increases the energy difference between states increases, one would expect the splitting to increase with pressure and ultimately to "saturate" when only the ground state had significant occupation probability. This indeed happens for many high spin ferrous systems as is illustrated in Fig. 13 for ferrous oxalate. There is a large number
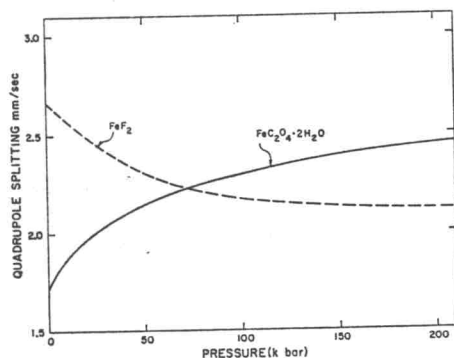

FIG. 13. Quadrupole splitting *versus* pressure—ferrous compounds.

of other examples in the literature (for example Champion *et al.*, 1967a). However, pressure may act to reduce the splitting among the t_{2g} levels and partially to equalize their occupation probability, thus reducing the quadrupole splitting as is shown for FeF_2, also in Fig. 13. For no change in relative distortion, it can be shown that the distorting field should increase as r^{-3} (or this term times a function of angle). Thus, one would expect more examples of increasing than of decreasing quadrupole splitting with increasing pressure for high spin ferrous compounds, and this is what is observed.

For high spin ferric compounds in a strictly cubic environment one would expect no quadrupole splitting. In almost all cases there appears to be some distortion, either trigonal, tetrahedral, or rhombohedral, since most high spin ferric compounds show small but measurable quadrupole splitting (0·3–0·6 mm/sec). Since the ferric quadrupole splitting responds directly to the ligand-metal distance (as r^{-3}), one would expect a large pressure effect. As typical data for K_3FeF_6 and $FeF_3 \cdot 3H_2O$ show (Fig. 14), this is indeed observed. Frequently, the increase in splitting with pressure is more rapid than r^{-3}, indicating that there is a tendency to increase the non-cubic component of the field with pressure.
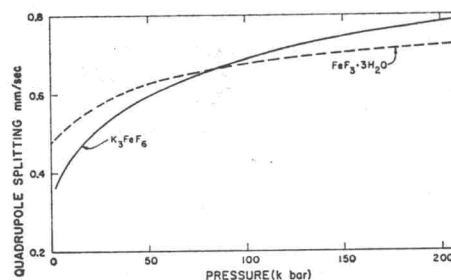
FIG. 14. Quadrupole splitting *versus* pressure—ferric compounds.

No general discussion of low spin compounds is possible, since these involve strong chemical binding and complex orbital occupation, but there are some special cases (not necessarily low spin) which deserve discussion. Firstly, ferrocene, which was mentioned briefly in the section on isomer shifts, is one of the most interesting and most thoroughly studied organometallic compounds. Iron is sandwiched between two C_5H_5 (dicyclopentadiene) rings to form a very stable molecule. The effect of pressure has been studied on both the optical and the Mössbauer spectrum of this compound (Zahner and Drickamer, 1961; Vaughan *et al.*, 1967a).

There have been a number of theoretical treatments of the electronic structure of ferrocene, but that of Dahl and Ballhausen (1961) forms the best basis for discussion of pressure effects. The application is discussed in detail by Vaughan and Drickamer (1967a). By estimating bond compressibilities from bond-force constants one can estimate orbital occupation as a function of pressure. One can show that there is a significant electron transfer from metal to ligand in the $e_{2g}(d \pm 2)$ orbitals with increasing pressure, and a reverse flow in the $e_{1g}(d \pm 1)$ orbitals. Using the treatment of Höfflinger and Voitländer (1963), one can show that this would predict a marked decrease in quadrupole splitting with increasing pressure. As shown in Fig. 15, the experimental and predicted splittings are in essentially quantitative agreement; as shown in Vaughan and Drickamer (1967a), the theory also predicts correctly the behaviour of the low energy optical transition as a function of pressure.

The compound α-Fe_2O_3 is one of the most studied of iron compounds. It has a rhombohedral crystal structure with each iron located in an octahedron of oxygen ions, although the iron is about 0·06 Å above the