where

$$\alpha = \tfrac{2}{3}\pi Z e^2 [R_E^2 - R_G^2] \cong \tfrac{4}{3}\pi Z e^2 [R\Delta R] \qquad (2)$$

which for iron $= 3 \cdot 52 \times 10^{10} \, (R\Delta R)$.

Here the $\psi^2(0)$ are the amplitudes of the wave functions of the source and absorber at the nucleus, and R_G and R_G are the radii of the nucleus in the ground and excited state. From the standpoint of nuclear physics the value of ΔR is of considerable interest; from the viewpoint of solid state structure and electronic behaviour, the changes in $\psi_S^2(0) - \psi_S^2(0)$ with changing conditions are of paramount importance.

The nuclear energy levels can be perturbed by an electric field gradient at the nucleus. The ground state of spin one-half will remain unsplit, but the excited state of spin three-halves will split into two levels as indicated in Fig. 1(c). Under these conditions two transitions are possible, and one sees two peaks. The size of the splitting is then a measure of the electric field asymmetry seen by the nucleus. As will be discussed later, this effect gives important information concerning the local symmetry at the ^{57}Fe site, and the distribution and spin states of the electrons in the partially filled $3d$ shell.

A magnetic field at the iron nucleus also interacts with the nuclear levels of iron, splitting the excited level into four states and the ground level into two. When the selection rules ($\Delta m = 0, \pm 1$) are applied, one sees that a six line spectrum results as is shown in Fig. 1(d). The splittings between pairs of lines measures the magnetic field strength at the nucleus. It is thus possible to study changes in magnetic field with changing temperature, pressure, and chemical environment.

Finally, we have said that the phonon spectrum of the lattice determines the probability of recoilless decay, so that from the measured fraction of recoilless decays (proportional to the area under the Mössbauer peak) one can gain information about the lattice dynamics in the neighbourhood of the iron atom or ion. A number of rather sophisticated treatments have been given (Maradudin, 1966; Housley and Hess, 1966), but in this paper only the Debye approximation will be briefly considered where the recoilless fraction f is related to the characteristic temperature θ_D by:

$$f = \exp\left[-\frac{6E_r}{k\theta_D}\left\{ \tfrac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x\,dx}{e^x - 1} \right\} \right] \qquad (3)$$

where E_r is the recoil energy of the free nucleus due to decay.

Transition metal ions in crystals will be considered in this paper and it is therefore desirable to review qualitatively some of the features of

ligand field and molecular orbital theory. These theories are discussed in detail in various literature (Griffith, 1964; Orgel, 1960; Ballhausen, 1962; Ballhausen and Gray, 1965).

The five $3d$ energy levels on a free transition metal ion are all degenerate. A $3d$ electron on such an ion may be in its ground state or in an excited state. The energy difference between these states can be expressed in terms of the Condon–Shortley parameters or more conveniently in terms of the Racah parameters A, B, C (see Fig. 2). These parameters can be calculated in principle, but are usually evaluated from atomic spectra; they depend on the repulsion among the $3d$ electrons on the ion.
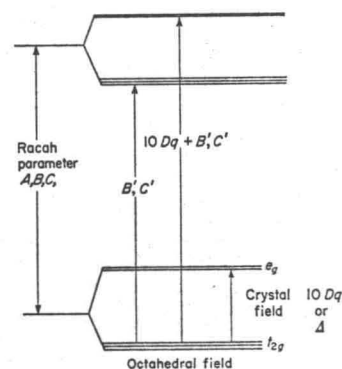

FIG. 2. Crystal field splittings and energies—octahedral symmetry.

If the ion is inserted into a crystal lattice, the surrounding ions provide a field of less than spherical symmetry. In this paper we shall discuss primarily octahedral symmetry wherein six ligands are arranged at the centres of the faces of a cube which has the iron at its centre, but we shall occasionally introduce the tetrahedral arrangement, where the ligands are at the corners of a regular tetrahedron surrounding the iron.

As seen in Fig. 2, these symmetries partially remove the degeneracy of the $3d$ levels. In octahedral symmetry the levels labelled t_{2g} (d_{xy}, d_{xz}, d_{yz}) lie below those labelled e_g ($d_{z^2}, d_{x^2-y^2}$); in tetrahedral symmetry this order is reversed.

The amount of splitting between these groups of levels depends on the intensity of the field supplied by the nearest neighbour ions (the