# Judd-Ofelt Theory and Analysis

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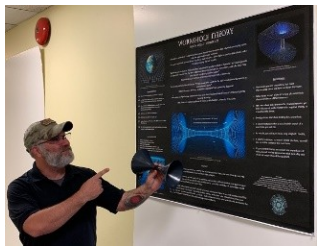
# About Me

- Student attending Pacific Lutheran University, B.S. in Applied Physics with minors in Math and Data Science (Spring 2021)
- Worked with: United States Marine Corps, United States Army, NASA LaRC Fall 2019



PACIFIC LUTHERAN UNIVERSITY

# Objective

The objective of this internship was to review the Judd-Ofelt theory and discuss how to conduct a Judd-Ofelt analysis of experimental data acquired from absorption spectra of a rare earth doped crystal. The analysis is accomplished by calculating the Judd-Ofelt parameters (, , ) and transition probabilities. The branching ratios and radiative lifetimes is calculated using a Judd-Ofelt Fitting Program created by Dr. Brian M. Walsh. The purpose of an analysis is to determine if a rare earth doped crystal is a valid candidate material for use in development of mid-infrared lasers, specifically in the 3-8 micrometer region.

# Introduction

In 1962, Brian R. Judd and George S. Ofelt simultaneously and independently published two identical formulations of a theory in separate publications. They had never met each other, and they were unaware of each other's interest in the intensities of rare earth ions in solids. Judd and Ofelt finally met each other along with B.G. Wybourne 40 years after their initial publications.

B.R. Judd G.S. Ofelt B.G. Wybourne

# Introduction

Brian R. Judd, of the University of California at Berkeley, referred to optical absorption and intensities of rare earth ions in his article.

PHYSICAL REVIEW VOLUME 127, NUMBER 3 AUGUST 1, 1962

## Optical Absorption Intensities of Rare-Earth Ions

B. R. JUDD
*Lawrence Radiation Laboratory, University of California, Berkeley, California*
(Received March 12, 1962)

Electric dipole transitions within the $4f$ shell of a rare-earth ion are permitted if the surroundings of the ion are such that its nucleus is not situated at a center of inversion. An expression is found for the oscillator strength of a transition between two states of the ground configuration $4f^N$, on the assumption that the levels of each excited configuration of the type $4f^N n'd$ or $4f^N n'g$ extend over an energy range small as compared to the energy of the configuration above the ground configuration. On summing over all transitions between the components of the ground level $\psi_J$ and those of an excited level $\psi'_{J'}$, both of $4f^N$, the oscillator strength $P$ corresponding to the transition $\psi_J \rightarrow \psi'_{J'}$ of frequency $\nu$ is found to be given by

$$P = \Sigma T_\lambda \nu (\psi_J \| U^{(\lambda)} \| \psi'_{J'})^2,$$

where $\mathbf{U}^{(\lambda)}$ is a tensor operator of rank $\lambda$, and the sum runs over the three values 2, 4, and 6 of $\lambda$. Transitions that also involve changes in the vibrational modes of the complex comprising a rare-earth ion and its surroundings, provide a contribution to $P$ of precisely similar form. It is shown that sets of parameters $T_\lambda$ can be chosen to give a good fit with the experimental data on aqueous solutions of $NdCl_3$ and $ErCl_3$. A calculation on the basis of a model, in which the first hydration layer of the rare-earth ion does not possess a center of symmetry, leads to parameters $T_\lambda$ that are smaller than those observed for $Nd^{3+}$ and $Er^{3+}$ by factors of 2 and 8, respectively. Reasons for the discrepancies are discussed.

# Introduction

George S. Ofelt, a PhD student at Johns Hopkins University in Baltimore, referred to crystal spectra and intensities of rare earth ions in his article.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 37, NUMBER 3 AUGUST 1, 1962

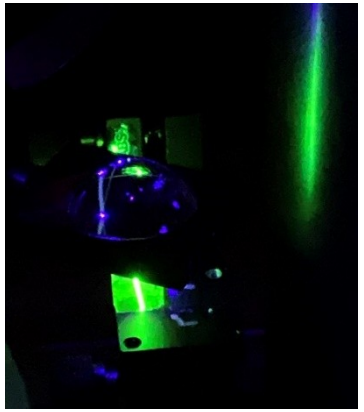
## Intensities of Crystal Spectra of Rare-Earth Ions*

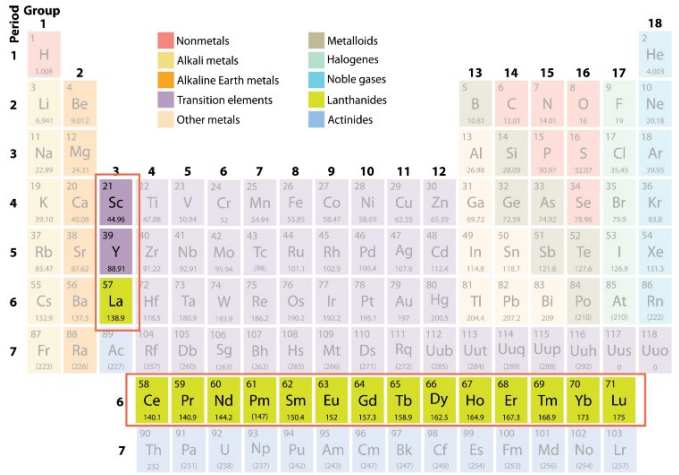
G. S. OFELT
*The Johns Hopkins University, Baltimore, Maryland*
(Received February 26, 1962)

Magnetic and electric dipole transitions between levels of the $4f^z$ configuration perturbed by a static crystalline field are treated. The expression obtained for the pure-electronic electric-dipole transition probability involves matrix elements of an even-order unit tensor between the two $4f^z$ states involved in the transition. The contributions to the transition probability from interactions, via the crystalline field, with the $nd^0 4f^{z-1}$, $4f^{z-1}nd$, $4f^{z-1}ng$ configurations are shown to add linearly, in such a manner as to multiply each odd $k$ crystal-field parameter $A_k^q$ by a constant. If "$J$ mixing" in the $4f^z$ configuration is neglected $\Delta J$ between the upper and lower $4f^z$ levels is restricted to six units or less. If "$L$ mixing" is neglected then $\Delta L$ is also restricted to six units or less. Application is made to the fluorescence spectra of $PrCl_3$ and $EuCl_3$. Many of the missing and weak transitions are explained.

# Background

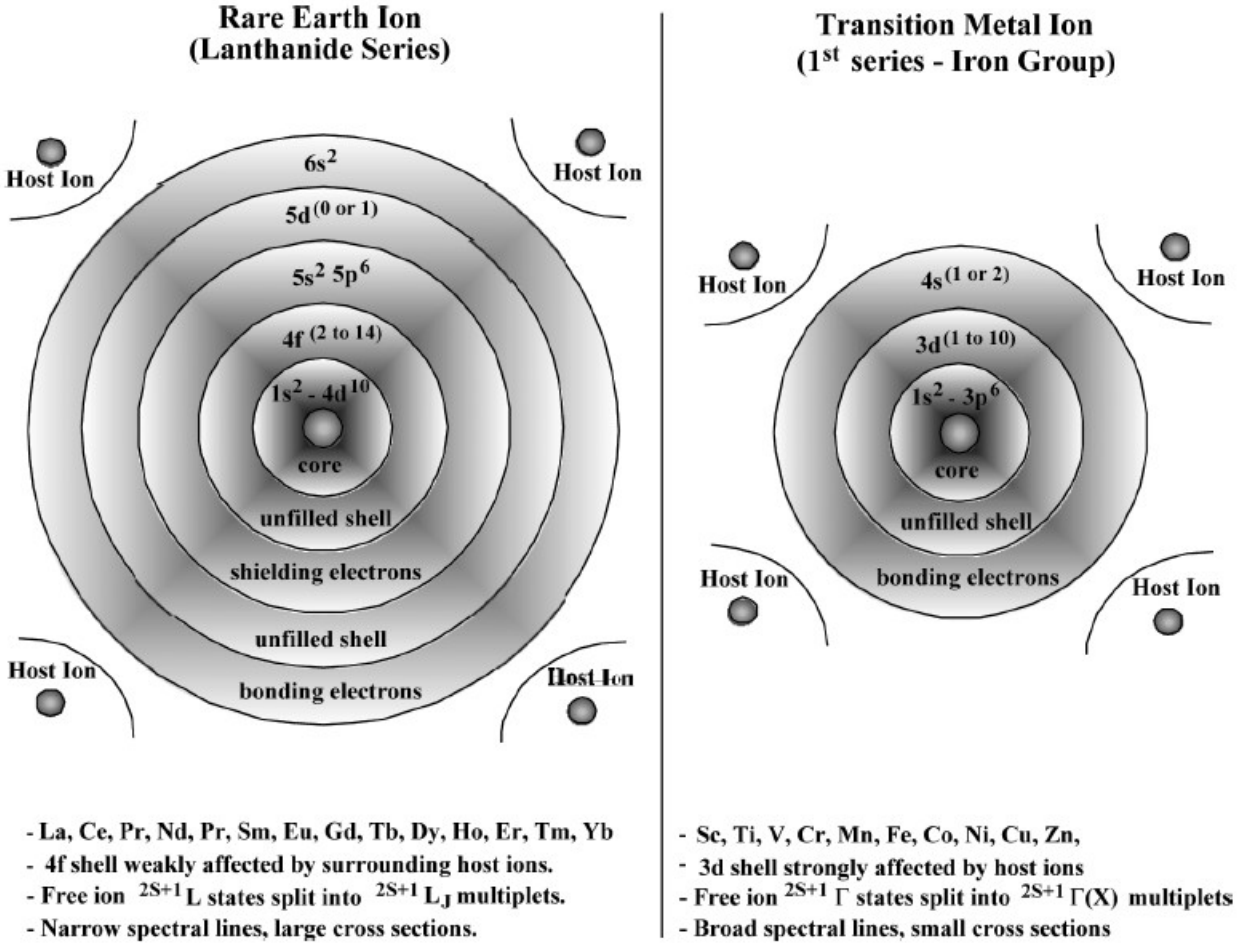
- Rare earth elements – Yttrium, Scandium, Lanthanum, Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, and Lutetium.
- The last 15 make up the lanthanide series. These elements are considered rare earths because of their scarcity and the difficulty associated with extracting them from earth.
- In their ionized state these elements are optically active making them possible candidates for use in lasers.





# Background

The atomic structure of rare earth ions in the lanthanide series and transition metal ions of the iron group are shown in the figure below.



# Theory in Principle

The Judd-Ofelt theory is based on the static, free-ion, and single configuration approximations. Simply stated, the Judd-Ofelt theory describes the intensities of lanthanide and actinide transitions in solids and solutions. The utility of the Judd-Ofelt theory is that it provides a theoretical expression for the line strength.

# Theory in Principle

The summation over  is known as the linestrength. This is the approximate solution of the Judd-Ofelt theory. It is often used to find ED matrix elements between mixed parity states for manifold-to-manifold transitions. What is usually done is to treat the Judd-Ofelt parameters as a set of phenomenological parameters to be determined from fitting experimental absorption measurements determined by the equation below with the theoretical Judd-Ofelt expression above.

# Theory in Principle

Judd-Ofelt theory makes 4 assumptions

1. The states of  are completely degenerate in
    - Assume an average energy for the excited configuration above the , that is, .
2. The energy denominators are equal
    - Assume that the difference of average energies, , is the same as the difference between the average energy of the  and the energy of the initial and final states of the .

    Advantages of these 2 assumptions are:
    - Energy denominators can be removed from the summations
    - Closure can be used
    - Angular parts of the electric dipole operator and crystal field can be combined into an effective tensor operator

# Theory in Principle

Judd-Ofelt theory makes 4 assumptions

3. Sum over Stark split J-levels
    - Assumes all Stark levels within the ground manifold are equally populated
4. Sum over dipole orientations
    - Assumes optically isotropic situation

Drawbacks of these assumptions

- The third assumption does not work at lower temperatures
- The fourth assumption is not valid for uniaxial or biaxial crystals, but this can be overcome by polarization averaging

# Theory in Practice: Example

The Judd-Ofelt theory allows for the calculation of manifold to manifold transition probabilities, from which the radiative lifetimes and branching ratios of emission can be determined. A Judd-Ofelt analysis relies on accurate absorption measurements, specifically the integrated absorption cross section over the wavelength range of several manifolds.

The mean wavelength, , can be found from the first moment of the absorption cross section data,

# Theory in Practice: Example

In practice, the Judd-Ofelt theory is used to determine a set of phenomenological parameters, , by fitting the experimental absorption or emission measurements, in a least squares difference sum, with the Judd-Ofelt expression. First, the linestrength is written as a 1xN column matrix, , and the Judd-Ofelt expression is also written in matrix form as,

where are components of a N x 3 matrix for the square matrix elements of U(2), U(4) and U(6). The are components of a 1 x 3 matrix for the Judd-Ofelt parameters , and . Note that N represents the number of transitions to fit, which depends on the number of absorption manifolds measured. Obviously, since there are only three Judd-Ofelt parameters, $N > 3$.

# Theory in Practice: Example

Next, the sum of the squared difference is formed,

and minimized by taking the derivative with respect to

# Theory in Practice: Example

The set of Judd-Ofelt parameters that minimizes the sum of the squared difference of measured and theoretical linestrength is written in matrix form, , where  is the adjoint of . Once the Judd-Ofelt parameters are determined, they can be used to calculate transition probabilities, , of all excited states from the equation,

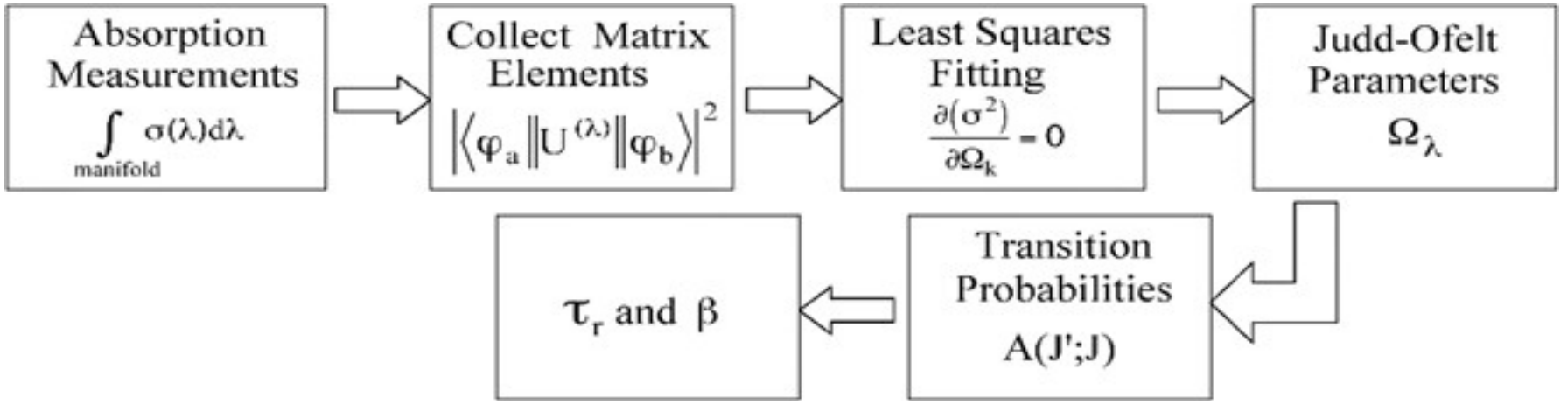
where  is the refractive index of the solid,  and  are the electric and magnetic dipole line strengths, respectively. In this equation  is the total angular momentum of the upper excited state. Electric dipole linestrengths, , are calculated from each excited manifold to all lower lying manifolds the Judd-Ofelt expression using the matrix elements, , and Judd-Ofelt parameters.

# Theory in Practice: Example

All the tools have been developed up to this point, and it is now a simple matter to find the radiative lifetimes, , and the branching ratio,

# Theory in Practice: Example

The procedure of a Judd-Ofelt analysis is represented in a simple flow chart shown in figure 7 below. This figure shows the major steps in the process, culminating in calculation of the transition probabilities and branching ratios. The details of all these steps have been covered and form, a hopefully clear and coherent, recipe for what is called a Judd-Ofelt analysis.



# Value Added

To NASA:

- Work at NASA Langley is focused on a systematic search for novel lanthanide-doped mid-infrared solid-state lasers using both quantum mechanical models (theoretical) and spectroscopy (experimental) techniques.
- Efforts to develop MIR lanthanide based solid-state lasers can be of substantial benefit in producing sources for the spectral ranges 3–8 μm, a region that is rich in many atmospheric molecular gasses. The impact is clear, and in the MIR region, broad spectral coverage buys access to chemical "fingerprints," where molecules can be detected and distinguished with great sensitivity.

# Value Added

To me:

- Developed key technical skills such as data analysis, optics, lasers, and various software platforms which will allow me opportunities to continue exploring necessary research skills as I transition into graduate school
- Gained confidence with teleworking, time management, and advanced topics in physics and chemistry in preparation for graduate school
- Attended seminars and video conferences throughout the summer to explore future possibilities for research and career interests

# Conclusion

- This analysis technique is integral to the theoretical modeling and a necessary tool for the future of MIR solid -state laser materials research.
- Thank you for this unparalleled opportunity to expand my skillset and knowledge base as I continue my scientific and academic journeys.

# Questions?

# Thank You!