

ligands) in the crystal. For historical reasons this energy difference is usually called $10 Dq$.

So far only arguments which depend on symmetry have been used. If one wishes to make even semiquantitative calculations, molecular orbitals combining realistic ligand and metal ion wave functions must be used to give orbitals which satisfy the symmetry requirements. Ballhausen and Gray have given a description of the process. A diagram such as Fig. 3 results, in which we see the combination of ligand

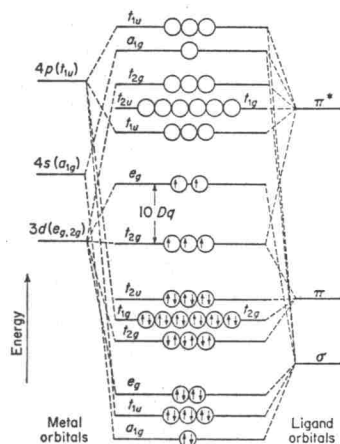


FIG. 3. Molecular orbital diagram—octahedral symmetry.

and metal ion wave functions to give bonding orbitals such as a_{1g} and t_{1u} , non-bonding orbitals such as t_{2u} , and anti-bonding orbitals such as t_{2g} and e_g . The separation between these last two is still a measure of the crystal field ($10 Dq$).

The $3d$ shell of iron is only partially filled. In the ideal case, the ferrous ion has six and the ferric ion five $3d$ electrons. There is more than one way to put the electrons in the levels; according to Hund's rule of atomic spectroscopy, the state of maximum spin should be lowest in energy. This case is illustrated in (a) and (b) of Fig. 4, and applies to most ionic materials. If the metal-ligand interaction is strong enough, energy may be saved by pairing spins as in (c) and (d). Potassium ferrocyanide and potassium ferricyanide are examples of this situation. For high spin ferric (a) and low spin ferrous (d) ions,

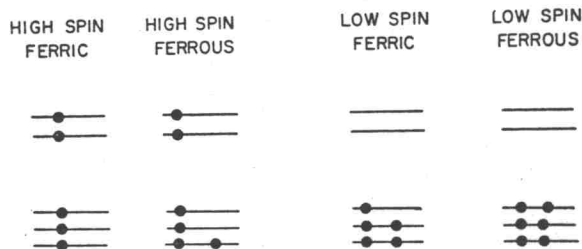


FIG. 4. Spin free and spin paired electron distributions for ferric and ferrous systems.

the $3d$ electrons present a field of spherical symmetry at the nucleus. For high spin ferrous and low spin ferric ions a strong probability of an asymmetric field exists. This is very important in understanding many aspects of quadrupole splitting.

A variety of different transitions are observed optically in crystals containing transition metal ions. There are $d-d$ transitions which measure $10 Dq$, or the Racah parameters B and C , or combinations of these two effects. These are of moderate intensity because they are allowed only due to vibrational interaction. Typically, $10 Dq$ is of the order of $5000-15,000 \text{ cm}^{-1}$ ($0.6-1.8 \text{ eV}$, $15-45 \text{ kcal}$) at one atmosphere. The combination peaks measuring both $10 Dq$ and B and C lie at somewhat higher energies, in the visible or near ultraviolet.

It is also possible to observe optical transitions which measure an electron transfer from a ligand level (ϵ_{2u}) to a predominantly metal level (ϵ_{2g}). This is an allowed transition and very intense, and the energy peak for such transitions typically lie at 25,000–40,000 cm^{-1} (3–5 eV), but they are broad, and the low energy tail sometimes extends through the visible and even into the infrared.

The effects of pressure on these transitions have been reviewed extensively elsewhere (Drickamer, 1963, 1965). In general, there is a marked increase in $10 Dq$ with pressure (10–15% in 100 kb). In the simplest order of theory, one would expect the crystal field to increase as R^{-5} , where R is the metal-ligand distance, and this is roughly what occurs. There is a measurable decrease in the Racah parameters with increasing pressure—7–11% in 100 kb. Apparently the $3d$ orbitals expand by interaction with the ligands, and this increases the average distance between electrons in the $3d$ shell, which reduces the repulsion between them.

The charge transfer peaks shift strongly to lower energy with increasing pressure, by as much as one half to 1 eV in 100 kb. This lowering