

# The fascination of the rare earths - then, now and in the future

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**Abstract.** The rare earths have long been a subject of fascination to chemists and physicists. Herein I comment on some of the prehistory leading up to the advent of the Judd-Ofelt theory of the intensities of their remarkable spectra, the origins of the Judd-Ofelt theory and its early applications. I then consider subsequent developments and extensions of the theory, its current status and its relevance to current problems of interest in rare earth spectroscopy and the future of rare earth studies.

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## 1. Introduction

Of all the groups in the periodic table of the chemical elements perhaps the most fascinating are those commonly known as the rare earth elements or the lanthanide series. They are noteworthy for both their similarity and their diversity. The study of their properties has been long, torturous and often controversial. Herein I wish to concentrate on those features that led eventually to the modern understanding of their spectroscopic behaviour in their solutions and crystals via what has become known as the Judd-Ofelt theory.<sup>a</sup> The theory was promulgated in 1962 and represented, in a sense, the end of a long search for a consistent theory of the intensities of transitions, in another sense it represented a beginning of understanding and like all good theories raised many further questions. Some of these questions have been answered and others remain unanswered or partially answered. In any major development there is a long pre-history contributed by many, mostly forgotten. But the present depends very much on the past. Here we sketch, in a very cursory manner, some of the pre-history associated with the development of the Judd-Ofelt theory, make some brief comments on the initial response to the theory, subsequent developments and look to future developments concluding with some remarks on my personally favourite rare earth ion, trivalent europium. Throughout I will endeavour to give a largely verbal rather than mathematical account referring the interested reader to original sources for the details.

## 2. Some Pre-History of Crystal Field Theory

*We must consider how very little history there is; I mean real authentick history -*  
Samuel Johnson 1775

In 1942, at a Spectroscopy meeting held at the University of Chicago, William F Meggers<sup>1</sup> critically reviewed the current status of the atomic spectra of the rare earth elements, first remarking “*The so-called “rare earth” elements are notorious for the trouble they have caused both chemists and physicists. It required more than a century to complete their discovery,<sup>b</sup> and even now most of them are not available in quantity nor in a state of spectroscopic purity. Satisfactory descriptions of the atomic emission spectra are still lacking for many of these elements, partly because pure samples of some have not been produced and partly because of the extreme complexity of the spectra in most cases.*” Meggers continued his review destroying much of the previous work with cutting remarks such as “It probably has no physical significance”, “...must be regarded as pure numerology”, “This analysis may also be rated as wholly fictitious”, “...his sharp and diffuse series are entirely artificial”.

<sup>a</sup> We note that in this year, 2003, the INSPEC Thesaurus has added the term *Judd-Ofelt theory*.

<sup>b</sup> Actually the discovery was not completed until 1944 with Promethium whose existence had been predicted by Branner in 1902, misdiscovered as the element Illinium in 1926 and finally produced using the Oak Ridge National Laboratories reactor.

Megger's review occurred at a turning point in rare earth spectroscopy. New developments in the separation of rare earths was shortly to remove the problems of impure samples that plagued much of the earlier work. Nevertheless our subject starts much earlier with the work of many unsung heroes many of whose names no longer appear in treatises devoted to rare earths<sup>2</sup>. In 1925 Friedrich Hund focussed attention on the magnetic properties of the rare earths<sup>3</sup> successfully predicting the groundstates of the trivalent rare earths. Bethe<sup>4,5</sup> introduced the *gruppen pest* to the subject and crystal field theory was born. With the initial theoretical work of Hund and Bethe the subject developed rapidly. Van Vleck and Amelia Frank<sup>6</sup> resolved *the previous glaring discrepancy between theory and experiment for  $Eu^{+++}$ , which marred the otherwise quite satisfactory Hund theory for the rare earths*. By 1932 Van Vleck<sup>7</sup> had published his comprehensive book on magnetic susceptibilities while Penney and Schlapp<sup>8</sup> started to formalise the practical calculation of crystal fields. Amelia Frank<sup>9,10</sup> applied their crystal field theory to the magnetic susceptibilities of  $Sm^{+++}$  and  $Eu^{+++}$ . She extends the crystal field theory of Penney and Schlapp to include  $J$ -mixing making use of Wigner's then recently published *Gruppentheorie*<sup>11</sup>.<sup>c</sup> Frank explored the effects of a breakdown from cubic symmetry to the lower rhombic symmetry and can be regarded as one of the pioneers, and unsung heroine, of crystal field theory.

### 3. Some Experimental Rare Earth Spectroscopy Pre-History

*History does not reveal causes; it presents only a blank succession of unexplained events.* Isaiah Berlin *The Hedgehog and the Fox* (1953)

Megger's 1942 review of line spectra of rare earths at Spectroscopy meeting held at the University of Chicago, was followed by Simon Freed's review of the spectra of ions in crystals and solutions and was almost entirely devoted to salts and solutions of compounds of the rare earth elements. Freed notes that *The ions of the rare earths conform rather closely to the case of weak coupling with the lattice because of the shielding afforded by the incomplete 4f shell by the filled 5s and 5p shells*. Furthermore, he sees that there is a very close connection between the energy levels of the gaseous ions and those observed in a crystalline or solution environment and that in the salts the spectral lines are remarkably sharp. Much of his review focusses on salts containing the ubiquitous  $Eu^{3+}$  ion. Freed and Spedding<sup>13</sup> as early as 1929 had commenced detailed studies of the line absorption spectra of rare earth salts down to liquid hydrogen temperatures. They had *outlined reasons for believing that the absorption spectra of the rare earths in the solid state would resemble the line spectra of ions in the gaseous state*<sup>14</sup>. The year 1937 saw Bethe and Spedding<sup>15</sup> collaborating on the absorption spectrum of  $Tm_2(SO_4)_3 \cdot 8H_2O$  and speculating on

<sup>c</sup> Wigner found himself greatly attracted to Amelia Frank, one of the young women members of the Wisconsin faculty. The two were married in December 1936. Unfortunately, she soon developed incurable cancer and died just a few months after their marriage, casting him into a deep depression.

the nature of the mechanisms giving rise to the observed transitions. They note *Two theoretical arguments may be given a priori for the transitions within the 4f shell: First, the sharpness of the absorption lines would be immediately evident in the case of a transition within an inner shell and second, the intensity of the absorption lines is extremely small .... This indicates that they are due to a "forbidden" transition which would be true for a rearrangement within the 4f shell.* They further note *There are therefore three possible types of transitions: (a) Ordinary quadrupole transitions ... (b) Dipole transitions caused by a natural lack of symmetry of the crystalline field ... (c) Dipole transitions caused by coupling with crystal vibrations ...*<sup>d</sup> Simultaneously, Van Vleck<sup>16</sup> had reached similar conclusions. By 1940 the seminal ideas of Bethe and Spedding and of Van Vleck were driving further experimental studies. Notably Spedding<sup>17</sup>, now at Ames, made a detailed experimental and theoretical study of the absorption of the  $Pr^{3+}$  ion in solutions and solids assuming the transitions occurred among the states of the  $4f^2$  electron configuration. Here Spedding makes one of the first intermediate coupling calculations using the complete spin-orbit matrices for the  $f^2$  configuration. More ambitiously, Spedding and co-workers<sup>18</sup> at Ames studied the absorption spectra of  $Eu^{3+}$  in hydrated salts prophetically noting ... *the spectra in their fine structure reflect the nature of the fields surrounding the rare earth ion and, accordingly, such spectra should prove to be a powerful tool for the study of the fields existing in solids and solutions.*<sup>e</sup> They also note that some transitions in salts containing  $Eu^{3+}$  ions are very sensitive to changes in their surroundings, perhaps the first hint of so-called *hypersensitive* transitions.

#### 4. The Stage Setting for the Judd-Ofelt Theory

*'Contrawise,' continued Tweedledee, 'if it was so, it might be; and if it were so, it would be; but as it isn't, it ain't. That's logic.'* Lewis Carroll (1865)

The post-World War II period saw major developments in both theory and experiment that were to greatly accelerate our understanding of the rare earths and many of their puzzling features. Here we note only a few of the many facets associated with these developments. New techniques for separating rare earth elements resulted in the ready availability of rare earths of spectroscopic purity. This gave a tremendous emphasis to the study of the rare earth ions in the gaseous, solution and solid states. Experimentally the spectroscopic range was greatly increased and now included far infrared and microwave spectroscopy. In 1940 Spedding *et al*<sup>18</sup> had quoted from Condon and Shortley<sup>19</sup>

<sup>d</sup> Remarkably they did not consider magnetic dipole transitions.

<sup>e</sup> The heroic nature of these early experiments can be seen in the remark: *A line marked 0 was so faint as to be invisible under the magnification of the comparator microscope while a line marked 1 was just discernible. These lines were observed through a jeweler's eyeglass and were scratched on the gelatine of the plate by means of a sharp fine needle. Measurements were then made from the scratches.*

*"All known features of atomic spectra are now at least semiquantitatively explained in terms of quantum mechanical treatment of the nuclear atom model."*

The problem was, in the case of the rare earths where the  $4f$  shell was dominant, to be able to make practical calculations. A major breakthrough came in 1949 with Giulio Racah's remarkable application of group theory and tensor operators to problems of complex spectra<sup>20f</sup>. He essentially created the tools required to make detailed spectroscopic calculations for systems involving the multitudinous states of the  $4f$  shell. This revolutionised the entire subject of rare earth spectroscopy. Nuclear physicists such as H A Jahn and J P Elliott rapidly applied the methods of Racah to nuclear shell and collective models. Atomic physicists reared upon the comprehensive book of Condon and Shortley were slower to take up Racah's methods. Among the early practitioners in rare earth crystal spectroscopy were physicists such as K W H Stevens, R J Elliott and B R Judd and in chemistry the remarkable Christian Klixbull Jørgensen. The techniques developed by Racah rapidly found applications in crystal field calculations, the calculation of free ion energy levels etc. The problems of diagonalising large matrices were largely overcome with the parallel development of high speed computers. The books of Fano and Racah<sup>22</sup> and of Edmonds<sup>23</sup> and shortly to be followed by Judd's book<sup>24</sup> were to make the methods of Racah available to a wider audience. Practical calculations were further assisted by the computer generation of tables of the angular momentum coupling coefficients<sup>25</sup>, essential to Racah's tensor operator algebra. The methods of applying Racah's methods to problems of rare earth ions in crystals were outlined by Elliott, Judd and Runciman<sup>26</sup>. Many of the ideas of Racah were taken up and applied to transition metal ions in the remarkable and comprehensive book by Griffiths<sup>27</sup> which was to play a role in the subsequent works of both Judd and Ofelt. And thus by 1962 the stage was set for the next major development in the spectroscopy of rare earth ions in solutions and crystals - the Judd-Ofelt theory of the intensities of the transitions.

## 5. Arrival of the Judd-Ofelt Theory of Intensities

*The art of being wise is the art of knowing what to overlook.* William James

The solution to what Van Vleck<sup>16</sup> had called "The rare earth puzzle" was supplied simultaneously and completely independently by Judd<sup>28</sup> and Ofelt<sup>29</sup>. The two papers were published in *Phys. Rev.* and *J. Chem. Phys.* respectively on 1 August 1962. Neither author was aware of the results of the other, one (BRJ) working at Lawrence Radiation Laboratory at the University of California, Berkeley on the West coast of the USA and the other completing his PhD thesis at Johns Hopkins near the East coast of the USA some 4000km apart. I suggest that the coincidence of discovery was indicative that the time was ripe for the solution of the problem. The two papers have similarities and diversities. Both considered the odd terms in the crystal field expansion to couple

<sup>f</sup> Racah's work was largely done in isolation. For a fascinating account of Racah's appointment to the Hebrew University in 1940 see reference [21].

the states of the  $4f^N$  configuration to states of excited configurations of the opposite parity and used a form of perturbation closure to produce effective operators whose matrix elements were to be evaluated between states of the  $4f^N$  configuration. Both recognised the idea of Griffith<sup>30</sup> in making use of a closure procedure and both made extensive use of Racah's tensor operator methods. Judd applied his formalism mainly to available experimental results on the absorption spectra of solutions of rare earth salts while Ofelt, reflecting the experimental studies of rare earth crystal spectra at Johns Hopkins, applied his results to single crystal measurements made on  $EuCl_3$  and the then recently discovered fluorescence of the anhydrous rare earth trichlorides<sup>9</sup>.

## 6. Impact of the Judd-Ofelt Theory

*Nothing can be more fatal to progress than too confident reliance on mathematical symbols; for the student is only too apt to take the easier course, and consider the formula and not the fact as the physical reality.* Lord Kelvin and P G Tait (1878)

The papers by Judd<sup>28</sup> and Ofelt<sup>29</sup> satisfied David Hilbert's criterion for a good paper, *One can measure the importance of a scientific work by the number of earlier publications rendered superfluous.* The two papers of 1962 represent the paradigm that has dominated all further work on the intensities of rare earth transitions in solutions and solids up to the present time. Among the first attempts to confront the Judd-Ofelt theory with an extensive set of rare earth data was the 1965 analysis by Carnall *et al*<sup>31</sup>. Their data involved solutions in a wide range of solvents as well as rare earths in molten salts and showed that the Judd-Ofelt theory could give a very satisfactory account of the intensities for different rare earths in widely differing environments.

The hallmark of a good paper is also its ability to stimulate further work. It is not my intention to review the multitudinous works devoted to extensions, limitations, verification, relativistic extensions etc of the Judd-Ofelt theory. The interested reader could well start with the 1998 review of Smentek<sup>32</sup> or the special issue of *Molecular Physics*<sup>33</sup> devoted to the 40th anniversary of the Judd-Ofelt theory.

## 7. The fascination of the $Eu^{3+}$ ion

*"It did, Mr Widdershins, until quantum mechanics came along. Now everything's atoms. Reality is a fuzzy business, Mr Widdershins. I see with my eyes, which are a collection of whirling atoms, through the light, which is a collection of whirling atoms. What do I see? I see you Mr Widdershins, who is also a collection of whirling atoms. And in all this intermingling of atoms who is to know where anything starts and anything stops. It's an atomic soup we're in, Mr Widdershins. And all these quantum limbo states only collapse into one concrete reality when*

<sup>9</sup> The fluorescence had been discovered by accident during studies of the absorption spectra of single crystals. Expecting to see just absorption lines on the photographic plate there was surprise at seeing also emission lines!

*there is a human observer*” -Pauline Mellville, *The Girl with the Celestial Limb* (1991).

The  $Eu^{3+}$  ion has been an object of fascination right to the present time and shows every likelihood of becoming of even greater interest in the future. Interest in its spectroscopic properties goes back to the earliest spectroscopic studies of the rare earths. In 1937, Spedding<sup>34</sup>, noting the sharpness of the absorption lines of europium salts, suggested their application in astronomical measurements of Doppler shifts and proposed that  $Eu^{3+}$  embedded in glass replace the commonly used didymium glass<sup>h</sup>. He noted that the groundstate of  $Eu^{3+}$  in the solid was  ${}^7F_0$  and a number of transitions should occur to upper states which have  $J$  values of 0 or 1 and that these were sharp at room temperature even in glass.

The energy levels of the  $Eu^{3+}$  ion involve the states of the  $4f^6$  electron configuration with the ground multiplet being  ${}^7F$  and the first excited multiplet being that of a  ${}^5D$ . Transitions between the states of these two multiplets in absorption and fluorescence have been of considerable interest. Both Judd<sup>28</sup> and Ofelt<sup>29</sup> discussed these transitions in their initial papers. Since that time a large number of papers have discussed particular features of the transitions as well as the corresponding transitions in solids containing the divalent samarium ion  $Sm^{2+}$ . The transitions  ${}^7F_0 \leftrightarrow {}^5D_1$ ,  ${}^7F_1 \leftrightarrow {}^5D_0$ ,  ${}^7F_0 \leftrightarrow {}^7F_1$  all involve some magnetic dipole character as well as the forced electric dipole character coming from the Judd-Ofelt model. The transitions  ${}^7F_{J_{odd}} \leftrightarrow {}^5D_0$  and  ${}^7F_0 \leftrightarrow {}^5D_{J_{odd}}$  are forbidden in the standard Judd-Ofelt second-order treatment, though not in third-order extensions<sup>35–38</sup>. These “forbidden” transitions provide a testing ground for extensions of the original Judd-Ofelt model. The transitions  ${}^7F_0 \leftrightarrow {}^5D_1$ ,  ${}^7F_1 \leftrightarrow {}^5D_0$  are predominantly magnetic dipole in origin and unlike the electric dipole transitions are relatively insensitive to environmental changes. Comparison of the magnetic dipole and electric dipole transitions can give a useful measure of environmental effects<sup>39,40</sup>. The situation for the other transitions is complicated by the existence of several competing mechanisms involving  $J$ -mixing, the so-called Wybourne-Downer mechanism<sup>35,36,41,42</sup>, and relativistic effects<sup>43–46</sup>. These various mechanisms introduce angular dependent factors that go beyond the original Judd-Ofelt model and can produce a very entangled situation that is still not fully resolved.

## 8. Back to the future with the ${}^7F_0 \rightarrow {}^5D_0$ transitions

*The most important discoveries of the next 50 years are likely to be ones which we cannot now even conceive* Sir John Maddox (1999)

As noted in the previous section the  ${}^7F_0 \rightarrow {}^5D_0$  transition in solids containing  $Eu^{3+}$  ions are highly forbidden though nevertheless are observed, albeit rather weakly.

<sup>h</sup> Didymium was a rare metal discovered in 1841. In 1885 didymium was found to be a composite of the two rare earth elements, Praseodymium (the “leek-green twin”) and Neodymium (the “new twin”).

Their origin lies in departures from the Judd-Ofelt model. This transition has recently assumed special significance in the possibility of realising quantum computers with rare earth ion doped crystals<sup>48–51</sup>. The rare earth ion  $Eu^{3+}$  doped in crystals of  $Y_2SiO_5$  is of particular interest<sup>52</sup>. The  ${}^7F_0 \rightarrow {}^5D_0$  transition in  $Y_2SiO_5$  is one of the narrowest, if not the narrowest, known optical resonance in a solid with a linewidth of  $\sim 100Hz$ . Here the highly forbiddenness of the transition comes as a positive feature. In projected applications to quantum computing the hyperfine levels of the  ${}^7F_0$  groundstate of the  $Eu^{3+}$  ions play a central role leading to lifetimes measured in hours with decoherence times of several milliseconds. The precursor to this work goes back to the theory of nuclear magnetic resonance in  $Eu^{3+}$  developed in the late 1950's by R J Elliott<sup>53</sup> and studies of the anomalous quadrupole coupling in europium ethylsulphate<sup>81</sup>. The hyperfine structure of the groundstate is largely due to the fact that both of the stable isotopes,  ${}^{151}Eu$  and  ${}^{153}Eu$  each having a nuclear spin of  $I = \frac{5}{2}$  and hence each possess both a nuclear magnetic moment and an electric quadrupole moment. Calculating the magnitude and sign of the hyperfine splitting is a non-trivial exercise. Elliott considered a mechanism involving  $J$ -mixing by the crystal field coupling the  ${}^7F_0$  state to the  ${}^7F_2$  state together with coupling between the same two states via the nuclear electric quadrupole moment. Such a mechanism readily leads to the correct ratio for the observed splittings in the groundstate but of twice the observed magnitude and the *opposite* sign. This problem was considered by Judd, Lovejoy and Shirley<sup>54</sup> in their study of the anomalous quadrupole coupling in europium ethylsulphate. As with the Judd-Ofelt theory the solution was sought, and largely found, via interactions outside of the  $4f^6$  configuration. There is clearly a need for further work on this subject. The year 1962 saw not only the introduction of the Judd-Ofelt theory but also the rather analogous problem of anomalous quadrupole coupling with both having a direct relationship to the fascinating properties of the  $Eu^{3+}$  ion.

## 9. Concluding Remarks

The Judd-Ofelt theory marked a turning point in our understanding of the fascinating spectroscopic properties of the rare earths. It has been in a very real sense the first step in the journey to an understanding of the rare earths and their much heavier cousins, the actinides, but like many journeys into the unknown, the end is not in sight.

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