

[CF models] supplementary to {13.1:434}

If the RE ions are truly independent and each of them is embedded in an identical local environment as prescribed by the point group of the site, the spectrum will consist of a series of lines whose positions and intensities are defined by the delta function and the matrix elements of (13.7), respectively. A common approach is to treat the crystal-field theory in terms of a model which can be either phenomenological or *ab initio* so that one may quantitatively compare the experimental data with theoretical prediction. Our purpose here is not to review the various theoretical treatments but rather to illustrate the basic neutron methodology. Therefore, it is suffice to confine ourselves to a crystal-field scheme of intermediate coupling using the spherical-tensor formalism. The method in general works reasonably well for most of the rare-earth and actinide compounds. The Hamiltonian for the crystal field effects is written as

$$H_{CF} = \sum_{k,q,j} B_q^k C_q^k(i), \quad (1)$$

Where the $C_q^k(i)$ are spherical tensor operators of rank k , and depend on the coordinates of the i th electron. The summation of the i is over all f electrons of the ion, and the B_q^k are the crystal-field parameters. The presumably real crystal-field potential and inversion invariance imply, respectively, that all parameters are real and of even rank, and for f electrons, $k \leq 6$. A consideration of the point-group symmetry of the RE site reduces further the number of non-zero parameters. In the case of TmPO_4 , only five parameters, $B_0^2, B_0^4, B_4^4, B_0^6$, and B_4^6 are of relevance. In order to account for the hierarchy energy structure, additional terms representing the electronic interactions within the free RE ion are included. The advantage of this approach is to enable the analysis of both the low-energy neutron data and the high-energy optical data over many crystal-field-split multiplets. If only neutron data concerning the ground-multiplet are of interest, the parameters corresponding to the free-ion terms, such as those corresponding to the Slater integrals and spin-orbit interaction, are fixed to the values in the literature previously determined from optical spectroscopy. Often, if only the low-lying states of the ground term are of interest, these parameters are completely ignored and a simplified *operator equivalents method*, originally introduced by K. W. H. Stevens, can be used to diagonalize the Hamiltonian of (1). However, if anomalous spin-orbit and/or the Coulombic interactions are of concern, e.g., via hybridization of the f - and conduction electrons or electrostatic screening of the Coulomb repulsion in some RE intermetallic compounds, intermultiplet transitions measured by neutron scattering, typically using instruments at spallation neutron sources, can shed light on the interesting physics involved.

Reference:

Furrer, A. and A. Podlesnyak (2006), "Crystal field spectroscopy", in Handbook of Applied Solid State Spectroscopy, Ed. D. R. Vij, Springer, Chapter 6, p. 257.