

This Week's Citation Classic®

Peacock R D. The intensities of lanthanide $f-f$ transitions.
Struct. Bond. 22:83-122, 1975.

[Department of Chemistry, King's College, University of London, England]

This paper reviewed the mechanisms whereby the Laporte-forbidden lanthanide ion $f-f$ transitions gain intensity. In particular, the possible physical causes of the phenomenon of "hypersensitivity" were considered. After assessing the various theories that had been proposed, it was concluded that only the ligand polarisation mechanism, in which the metal ion transitions gain intensity from the allowed ligand transitions, could account for all the experimental facts. [The SCI® indicates that this paper has been cited in over 205 publications.]

The Intensities of Lanthanide Spectra

Robert D. Peacock
Department of Chemistry
University of Glasgow
Glasgow G12 8QQ
Scotland

July 12, 1988

My PhD work at the University of Dundee involved the synthesis of new heteropoly anions containing lanthanide elements. During the course of my work, I became more and more interested in the spectroscopy of the lanthanide ions and particularly in the intensity of the $f-f$ transitions. It was (and is) frequently said that $f-f$ spectra are uninteresting because they depend little on the chemical environment of the ion, due to the strong shielding effect of the 5s and 5p electrons. It is certainly true that for lanthanide complexes in solution the energies of the $f-f$ transitions are fairly similar from compound to compound, but this is certainly not true of the intensities. In par-

ticular there are certain $f-f$ transitions, called *hypersensitive* by C.K. Jørgensen and B.R. Judd,¹ whose intensities are very sensitive to the environment: for example, the $^4I_{9/2} \rightarrow ^4G_{5/2}$ transition of Nd^{3+} is about 100 times larger in gas-phase NdI_3 than in the Nd^{3+} aqua ion. Shortly before I started my research, a general theory of lanthanide intensities had been published by Judd² and by G.S. Ofelt.³ Although the Judd-Ofelt theory is the basis for understanding lanthanide intensities, it does not in itself explain hypersensitivity.

After my PhD I went to King's College, London, on an SRC/NATO fellowship to work with S.F. Mason. I decided to look at all the suggestions that had been put forward to explain hypersensitivity and, where appropriate, test them experimentally. Finally, in conjunction with Mason and Brian Stewart, I proposed our own solution to the problem—Ligand Polarisation Theory.⁴ While this work was in progress, it became clear that there was a lack of a suitable review on the subject of lanthanide intensities and in particular of one that explained the various theories and suggestions in language that chemists could understand.

I think there are various reasons the review has been successful. First of all, it came at just the right time. There had been a good deal published on the subject during the decade or so before 1975 but few^{5,6} major theoretical advances since, so it still essentially represents the state of the subject. Second, it is a critical review—indeed, it was specifically designed as such. Third, it attempted to make a subject that had largely been developed by physicists and mathematicians comprehensible to chemists (and especially the author!). I would like to believe that the last reason is the main explanation for the review's success.

1. Jørgensen C K & Judd B R. Hypersensitive pseudoquadrupolar transitions in lanthanides. *Mol. Phys.* 8:281-90, 1964. (Cited 230 times.)
2. Judd B R. Optical absorption intensities of rare-earth ions. *Phys. Rev.* 127:750-61, 1962. (Cited 685 times.) [See also: Judd B R. Citation Classic. (Thackray A, comp.) *Contemporary classics in physical, chemical, and earth sciences*. Philadelphia: ISI Press, 1986. p. 21.]
3. Ofelt G S. Intensities of crystal spectra of rare-earth ions. *J. Chem. Phys.* 37:511-20, 1962. (Cited 530 times.)
4. Mason S F, Peacock R D & Stewart B. Ligand polarisability contributions to the intensity of hypersensitive trivalent lanthanide transitions. *Mol. Phys.* 30:1829-41, 1975. (Cited 105 times.)
5. Stewart B. Anisotropic ligand polarisation contributions to the Laporte-forbidden transition probabilities of open-shell metal complexes. *Mol. Phys.* 50:161-71, 1983. (Cited 10 times.)
6. Reid M F & Richardson F S. Paramagnetization of electric-dipole intensities in the vibronic spectra of rare-earth complexes. *Mol. Phys.* 51:1077-94, 1984. (Cited 10 times.)