SPECTROSCOPIC PROPERTIES OF RARE–EARTH DOPANTS IN SEMICONDUCTORS

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The electronic properties of rare-earth ions in solids are very much atomic-like in nature due to the fact that the relevant 4f electrons are shielded from outside influences by the screening by 5s and 5p electrons. The effects of ligand ions are treated successfully by adding crystal fields to the Hamiltonian. Equations are traditionally solved by analytical means. In spite of obvious great successes this method has the handicap of being applicable only to cases of high symmetry, such as in cubic or axial structures. For lower symmetries, and especially for ions with high spin, the mathematical problem of solving equations becomes a handicap. This can only be slightly improved by applying methods of perturbation theory.

In a basically different approach the equations are solved by numerical methods, eliminating limitations of the analytical formulation. Ligand fields of lower symmetry, such as orthorhombic and monoclinic, and of arbitrary strength, can be applied. By diagonalization, energy levels and wave functions are obtained allowing optical spectra to be analyzed. Upon adding a magnetic field to the Hamiltonian the spectra from magnetic resonance become accessible for interpretation. The numerical method is applicable equally well to all rare-earth ions embedded as an impurity in semiconductor and insulator crystals.

As a specific example the rare-earth impurity Er^{3+} in its $4f^{11}$ electron configuration, with orbital momentum L = 6 and spin S = 3/2, is considered in some detail. A large amount of experimental data on optical spectra measured by photoluminescence was analyzed in the computational framework. The lifting of the 16-fold degeneracy of the $^4I_{15/2}$ spin-orbit ground state was calculated in a near systematic fashion for arbitrary combinations of crystal-field potentials. Crystal field parameters B_j^k are obtained from the analysis. Complex features such as due to level anticrossings do not require any special care. Admixture of higher spin-orbit field states $^4I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ is possible by using a larger basis set, i.e., increasing the size of the interaction matrix to dimension 52.

Once optical spectra are interpreted, the magnetic properties of the states are known as well, allowing, e.g., the prediction of corresponding electron paramagnetic resonance spectra. As the calculations include all interactions simultaneously the magnetic field can be of arbitrary strength covering both the linear low-field region with constant g tensors as well as high field with non-linear dependence. By the Zeeman effect all (Kramers) degeneracy is lifted eliminating all problems associated with doublet and quartet levels. Results allow a convincing interpretation of nearly 100 EPR spectra as reported in the literature for the erbium ion in a great variety of host crystals. By also calculating expectation values for the spin, the sign of g values can be evaluated. An empirically established rule of constant trace $g_{//} + 2g_{\perp}$ of axial g tensors upon trigonal or tetragonal distortion of cubic centers is supported by the calculations.

The numerical calculations have shown to be a versatile modern tool for the analysis of data from spectroscopy of rare-earth ions. In optical experiments this includes straightforward photoluminescence as well as magneto-optics (Zeeman spectroscopy) and optical detection of magnetic resonance (ODMR). The smaller energy separations as measured in magnetic resonance spectra are also analyzed without applying perturbation methods, for ground states as well as for excited states.