



Figure 4.  $^{57}\text{Fe}$  spectrum of synthetic magnetite,  $\text{Fe}_3\text{O}_4$ , at room temperature. Note the evidence for at least two different iron sites, with different magnetic fields and isomer shifts.

has shown that when ligands are adequately weak that the compound is "high-spin", the ligands do not contribute importantly to the electric field gradient tensor. Very strong ligands, such as cyanide, overshadow the uncompensated  $3d$  electron contribution.

The electric field gradient contains information concerning structure and bonding. The gradient of a vector is a tensor, which in this case has nine components:

$$\text{e.f.g.} = - \begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{pmatrix}$$

Only two independent components remain after rotation into the principal axes, plus the consideration that the trace vanishes. The axes are then re-named such that the absolute values of the diagonal elements decrease in the order,  $zz$ ,  $yy$ , and  $xx$ . The parameters are then chosen as  $V_{zz}$  and  $\eta$ ,<sup>(9)</sup> which ranges from zero for axial symmetry to a maximum value of one. The quadrupole splitting is proportional to  $V_{zz}(1 + \eta^2/3)^{1/2}$ , so that a measurement of this splitting measures neither parameter. The only generally promising method for the extraction of both parameters is the magnetic perturbation method.<sup>(10)</sup> A large magnetic field is used to split the degeneracies remaining after quadrupole splitting. Even with a powder sample, characteristic distortions are produced and these enable the determination of the parameters of the electric field gradient tensor.<sup>(11)</sup>

The identification and measurement of corrosion products is quite practical. The usual lack of well-formed crystallites, which hinders X-ray evaluation, is less of a burden for Mössbauer analysis. There is an observable effect of stress on the Mössbauer spectrum, too. The stress change "s" electron density at the nucleus, and so shifts the spectrum. Compression shifts the spectrum to lower energy,  $-5.43 \times 10^{-8}$  mm/s/psi.<sup>(12)</sup> A second and smaller effect is that the magnetic splitting varies with stress:

$$\frac{1}{H} \left( \frac{\partial H}{\partial P} \right)_T = -1.15 \times 10^{-8} / \text{psi}$$

These effects are small and require care to measure with any precision. The line width of the  $^{57}\text{Fe}$  Mössbauer line is nominally