

three categories: those connected with Mössbauer resonance; those connected with nonhydrostaticity and shear; and those associated with metastability, which may be inherent in solid state reactions.

The relative amounts of the various states are established from the area measured by fitting the data with Lorentzian or pseudo-Lorentzian peaks. It is necessary to assume equal f number at the two sites. This is always a possible source of error. Self absorption in the sample can change the apparent relative amounts of two states. This may be a source of significant error in the earlier work where the degree of dilution was not closely controlled. If high dilutions are used and care is taken to run a series of similar compounds at the same dilution, this error can be eliminated. A third possible inaccuracy arises from fitting asymmetric peaks as in the hemiporphyrins. Under the best conditions the conversions can be reproduced to $\sim \pm 2\%$.

The pressure is clearly not completely hydrostatic. Under these conditions there is a question of the degree to which conversions are due to shear rather than pressure. There are a number of reasons to believe that pressure per se is the major factor in the great majority of cases:

1. Isobaric runs show a large effect of temperature on conversion at constant pressure. With no change in pressure, change in shear should be minimized.
2. Studies involving a series of related compounds with apparently similar shear properties sometimes gave very different conversions, conversions which correlated well with other electronic differences, as discussed below.
3. For some compounds with distinctive shear products it is possible to make pressure runs where little or no shear product is produced at any pressure.
4. The change in integrated intensity (area) under optical charge transfer peaks with pressure mirrors the conversion obtained by Mössbauer studies. Shear is minimized in the optical apparatus.
5. The conversions were generally in some sense reversible. When the applied pressure is removed there is still considerable strain in the pellet. However, for some systems (hemin, hematin) the spectrum on releasing all the applied pressure was substantially identical with the atmospheric. For most systems the spectrum was returned 60–80% of the way to the original. It is possible to cut the center from the pellet and to relieve the strain by chopping it with a sharp blade, although with such a small amount of material the efficiency of the operation is low. This chopped material exhibits an 80–100% return to the original spectrum for most materials.

Except possibly for one or two systems it is probable that the lack of immediate reversibility is primarily due to stored strain in the crystals because of modified local geometry, especially at high conversions. This raises the question of establishing true equilibrium in solid state systems where electron

transfer or other chemical processes involving local deformation occur. The conversions were not time dependent in the sense that readouts over a period of time at the same pressure gave the same conversion, even over periods of several days. However, if two states of only moderately different energy are separated by a reasonably high potential barrier, the system could stay metastably in the higher energy state for an indefinite period.

We discuss three types of electronic transitions in iron compounds: $\text{Fe(II)}_{\text{HS}} \rightarrow \text{Fe(II)}_{\text{LS}}$; $\text{Fe(II)}_{\text{LS}} \rightarrow \text{Fe(II)}_{\text{HS}}$; and $\text{Fe(III)}_{\text{HS}} \rightarrow \text{Fe(II)}_{\text{HS}}$. In the high spin to low spin transition the increase in ligand field with pressure is sufficient to cause a rearrangement of electrons among the $3d$ orbitals. For the low spin to high spin transition the ground state of the ligand is modified at high pressure by significant thermal occupation of the ligand π^* orbitals by ligand π electrons. This reduces the possibility of metal $d_{\pi} \rightarrow$ ligand π^* back-donation, which decreases the ligand field so that a high spin state becomes more favorable. Ferric iron reduces to ferrous iron because the energy of the metal d_{π} orbitals reduces vis à vis that of the ligand nonbonding orbitals so that thermal electron transfer takes place.

Spin changes.—According to Hund's rule the ground state of a free ion is that of maximum multiplicity. This configuration also obtains in many crystals, since the repulsive energy involved in pairing spins is larger than the splitting among orbitals of different symmetry due to the ligand field. Since, for high spin compounds, the ligand field increases with pressure by as much as 15–20% in 150 kbar, ultimately it may become energetically economical to pair spins. For systems of octahedral symmetry Griffith (69) has shown that the intermediate spin configuration is higher in energy than either the high or low spin states. For systems of lower symmetry an intermediate spin ground state is possible, as we shall discuss later.

An example of the high spin to low spin transition is the behavior of Fe(II) as a dilute substitutional impurity in MnS_2 (70). MnS_2 has a cubic structure isomorphous to FeS_2 . Iron in FeS_2 is low spin at all pressures. Since the lattice parameter of MnS_2 is significantly ($\sim 10\%$) larger than that of FeS_2 it is not surprising that the Fe impurity is high spin even though there is probably local relaxation near the iron. At a pressure of about 40 kbar a measurable amount of low spin appears. By 130 kbar the iron is completely converted to low spin. The process is reversible in the sense discussed above.

The complexes of ferrous iron with 1,10-phenanthroline form a widely studied series of compounds (71–73). There are two types of octahedral or nearly octahedral complexes. The bis complexes involve two phenanthrolines each coordinated to the iron through the nitrogens, plus two other ligands to fill out the six positions. The tris complexes have the iron coordinated to three phenanthroline molecules with the anions outside the coordination sphere. The bis complexes usually have ligand fields of 10–13 kK, just below the cross-over value of ~ 14 kK, and are high spin. The tris complexes have ligand fields in the range 16–19 kK and are low spin. These complexes form an