

Judd B R. Optical absorption intensities of rare-earth ions.

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[Lawrence Radiation Laboratory, University of California, Berkeley, CA]

Electric-dipole transitions within configurations of f electrons are allowed if the ion involved is situated at a site that does not possess inversion symmetry. For a rare-earth ion in solution, the intensities involve only three parameters. [The SC1® indicates that this paper has been cited in over 480 publications since 1962.]

B. R. Judd
Department of Physics
Johns Hopkins University
Baltimore, MD 21218

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"While a graduate student at Oxford University in the early 1950s, I was working on the paramagnetic resonance of rare-earth ions in crystals. In order to obtain reasonably good eigenfunctions for the low-lying states of the configurations $4f^N$, I began searching for optical data that could be used in my analyses. It soon became clear that almost nothing was known about the optical transition probabilities for electric-dipole radiation within the f shell. I realized that the noncentrosymmetric part of the crystal-field potential could admix states of opposite parity (such as those of $4f^{N-1}5d$) into $4f^N$, and thus allow the transitions to take place. The effective transition operator would have to have even rank, and I experimented with a sixth-rank tensor taken between the ground level of the Nd^{3+} ion and the levels of the $4F$ multiplet.

"By a remarkable piece of good fortune, I was sharing a room with several other researchers, and one of them, D. Bijl, had a copy of Hoogschagen's 1947 Leiden thesis¹ on the absorption spectra of the rare earths

in solution, which gave the experimental results for the transitions in question. The relative intensities of the four lines were not too far from the numbers I had calculated. However, the methods I had used were based on determinantal product states and were extremely tedious. I also took no account of deviations from pure Russell-Saunders coupling, and it was clear that this would have to be corrected if it was going to be possible to account for transitions involving a change in the total spin quantum number.

"I was further deflected at that time by the need to write a thesis, and the problem of the intensities lost its priority for my attention. Seven years later, in 1961, I emerged from writing a book entitled *Operator Techniques in Atomic Spectroscopy*,² and I was anxious to make a contribution to the research literature. By that time I had learned the tensorial techniques of Racah,³⁻⁵ and it was much easier for me to cope with the mathematics. In the meantime, Wybourne⁶ had carried out the intermediate-coupling analysis for the f^3 configuration of the neodymium ion, so accurate eigenfunctions were available. It only took me a few weeks to put the pieces together and work out the parameters that gave the best fit to the neodymium data. I then went to the complementary configuration, f^{11} , and did a similar analysis for the erbium ion in solution. Just three parameters, corresponding to the three possible tensors of even rank, seemed to be sufficient to fit the many data for each ion extremely well. And so it has turned out: not only for other rare-earth ions, but also for the members of the actinide series. The frequent citation of my article merely reflects the interest in understanding the spectroscopic properties of f -electron ions.

"For a recent review, see Hessler and Carnall."⁷

1. Hoogschagen J. *De absorptiespectra van de zeldzame aarden.*

Amsterdam: Noord-Hollandsche Uitgevers Maatschappij. 1947. 119 p.

2. Judd B R. *Operator techniques in atomic spectroscopy.* New York: McGraw-Hill, 1963. 242 p.

3. Racah G. Theory of complex spectra. II. *Phys. Rev.* **62**:438-62, 1942. (Cited 790 times since 1955.)

4. Theory of complex spectra. III. *Phys. Rev.* **63**:367-82, 1943. (Cited 585 times since 1955.)

5. Theory of complex spectra. IV. *Phys. Rev.* **76**:1352-65, 1949. (Cited 360 times since 1955.)

6. Wybourne B G. Analysis of the solid-state spectra of trivalent neodymium and erbium.

J. Chem. Phys. **32**:639-42, 1960. (Cited 85 times since 1960.)

7. Hessler J P & Carnall W T. Optical properties of actinide and lanthanide ions. *ACS Symp. Ser.* **131**:349-68, 1980.