This Week's Citation Classic

Stevens K W H. Matrix elements and operator equivalents connected with the magnetic properties of rare earth ions.
Proc. Phys. Soc. London A **65**:209-15, 1952.
[Clarendon Laboratory, Oxford, England]

This paper describes a relatively simple way of obtaining crystal field matrix elements for use with rare earth ions, and tables of the most often needed elements are included. [The *SCI*® indicates that this paper has been cited in over 580 publications since 1961.]

K.W.H. Stevens
Department of Physics
University of Nottingham
Nottingham NG7 2RD
England

July 25, 1983

"By the late 1940s, electron spin resonance at the Clarendon Laboratory was moving toward the study of rare earth ions. The problem of working at helium temperatures had been overcome and a wealth of spectra were being observed on the ethyl sulphates. It was not known that crystal field theory would account for the results, which were certainly not characteristic of small departures from cubic symmetry. Indeed, it was later learned that J.H. van Vleck, from an examination of the macroscopic magnetic properties of the ethyl sulphates, had concluded that they could not be interpreted using crystal field ideas. Fortunately, this was not known in Oxford, and it was a natural step to apply crystal field ideas to the D_{3h} symmetry of the ethyl sulphates.

"Techniques for evaluating matrix elements were available, but they were extremely tedious to use. By chance I had become interested in two apparently disparate topics, group theory and nuclear quadrupole interactions. The latter had recently been recognised[1,2] in the spectra of iron group ions, and I had been puzzled as to how electrostatic interactions could be rewritten in terms of angular momentum operators. The original reference (which was reprinted in 1963) was to a prize essay, written in 1936 by H.B.G. Casimir,[3] and virtually unobtainable. However, a copy was eventually found and there it was shown how second order spherical harmonics could be reexpressed in angular momentum form, using the Wigner-Eckart theorem, with which I was already familiar. The way was immediately open to do something similar with the higher order potentials of the crystal fields. There remained the question of finding the equivalence factors, and this could be done by a trick. It was necessary to work out all the relevant operators, their matrix elements, and the equivalence factors, but within a few weeks R.J. Elliott and I knew we could account for many of the observations.

"Only one British journal had previously carried a paper[4] on rare earth crystal fields; my manuscript was rejected as being of insufficient interest! It lay in a drawer for some time after, while the technique was happily exploited. Indeed, it might still be there had B. Bleaney not suggested trying the Physical Society.

"I have been asked why I didn't use a different normalisation, that more appropriate to change of axes. The simple answer is that we had enough to do with the obvious axes and there was no desire to rotate. That all came much later, along with recognising the relevance of Racah's work.[5] So why is the method still used and why is it highly cited? Presumably because it is simple. Will it be superceded? To some extent it has been, but the use of noncommuting operator expressions to form bases of irreducible representations seems likely to remain.

"The operators were originally obtained from crystal field theory. More recent work[6] has shown that they also arise in a more basic theory of magnetic insulators, which avoids the criticisms of crystal field theory. The origin of the parameters is different, which is an attraction for they have never been satisfactorily derived using crystal field theory!"

1. **Penrose R P.** Hyperfine structure in the solid state. *Nature* **163**:992, 1949.
2. **Bleaney B.** Nuclear specific heats in paramagnetic salts. *Phys. Rev.* **78**:214-15, 1950.
3. **Casimir H B G.** *On the interaction between atomic nuclei and electrons.* San Francisco, CA: W.H. Freeman, 1963. 90 p.
4. **Kynch G J.** Multiplet structure in a crystalline electric field of cubic symmetry. *Trans. Faraday Soc.* **33**:1402-18, 1937.
5. **Fano U & Racah G.** *Irreducible tensorial sets.* New York: Academic Press, 1959. 171 p.
6. **Stevens K W H.** Exchange interactions in magnetic insulators. *Phys. Rep.—Rev. Sect. Phys. Lett.* **24C**:1-75, 1976.

© 1983 by ISI®