Figure 8.   Isomer shift *vs.* pressure diagram for ferrocene.

Figure 9.   Shift of optical absorption peak *vs.* pressure diagram for ferrocene.

The change in the isomer shift with pressure can result from changes in orbital occupation or distortion of the wave function, as discussed above.   There is a negligible change in occupation of the 4s orbital predicted, and only a small net decrease in 3d occupation.[29]   Using the Walker, *et al.*, calibration[15] for the effect of the change in 3d shielding, the predicted change in the isomer shift due to change in orbital occupation is plotted in Figure 8. This accounts for only a portion of the experimental shift.   The SCF–LCAO treatment does not, however, lend itself to a consideration of the orbital distortion effects.   This mechanism would be expected to predict an increase in s electron density (as is discussed elsewhere in this paper) and improve the agreement with experiment.

Zahner and Drickamer[33] have reported the shift in the optical absorption peak near 24,000 cm^{-1} with pressure in ferrocene.   This transition is attributed to the $e_{2g} \rightarrow e^{*}_{2g}$ (A_{2g}) transition by Dahl and Ballhausen, and the effect of pressure on this transition can be obtained from the shift in the e_{2g} and e^{*}_{2g} orbital energies.[29]   This is plotted along with the Zahner and Drickamer data in Figure 9.

Thus, an approximate molecular orbital treatment predicts the proper direction and order of magnitude of the pressure-induced shifts in all parameters of the electronic distribution of ferrocene for which experimental data exist.   The agreement between theory and experiment is in some cases much better than the approximation made would indicate, and is probably in part fortuitous.

α-Fe$_2$O$_3$

The Mössbauer effect allows one to follow pressure-induced changes in both the magnetic configuration and local environment in α-Fe$_2$O$_3$.[34]

There is a large internal magnetic field present in α-Fe$_2$O$_3$ due to the antiferromagnetic spin arrangement and there are, therefore, both magnetic dipolar and electric quadrupolar effects present in the Mössbauer spectra.   The electric field gradient is axially symmetric,
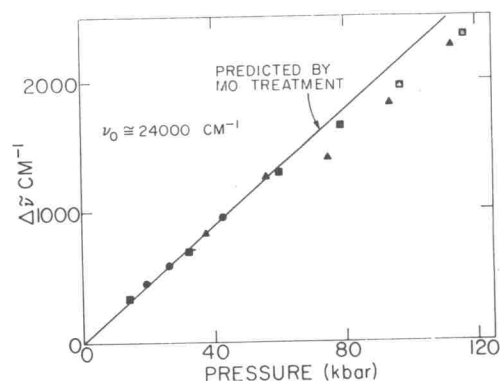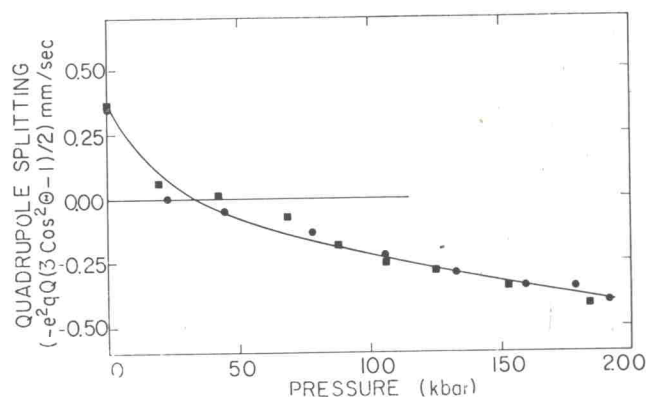

Figure 10.   Quadrupole splitting *vs.* pressure diagram for α-Fe$_2$O$_3$.

and the electric quadrupole interaction is much smaller than the magnetic dipole interaction.   In this special case the shift of the nuclear energy levels by the simultaneous existence of both interactions is[2]

$$\Delta_\epsilon = -gu_n Hm_I + (-1)^{m_I + 1/2}[1/_8 e^2 qQ(3\cos^2\theta - 1)]$$

The second term, which represents the effect of the quadrupole interaction, contains an angular factor, $(3\cos^2\theta - 1)$, where θ is the angle between the direction of the magnetic field and the symmetry axis of the electric field gradient.   This orientation factor becomes particularly important in the case of α-Fe$_2$O$_3$ because there is a change in the antiferromagnetic orientation, and thus a change in the direction of the internal magnetic field, near 260°K[35] at 1 atm.   From the antiferromagnetic Néel temperature, near 950°K, to about 260°K the direction of the internal magnetic field is perpendicular to the (111) or body diagonal of the rhombohedral unit cell, while at the transition temperature the internal magnetic field rotates 90°, and below this temperature it is parallel to the (111) or body diagonal.   As the symmetry axis of the electric-field gradient is along the (111), the angular factor in the above equation, $(3\cos^2\theta - 1)$, changes from -1 to $+2$ in going through the transition.   This produces a marked effect on the quadrupole splitting when the sample is

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cooled through the transition temperature. Ôno and Ito[36] reported a broadening of the Mössbauer peaks as the transition temperature was reached due to the simultaneous existence of both antiferromagnetic phases and the predicted change in sign and doubling in magnitude of the quadrupole splitting.

The effect of pressure on the quadrupole splitting is shown in Figure 10; the splitting passes through zero near 30 kbars, changes sign, and then grows with increasing pressure to about the original magnitude by 200 kbars. Measurements have indicated that the temperature of the Morin transition does increase with pressure,[37,38] and Worlton, et al.,[39] have recently reported that it reaches room temperature near 30 kbars. This agrees well with the point where the quadrupole splitting goes through zero, but if the explanation of the quadrupole splitting data were simply the occurrence of the Morin transition with increasing pressure, the peak broadening reported by Ôno and Ito should be detectable and the observed quadrupole splitting should have grown to nearly twice the original size.

The absence of these phenomena indicates that a reduction has occurred in the electric-field gradient before or during the Morin transition. One can interpret this reduction in the electric-field gradient in terms of local movement of ions within the unit cell using a point dipole model for the α-Fe_2O_3 structure. A calculation of this effect[34] indicates that a movement of the iron ion of only 0.04 Å along the body diagonal of the rhombohedral unit cell is sufficient to account for the abnormalities noted in the Mössbauer spectra.

Worlton and Decker[40] have, however, shown that these Mössbauer results, as well as neutron diffraction studies to 40 kbars, can be more plausibly explained by assuming a continuous change in the angle of the antiferromagnetic axis with respect to the (111) axis of the crystal with increasing pressure.

This relatively brief presentation illustrates the power of high-pressure Mössbauer resonance as a tool for uncovering new generalizations about electronic behavior in solids as well as for investigating the electronic structure of specific systems.

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