Outline of Crystal field theory

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Crystal field theory describes the origins and consequeces of interaction of the surroundings on the orbital energy levels of a transition metal ion.

1 Orbitals

- Principal quantum number n
- Azimuthal quantum number l
- Magnetic quantum number m_l
- Spin quantum number m_s
- Spin-orbit coupling

2 Shape and symmetrys of Orbitals

- 's'orbital: sphereical symmetry
- 'p'orbitals: p_x, p_y, p_z
- 'd'orbitals: $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{xz}

3 Application of group theory on crystal field splitting

Group Theory plays a major role in finding the degeneracy and the symmetry types of the electronic levels in the crystal field.

- Splitting of the energy levels.
- Symmetry types of the split levels.
- Choice of basis functions to bring the Hamiltonian H into block diagonal form. Spherical symmetry results in spherical harmonics $Y_{lm}(\theta, \phi)$ for basis functions.

The Hamiltonian for the impurity ion in a crystalline solid

$$H = \Sigma_i(\frac{p_i^2}{2m} - \frac{Ze^2}{r_{i\mu}} + \Sigma_j \frac{e^2}{r_{ij}} + \Sigma_j \xi_{ij} l_i \cdot s_j + \gamma_{i\mu} j_i \cdot I_\mu) + V_{xtal} \tag{1}$$

Here $\xi_{ij} l_i \cdot s_j$ is the spin-orbit interaction of electrons on the impurity ion and $\gamma_{i\mu} j_i \cdot I_\mu$ is the hyperfine interaction of electrons on the ion. The perturbing crystal potential V_{xtal} of the host ions acts on the impurity ion and lowers its spherical symmetry.

- Weak field. V_{xtal} is small compared with spin-orbit interaction. Rare earth and ionic host crystals.
- Strong field. V_{xtal} is strong compared with spin-orbit interaction. Transition metal.

4 Crystal field splitting in octahedral coordination

Most interesting 3d transition metal, e_g and t_{2g}. Since lobes of the e_g orbitals point towards the ligands, electrons in these two orbitals are repelled to a greater extent than are those in the three t_{2g} orbitals that project between the ligands.Therefore, the e_g orbitals are raised in energy relative to the t_{2g} orbitals. The energy separation between the t_{2g} and e_g orbitals is termed the crystal field splitting and is designated by Δ_0. Alternatively, the symbol $10Dq$ utilized in ligand field theory is sometimes used, and $\Delta_0 = 10Dq$.

Crystal field splitting in different coordinations:

- Cubic coordination: $\Delta_c = -\frac{8}{9}\Delta_0$
- Tetrahedral coordination: $\Delta_t = -\frac{4}{9}\Delta_0$
- Dodecahedral coordination: $\Delta_d = -\frac{1}{2}\Delta_0$

5 The 10Dq parameter

The magnitude of the crystal field splitting parameter, $10Dq$, may be estimated by two independent methods. The conventional way is from positions of absorption bands in visible-region spectra of transition metal compounds.The second method for estimating the value of A is from plots of thermodynamic data for series of similar compounds of transition elements.

Factors influencing values of $10Dq$:

- Type of cation: $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Mn^{4+}$
- Type of ligand: $I^- < Br^- < Cl^- < SCN^- < F^- < urea = OH^- < CO_3^{2-} = oxalate < O^{2-} < H_2O < pyridine < NH_3 < ethylenediamene < SO_3^{2-} < NO_2^- < HS^- < S^{2-} < CN^-$
- Interatomic distance
- Pressure: $10Dq \sim V^{-5/3}$
- Temperature