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The Oxidation State of Iron at High Pressure

Fe(III) reduces to Fe(II) in solids at high pressure;
the process is reversible.

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I. Introduction

Mössbauer resonance is a convenient tool for studying the electronic behavior of iron in various environments. High pressure Mössbauer studies in this laboratory (1-7) have shown that, in a wide variety of compounds, ferric ion reduces to the ferrous state with increasing pressure, and that this is a reversible process. Before describing and analyzing these results, it will be useful to review briefly the relevant features of the Mössbauer effect, to outline some aspects of ligand field and molecular orbital theory and to mention the results of some high pressure optical studies which will be helpful in the interpretation of the experiments discussed in this paper.

II. Mössbauer Resonance

There are available excellent expositions of the principles of Mössbauer resonance (8, 9) so that we confine ourselves to a short discussion of those features important in determining the oxidation state of iron. When a free atom decays emitting a gamma ray, it recoils to conserve momentum. As a result of energy conservation, the energy of the emitted gamma ray no longer corresponds exactly to that of

the nuclear transition, and, in addition, the energy spectrum is Doppler broadened. A similar argument applies to the absorption of a gamma ray by a free atom. If the atom is fixed in a crystal where the lowest quantum of vibrational energy (lowest phonon energy) is large compared to the recoil energy, an appreciable fraction of the decays are recoilless. Since the atom vibrates around an equilibrium position, the peak is not Doppler broadened and presents a very nearly monochromatic measure of the energy difference between the ground and the excited states of the nucleus. This difference (the isomer shift) is measurably affected by the electronic wave functions having non-zero amplitude at the nucleus (*s* electrons). Changes in the environment are reflected in the isomer shift through changes in occupation of the 4*s* levels and changes in the degree of shielding of the 3*s* orbitals by the 3*d* electrons. The ferrous ion nominally has six 3*d* electrons and the ferric ion five. Therefore these two states typically exhibit distinctly different isomer shifts and are easily distinguishable in a Mössbauer spectrum.

An electric field gradient at the nucleus interacts with the nuclear quadrupole moment to split the state of spin 3/2 and give two peaks in the spectrum. In the usual "ionic" complex, according to Hund's rule, the 3*d* states are occupied in a manner which gives maximum multiplicity (high spin).

The aspherical distribution of the six electrons of the ferrous ion gives a significant electric field gradient at the nucleus, and thus a large quadrupole splitting. The spherically symmetric ferric state exhibits small quadrupole splitting. This effect also helps to distinguish the two states.

In very covalent compounds with a very strong ligand field, such as potassium ferricyanide the iron ions tend to pair their spins. For these low spin materials, the difference between the Mössbauer spectra of the ferrous and ferric states is less spectacular, but the determination can still be made. In the first order, the relative areas under the two sets of peaks give a reasonable measure of the amounts of ferrous and ferric ion present.

III. Transition Metal Ions in Crystals

The energy states of a 3*d* electron on a free transition metal ion are fivefold degenerate. The separation between the ground and excited states is due to the repulsion among the 3*d* electrons, and can conveniently be expressed in terms of the Racah parameters *A*, *B*, and *C* which we here consider as established empirically. When the ion is placed in a crystal where the field is less than spherically symmetric, the degeneracy is partially removed. We shall phrase this discussion in terms of an octahedral field, although the ideas are not qualitatively different for other symmetries. [Nor is the reduction of Fe(III) to Fe(II) which is the main theme of this paper.] The 3*d* levels split into two states, a triply degenerate level labeled *t_{2g}* and a doubly degenerate level of higher energy labeled *e_g*. The energy difference is commonly called 10 *Dq* or Δ . Optical absorption peaks of moderately low intensity in the near infrared and visible spectrum measure 10 *Dq* as well as the values of *B* and *C* in the crystal. These latter parameters are generally lower in the crystal than in the free ion by an amount that depends on the type of ligand. With pressure, the crystal field parameter 10 *Dq* increases because of the increased field of the ligands, roughly as predicted by

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