Eu$^{3+}$, and the predominantly visible wavelengths that involved here, there would be many phonons required for non-radiative decay, compared to the single photon required for radiative decay. The probability of the creation of many phonons is less than the creation of a single photon; this is part of the reason that LaF$_3$ is considered a good host for the other rare-earths.

Absorption in Eu$^{3+}$:LaF$_3$ occurs in the ultra-violet (UV) below the wavelength of approximately 400 nm [55, 64]. Exciting in this band causes luminescence to be observed at a number of wavelengths; a selection of these is shown in Figure 5.5.

### 5.2.2 Fluorescence in Nanoparticles

Nanoparticles are somewhat different to bulk samples in behaviour, as shown in section 4.2. This is seen in a number of properties; one of the more important is the increased relevance of surface effects. The depth at which surface effects become unimportant can vary with the properties being measured, but is generally considered to be approximately three atoms [53, § 17.1], or for our rare earth ions approximately 6 Å (0.6 nm) [64, p.4-122]. Thus, while a 1 μm sphere will have approximately 1 part in $10^{10}$ affected by the surface, a 100 nm sphere will have approximately 1 part in $10^7$, a 10 nm sphere 1 in $10^4$, and a 10 nm sphere 1 in 5 part of its volume in the "surface volume." It is thus easy to see why in macroscopic sample the surface effects can be dispensed with, while nanoparticles have much more significant surface effects.

For ligand-capped rare-earth nanocrystals, a common model used it that of a core, at a distance from the surface, and a shell consisting of the surface. This relates to the depth at which the ligand ceases to have an effect on the properties of the crystal [48, 49]. This is a simple yet effective model of the properties of the nanocrystals in the range where it is valid.

With nanoparticles, the luminescence lifetime is dependent on the refractive index of the particle and the surrounding medium [71], as shown in section 4.4. This is useful in varying the radiative lifetime of the radia-
5.2. LUMINESCENCE IN TRIVALENT EUROPIUM

Figure 5.5: The spectroscopic levels in single crystal 0.5% Eu$^{3+}$:LaF$_3$, with some of the relevant transitions shown. The energy axis is to scale. The large (365 nm) arrow is the wavelength of the pump; this acts on the un-shown states of the TTA ligand, which decays to transfer energy to the Eu$^{3+}$ as shown in figure 2.3. The $^{7}F_{5}$ level is shown as a box as it is poorly resolved in the reference; this is only included as there is a transition in the range of interest (550 nm to 720 nm) that ends on it.

After Kumar et al. \cite{55}.
ive lifetime without modifying the spectral properties of the nanoparticles used. In Y$_2$SO$_4$, Eu$^{3+}$ ions the radiative lifetime $\tau_R$ was shown to follow the relationship\cite{71}

$$\tau_R = \frac{1}{f_{fi}} \frac{\lambda_0^2}{\left( \frac{3}{4} (n^2 + 2)^2 \right) n},$$

where $f_{fi}$ is the electric dipole oscillator strength between final and initial levels $f$ and $i$, $\lambda_0$ is the vacuum wavelength and $n$ is the effective refractive index for a volume fraction $x$ of the space occupied by the particles

$$n = xn_{\text{particle}} + (1 - x)n_{\text{medium}}.$$

This is strictly valid for the case where the average size of the particles is much less than the wavelength of the light used. It does however show that, all else being equal, the lifetime has a dependence of

$$\tau_R \propto \frac{1}{n^5}.$$

This means for our measurements, performed in air ($n_{\text{air}} \approx 1.00$), the recorded lifetimes can be expected to be somewhat longer than those reported in other materials.

The fluorescence lifetime of Eu$^{3+}$:LaF$_3$ can be modelled with a two-part exponential\cite{49,48}

$$I = A_1 \exp \left( \frac{t}{\tau_1} \right) + A_2 \exp \left( \frac{t}{\tau_2} \right),$$

where $\tau_1$ and $\tau_2$ relate to the radiative decay lifetimes of two types of Eu$^{3+}$ ions in our model, with respective contributions of $A_1$ and $A_2$.

A useful parameter is ratio between the integral of the different spectral lines. In Eu$^{3+}$, the two most intense of these transitions are also two of the more interesting: $^5D_0 \rightarrow ^7F_1$ about 592 nm and $^5D_0 \rightarrow ^7F_2$ at about 613 nm. The former is a magnetic dipole-dipole interaction, which makes it quite insensitive to the electronic environment surrounding it. It is therefore often used as an “internal reference” for comparisons with other lines in the ion\cite{49,111,9}. This contrasts with the latter transition, which is a purely electric dipole-dipole transition, which in a centro-symmetric site is strictly forbidden, and so is a sensitive gauge of the symmetry and electric environment of the ion\cite{9,10}. Changing the environment has a significant effect on the magnitude of this, relative to the internal reference $^5D_0 \rightarrow ^7F_1$.

We can define a ratio $R_{ij}$ between the integrals of the lines in the spectra
\[ \Psi \text{ as } R_{ij} = \frac{\int_i \Psi \, d\lambda}{\int_j \Psi \, d\lambda}, \quad (5.5) \]

where the \( i,j \) relate to the transitions \( ^5D_0 \rightarrow ^7F_{i,j} \). With this definition, a larger \( R_{21} \) means the 613 nm, \( ^5D_0 \rightarrow ^7F_2 \), band is of greater relative intensity.

It is possible to interpret this ratio as a measure of the dis-symmetry of the ion site: certainly, that it exists at all shows that there is a distortion in the lattice of the host. However, there are also other effects that can change the electronic surroundings of the ions. For example, the ligand TTA is a somewhat polar molecule. This causes an asymmetry that is not related to the crystal site[9]. Thus, while this ratio is related to the symmetry of the ions, there are other factors that affect the preclude using this solely as a measure of dis-symmetry. This notwithstanding, the ratio can be used to compare the different samples, providing that one remembers that there will also be distortions from the TTA, which is assumed to be constant for the TTA-capped and non-TTA-capped samples, and that increasing the concentration of the dopants will increase the distortion in the lattice.

## 5.3 Europium Trifluoride Nano-crystals

Here we will look at the materials and methods used to investigate the luminescence in nanoparticles capped with oleic acid (OA).

### 5.3.1 Materials Used

The samples we have are of europium-doped lanthanum trifluoride nanoparticles, capped with oleic acid (\( 9\text{-octadecenoic acid, } C_{18}H_{34}O_2 \)). These were prepared using the method of section 4.5 with three doping rates or europium: 1%, 5% and 10%.

Oleic acid is used as a capping agent to enable better mixing of the nanocrystals in polymers and other organic materials[97]. They play little rôle in the optical properties of the nanocrystals, and are ignored for much of this work.

### 5.3.2 Results

Because of the arrangement of the apparatus, the collection of data preferred either the lifetime data or the spectral data: it proved impossible to get a large signal to noise ratio for both. This is a result of the physical constraints
in building the system. Therefore, to ensure the maximum possible accuracy in the data collected, the apparatus was aligned to have the lifetime data most accurate, with the spectral data less so, and then the same measurements repeated, but aligned for maximum spectral data, with the lifetime data less so.

This duplication had the effect of increasing the reliability of the data by allowing comparisons to be made between the same samples. Furthermore, it enabled a consistency check on the performance of the 3 kHz low-pass filter used on the PMT (Figure 5.3). For the measurements taken primarily for spectral results, the filter was removed and the measured fluorescent lifetimes recorded.

The measurements taken were to find if the changes were dependent on the total amount of energy put into the sample. To do this, we defined the fluence to be the optical power per unit area integrated over time

\[ f = \int_0^t \frac{P_{opt}}{A} \, dt. \]  
(5.6)

This gives a quantity with units of J/cm². The traditional spectroscopic units of cm were used to enable easy comparison with the literature. 1 J/cm² = 1 × 10⁻⁴ J/m².

**Lifetimes**

The fluorescence lifetime recorded is shown in Figure 5.6 with a fit to equation 5.4. The fit was computed with the method of least squares, having normalised the amplitude of the data.

The parts of the decay curves fitted to are shown in Figure 5.7.

The parameters found in fitting the data to equation 5.4 are shown in figures 5.8 and 5.9. This shows the expected relationship: the greater the concentration of dopant, the shorter the lifetime. This is because a greater concentration of ions causes a greater amount of inter-ion energy transfer, which provides non-radiative decay mechanisms.

Due to the amount of data for these fittings, a number of simplifications and automations were required for computational efficiency; these, and the noise in the data collected, are responsible for the noise present in the fitted parameters. However, the number of data collected in turn mean that it is possible to average these fluctuations successfully.
Figure 5.6: Fluorescence lifetime measurements of OA-capped samples, with the crosses showing the collected data and the lines the fit to these, at different fluence as shown by the colours. It can be seen that the little change evident is due to the “noise” in the data and thus the fit, rather than any significant physical process.
Figure 5.7: Decay of fluorescence as measured by the PMT and recorded by the oscilloscope. The top trace is the voltage across the PMT as recorded, offset by 1 V for clarity. The bottom trace shows parts of the curve fitted to. To determine the amplitude, the mean of the “foreground” and “background” levels was taken. These levels were picked so that the transient parts were excluded. The length of the data fitted to was varied among the different classes of sample to avoid as much of the background noise as possible.
5.3. EUROPIUM TRIFLUORIDE NANO-CRYSTALS

Figure 5.8: Lifetimes $\tau_1$ and $\tau_2$ from fitting data to the bi-exponential equation [5.4]. The legend refers to both the upper and lower plots. Throughout this thesis, the same colours are used for each of the samples where is necessary to distinguish between them, as in these plots.
Figure 5.9: Amplitudes of each component in equation 5.4 when fitted to the lifetime data. $A_1$ relates to the longer lifetime $\tau_1$. 

$A_1$ relates to the longer lifetime $\tau_1$. 

$1\% \text{Eu}^{3+}: \text{LaF}_3$  
$5\% \text{Eu}^{3+}: \text{LaF}_3$  
$10\% \text{Eu}^{3+}: \text{LaF}_3$
5.3. EUROPIUM TRIFLUORIDE NANO-CRYSTALS

Spectra

The spectra, corrected for dark counts and temperature variations, are shown in Figure 5.10. Just as there is a change in the lifetimes with fluence, there is a change in the spectra: a slight increase in the intensities of the peaks.

Change in Intensity

In the spectral data is clear that the intensity of the luminescence changes. This is confirmed by the data collected to monitor the lifetime which also recorded the amplitude of the emission at $613 \pm 3.5 \text{ nm}$. The change in intensity from the PMT is shown in Figure 5.11.

Change in Ratio of Transition Intensity

It is useful to consider the ratio of the different peaks in order to determine some properties of the site of the Eu$^{3+}$. The ratio, per equation 5.5, is shown in Figure 5.12. The integration was performed numerically, using the trapezoidal rule.

There is a slight decrease in the ratio $R_{21}$, which continues to decrease at a decreasing rate. This is more pronounced in the samples with greater dopant rates.

5.3.3 Discussion

There are a number of possible changes occurring in the systems that effect the results we see. A schematic of the parts of the system in the nanocrystals is shown in Figure 5.13. We will go through each of these parts and interactions in turn and consider what might be occurring.

In figures 5.8 and 5.9 there is a sizeable amount of noise, despite being averaged; this is an artefact of the computational compromises made to ensure the fitting completed in a timely fashion. It is possible to take a longer average, but at the cost of hiding any short-term features, however, we can generate an “average” lifetime which does not have the same amount of noise.

We define the fractional contribution of each of the components of the exponential [57]

$$f_i = \frac{A_i \tau_i}{\sum A_j \tau_j};$$

(5.7)
## CHAPTER 5. LUMINESCENCE

<table>
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<tr>
<th>Wavelength (nm)</th>
<th>Intensity (counts)</th>
<th>Fluence (kJ/cm$^2$)</th>
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<tr>
<td>700</td>
<td>0</td>
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</tr>
</tbody>
</table>

(a) 1% Eu$^{3+}$ : LaF$_3$

(b) 5% Eu$^{3+}$ : LaF$_3$

(c) 10% Eu$^{3+}$ : LaF$_3$

Figure 5.10: Spectra as recorded for the OA-capped samples, at number of logarithmically spaced fluences. This is a representative sub-plot of 100 of the 5670 recorded sets. The data was recorded over 500 ms. Note that the signal to noise ratio of 5.10b is much greater than 5.10a and 5.10c, this is due to a combination of greater intensity than 5.10a and better alignment than 5.10c.
5.3. EUROPIUM TRIFLUORIDE NANO-CRYSTALS

Figure 5.11: The amplitude, as defined in Figure 5.7, of the 613 ± 3.5 nm fluorescence from the PMT, viz. the difference in the mean of the “foreground” and “background” levels. This has been smoothed by a moving average of 49 points. There is a slight increase in the intensity seen for these OA-capped particles.

From this, an effective (or weighted average) lifetime $\tau_{av}$ can then be calculated:\[57\]:

$$\tau_{av} = \sum \tau_i f_i = \frac{\sum_i A_i \tau_i^2}{\sum_j A_j \tau_j}.$$  \hspace{1cm} (5.8)

Using this, the effective lifetimes are plotted in Figure 5.14. The short traces were taken with the UV power at the sample attenuated by half, to 36 ± 2 mW, and run for the same amount of time. This shows that the changes are a function of fluence, not merely of time exposed.

Surface Defects Removed

One possibility is that the surface of the nanoparticles change. It has been seen that ionising radiation can cause a decrease in the surface defects of nanocrystals\[30\].

In one way, the presence of a surface is a defect in itself when regarding a crystal. However, it is possible to have rougher and coarser surfaces: for instance, the difference between the surface of a tennis ball and a cricket ball. For a carefully grown single crystal, it is possible to have the crystal structure
Figure 5.12: The ratio $R_{21}$ of the integrated intensity of the electric-dipole transition $^5D_0 \rightarrow ^7F_2$ at 600–624 nm to the magnetic dipole transition $^5D_0 \rightarrow ^7F_1$ at 585–600 nm. The short traces are recorded with half the incident radiant flux, to determine if the changes are a function of fluence or time.
very close to uniform; for our crystals, this is not likely to be the case. The nanocrystals are grown, but then clump together to form macroscopic groups of nanocrystals. Because each of the nanocrystals is capped with oleic acid, there is no reason to assume the inter-crystal bonds are as strong as the intra-crystal bonds; therefore, when milled to a smaller size in the roller mill, there is likely to be a very irregular surface on the resultant particles, which are still not single nano-crystals, but merely small clumps of nanocrystals, each crystal separated from the others by a layer of oleic acid. While generally the shape of a particle tends toward the lowest possible energy, in this case it is not unreasonable to suggest that the nanocrystals have found a local minimum energy rather than the global minimum, and would require more energy to escape these local minima. One method to do this could be to heat the nanocrystals, thus introducing energy to the lattice; another could be through the use of light.

The UV light, then, may have sufficient energy to excite the ions out of their local minima into a global minimum energy, which is likely to be the sites leading to the total minimum amount of distortion in the crystal lattice for each of the ions involved. To be clear, I mean here that all of the ions in the nanocrystals are involved in this process, not only the dopant Eu$^{3+}$.

**Europium moves around**

Similar to the removal of surface defects, it is possible that the Eu$^{3+}$ moves within the nanocrystal. The commonly used model for nanocrystals is one of a surface “Shell” surrounding a central “core”, which can account for the
Figure 5.14: The average/effective lifetimes of the samples fitted with equation 5.4 using equation 5.8. These are un-smoothed; contrast with the smoothed and yet much noisier figures 5.8 and 5.9. In this figure the noisier sets were recorded with the 3 kHz low-pass filter on the PMT removed; some of the difference between the “filtered” and “un-filtered” data can be attributed to the 0.3 ms time constant of this filter.
5.3. EUROPIUM TRIFLUORIDE NANO-CRYSTALS

significant surface effects\cite{49, 48}. It is possible that the Eu$^{3+}$ moves from one to the other, but this is unlikely, requiring somewhat more energy that the surface modifications would.

**Contamination**

Contamination of the samples is unlikely. The reagents and process used are of the highest quality, and there is limited scope for contamination from outside sources.

It is also possible that there is a heretofore undiscovered reaction between LaF$_3$, toluene nalgene and zirconium; this is discounted as extremely unlikely.

**Oleic Acid Changes**

It is possible that the Oleic Acid capping ligand changes; however, as well as there being no mention in the literature of UV instability of OA, there is the fact it has no direct rôle in the luminescence of Eu$^{3+}$. This is therefore discounted as a possibility.

**Colour Centres**

The formation of *colour centres* in the nanocrystals is a distinct possibility. Colour centres are defects in a crystal lattice that lead to observable colours in otherwise clear/colourless crystals.

Colour centres were observed by Thomas J. Pearsall, an assistant to Michael Faraday at the Royal Institution, in 1830, but were not investigated in any depth until the 1920s and 1930s. Many of these investigations were performed in alkali halides. To this day, the cast majority of investigations of defects in crystals have been performed with the alkali halides.

It is thus unsurprising that the study of these *Farbenzentrum*\cite{91} in the alkali halides led to the nomenclature used to describe them. For instance, the prototype colour centre, an absent alkali ion whose lattice point has been filled solely by an electron is called an “F-centre”. This also extends to the other types of defects; two that are relevant here are the $V_K$-centre and the H-centre. Note that the notation for these defects is not standardised, although there are two predominant schemes that are used: the original, non-systematic system that has arisen from use; and a somewhat systematic system that was proposed by Sonder and Sibeley\cite{91} in 1972, which has not been widely adopted.

\footnote{\textbf{91}From the German \textit{farbe} “colour” and \textit{zentrum} “centres.”}
CHAPTER 5. LUMINESCENCE

Colour centres are known in Eu\textsuperscript{3+}:LaF\textsubscript{3}\textsuperscript{[24]. Thus far, these have only been seen for exposure to ionising radiation; the cited results are for incident energy of mega-electron-volts, which correspond to a wavelength of picometres or less. However, colour centres have been seen to form in other materials for incident energy of much less than this; for example in rare-earth doped glasses\textsuperscript{[31].}

The colour centres observed in Eu\textsuperscript{3+}:LaF\textsubscript{3} in \textsuperscript{[105]} were formed using γ-radiation of energy approximately 1.25 MeV, from a \textsuperscript{60}Co source. The samples were irradiated at a temperature of 20 K, and the thermoluminescence measured. Investigation of these found that the defects formed here were of the V\textsubscript{k} and H types.

Thermoluminescence is the luminescence of a crystal as it is heated; this comes from the increasing energy in the crystal lattice allowing stresses that had accumulated to be released, with the emission of light, usually in the visible spectrum.

A V\textsubscript{k}-centre (or [X\textsuperscript{−}]\textsubscript{2}-centre, with X denoting the host halide) is a “self-trapped hole”: a simple charge defect there are no extra or missing ions in the lattice, but a single electron missing.

An H-centre is an interstitial ion or molecular ion in a lattice location where there ought to be a halide ion, which here is fluoride.

The broad under-band of our measured spectra are quite similar to the F\textsuperscript{+}\textsubscript{2} luminescence seen in KCl\textsuperscript{[1, 2]} and other alkali halides\textsuperscript{[102]}. Unfortunately, the primary method of characterising colour centres and self-trapped excitons and holes is by absorption measurements and with Electron Paramagnetic Resonance (EPR), to obtain data on the site and concentration of the ions. We are unable to perform these measurements; this is however, a perhaps promising direction for future investigations.

Change in Oxidation State

The divalent Eu\textsuperscript{2+} ion has long been known to have a broad indistinct luminescence band. Historically, this was a problem for spectroscopists, because it obscured the much more interesting Eu\textsuperscript{3+} lines\textsuperscript{[23, 15].}

In K\textsubscript{4}CaSi\textsubscript{3}O\textsubscript{9}, the Eu\textsuperscript{2+} ion has a band with a sharp centre at 522 nm and a half-width at half-maximum (HWHM) of 60 nm\textsuperscript{[108]}. In mixture with strontium chloride (SrCl\textsubscript{2}), europous chloride (EuCl\textsubscript{2}) has fluorescence at approximately 405 ± 15 nm and from 670 nm to 830 nm\textsuperscript{[35]}. In complexes with crown ethers and cryptands, the centre of the band is at approximately 495 nm, with a HWHM of 30 nm\textsuperscript{[104]}. Analysis of our results is hindered in this by the 532 nm long-pass filter, which was intended to remove the UV light of the pump. This truncates the
signal at the wavelengths where the Eu$^{2+}$ would become obvious. Unfortunately, the importance of this was only realised after the data collection was complete; and furthermore, the most significantly affected samples were the last to be collected.

The transformation of the Eu$^{3+}$ would explain a number of the changes seen: the decrease in the intensity of the Eu$^{3+}$ lines, the increase in the lifetimes and the formation of the “brown” colour in the samples.

The UV photo-reduction of Eu$^{3+}$ has been seen for high-energy ($\lambda < 250$ nm) photons \cite{109}. However, with ultra-short pulses of lower energy, this has also been seen, which may be due to the presence of multi-photon processes.\textsuperscript{75}

5.3.4 Conclusion

We conclude that the non-TTA-capped nanoparticles change in luminescence slightly. Movement of the Eu$^{3+}$ ions and changes in the oleic acid are discounted; furthermore, there is evidence the Eu$^{3+}$ undergoes photoreduction to Eu$^{2+}$, our measurements are insufficient to determine if this is the case. The formation of colour centres in the nanocrystals and the removal of surface defects are the most likely changes; it is possible that a combination of these is occurring.

5.4 Europium-TTA Complexes

The use of rare-earth $\beta$-diketonates is a common method to increase the intensity of luminescence seen. Here we repeated the measurements reported above on a sample of (Eu(tta)$_3$) : PMMA in amorphous polycarbonate.

5.4.1 Materials

The sample measured here is of a (Eu$^{3+}$:LaF$_3$)$_{10}$ complex suspended in amorphous polycarbonate. This was in the form of a short cylinder, with flat sides set at an angle to each other. The diameter of this “cylindrical wedge” was approximately the same as the vials used for the powder. This made mounting a matter of removing the vial and inserting the cylinder.

5.4.2 Luminescence

Because the ligands are in intimate contact with the Eu$^{3+}$ ion, the efficiency of energy transfer is very high; it follows the path shown in Figure 2.4.
CHAPTER 5. LUMINESCEENCE

Figure 5.15: Measured luminescence lifetime of the (Eu(tta)\textsubscript{3} 1\%) : PMMA sample. There is little change in the data. The shape of this has not been explained. Note the logarithmic axes. This is a representative subset of 10 from the total 5670 traces collected for each sample.

5.4.3 Method and Apparatus

The method is the same as described in section 5.1. Because the emitted light was much stronger than for the nanocrystal samples, the pump power was set to 34 ± 5 mW, and a neutral density filter of optical density 4 was inserted between the two lenses leading to the photo-multiplier. This reduced the signal to approximately 40% of the actual level. This has not been compensated for in the presented data, so to remain within a similar range of values as the other samples. The spectrometer had sufficient reserve that it did not need a filter; the results presented for it are the actual level seen.

5.4.4 Results

Lifetime

The fluorescence decay curves measured are shown in Figure 5.15. It can be seen that the decay does not follow the exponential of equation 5.4, therefore it was not fitted to this data. There are a number of possibilities for this. We exclude the possibility of the machine malfunctioning, as our other measurement were performed with the same apparatus before and after this one. It is possible that these are saturation effects; in any case, all that we care about with this complex is the change (or lack of) that is seen with fluence.
Figure 5.16: Spectrum of (Eu(tta)$_3$ 1%) : PMMA. The transitions $^5D_0 \rightarrow ^7F_J$ in the Eu$^{3+}$ ion are clearly visible; from the left these are to lower levels $J = 0, 1, 2, 3, 4$. The transitions to $J = 5, 6$ are not visible with this pumping energy. The level decreases slightly toward the end of measurements. This is a representative sub-plot of 10 of the 5670 recorded sets, each recorded over 500 ms.

### Intensity and Spectrum

Similarly to the lifetime, the spectra (Figure 5.16) shows little change with fluence, both in absolute intensity and in the ratio of the peaks.

The different transitions from the $^5D_0$ level of Eu$^{3+}$ are clearly visible in the spectra.

### 5.4.5 Discussion

It is immediately apparent that the Eu$^{3+}$ in complex with TTA is stable with respect to fluence when in APC. This contrasts with both the non-TTA-capped nanocrystals above and the TTA-capped samples below, at least over the range of fluence that we measured.

One of the possible reasons for this is that the APC acts to fix the TTA molecule in space, so that the bond length cannot change and thus causes the resonant energy of the molecule to remain constant.

It is also seen from the spectra that the ratio $R_{21}$ (equation 5.5) of the different transitions is approximately 17, which is comparable with the values of 15–20 in the literature [9, p.175]. This can be accounted for by considering the distortions in the environment of the Eu$^{3+}$ ion, as there are three TTA ligands attached to it causing the centro-symmetrically “forbidden” $^5D_0 \rightarrow ^7F_2$ transition to become allowed.

The strength of the transition also allows observation of all of the $^5D_0 \rightarrow ^7F_J$ transitions, from $J = 0$ to $J = 4$. The weak transitions to the $^7F_5$ and $^7F_6$
levels are not visible; this is as expected for transitions pumped with UV light\cite{53}.

What is less readily apparent is the reason for the unusual luminescence decay rate. This is an unknown matter which is worthy of further investigation; we do not do this here, as for our investigation of nanocrystals it suffices to find that the luminescence does not change with fluence.

5.5 TTA-Capped Nanocrystals

5.5.1 Materials Used

For these measurements, nanoparticles which had been sensitised with a \(\beta\)-diketonate ligand were used, with the same measurements performed as for the previous samples. The nanocrystals are made following the method in section 5.3.1, then a partial exchange of the oleic acid ligand for thenoyltrifluoroacetone (TTA) was carried out. This results in a nanoparticle that has both OA and TTA ligands attached\cite{48, 49}.

5.5.2 Method and Apparatus

The same method and apparatus were used for these data as in section 5.1.

5.5.3 Results

The fluorescence decay in the TTA-capped nanoparticles can be modelled by a three-part exponential of the form\cite{48}

\[
I = A_1 \exp \left( \frac{-t}{t_1} \right) + A_2 \exp \left( \frac{-t}{t_2} \right) + A_3 \exp \left( \frac{-t}{t_3} \right),
\]

(5.9)

with the first two terms relating to the interaction between OA/TTA/Eu\(^{3+}\), while the third is a result of the presence of TTA. However, the third component has a strong dependence on temperature and at room temperature is very small. In our samples this was not obviously seen, and so to reduce error in the fit, a two-part exponential of the form of equation 5.4 was used.

The data collected and the resultant fit is shown in Figure 5.17.

It can be seen that the lifetime varies with fluence, and that the lower concentration of Eu\(^{3+}\) results in a greater change.

\(^{11}\) Also TTFA.
5.5. TTA-CAPPED NANOCRYSTALS

Figure 5.17: Luminescence decay in the TTA-capped samples. Note the logarithmic axis. These have a sizeable noise level at low intensity; this is due to limitations in the dynamic range of the oscilloscope used to collect the data. This is a representative subset of 10 from the total 5670 traces collected for each sample.
The parameters of the fit are plotted in figures 5.18 and 5.19 along with the non-TTA-capped nanoparticles.

The spectra were corrected in the same way as stated in section 5.1. The results are shown in Figure 5.21. These show a significant decrease in intensity for all of the peaks. There is also an “under-band” that arises from below 710 nm. This is shown as decreasing from ca. 590 nm to zero at ca. 530 nm; this shares a similar shape with the transmission band of the long-pass filter used (refer Figure 5.2), and is likely to be due to this. Private communications with Dr. Quilty at IRL lend to weight to this thought: he has subsequently performed similar measurements and has observed the under-band continuing to increase to at least 300 nm.
Figure 5.19: Amplitudes of each component in equation 5.4 when fitted to the lifetime data collected for the TTA-capped samples. $A_1$ relates to the longer lifetime $\tau_1$, and $A_2$ correspondingly to $\tau_2$. 
Figure 5.20: The average/effective lifetimes of the samples fitted with equation 5.4 using equation 5.8. These are un-smoothed; contrast with the much noisier figures 5.18 and 5.19. In this figure the lower (noisier) traces were recorded with the 3 kHz low-pass filter on the PMT removed; some of the difference between the “filtered” and “un-filtered” data can be attributed to the 0.3 ms time constant of this filter. The short traces relate to the measurements made with the intensity halved. It can be seen that the average lifetime depends on the fluence rather than on the time of exposure.
5.5. **TTA-CAPPED NANOCRYSTALS**

![Graph of TTA-capped nanoparticles spectra]

Figure 5.21: Spectra of the TTA-capped nanoparticles. Notice that a broad under-band forms in all three samples, being most noticeable with the lower concentration of Eu$^{3+}$, and that the intensity of the peaks at 613 nm and 700 nm change much more rapidly than the 592 nm peak.

This is a representative sub-plot of 10 of the 5670 recorded sets.
Change in Intensity

There is also a significant decrease in the intensity of the luminescence seen, which is obvious from the spectra shown above. We also recorded the amplitude of the luminescence seen by the PMT, at 613 ± 3.5 nm. The changes in this are shown in Figure 5.22.

Change in Ratio of Transition Intensity

It is seen in the spectra that the ratio of the peaks change significantly here. The integral equation 5.5 was performed numerically using a trapezoidal method, and is plotted in Figure 5.23. It is seen that there is a very sharp decrease in the ratio $R_{21}$ for the TTA-capped nanoparticles, and that it approaches, but does not meet, the non-TTA-capped nanoparticles.

5.5.4 Discussion

The system in the TTA-capped nanocrystals has one further participant compared to the non-TTA-capped nanoparticles. This is shown schematically in Figure 5.24. We will consider the changes in each of these in turn, comparing
Figure 5.23: The ratio $R_{21}$ of the spectral integral of the two interesting peaks at 613 nm and 592 nm. It can be seen that the samples with lowest concentration of Eu$^{3+}$ change more rapidly than the higher ones.
CHAPTER 5. LUMINESCENCE

Figure 5.24: Energy transfer in the TTA-capped nanocrystals. The LaF$_3$ crystal transfers little to no energy to the Eu$^{3+}$ or to the TTA molecule, but “collects” energy from the decay of the lower levels of the Eu$^{3+}$ and from non-radiative decay in the TTA molecule. The interaction between the TTA and the Eu$^{3+}$ is the interesting one, that appears to change with exposure to the UV pump.

There is great change seen in the luminescence; especially in the absolute and relative intensities of the spectral lines. Before this was analysed, it was considered possible that the processes occurring in the Eu$^{3+}$:LaF$_3$ and (Eu$^{3+}$:LaF$_3$)$_{TTA}$ were the same, with the changes in the non-TTA-capped samples were happening much slower than in the TTA-capped samples, because the TTA increased the absorption cross-section increasing the amount of energy absorbed from the UV source. We can see, however, that this conjecture is not supported by the results: the most significant of which here is that the sign of the changes in the intensity of luminescence is different; in Figure 5.21 in the TTA-capped samples, the there is a decrease in the intensity whereas in the non-TTA-capped samples (Figure 5.10) there is a slight increase to a constant level.

Despite these great changes, there are some similarities which suggest that there are some of the same processes occurring. For example, the initially the lifetime increases in the non-TTA-capped samples, then stops changing. For the 5% and 10% Eu$^{3+}$ samples, the lifetime also increases in a similar way with fluence, before decreasing. This is not inconsistent with a process that
affects only the Eu$^{3+}$→LaF$_3$ system affecting both of the types of samples, which is then overwhelmed by some other change in the TTA→Eu$^{3+}$:LaF$_3$ system, which would of course not occur in the samples without TTA.

**Surface Defects Removed**

As in section 5.3.3, it is possible that the surface defects are modified. There is also the possibility that the surface is affected by the presence of a different ligand, as well as the increased effective absorption cross section increasing the power, and so increasing the rate at which changes occur.

**Europium moves around**

If the Eu$^{3+}$ were to move around, the increases absorption cross-section due to the TTA would increase the amount of energy in the system, possibly increasing the rate of movement. The method for this is still unknown; it is also unlikely as it would require the crystal structure to be changed, as the Eu$^{3+}$ substitutes for the La$^{3+}$ in the host.

**Contamination**

In addition to the discounted possibility of contamination in section 5.3.3, there is a very slight chance that there is a heretofore unknown reaction between the organic nalgene and the TTA. As well as being very unlikely, this is also not in the scope of this thesis to investigate.

**Ligands Detach**

The bond between the host (Eu$^{3+}$ or La$^{3+}$) and TTA-ligand is generally considered to be between the oxygen atoms in the molecule and the rare-earth[9]. If the incident photons are of higher energy than the bond between the ligand and the host, it is possible that the ligand is detached, but otherwise unchanged. However, it is probable that the sample with the ligands detaching would tend toward the luminescence seen in the samples without TTA. The absorption spectra would remain the same as the the TTA is still intact and absorbing, but this is reduced to ligand fluorescence and other non-radiative decay, as there is no way to transfer the energy to the Eu$^{3+}$:LaF$_3$ host.

This, however, is not observed. The relative intensities of the spectral peaks in the nominally TTA-capped samples do not become like the non-TTA-capped samples. Likewise, the fluorescence lifetime remains somewhat less for the TTA-capped samples than it is for the non-TTA-capped samples,
which suggests that there is an energetic connection remaining between the ligand and host.

One could therefore tentatively conclude that the TTA does not become detached in any significant way from the nanocrystals.

Ligands Change

One way the ligand could change is if the triplet state starts above the level of the $^5\text{D}_0$ level of the Eu$^{3+}$, but falls after exposure to the UV light.

It is known that the triplet levels vary between ligands, and are also temperature dependent\cite{9}, which can be used to tune the amount of luminescence observed.

It is likely that the levels in the TTA are dependent on the size and shape of the molecule. If the molecule changes shape with exposure to UV even a little, it could have significant effects on the energy levels. It is also possible that the singlet level will change. The reflectance of the samples was measured before exposure to the UV, and is shown in Figure 5.25. The diffuse reflectance was measured rather than the absorption as we are dealing with a powder, which is difficult to measure transmissivity through in a repeatable fashion. This was done in a dual beam spectrophotometer\cite{12} with certain optical modifications for the very small amount of sample we had. The TTA-capped samples show a broad band of absorption below approximately 400 nm, from the TTA. Note that the power of light from the spectrophotometer is very small; there was no significant change seen in the spectra over the three averages taken.

For our main measurements, we were pumping at 365 nm, which is at the long edge of this absorption band. A slight shift in this band toward higher energy could cause a great change in the absorption. D\textsuperscript{22} Quilty and Clarke at IRL, related in a private communication, have said that for irradiance at 325 nm, the absorption does not change. This suggests that the band does not move toward longer wavelengths, as 325 nm is toward the shorter end of the absorption band. However, this does not imply that the band does not change. Measurements of this are to be performed by the D\textsuperscript{22} presently.

As we have measured above, the Eu$^{3+}$-TTA complex is stable in luminescence when exposed to UV light. However, there are few measurements of the stability of $\beta$-diketonate-capped nano-particles in the literature.

\cite{12}Shimadzu UV3100-PC, with MPC-3100 large sample box and associated integrating sphere.
Figure 5.25: The reflectance of the various samples, before exposure to UV light. The increased absorption from the TTA ligand is immediately obvious.
CHAPTER 5. LUMINESCENCE

Colour Centres

The formation of colour centres, as described in section 5.3.3 is still possible, and is possibly accelerated by the increase of absorption caused by the TTA. This is supported by a slight change in the colour of the samples after exposure to the UV light.

Change in Oxidation State

Although the broad under-band does not seem to correspond to the emission spectrum of Eu$^{2+}$, it would provide an explanation for the presence of the band in the TTA-capped samples but not the non-TTA-capped samples.

The decrease in the Eu$^{3+}$ lines relative to the increased under-band was most significant for the (1% Eu$^{3+}$ : LaF$_3$)$_{100}$, compared to the other concentrations of Eu$^{3+}$. The reduction rate of Eu$^{3+}$ is likely to be dependent on the intensity of the UV irradiance. Therefore in a sample fewer Eu$^{3+}$ ions to begin with, the fractional change will be higher than the fractional change seen in a sample with a large number of Eu$^{3+}$ initially. This we observed.

A possible reason the under-band is not seen in the non-TTA-capped samples could be because the reduction of Eu$^{3+}$ to Eu$^{2+}$,

$$\text{Eu}^{3+} + e^- \rightarrow \text{Eu}^{2+},$$

(5.10)

requires an electron. The provenance of this electron is difficult to explain; as conjecture, however, it is possible the non-TTA-capped particles have only enough electrons to associate with the ions in the crystal. In the TTA-capped samples, the ligand molecule could partially yield an extra electron, possibly from the oxygen bonding atoms, to decrease the oxidation state.

5.6 Conclusions

In this chapter, we measured the emission of light from a number of transitions in Eu$^{3+}$ nanoparticles. The OA-capped particles were shown to be reasonable stable in emission with incident fluence, as was the Eu$^{3+}$-TTA complex in PMMA. The TTA-capped nanoparticles however did not have constant emissions. The changes were shown to be a function of the fluence of the pump, over the range we measured. This could be a result of a few things; however, the lifetime measurements suggest that the TTA ligands do not detach from the nanoparticles. Comparing the TTA-capped nanocrystals and the Eu$^{3+}$-TTA complex, it is possible that the ligand undergoes a
5.6. CONCLUSIONS

structural change on the nanocrystals which inhibits it transferring energy to the Eu$^{3+}$.

From this, there are doubts raised about the viability of TTA-capped Eu$^{3+}$ nanoparticles as a gain source; it is possible mounting these polymer hosts, as done for the (Eu(tta)$_3$) : PMMA sample, could retain the desirable qualities, viz. the large emission at 613 nm.
Chapter 6

Scattering and Gain

In making amplifiers, maximum nett gain can be reached when the losses within the system are minimised. Scattering can be a major source of losses. The scattering cross-section is a measure of scattering from a particle; nano-particles by virtue of their small size can be expected to have very small scattering cross-sections.

In the films we measured, they weren’t, and in this chapter we investigate how great they were, how big they could be expected to be and and what implications this has for the manufacture of amplifiers.

6.1 How big $\alpha$ is: Measurements

To measure scattering losses in the film, we coupled light in with a prism, as shown in figure 6.1.

We performed measurements on the APC films doped with nanoparticles, and on two other films, using helium-neon laser light of $\lambda = 632.8$ nm. The HeNe was to be used for alignment, to be replaced by the dye laser source at the expected gain wavelength, 613 nm. In light of the results this was not necessary.

The results of coupling into the film, shown in figure 6.2, were so disappointing that it was thought the method of figure 6.1 was flawed. It can be seen the light coupled in is scattered immediately; within 2 mm of the edge of the coupling prism.

To check the method, two other films were chosen from some at hand; polymide tape and ordinary office-grade cellulose tape. These have refractive

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1RS 14 number 109-781, 60$\mu$m thick, same material as DuPont “Kapton” brand; and Sellotape “Golden Original” brand, 47.5$\mu$m thick, respectively.
Figure 6.1: Arrangement for coupling light to measure scattering. Using ray optics, the angle of the incident light was required to satisfy $\theta < 7.8^\circ$, for 632 nm light and APC film (i.e. $n_0 = 1.52$, $n_1 = 1.56$, $n_2 = 1.0003$, $n_3 = 1.965$.) A thumbscrew provided pressure in the direction indicated to ensure the film was in intimate contact with the prism. Leaky rays are not considered here. Scale distorted for clarity.
Figure 6.2: Coupling light to the nanocrystal-containing film. The incoming beam is from the right. There is what appears to be a short width of light guided through the film; this is in fact light coming through the front face of the prism, as checked by removing the prism from the film surface and observing the light still being there. The glass substrate is $25 \times 25 \times 1$ mm.
CHAPTER 6. SCATTERING AND GAIN

(a) Polyimide.

(b) Cellulose.

Figure 6.3: Polyimide and cellulose tapes used as waveguides. In both cases the beam enters from the right; the prism is obscured in its mount. The beam is guided for most of the length of the tape; in both cases imperfections (e.g. dust) cause the beam to be seen along its length. A green box is drawn to show the path of the beam; being good waveguides, little light escapes to photograph.

indices of $n = 1.70^{28}$ and $1.469^{50}$ respectively. Coupling light into these films mounted (stuck) onto slides was quite simple, as shown in figure 6.3.

To investigate this, the APC film with (5% Eu$^{3+}$ : LaF$_{3}$)$_{113a}$, and another of plain APC, were looked at under a microscope, as shown in figure 6.4. What can be seen is that there were a large number of rather large bubbles present: these are not conducive to transmission. Poor transmission can also be seen in the appearance of the films, as in figure 6.5. It can be seen that, in addition to the bubbles, the nanocrystals seem to make the films less transparent still.

We therefore see that the films we were supplied with are inadequate to perform measurements with, as a result of the presence of bubbles in them.
6.1. MEASUREMENTS

(a) (5% Eu$^{3+}$ : LaF$_3$)$_{110}$ in APC.  

(b) APC alone.  

Figure 6.4: Bubbles in the films; on the left the film with Eu$^{3+}$:LaF$_3$, the right the APC alone for comparison. The bubbles can be seen as dark spots in the APC film; the white spots are those bubbles bisecting the focal plane of the microscope. The scratches in the right hand film are believed to be from the coupling prism. In both films it can be seen that the bubbles are widely distributed. The field of view is approximately 500 $\mu$m across.  

Figure 6.5: A comparison of the APC films with (right) and without (left) nanocrystals. This shows three aspects of the films: the scattering due to the nanocrystals, the difficulty in ensuring adhesion, and the non-uniformity of the edges. The green mark is to indicate orientation.
6.2 How big $\alpha$ ought to be: Theoretical Scattering

Knowing the films we have are inadequate, we put them aside except as a reference for reasonable parameters, and use theory to predict what losses might be expected. We first find the refractive indices of the materials, which are required for the calculations, and then the expected losses using a set of reasonable parameters and the Mie theory of scattering from particles.

6.2.1 Refractive Index

The APC films have been measured\footnote{Cargille Labs Inc. “A”-series, certified to $n \pm 0.0002.$} as $n = 1.57$; the refractive index of the nanoparticles has not. As described in section 4.3, this can be sensitive to the composition of the particles and especially the size. We therefore made the apparatus in figure 6.6 to measure the refractive index by putting particles into oils of different refractive indices and directly measuring the scattering. We used 750\(\mu l\) of refractive index matching oil\footnote{2} and 70 mg of \((5\% \text{ Eu}^{3+} : \text{LaF}_3)_{\text{ta}}\) nanoparticles in each vial.

For different refractive indices, the results are shown in figure 6.7. There

Figure 6.6: The scattering apparatus, from the side. The entire arrangement was encased to keep out room lights.
6.2. THEORETICAL SCATTERING

Figure 6.7: Scattering of 10 mg of 5% Eu$^{3+}$ : LaF$_3$ nanocrystals in 750 µl of various refractive index oils. There is a local minimum at $n = 1.52$, which corresponds to that of the glass vial used; the global minimum at $n = 1.56 ± 0.005$ reflects the effective refractive index of the nanoparticles. The curve is a fitted shape-preserving polynomial.

are two minima in the scattering, at $n = 1.52$ and $n = 1.56$, with the latter the smallest.

It is unlikely that there is two refractive indices from the same substance; however, the refractive index of the glass vial used is $n = 1.52^{[33]}$. Considering this, we can explain the results seen. First consider a refractive index oil away from the minima and the glass, say, $n = 1.62$. Here, the light is scattered by the nanoparticles and encounters two optical interfaces between the beam and free space: between the oil and glass, and between the glass and air. From both of these interfaces, there are Fresnel reflections of the scattered light, which causes more than just the initially scattered light to be caught by the detector.

At $n = 1.52$, there is effectively one interface: between the air and glass. This means that only one source of Fresnel reflections, so that more of the scattered light escapes at once rather than “bouncing around”.

Considering this, the refractive index of the nanoparticles is found to be $n = 1.56 ± 0.01$. 
6.2.2 Calculations of Scattering

Knowing the refractive index of the nanoparticles, we can now calculate the extinction coefficient $\alpha$ from Beer’s Law,

$$\frac{I_f}{I_i} = e^{-\alpha z}, \quad (6.1)$$

for non-absorbing particles. This is the case for our measurements made with the HeNe at $\lambda = 632.8$ nm in Eu$^{3+}$ ions; of course, on the transitions there is rather great absorption. We treat this absorption separately, when we consider the transition rates and the expected gain in the ions.

We assume single scattering, so that the extinction coefficient $\alpha$ is directly proportional to the extinction cross-section $C_{\text{ext}}$, and the number density of particles $N_s$.

We’ll first calculate the value of $\alpha$ that might be expected from our nanoparticle-containing films, and then vary the parameters a little to see what effect this has on the extinction.

We assume single scattering, so that we have

$$\alpha = N_s \cdot C_{\text{ext}}. \quad (6.2)$$

$N_s$ can be calculated geometrically; $C_{\text{ext}}$ is a complicated function, which we derive (using Mie scattering theory) in appendix B and calculate numerically using the program in appendix C. We assume single scattering on the basis of the small particle size, the close refractive index between film and nanoparticles, and the low weighting of nanoparticles resulting in a small number density, and the nanoparticles being trapped in a waveguide, where it assumed that any light scattered is sent outside the waveguide volume. As we found above, this is invalid for our real films, due to the large number of bubbles.

If we take a monodispersed mass of particles with radius $a$ and density $\rho_d$, weighted into a polymer substrate with density $\rho_f$ as $x : 1$, we get

$$N_s = \frac{3x}{4\pi a^3} \left( \frac{1}{\rho_f} + \frac{x}{\rho_d} \right). \quad (6.3)$$

For our rare-earth-doped rare-earth nanoparticles Eu$^{3+}$:LaF$_3$, we assume the density to be a linear combination of EuF$_3$ ($\rho = 6790$ kgm$^{-3}$) and LaF$_3$.  

$^3$The subscript “$s$” here denotes “spheres”; we will later introduce a number density of ions $N_i$.  

(ρ = 5940 kgm\(^{-3}\))\[\text{[13]}\], to give \(ρ_d = 850x' + 5940 \text{kgm}^{-3}\). \(x'\) is the doping rate of Eu\(^{3+}\) in Eu\(^{3+}\):LaF\(_3\).

We start with the parameters of the films as supplied: \(a = 7 \text{nm}, ρ_d = 5982.5 \text{kgm}^{-3}, ρ_f = 1200 \text{kgm}^{-3}, n_1 = 1.56, n = 1.557\)\[\text{[83]}\]. With a weighting of \(x = 0.1\), we find an expected extinction coefficient of \(α = 4 \times 10^{-3} \text{m}^{-1}\). The results above show the light being scattered totally in less than 2 mm. This gives a measured extinction coefficient of ca. \(10^3\), which is substantially more than we calculate; in fact it is rather small in a general sense. For example, certain polymer fibres\[4\] have losses of ca. \(18 \times 10^{-3} \text{m}^{-1}\).

Starting from these values, we vary them a little, from \(a = 1 \text{nm}\) to \(a = 150 \mu\text{m}\). This is the range of possible sizes from the various types of nanoparticles in we were supplied with.

This is shown in figure 6.38.

Assuming the refractive index \(n_1\) of the nanoparticles is fixed and that of the medium \(n\) changes, we vary the difference in this over a range of \(-0.1 < δn < 0.1\). This is a very broad range, which takes into account the refractive index changing with the particle size\[60\]. The graph is nominally asymmetric, although over our range this is not readily apparent. It shows that the extinction coefficient is strongly dependent on \(δn\), but the dependence becomes weaker with increasing \(δn\). We also vary the weighting \(x\); as is expected with our single scattering model, \(α\) is linear as a function of \(x\).

Considering this, we can see that while \(α\) has a strong dependence on the particle size, it has a much stronger dependence on the difference in refractive index between polymer and nanoparticles. Furthermore, although \(α\) cannot be zero for a non-zero particle size, we are able to adjust the refractive index continuously, and so are able to come arbitrarily close to zero scattering by changing the refractive index of the medium.

### 6.3 Gain Calculations

Because the amount of loss is small, the amount of optical gain required to reach nett optical transparency is also small. Furthermore, with the rare-earth ions the long lifetimes mean that it is relatively easy to obtain total population inversion.

In this section, we will calculate two requirements: the population inversion required for nett optical transparency, and the incident pump power required for this; as well as the possible gain available for total population inversion. This is done for the two strongest transitions: \(^5\text{D}_0\to^7\text{F}_2\) and \(^5\text{D}_0\to^7\text{F}_1\).

\[\text{[4]}\]Thorlabs GIPOF50, 50μm graded index perfluorinated polymer optical fibre.
Figure 6.8: The effects of varying the particle size, refractive index difference and weighting on the calculated extinction coefficient $\alpha$. 

(a) $\delta n = 0.001$, $x = 0.1$. 

(b) $\alpha$ as indicated; $x = 0.1$. 

(c) $\delta n$ as indicated; $a = 10 \text{ nm}$. 

Figure 6.8: The effects of varying the particle size, refractive index difference and weighting on the calculated extinction coefficient $\alpha$. 

![Graph showing the effects of varying particle size, refractive index difference, and weighting on the extinction coefficient $\alpha$.](image-url)
6.3. GAIN CALCULATIONS

6.3.1 Number Density of Ions

The number density of ions is needed for these calculations. In the nanocrystal containing films, this is given by

\[ N_i = \frac{xN_1}{M_d \left( \frac{1}{\rho_f} + \frac{x}{\rho_d} \right)}, \quad (6.4) \]

where \( x, \rho_d \) and \( \rho_f \) are the weighting and densities as in equation 6.3. \( N_1 \) is Avagadro’s number; and \( M_d \) is the molar density of the nanocrystals in kg mol\(^{-1}\). We again take Eu\(^{3+}\):LaF\(_3\) to be a linear combination of EuF\(_3\) and LaF\(_3\), so that \( M_d = 0.013058x' + 0.19590 \text{ kg mol}^{-1} \); for our 5\% Eu\(^{3+}\)-doped films, this is 0.1966 kg mol\(^{-1}\). In our 10\% weighted films then, the number density of ions is \( N_i = 3.6 \times 10^{26} \text{ m}^{-3} \).

6.3.2 Lineshape, Spontaneous Emission Rate and Quantum Efficiency

The gain coefficient \( \gamma(\nu) \) is introduced in section 3.4 as

\[ \gamma(\nu) = \left[ A_{21} \frac{c^2}{8\pi n^2 \nu^2} g(\nu) \right] \left[ N_2 - \frac{g_2}{g_1} N_1 \right]. \quad (6.5) \]

Of the parameters in this, we know the speed of light \( c \) and the refractive index \( n \) of the medium. We have measured the frequency \( \nu \) of the transition in chapter 5, and from this can determine the lineshape \( g(\nu) \). The spontaneous emission rate does not vary with material, and can be found from calculated values.

The lineshape function can be defined as the probability density of photon emission as a function of frequency. We have recorded this as shown in figures 5.6, 5.15 and 5.17. Normalising the area under each transition we can find the lineshape function as shown in figure 6.9.

It will be recalled that the luminescence from the TTA-capped samples was seen to change quite significantly, although monotonically, in chapter 5. To see if this was important here, we found the lineshape function for both high and low fluence. As can be seen, there is greater noise in the data for high fluence, which is a result of the signal being substantially smaller than in the low fluence case, but otherwise the lineshapes are similar.

The values we will use for the lineshape function and the frequencies of the transitions are shown in table 6.1.

Also shown is the linestrength and spontaneous emission rate for each
Figure 6.9: The lineshape of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ levels. The traces are for the high and low fluence cases as indicated.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\nu$ (THz)</th>
<th>$g(\nu) \times 10^{-13}$ s</th>
<th>$S_{21} \times 10^{-65}$ C${}^2$m$^2$</th>
<th>$A_{21}$ m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5\text{D}_0 \rightarrow ^7\text{F}_1$</td>
<td>507</td>
<td>1.5</td>
<td>10</td>
<td>1.4</td>
</tr>
<tr>
<td>$^5\text{D}_0 \rightarrow ^7\text{F}_2$</td>
<td>488</td>
<td>1.2</td>
<td>3.8</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Table 6.1: The values of the transition frequency, lineshape function and spontaneous emission coefficient used in our calculations. The lineshape function is from [59].
of the transitions. The linestrengths were calculated\[59\] for Eu$^{3+}$ in LaF$_3$; these were transformed to the emission rate as\[44\]

$$A_{21} = \frac{16\pi^3 \nu_2^3}{3g_2\varepsilon_0hc^3}S_{21},$$

(6.6)

where $g_2$ is the degeneracy factor of the upper level: $g_J = 2J + 1$. The linestrengths and spontaneous emission rates are also shown in table 6.1.

### 6.3.3 Gain Schema and Calculations

The basic scheme of our nano-particle-ligand system can be approximated as a selectively-pumped four-level laser system, as shown in figure 6.10.

In this scheme we ignore the processes causing the population of the $T_1$ level, $M_1$, since the singlet state $S_1$ is directly populated by the UV pump and rapidly transfers energy to the triplet state. The $T_1$ state then undergoes a fast energy transfer to excite the metastable $^5D_0$ state in Eu$^{3+}$. The population of the $^5D_0$ state is denoted $N_2$. This decays radiatively to the lower states $^7F_{1,2}$, which in turn rapidly relax to the ground state. We consider the lower states separately, but denote their population with the same $N_1$ for the sake of notational convenience. Because the lower states decay quickly, it is a suitable approximation to assume a negligible population of the lower levels, so that $N_1 = 0$.

We also make the assumption that the ground state is unpopulated, as the transfer of energy between the ligand an ion is very efficient.

For nett optical transparency, the gain coefficient $\gamma(\nu)$ equals the extinction coefficient $\alpha$. Doing this, we find

$$\left[ N_2 - \frac{g_2}{g_1}N_1 \right] = \frac{8\pi n^2\nu^2\alpha}{A_{21}c^2g(\nu)}.$$  

(6.7)

If we assume the only losses are from scattering from the nano-particles, ignoring any absorption and scattering from the polymer waveguide, we can take $\alpha = 4.12 \times 10^{-3} \text{m}^{-1}$. The results of this calculation are shown in table 6.2. Assuming the population $N_1 = 0$, we can also find the proportion of ions required to excited for nett optical transparency, which is also shown in the table. Nett optical transparency requires only a small portion of the Eu$^{3+}$ions to be in the excited state.

The quantum efficiency $\eta$ of (5% Eu$^{3+}$ : LaF$_3$)$_{tta}$ has been measured as 0.6\[47\]. Knowing this, we can calculate the required rate of pumping to maintain the population inversion; if we are using a $\lambda = 365 \text{nm}$ pump, the
Figure 6.10: Approximation to our system. The solid arrow represents optical processes, and the dashed non-radiative processes. The y-axis is to scale. The processes leading to the population of the T\textsubscript{1} triplet state of the ligand are simplified as in the text. The T\textsubscript{1} state rapidly undergoes an energy transfer to the metastable excited \textit{5D}\textsubscript{0} state of the \textit{Eu}\textsuperscript{3+} ion. This relaxes radiatively to the \textit{5D}_{1,2} states which quickly decay to ground in a phonon-mediated process. \(N_{0,1,2}\) are the populations of the ground lower and excited levels of the \textit{Eu}\textsuperscript{3+} ion; \(M_{0,1}\) are the populations of the ground and excited \textit{T}1 states of TTA ligand.

<table>
<thead>
<tr>
<th>Transition</th>
<th>(\lambda) (nm)</th>
<th>(N_2 - \frac{g_2}{g_1}\times10^2) m\textsuperscript{-1}</th>
<th>(\frac{N_2}{N_1})</th>
<th>(P) W cm\textsuperscript{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5D_0\rightarrow7F_1)</td>
<td>592</td>
<td>4.8</td>
<td>0.013</td>
<td>2.6</td>
</tr>
<tr>
<td>(5D_0\rightarrow7F_2)</td>
<td>613</td>
<td>9.7</td>
<td>0.027</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 6.2: Requirements for nett optical transparency; the third column shows the degree of population inversion required; the fourth the fraction of total ions in the excited state \(5D_0\), and the fifth the pump power required, as explained in the text.
6.3. GAIN CALCULATIONS

<table>
<thead>
<tr>
<th>Transition</th>
<th>Transition</th>
<th>$\lambda$</th>
<th>$\gamma_{\text{nett}}$</th>
<th>$P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5D_0 \rightarrow ^7F_1$</td>
<td></td>
<td>592</td>
<td>0.429</td>
<td>169</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_2$</td>
<td></td>
<td>613</td>
<td>0.125</td>
<td>54.7</td>
</tr>
</tbody>
</table>

Table 6.3: The parameters for maximum gain, where $N_2 = \mathcal{N}_i$: the nett gain after scattering losses $\gamma_{\text{nett}}$ and an estimate of the optical pump power required for this.

The required pump power is given by

$$P = \eta \cdot \frac{hc}{\lambda} \cdot A_{21}N_2,$$

(6.8)

which we also present in table 6.2.

In optical fibres, damage thresholds are conventionally given in the useful form of cross-sectional intensity. This is difficult to compare with our parameters, in terms of volume; however, we can consider the magnitude of these and draw tentative conclusions from this. A typical damage threshold is of the order of $10^6$ W per square centimetre; in a 400 μm fibre, which is a typical size for a polymer fibre, this corresponds to an input power of order 100 W. This is much greater than the power required for optical transparency.

We also consider an upper limit on the possible gain, where all of the Eu$^{3+}$ ions are excited to the $^5D_0$ level, so that $N_2 = \mathcal{N}_i$. Although it is not possible at all in a two- or three-level system to obtain this complete population inversion, in this selectively-pumped four-level scheme it is not implausible. We do note that the approximations made are likely to become less valid with the extreme conditions required; nevertheless this provides an insight into what might be required to obtain the greatest gain, and what might be required for this to occur.

We again assume $N_1 = 0$, and set $N_2 = \mathcal{N}_i$ in the gain equation 6.5. Subtracting the scattering losses $\alpha$, we obtain a nett gain, which is given in table 6.3. We also calculate the power required for this, as defined previously.

We see the gain is quite large; we also see that the power requirements are very large.

When considering this, we also have to consider the quantum deficit between the pump (3.4 eV) and the signal (ca. 2 eV). This deficit of energy has to be dissipated, into the polymer or cladding (in a fibre). The heat capacity of APC is $1.2 \text{kJK}^{-1}\text{kg}^{-1}$, the density is $1200 \text{kgm}^{-3}$, and thus the volume heat capacity of APC is approximately $14 \text{JK}^{-1}\text{cm}^{-3}$. 
The glass transition of APC is at $215\,^\circ\text{C}$, but it is recommended that the operating temperature not exceed $120\,^\circ\text{C}$, or $95\,\text{K}$ above room temperature. This means that pumping the $592\,\text{nm}$ transition at this rate would cause the polymer to overheat in approximately $0.2\,\text{s}$, or $2\,\text{s}$ for the $613\,\text{nm}$ transition, unless the fibre was cooled in such a way as to avoid this. Of course, the power required for the nett transparency is sufficiently low that the fibre cladding might be able to absorb the surplus energy.

### 6.4 Conclusions

In this chapter we measured the losses in nanoparticle-containing polymer films, with the intention of making measurements of the gain. However, the films we were supplied with were found to contain large numbers of bubbles, which precluded the transmission of light.

We then turned to theory to predict the losses that we perhaps ought to see for scattering off the nanoparticles. This was found to be quite low, comparable to the absorption in certain polymers.

Having found the losses, we then calculated the pump power required for nett optical transparency, using a four-level approximation to our system, and found it to be reasonable. This is in part due to the properties of the rare-earth ions, which have a long radiative lifetimes and thus small spontaneous decay rates. We also calculated the approximate power required to obtain a total inversion; this was much higher, and indeed is sufficient to melt the polymer in a short time due to the large quantum deficit in our material.

We can conclude then that there is potential for the use of these nanoparticle-containing polymers for creating modest gain, either as films or as fibres, should the manufacture be improved. This because the nanoparticles provide a quasi-crystalline environment for the rare-earth ions and theoretically have the potential to cause very little scattering.
Chapter 7

Conclusions

In this work, we have investigated the luminescence stability of a number of variations of rare-earth nanocrystals, primarily \( \text{Eu}^{3+} \) in \( \text{LaF}_3 \), as well as \( \text{Eu}^{3+} \) in complex with TTA molecules as sensitising agents to increase the absorption of light.

The \( \text{Eu}^{3+} \) emissions were found to be stable, with pump fluence, as was the \( \text{Eu}^{3+} \)-TTA complex. The TTA-capped \( \text{Eu}^{3+}:\text{LaF}_3 \) nanoparticles, however, were not. Although their lineshape and frequency of the transitions remained constant, their emissions decreased quite significantly in intensity, as did the relative intensities of various transitions in the ion. Though this can be used as an indication of the site symmetry of the ion, the smallness of the nanoparticles introduces complications to this, making it dubious to do so.

We furthermore attempted to couple light into nanoparticle-containing polymer films to measure the transmission. We were stymied in this by the presence of bubbles, which heavily scattered the light. We then used the Mie scattering theory to calculate the losses that might be expected from the nanoparticle-containing films, and found this to be very small. We then calculated the gain parameters required for nett optical transparency in the films, and found the pump power for this to be correspondingly small.

There are a number of further researches that could continue from this: amongst these would be using the polymer film for actual gain, which would require the manufacturing process of the films to be improved; a possibility for this would be to create fibres rather than the films that were supposed to be easier to work with in small amounts.

A more pressing matter would be to further investigate the process behind the decay of the fluorescence seen: why it is seen in the nanoparticles, but not in the complex.

In conclusion, then, we have seen that in their present form TTA-capped
Eu$^{3+}$:LaF$_3$ nanoparticles are not suitable for gain, either as a small signal amplifier or as laser medium. However, the insertion of nanoparticles into polymers should create little scattering losses, and so is a possible route to the creation of amplifiers.
Appendix A

History, Uses and Occurrence of the Rare Earths

A.1 History

The history of the rare earths begins in 1751, with Axel Fredrik Cronstedt finding a mineral of unknown composition at the Bastnäs mine in Sweden. After an indeterminate examination in 1766 by Carl Wilhelm Scheele, who called it tungsten Bastnäs (the heavy stone of Bastnäs) and decided that, although it might contain wolfram (tungsten), it had nothing new in it, and so it languished for half a century unnoticed.

Meanwhile, in 1788, a Swedish army Lieutenant found an unusual black rock near the mines of Ytterby. Lt. Arrhenius sent this sample, that he called Ytterbite, to the famous Finn Johan Gadolin for analysis. In 1794 Gadolin found that it contained 38% of a theretofore unknown earth. Anders Gustaf Ekeberg confirmed Gadolin’s analysis, and called the new-found earth Gadolinite in his honour.

In the first years of the 19th century, gadolinite was investigated quite

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1The information in this section is primarily from [98], with further details from [73, 76, 64, 20, 21], unless otherwise attributed. It also came to my attention after writing this that an excellent history of the rare earths has been published, reference [32].

2Throughout this history, I shall use the language as used at the time. Historically, an Earth was a metallic oxide, which is the form in which much of the minerals on earth are found.

31722–1765, Swedish chemist and mineralogist.

41742–1786, Swedish pharmacist and chemist, discoverer of oxygen and of numerous natural acids.

51757–1824; not of Arrhenius equation fame.

61760–1852, chemist at University of Åbo.

71767–1813, scholar of science and the arts, first finder and name of tantalum.
independently by Ekeberg, Martin Heinrich Klaproth and Nicholas-Louis Vauquelin. They found that it contained a separate mineral, which came to be called yttria.

In 1803, Klaproth was investigating the mineral found by Cronstedt at Bastnäs, which by this time had been looked at by Scheele and been declared un-interesting, and found a new earth, which he called terre ochorite.

At the same time, the Bastnäs mineral was being investigated by William Hisinger and Jöns Jacob Berzelius. They subjected the Bastnäs mineral to the same tests as used to find yttria; instead of yttria, they found a new mineral which was called ceria in honour of the then recent discovery of the asteroid Ceres. It was then found that this was the same as Klaproth’s terre ochorite.

To skip ahead in time, the discovery of this ceria led to attempts to get the pure metal cerium. Vain attempts were made by Gahn and Vauquelin; in

---

91743–1817, German verifier of the discovery of Tellurium and Titanium, considered to be one of the finest analysts of all time.

101766–1852, Swedish mineralogist, geologist and noble.

111779–1848, Swedish physician and chemist, made the first accurate measurements of atomic weights, had interesting domestic arrangement with his late mentor’s sisters.
Figure A.2: The derivation of the elements found in Arrhenius' Gadolinite. Reproduced from [73] with the kind permission of the publisher.
1811 Carl Gustaf Mosander made a the very impure metal; in 1875 Wöhler, Hillebrand and Norton obtained a somewhat pure metal, but it was not until 1911 that Alan Hirsch succeeded after three years of work in obtaining 98% pure cerium metal.

Returning to the 1830s, with further investigations, both ceria and yttria were found to not be simple substances, a proof of which was given by Mosander in 1839. Cerium nitrate was dissolved in nitric acid, giving two components: a soluble one called lanthana, after the Greek for “hidden”, and an insoluble one, which continued to be ceria. Simultaneously, at the same institute, Axel Erdman found the same fact.

Then after two years of “purifying” ceric oxide, Mosander then separated his lanthanum into two parts, one called lanthanum again, the other called didymia, from the Greek for “inseparable twin”.

Then, considering the success of decomposing ceria with nitric acid, in 1843 Mosander did the same to yttria: lo and behold, after removing all of the ceria, lanthana and didymia from the sample there was still at least three earths remaining. These were separated by colour: the colourless earth kept the name yttria; the yellow earth he called erbia; and the rose-coloured earth he called terbia, all after the place where the original mineral was found.

These results lead to a renewed interest in the rare earths. Over the next 40-odd years the results were confirmed by Jean-Charles Galisard de Marignac, his student Marc Delafontaine, Paul Émile (dit François) Lecoq de Boisbaudran, J. Lawrence Smith and Per Theodor Cleve.

After this time there was a confusing swap of names: Mosander’s yellow earth “erbia” was by 1880 commonly called terbia; similarly, the rose earth “terbia” was, by 1860, called erbia. There has not, to the author’s knowledge, been a good reason for this given.

---

12 1797–1858, army surgeon, chemist and mineralogist, discoverer of lanthana and didymia.
13 1792–1841, discoverer of lithium.
14 The name didymia was chosen by Mosander to give it a symbol unlike any in use at the time, even though it was unpopular amongst his colleagues. He was partly successful; although there are still only two elements with “D” symbols, didymium is not one of them!
15 1817–1894, Swiss discoverer of ytterbia and gadolinia, proved tantalum and columbium (now niobium) are different elements.
16 1837–1911.
17 1838–1912, decendent of Protestant nobility, discoverer of gallium, samarium and dysprosium, and founder, with Bunsen, Kirchoff and Crookes, of spectroscopy, which he used to discover gallium.
18 1814–1883, U.S.A.
19 1840–1905, Swedish discoverer of thulium, and independent discoverer of holmium, known for his broad interests, love of nature and “pleasing writing style.”
In 1878, de Marignac separated the rose-coloured oxide of erbia into two: a red oxide, which kept the name erbia, and a colourless oxide which he called ytterbia. Then in 1879, Lars Fredrik Nilson separated ytterbia into two oxides: one keeping the original name, ytterbia, and another named after his homeland scandia. This last was proven by Cleve to be identical to the ekaboron predicted by Mendeleev’s periodic table, thus helping to establish the table’s usefulness and correctness.

After scandia and ytterbia were removed, though, there was still a composite erbia. This was resolved by Cleve into holmia, after his native Stockholm, thulia, after the ancient name for Scandianvia, and a fourth iteration of erbia. Each of these was later found to be a simple substance, the (oxides of the) pure elements holmium, thulium and erbium, respectively.

Even in the 1850s, de Marignac thought that didymia was not a pure substance; using the recent innovation of spectroscopy, Delafontaine and Lecoq de Boisbaudran found the spectrum of didymia varied depending on the source of it. Using this knowledge, Lecoq de Boisbaudran they separated didymia into didymia and samaria, named for the mineral samarskite in which it was found, in 1879; in 1886, this samaria was then separated into a new samaria and gadolinia, named after Gadolin who started of all of this.

Still, Lecoq de Boisbaudran, Cleve and Bohuslav Brauner believed that didymium was a mixture of elements. The separation of these proved to be very difficult. Brauner found that there were two groups in the spectrum of didymium: a blue one at 443 nm to 449 nm, and a yellow one at 586 nm to 590 nm.

It was in 1885 that Carl Auer, Freiherr von Welsbach separated didymia into neodymia, the new dydimia, and praseodymia, the green dydimia. These were subsequently found to be the oxides of the elements neodymium and praseodymium.

Shortly after this, Lecoq de Boisbaudran separated holmia by fractional precipitation into holmia and dysprosia, the so-called “difficult one”. These were, of course, the oxides of the elements holmium and dysprosium.

It was Eugène-Anatole Demarçay, who fractionated samaria magnesium

---

201840–1899, agriculturalist and discoverer of scandium, known for refusing to mix his work into his recreation.
211855–1935, professor of chemistry at the Bohemian University of Prague, predictor of the element illinium, now called promethium.
221858–1929, discoverer of praseodymium and neodymium, creator of the Welsbach gas lamp mantle (called the “Auerlicht” in German-speaking countries) and the automatic gas lighter.
231852–1904, French discoverer of europium, spectroscoper of radium for M. & Mme Curie, and of many organic substances, who was wounded in a lab explosion to his continued ill-health, but who carried on with his researches regardless.
nitrate to find two components: samaria and europia, named after the continent of Europe. Death halted his research into Europium.

Those who have been keeping count will realise that there are still three elements un-accounted for; it was Georges Urbain\footnote{1872–1938, French chemist, painter, sculptor and musician.} who, in 1907, fractionally crystallised ytterbium into two oxides: neodytterbia, the new ytterbia, to continue to credit de Marignac, and lutecia, after the ancient name for Paris, the home of all Frenchmen. At the same time von Welsbach found the elements which he called “alderbaranum” and “casseopium”, after stellar constellations; his names did not stick. Also at the same time, Charles James (1880–1928, U.S.A. Innovative and ingenius specialist in rare earths) discovered lutetium; however he delayed publication of his results to check them over; in doing so he gave primacy of discovery to Urbain.

There is only one further of the rare-earths, which was predicted by Moseley in 1902, once the concept of atomic numbers was known: element 61. For the next few decades there were searches for this element, many of which were thought to have found it as a component in the naturally occurring rare earths. These were almost certainly incorrect, as in 1941 at Ohio State University in the U.S.A. it was found, and found to be radioactive, with the longest-lived isotope having a half-life of 17.7 years. It was only in 1945 that Marinsky, Glendenin and Coryell identified it positively, giving it the name promethium, after the titan Prometheus who stole fire from the gods in Greek mythology. This name supplanted others that had been proposed, such as illinium, florentium and cyclonium, although books of that era still use these other names from time to time.

The evolution and discovery of the rare earths is shown in figures A.1 and A.2.

\section*{A.2 Uses}

For much of their early history, the rare earths had little practical application. An exception to this was the mixture didymium, which was used in forging and glass-blowing safety goggles as a band-stop filter for the intense sodium $D$ lines.

Cerium was heavily used in von Welsbach’s \textit{Welsbach Mantle}, although this has been reduced recently with the rise of electric lighting. The alloy \textit{mischmetall} is a mixture of $\sim 70\%$ cerium, with other rare earths (often Lanthanum, praseodymium and neodymium) and $\sim 1$–$5\%$ iron. This has a pyrophoric nature which lead to its use in cigarette lighters, gas lighters, tracer bullets and others\cite{76}.  

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figureA.1.png}
\caption{Evolution and discovery of the rare earths.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figureA.2.png}
\caption{Uses of the rare earths.}
\end{figure}
For film projection lamps, carbon arcs with rare earths were used to provide a brilliant light very that is nearly white\cite{76}. The bright colours of the oxides meant that some of the rare-earth elements were used as decorative glazes for pottery.

One of the first widespread uses of europium was as the red phosphor in cathode ray tube televisions. Although this has been supplanted by changing technology, europium is still used in fluorescent mercury discharge lamps as a down-conversion phosphor to create white light\cite{80}.

Recently, however, the rare-earths have found new uses in high technology, as sources of narrow-band light and for high-strength low weight magnets. Furthermore, because the a number of the lanthanides react with biology in a similar way to calcium, they are used as probes for reactions and investigations into the role of calcium in the body.

The high magnetic moment of dysprosium and neodymium means that large permanent magnetic fields can be obtained from physically small and light-weight permanent magnets\cite{51}. These are used in such things as magnetic computer hard-drives and electric vehicle motors\cite{84}.

There is also a great deal of pure research investigating the use of rare earths for quantum computing\cite{66, 68, 61, 67}.

Until the 1950s the separation of the rare earths was a difficult process; in that decade Spedding et al. developed the ion-exchange methods that are now used for much of the production of pure rare earths.

### A.3 Occurrence

The name “rare earth” is something of a misnomer; although the use of “earth” to describe stable, dry, non-volatile odourless mineral oxides\cite{88} has simply fallen out of fashion in the past century or so, the use (or misuse) of “rare” is more a matter of changing knowledge.

Until the end of the 19th century, there was justification for this usage, as many of the rare earth elements had only been found in Scandinavia, and specifically so in two mines in Sweden. However, after this it was found that the “rare earths” are really quite common; more abundant in the earth’s crust than, for example, mercury, arsenic, cadmium, gold, platinum, zinc and selenium\cite{20}. The only truly rare rare-earth is the radioactive promethium, for obvious reasons.

Furthermore, they are not isolated to certain places, either: they are found in commercially profitable amounts in the USA, Brazil, China, the former USSR, Greenland, Madagascar and Australia. The most common source of rare earths today is China, although this is for two main reasons:
they are plentiful in that country, and the labour required to extract them is cheaper than in much of the rest of the world.

A relatively novel thought is to extract the rare earths from the mud on the sea-floor of the Pacific\cite{51}. Although there are great deposits on the bed of the Pacific Ocean, there are still a number of technical difficulties to be resolved in this proposal.
Appendix B

Mie Calculations

The procedure shown here is essentially that shown in reference [12], with appropriate restrictions to our cases and with additional calculations where necessary. Additional explanations are from [12].

We take a single homogeneous isotropic spherical particle of radius $a$ inside a (different) homogeneous isotropic medium.

We begin with an electromagnetic field $(E_1, H_1)$ inside of the sphere and a field $(E_2, H_2)$ outside which is a superimposition of the incident field $(E_i, H_i)$ and the scattered field $(E_s, H_s)$. The incident field has the form

$$E_i = E_0 e^{i k x - i \omega t}, \quad H_i = H_0 e^{i k x - i \omega t},$$

and varies slowly enough that we can assume it is quasi-static.

These fields must satisfy Maxwell’s equations

$$\nabla \cdot E = 0, \quad \nabla \times E = i \omega \mu H,$$
$$\nabla \cdot H = 0, \quad \nabla \times H = i \omega \epsilon H,$$

at all points where the permittivity $\epsilon$ and permeability $\mu$ are continuous.

Taking the curl of the last two and using a suitable vector identity we obtain

$$\nabla^2 E + \omega^2 \epsilon \mu E = 0; \quad \nabla^2 H + \omega^2 \epsilon \mu H = 0,$$

which are Laplace’s wave equations (the general form of Poisson’s equations) for materials with no free charge.

We said that Maxwell’s equations (B.2) hold where $\epsilon$ and $\mu$ are continuous; at the edge of a particle or an interface between a particle and the surrounding medium these change over the scale of an atom or so. Therefore, to a good approximation we assume that these changes are instantaneous and enforce the boundary conditions that the tangential components of the
fields \((E, H)\) are continuous. This is simple to show either with the “phar-
maceutical” method of pill-boxes and loops through the surface, or through
the conservation of energy and the Poynting vector \(S = \frac{1}{\mu} E \times B = E \times H\).

We can construct from a scalar function \(\psi\) and an arbitrary constant
vector \(c\) a vector function \(M = \nabla \times (c\psi)\). The divergence of a curl is always
zero; making use of vector identities we can show that

\[
\nabla^2 M + k^2 M = \nabla \left[ c(\nabla^2 \psi + k^2 \psi) \right],
\]

(B.5)

where \(k^2 = \omega^2 \mu \epsilon\). This satisfies Laplace’s equations (B.4) for \(M\) if \(\psi\) is a
solution to the wave equation \(\nabla^2 \psi - k^2 \psi = 0\).

From \(M\) we can also construct another vector

\[
N = \frac{\nabla \times M}{k},
\]

which has zero divergence and also satisfies the wave equation. The curl of
this construction,

\[
\nabla \times N = kM = i\omega^2 \epsilon \mu M,
\]

bears an uncanny resemblance to Maxwell’s equations.

Thus these \(M\) and \(N\) satisfy the wave equation and are acceptable phys-
ical waves. The choice of guiding vector \(c\) is not at all obvious; however,
spherical polar co-ordinates are natural for dealing with a sphere, and it
turns out the radial vector \(r = \hat{e}_r\) is an appropriate choice to find \(M\) as
solutions to the spherical wave equation.

The spherical polar co-ordinates used are \((r, \theta, \phi)\) such that \(r\) is the radial
distance, \(\theta\) is the polar angle and \(\phi\) is the azimuthal angle.

To solve for the generating function \(\psi\), we solve the spherical polar wave
equation

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} + k^2 \psi = 0.
\]

(B.6)

We can solve this by separation of variables such that

\[
\psi(t, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi);
\]

(B.7)

when substituted into [B.6] these yield

\[
\frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0,
\]

(B.8)
\[
\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ n(n + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0, \quad (B.9)
\]
\[
\frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ k^2 r^2 - n(n + 1) \right] R = 0, \quad (B.10)
\]
with \( m \) and \( n \) separation parameters that depend on the conditions that \( \psi \) must satisfy.

Linearly independent solutions to \( B.8 \) are
\[
\Phi_e = \cos m\phi, \quad \Phi_o = \sin m\phi, \quad (B.11)
\]
with \( e \) denoting an even function and \( o \) denoting an odd function. The spherical symmetry of the situation requires that \( \psi \) be single-valued function of the azimuthal angle
\[
\lim_{\nu \to 2\pi} \psi(\phi + \nu) = \psi(\phi); \quad (B.12)
\]
this requires that \( m \) is an integer or zero; the positive integers are sufficient to generate the linearly independent solutions to \( B.8 \).

The solutions to \( B.9 \) have to be finite at \( \theta = 0 \) and \( \theta = \pi \); these solutions are the associated Legendre functions of the first kind of degree \( m \) and order \( n \), \( P^m_n(\cos \theta) \), with \( n = m, m + 1, \ldots \). The Legendre functions are orthogonal, and if \( m = 0 \) they become the Legendre polynomials \( P_n \).

If we define \( Z = R\sqrt{\rho} \), with \( \rho = kr \) (a dimensionless variable), \( B.10 \) becomes
\[
\rho \frac{d}{d\rho} \left( \rho \frac{dZ}{d\rho} \right) + \left[ \rho^2 - (n + \frac{1}{2})^2 \right] Z = 0. \quad (B.13)
\]
The solutions to this are the Bessel functions of the first and second kinds \( (J_\nu \) and \( Y_\nu \) respectively); \( \nu = n + \frac{1}{2} \) is half-integral. From this, the solutions to \( B.10 \) are the spherical Bessel functions of the first and second kinds
\[
j_n(\rho) = \sqrt{\frac{\pi}{2\rho}} J_{n+\frac{1}{2}}(\rho); \quad y_n(\rho) = \sqrt{\frac{\pi}{2\rho}} Y_{n+\frac{1}{2}}(\rho); \quad (B.14)
\]
where the factor of \( \sqrt{\frac{\pi}{2\rho}} \) is used to make the mathematics convenient.

If we allow \( z_n \) to describe any spherical Bessel function, they satisfy the
APPENDIX B. MIE CALCULATIONS

Recursion equations

\[ z_{n-1}(\rho) + z_{n+1}(\rho) = \frac{2n + 1}{\rho} z_n(\rho), \]
\[ (2n + 1) \frac{d}{d\rho} z_n(\rho) = n z_{n-1}(\rho) - (n + 1) z_{n+1}(\rho). \]

Thus, knowing the first two values of each

\[ j_0(\rho) = \frac{\sin \rho}{\rho}, \quad j_1(\rho) = \frac{\sin \rho}{\rho^2} - \frac{\cos \rho}{\rho}, \]
\[ y_0(\rho) = -\frac{\cos \rho}{\rho}, \quad y_1(\rho) = -\frac{\cos \rho}{\rho^2} - \frac{\sin \rho}{\rho}, \]

it is possible to calculate all of the spherical Bessel functions.

As a future labour-saving tool, we introduce the spherical Bessel functions of the third kind, also known as the spherical Hankel functions, \( h_n^{(1)}(\rho) \) and \( h_n^{(2)}(\rho) \). Any linear combination of the independent solutions to an equation are themselves solutions; therefore

\[ h_n^{(1)}(\rho) = j_n + iy_n(\rho) \quad \text{and} \quad h_n^{(2)}(\rho) = j_n(\rho) - iy_n(\rho) \quad (B.15) \]

are solutions to \( B.10 \) as well. These will be used later.

Combined, these give us solutions to the scalar wave equation \( B.7 \)

\[ \psi_{emm} = \cos m\phi \ P_n^m(\cos \theta) z_n(kr), \]
\[ \psi_{omm} = \sin m\phi \ P_n^m(\cos \theta) z_n(kr). \quad (B.16) \]

Since the Bessel functions, Legendre functions and the trigonometric functions are all complete in the sense that they have real, if not necessarily rational, solutions over all of their range, any function that satisfies the scalar wave equation can be expanded in terms of \( B.16 \). We can thus express our vector spherical harmonics \( \mathbf{M} \) and \( \mathbf{N} \) in terms of these (reasonably) straightforward expressions.

We assume the incident wave is plane; therefore to use the above vector spherical harmonics it is necessary to express this in the spherical co-ordinate system. This reasonably tedious co-ordinate transformation results in the incident electric wave being

\[ \mathbf{E}_i = E_\phi \sum_{n=1}^{\infty} i_n \frac{2n + 1}{n(n+1)} \left( M_{\phi 1n}^{(1)} - i N_{\phi 1n}^{(1)} \right), \quad (B.17) \]
where \(^{(1)}\) means that only the Bessel functions of the first kind \((j_n)\) were used (since \(y_n\) is infinite at the origin), and we have recognised that the coefficients in the expansion of the vector harmonics vanish for \(m \neq 1\). The curl of this is the magnetic field

\[
H_i = \frac{-k}{\omega \mu} E_0 \sum_{n=1}^{\infty} i_n \frac{2n+1}{n(n+1)} \left( M_{e1n}^{(1)} - i N_{o1n}^{(1)} \right).
\]  

(B.18)

At the boundary between the sphere and the medium we require that the tangential components inside and out be equal (the boundary conditions)

\[
(E_i + E_s - E_1) \times \hat{e}_r = (H_i + H_s - H_1) \times \hat{e}_r = 0.
\]  

(B.19)

The expansion of the “internal” field is thus

\[
E_1 = \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} E_0 \left( c_n M_{o1n}^{(1)} - id_n N_{e1n}^{(1)} \right),
\]  

(B.20)

\[
H_1 = \frac{-k_1}{\omega \mu_1} \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} E_0 \left( d_n M_{e1n}^{(1)} - ic_n N_{o1n}^{(1)} \right),
\]  

(B.21)

with \(\mu_1\) the permeability of the sphere.

It is convenient to use the spherical Hankel functions for the scattered fields. The scattered wave will be outgoing in the far-field of the particle; therefore we use only the first type \(h^{(1)}\). The derivative of this is

\[
\frac{dh_n^{(1)}(\rho)}{d\rho} \simeq \frac{(-i)^n e^{i\rho}}{\rho} \quad \text{for } \rho \ll n^2.
\]

Using \(^{(3)}\) to denote the use of the spherical Hankel functions, the scattered field \((E_s, H_s)\) is of the form

\[
E_s = \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} E_0 \left( i a_n N_{e1n}^{(3)} \right),
\]

\[
H_s = \frac{k_1}{\omega \mu_1} \sum_{n=1}^{\infty} i^n \frac{2n+1}{n(n+1)} E_0 \left( i b_n N_{o1n}^{(3)} + a_n M_{e1n}^{(3)} \right).
\]

The coefficients \(a_n, b_n, c_n, d_n\) are distinctive scattering properties of the particles and medium, and will be calculated below.
For computational convenience, we define

$$\pi_n(\theta) = \frac{P'_n}{\sin \theta}, \quad \tau_n(\theta) = \frac{dP'_n}{d\theta}.$$  \hfill (B.22)

The prime denotes differentiation with respect to the argument of a function.

These are determined by upward recurrence, starting from $\pi_0 = 0$ and $\pi_1 = 1$, using the recurrence relations

$$\pi_n(\theta) = \frac{2n-1}{n-1} (\cos \theta) \pi_{n-1} - \frac{n}{n-1} \pi_{n-2},$$ \hfill (B.23)

$$\tau_n(\theta) = n (\cos \theta) \pi_n - (n+1) \pi_{n-1}.$$ \hfill (B.24)

These are not orthogonal to each other or themselves; their sums and differences, however, are orthogonal:

$$\int_0^\pi (\tau_n + \pi_n)(\tau_m + \pi_m) \sin \theta \, d\theta = \int_0^\pi (\tau_n - \pi_n)(\tau_m - \pi_m) \sin \theta \, d\theta = \delta_{mn}.$$ \hfill (B.25)

Using these functions, we can expand the vector spherical harmonics

$$M_{o1n} = \cos \phi \pi_n(\cos \theta) z_n(\rho) \hat{e}_\theta - \sin \phi \tau_n(\cos \theta) z_n(\rho) \hat{e}_\phi,$$ \hfill (B.26)

$$M_{e1n} = -\sin \phi \pi_n(\cos \theta) z_n(\rho) \hat{e}_\theta - \cos \phi \tau_n(\cos \theta) z_n(\rho) \hat{e}_\phi,$$ \hfill (B.27)

$$N_{o1n} = \sin \phi \, n(n+1) \sin \theta \pi_n(\cos \theta) \frac{z_n(\rho)}{\rho} \hat{e}_r$$

$$\quad + \sin \phi \, \tau_n(\cos \theta) \frac{[z_n(\rho)]'}{\rho} \hat{e}_\theta + \cos \phi \, \pi_n(\cos \theta) \frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\phi,$$ \hfill (B.28)

$$N_{e1n} = \cos \phi \, n(n+1) \sin \theta \pi_n(\cos \theta) \frac{z_n(\rho)}{\rho} \hat{e}_r$$

$$\quad + \cos \theta \, \tau_n(\cos \theta) \frac{[\rho z_n(\rho)]'}{\rho} \hat{e}_\theta - \sin \phi \, \pi_n(\cos \theta) \frac{\rho z_n(\rho)}{\rho} \hat{e}_\phi,$$ \hfill (B.29)

which then can be inserted into equations B.20 and B.21 to find the fields. The prime ' again signifies differentiation with respect to the argument in parentheses.

Since $m = 1$ for any real cases, for a given $n$ in the series B.20 and B.21 there are four values of $a_n$, $b_n$, $c_n$, $d_n$ to find; these require four independent
equations, which are found from the boundary conditions \[ \text{(B.19)} \]

\[
\begin{align*}
E_{\theta} + E_{s\theta} &= E_{\theta} \\
E_{\phi} + E_{s\phi} &= E_{\phi} \\
H_{\theta} + H_{s\theta} &= H_{\theta} \\
H_{\phi} + H_{s\phi} &= H_{\phi}
\end{align*}
\]

for \( a = r \). \[ \text{(B.30)} \]

After interminable algebra, remembering that \( \sin \theta \perp \cos \theta \) and a number of the relations and expansions above, four linear equations in the coefficients are obtained. The internal coefficients \( c_n \) and \( d_n \) do not interest us, dealing with a field we cannot measure; solving for the scattering coefficients we obtain

\[
a_n = \frac{\mu m^2 j_n(mx)[xj_n(x)]' - \mu_1 h_n(x)[mxj_n(mx)]'}{\mu m^2 j_n(mx)[xh_n^{(1)}(x)]' - \mu_1 h_n^{(1)}(x)[mxj_n(mx)]'},
\]

\[
b_n = \frac{\mu_1 j_n(mx)[xj_n(x)]' - j_n(x)[mxj_n(mx)]'}{\mu_1 j_n(mx)[xh_n^{(1)}(x)]' - \mu_1 h_n^{(1)}(x)[mxj_n(mx)]'},
\]

where \( \mu_1 \) is the permeability of the sphere, \( \mu \) is the permeability of the medium, \( x \) is the size parameter and \( m \) is the relative refractive index. The last two are defined such that

\[
x = ka = \frac{2\pi Na}{\lambda} \quad \text{and} \quad m = \frac{k_1}{k} = \frac{N_1}{N},
\]

with \( N \) and \( N_1 \) the refractive indices of the medium and sphere respectively, \( a \) is the diameter of the sphere, \( \lambda \) is the wavelength of the incident light, and \( k \) denotes the wavevector.

By introducing the Riccati-Bessel functions

\[
\psi_n(\rho) = \rho j_n(\rho), \quad \xi_n(\rho) = \rho h_n^{(1)}(\rho),
\]

we can simplify the coefficients \( a_n \) and \( b_n \)

\[
a_n = \frac{m\psi_n(mx)\psi'_n(x) - \psi_n(x)\psi'_n(mx)}{m\psi_n(mx)\xi'_n(x) - \xi_n(x)\psi'_n(mx)},
\]

\[
b_n = \frac{\psi_n(mx)\psi'_n(x) - m\psi_n(x)\psi'_n(mx)}{\psi_n(mx)\xi'_n(x) - m\xi_n(mx)\psi'_n(mx)}.
\]

From these it is possible to calculate the cross-sections.

To introduce the notation, we consider our single particle, and about it construct an imaginary sphere of radius \( r \), which has surface area \( A \). The flow of energy \( W_n \) through this sphere is the integral of the Poynting vector

\[ ^1 \text{Note that for these calculations we use the unconventional uppercase } N \text{ for refractive index, to distinguish it from the indices } n \text{ in our summations.} \]
over the surface

\[ W_a = - \int_A \mathbf{S} \cdot \hat{e}_r \, dA. \]  \hspace{1cm} (B.35)

The Poynting vector is the sum of three (vector) terms \( \mathbf{S} = \mathbf{S}_i + \mathbf{S}_s + \mathbf{S}_{\text{ext}} \), where \( \mathbf{S}_i \) relates to the incident field, \( \mathbf{S}_s \) relates to the scattered field, and we call the \( \mathbf{S}_{\text{ext}} \) the extinction term, which relates to the removal of energy from the incident beam due to the particle.

We can thus expand \( W_a \) in three terms, to give \( W_i, W_s \) and \( W_{\text{ext}} \). For a non-absorbing medium, \( W_i = 0 \); from the sign conventions of \( \mathbf{S}_s \) and \( \mathbf{S}_{\text{ext}} \) we find \( W_{\text{ext}} = W_a + W_s \), where we take the incident field \( \mathbf{E}_i \) to be \( x \)-polarised for simplicity. It will be generalised to arbitrary polarisation later on.

For a non-absorbing medium, the radius \( r \) of our sphere is of no consequence; we can therefore assume it is large such that

\[ \mathbf{E}_s \sim e^{ik(r-z)} \mathbf{X} \mathbf{E}, \quad \mathbf{H}_s \sim \frac{k}{\mu_0} \hat{e}_r \times \mathbf{E}_s. \]  \hspace{1cm} (B.36)

The vector scattering amplitude is defined as

\[ \mathbf{X} = (S_2 \cos \phi + S_3 \sin \phi) \hat{e}_{\parallel s} + (S_4 \cos \phi + S_1 \cos \phi) \hat{e}_{\perp s}. \]  \hspace{1cm} (B.37)

The scalar amplitudes scattering matrix elements \( S_i \) relate the incident and scattered fields as

\[ \begin{pmatrix} E_{\parallel s} \\ E_{\perp s} \end{pmatrix} = e^{ik(r-z)} \begin{pmatrix} S_2 & S_3 \\ S_4 & S_1 \end{pmatrix} \begin{pmatrix} E_{\parallel i} \\ E_{\perp i} \end{pmatrix}, \]  \hspace{1cm} (B.38)

and depend on the scattering angle \( \theta \) and azimuthal angle \( \phi \). These are difficult to measure directly, depending as they do on amplitude and phase, but can be found indirectly through other measurements.

After much manipulation of \( \text{B.36} \) we obtain an expression for \( W_{\text{ext}} \) in terms of the incident intensity and the vector scattering amplitude. Taking the ratio of the ratio of “lost” energy to the incident energy we obtain the extinction cross section

\[ C_{\text{ext}} = \frac{W_{\text{ext}}}{I_i} = \frac{4\pi}{k^2} \Re \left[ (\mathbf{X} \cdot \hat{e}_x)_{\theta=0} \right]. \]  \hspace{1cm} (B.39)

This shows a particular form of the optical theorem, which, perhaps counter-intuitively, says that the extinction from all manner of scattering types (optical, acoustic, particle) depends only on the amplitude of the scattering in

\( \cdot \)
the forward direction$^2$.

We can write $C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}}$, the sum of the scattered and absorbed energy; from (B.39) we can then calculate the scattering amplitude to be

$$C_{\text{sca}} = \int \frac{|X|^2}{k^2} \, d\Omega,$$  \hspace{1cm} \text{(B.40)}

where $|X|^2/k^2$ is also known as the differential scattering cross section $\frac{dC_{\text{sca}}}{d\Omega}$.

For arbitrarily polarised light $E_i = E_x \hat{e}_x + E_y \hat{e}_y$, we introduce $T = E_i \mathbf{X} + E_y \mathbf{Y}$, with $\mathbf{Y}$ defined similarly to $\mathbf{X}$, but for $y$-polarised light. With this, we get

$$C_{\text{ext}} = \frac{4\pi}{k^2} |E_i - i|^2 \Re \left[ \left( E_i^* \cdot T \right)_{\theta=0} \right], \quad C_{\text{sca}} = \int \frac{|T|^2}{k^2 |E_i|^2} \, d\Omega.$$ \hspace{1cm} \text{(B.41)}

Of course, for a sphere the polarisation of the incident light is somewhat irrelevant; for the consideration of more complicated particles it is worth remembering however.

Returning to considering the incident field as $x$-polarised, we can find $W_{\text{ext}}$ and $W_{\text{sca}}$ in terms of the incident and scattered fields; these in turn give us

$$C_{\text{sca}} = \frac{W_{\text{sca}}}{I_i} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \left( |a_n|^2 + |b_n|^2 \right) \hspace{1cm} \text{(B.42)}$$

$$C_{\text{ext}} = \frac{W_{\text{ext}}}{I_i} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n + 1) \Re \left( a_n + b_n \right) \hspace{1cm} \text{(B.43)}$$

To do this note that the Riccati-Bessel functions $\psi_n(\rho)$, $\xi_n(\rho)$ and $\chi_n(\rho)$ ($= -\rho y_n(\rho)$) are real for real arguments, and so we can use the Wronskian $\chi_n \psi'_n - \psi_n \chi'_n = 1$.

We can also introduce scattering efficiencies

$$Q_{\text{ext}} = \frac{C_{\text{ext}}}{G}, \quad Q_{\text{sca}} = \frac{C_{\text{sca}}}{G}, \quad Q_{\text{abs}} = \frac{C_{\text{abs}}}{G},$$  \hspace{1cm} \text{(B.44)}

where $G$ is the “geometric” cross-section of the particle; specifically the cross-sectional area of the projection of the particle onto the plane orthogonal to the axis of propagation of the incident beam: for example, a sphere of radius $a$ gives $G = \pi a^2$.

---

$^2$Refer to Newton [74] for a history of this theorem, and to van de Hulst [45] for details and a good, intuitive example.
This shows the inadequacy of ray optics; if ray optics were correct all particles would have scattering efficiencies of unity; the past few pages have strongly suggested otherwise.

To obtain the Rayleigh scattering, we truncate the power series expansion of the Bessel functions

\[
j_n(\rho) = \frac{\rho^n}{1 \cdot 3 \cdot 5 \cdots (2n + 1)} \left[ 1 - \frac{\frac{1}{2} \rho^2}{1!(2n + 3)} \right. \left. + \frac{\left(\frac{1}{2} \rho^2\right)^2}{2!(2n + 3)(2n + 5)} - \cdots \right], \quad (B.45)
\]

\[
y_n(\rho) = \frac{1 \cdot 3 \cdot 5 \cdots (2n + 1)}{\rho^{n+1}} \left[ 1 - \frac{\frac{1}{2} \rho^2}{1!(1 - 2n)} \right. \left. + \frac{\left(\frac{1}{2} \rho^2\right)^2}{2!(1 - 2n)(3 - 2n)} - \cdots \right]. \quad (B.46)
\]

Using these we can expand the scattering coefficients [B.34]. Taking the first four terms \(a_{1,2}, b_{1,2}\), and assuming (as always) that the permeability of the sphere is equal to that of the medium around it, we can construct a scattering matrix accurate with terms to order \(x^6\); from this we find that the (un-polarised) incident irradiance \(I_i\) gives scattered irradiance

\[
I_s = \frac{8\pi^4 Na^6}{\lambda^4 r^2} \left[ \frac{m^2 - 1}{m^2 + 2} \right]^2 \left(1 + \cos^2 \theta\right) I_i. \quad (B.47)
\]
Appendix C

Scattering Calculations

*Everyone who uses a computer frequently has had, from time to time, a mad desire to attack the precocious abacus with an axe.*
— John D. Clarke in [17, p. 97].

The MATLAB script used to calculate the classical scattering is listed here. It is a translated version of the FORTRAN *bhmie* from ref [12]. In order to test the translation, the example output in the book was replicated using this script. The physics and mathematics behind it are explained in appendix [B]. A wrapper script *genCext* that takes in physically interesting parameters is used to call *bhmie*.

```
function Cext = genCext(a,N,N1,lambda)

[S1 S2 Qext Qsca Qback] = bhmie(2*pi*N*a/lambda, N1./N, 181);
Cext = Qext * pi * a^2;
return
```

Note that, due to the optical theorem, this generates more outputs than we need: the values returned for $S_1$ and $S_2$ can be used to find the angular and phase distribution of the scattered light, which is not a problem that we are concerned with here.

% We make a Matlab function that does the same as BHMIE does in Fortran.
% This takes a set of three numbers:
% x --- The size parameter;
% refrel --- the relative refractive index;
% nang --- the number of angles to calculate the mie scattering for.
% It returns two matrices and three extinction efficiencies:
% s1 & s2 --- the coefficients used to create scattering matrix entries
% Qext --- The extinction efficiency;
% Qsca --- The scattering efficiency;
% Qback --- The back-scatter efficiency.
Based exclusively on the code in appendix A of Bohren and Huffman, "Absorption and Scattering of Light by Small Particles", Wiley, 1983.

Gavin King, 7th of February, MMXIII

function [S1 S2 Qext Qsca Qback] = bhmie(x, refrel, nang)

dx = x;
y = x*refrel;

% Figure out when to terminate:
xstop = x + 4*x^(1/3) + 2;
nstop = round(xstop);
ymod = abs(y);

nmx = round(max([xstop ymod]) + 15);
dang = 1.570796327/(nang - 1);

theta = nan*ones(1, nang);
for ii = 1: nang
    theta(ii) = (ii - 1)*dang;
end
amu = cos(theta);

% Logarithmic derivative is calculated by downward recurrence: start with
D(nmx) = complex(0, 0);
nn = nmx - 1;
for n = 1: nn
    rn = nmx - n + 1;
    fn = (2*rn + 1)/(rn*(rn + 1));
    psi = (2*dn - 1)*psi1/dx - psi0;
    apsi = psi;
    chi = (2*rn - 1)*chi1/x - chi0;
    xi = complex(apsi, -chi);
    an = (D(n)/refrel + rn/x)*apsi - apsi;
    bn = (refrel*D(n)+rn/x)*apsi - apsi;
end
Pi0 = zeros(1, nang); % we use Pi rather than pi to avoid Matlab's value.
Pi1 = ones(1, nang);
S1 = complex(zeros(1, 2*nang - 1));
S2 = complex(zeros(1, 2*nang - 1));

% Ricatti-Bessel functions with real argument z calculated with upward
% recurrence:
psi0 = cos(dx);
psi1 = sin(dx);
chi0 = -sin(x);
chi1 = cos(x);
apsi0 = psi0;
apsi1 = psi1;
xio = complex(apsi0, -chi0); %#ok<NASGU>
xil = complex(apsi1, -chi1);
Qsca = 0;

n=1;
while (n-1-nstop)< 0.0
    dn = n;
    rn=n;
    fn = (2*rn+1)/(rn*(rn+1));
    psi = (2*dn-1)*psi1/dx - psi0;
    apsi = psi;
    chi = (2*rn-1)*chi1/x - chi0;
    xi = complex(apsi, -chi);
    an = (D(n)/refrel+rn/x)*apsi - apsi;
    bn = (refrel*D(n)+rn/x)*apsi - apsi;
end
bn = bn /((refrel*D(n)*rn/xi*xi1);
Qsca = Qsca + (2*rn+1)*abs(an)*abs(an)*abs(bn)*abs(bn));
Pi = zeros(1,nang);
tau = zeros(1,nang);
for J = 1:nang
    JJ = 2*nang - J;
    Pi(J) = Pi1(J);
    tau(J) = rn*amu(J) - (rn+1)*Pi0(J);
    p = (-1)^n;
    S1(J) = S1(J)*fn*an*Pi(J) + bn*tau(J);
    t = (-1)^n;
    S2(J) = S2(J)*fn*bn*Pi(J) + bn*Pi(J);
    if J==JJ
        continue
    end
end
psi0 = psi1;
psi1 = psi;
apsi1 = psi1;
chi0 = chi1;
chi1 = chi;
x1 = complex(apsi1,-chi1);
n = n+1;
for J = 1:nang
    Pi1(J) = ((2*rn-1)/(rn-1))*amu(J)*Pi(J);
    Pi1(J) = Pi1(J) - rn*Pi0(J)/(rn-1);
    Pi0(J) = Pi(J);
end
Qsca = (2/(x^2))*Qsca;
Qext = (4/(x^2))*real(S1(1));
Qback = (4/(x^2))*abs(S1(2*nang-1))*abs(S1(2*nang-1));
Bibliography


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