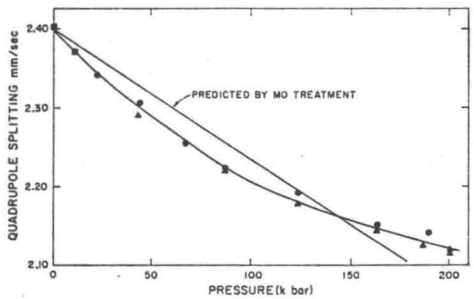

FIG. 15. Quadrupole splitting *versus* pressure—ferrocene.

centre of the octahedron. The material is antiferromagnetic below 950°K; from 950°K to about 260°K the internal magnetic field is perpendicular to the (111) body diagonal of the unit cell. Below this temperature (called the Morin temperature) it reorients through 90° and becomes parallel to the body diagonal. In such a crystal the equation for the quadrupole splitting contains a factor $(3\cos^2\theta - 1)$ which changes from -1 to $+2$ as one goes from a temperature above to one below the transition. This change in quadrupole splitting as a function of temperature has been observed by Ôno and Ito (1962).

The effect of pressure on the quadrupole splitting has been observed by Vaughan and Drickamer (1967b) using Mössbauer resonance; the low pressure region has also been studied by Worlton *et al.* (1967) using neutron diffraction. Figure 16 shows the observed splitting as a function of pressure. A sign change is obtained at about 30 kb. This has

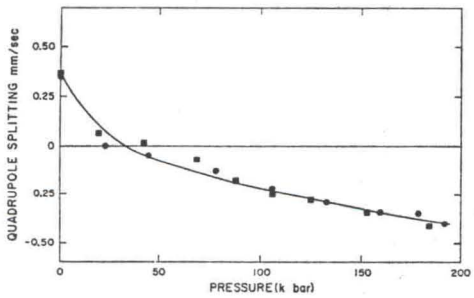

FIG. 16. Quadrupole splitting *versus* pressure—Fe_2O_3.

the qualitative features of a Morin transition, although there are several anomalous points. The transition is smeared out over a considerable range of pressure and in this transition region one does not observe the peak broadening which Ôno and Ito saw in the temperature region where two phases were present. Finally, in the high pressure region the magnitude of the splitting is not twice the atmospheric pressure value. These observations can be explained by a small movement of the iron ion in the oxygen octahedron. It is possible to show that a shift of only 0·04 Å in the position of the iron in a direction towards the centre of symmetry would be enough to cause the quadrupole splitting to go to zero. A slight shift accompanied by the Morin transition would account for the results. Worlton and Decker (1968) have shown that a more plausible argument involves the continuous change of the angle between the antiferromagnetic axis and the (111) axis of the crystal.

C. MAGNETISM

In the introduction it was pointed out that a magnetic field at the iron nucleus removed the degeneracy of both the ground state and the excited state. When one considers the selection rules, one can account for the observed six line spectrum. The changes in splitting of pairs of these lines with pressure measure the change in magnetic field. To date there have been only a limited number of Mössbauer resonance studies of magnetic fields at high pressure. We shall discuss briefly only two cases: ferromagnetism in iron, cobalt and nickel, and antiferromagnetism in cobalt oxide.

The magnetic field in iron as a function of pressure has been studied by Pound *et al.* (1961), Nicol and Jura (1963), Pipkorn *et al.* (1964), and Moyzis and Drickamer (1968a). A plot is shown in Fig. 17; the solid line in the figure represents the results of zero field n.m.r. measurements by Litster and Benedek (1963). It is interesting to see the very close agreement to 60 kb, the limit of the n.m.r. measurements, as this represents a check on both measurements but also yields additional information. The n.m.r. measurements are sensitive only to atoms at the surface of a domain, while Mössbauer resonance reflects the average field of all of the atoms in the domain. Apparently, the effects of pressure are very uniform throughout the domain. It should also be mentioned that the high pressure Mössbauer studies have shown that the high pressure (h.c.p.) phase of iron is paramagnetic at least at room temperature.

The magnetic field in nickel and in cobalt has been studied as a function of pressure, using ^{57}Fe produced by the decay of ^{57}Co as a probe by