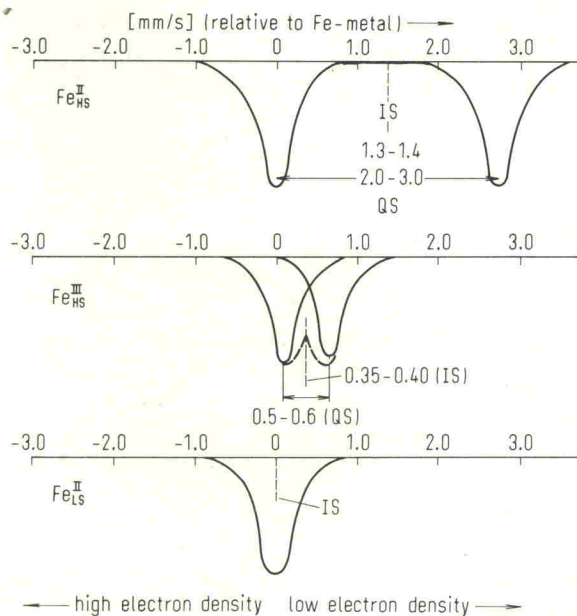




[A 978.6]

Fig. 6. Characteristic Mössbauer spectra.

has a smaller isomer shift, and, since the field of the 3d shell is spherical, only a small quadrupole splitting. The low-spin ferrous ion has a spherical electric field and thus a small quadrupole splitting. The low value of the isomer shift reflects the delocalization of the 3d electrons by "back donation" as discussed in Section 2.1, and the resultant high electron density at the nucleus. Our discussion will be largely limited to three transitions: 1. $\text{Fe}_{\text{HS}}^{\text{II}} \rightarrow \text{Fe}_{\text{LS}}^{\text{II}}$ (high spin) $\rightarrow$ $\text{Fe}_{\text{LS}}^{\text{II}}$ (low spin); 2. $\text{Fe}_{\text{LS}}^{\text{II}} \rightarrow \text{Fe}_{\text{HS}}^{\text{II}}$; 3. $\text{Fe}_{\text{HS}}^{\text{III}} \rightarrow \text{Fe}_{\text{LS}}^{\text{III}}$.

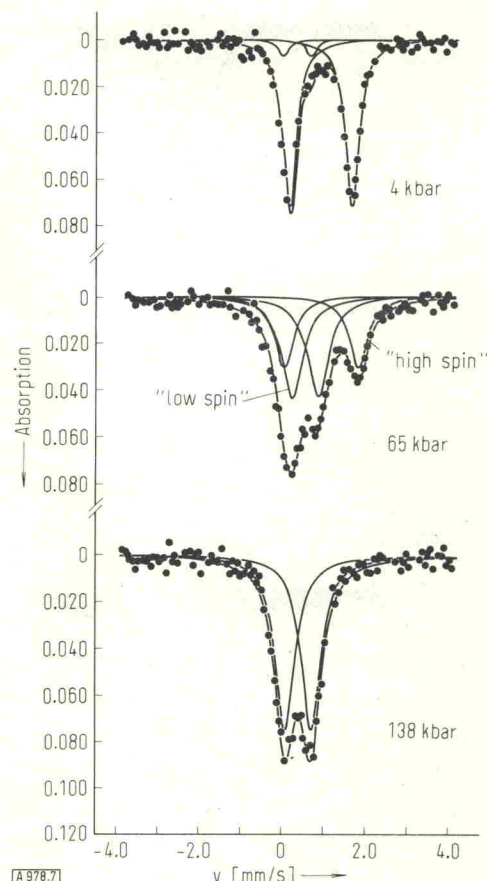
3.1.1. Spin Changes

We consider first the high-spin to low-spin transition. Since, as shown in Section 2.1, the ligand field increases with pressure, one might expect that at some pressure, Δ could become larger than the spin-pairing energy. One example is Fe(II) as a dilute substitutional impurity in MnS_2 . In the isomorphous FeS_2 (pyrites), iron is low spin at all pressures. Since the lattice parameter of MnS_2 is distinctly larger than that of FeS_2 it is not surprising that iron in MnS_2 is high spin. One can think of the Fe(II) as being under a large negative pressure in MnS_2 relative to its situation in FeS_2 . Figure 7 shows the Mössbauer spectra as a function of pressure. At low pressure (up to 40 kbars) one sees only the $\text{Fe}_{\text{HS}}^{\text{II}}$ spectra. At 65 kbars the iron is over 50% converted to low spin. At 138 kbars the conversion is complete. The process is reversible with some hysteresis. This is, then, a transition from a paramagnetic to a diamagnetic ground state.

Let us now consider the transition from $\text{Fe}_{\text{LS}}^{\text{II}}$ to $\text{Fe}_{\text{HS}}^{\text{II}}$ with increasing pressure. We first look at the evidence for this somewhat surprising event. We consider complexes of iron with 1,10-phenanthroline. In tris complexes each of three phenanthrolines complexes through two nitrogens so that the Fe(II) is in an approximately octahedral field of six nitrogens. Because of back donation (see Section 2.1) to the ligands Δ is 2.0–2.5 eV and the iron is low spin. Figure 8 shows Mössbauer spectra as a function of pressure. At low pressure one observes only low spin iron. Above ~ 40 kbars a measurable amount of $\text{Fe}_{\text{HS}}^{\text{II}}$ appears; and at 140

kbars there is about 30% conversion. Complexes involving substituted phenanthrolines may exhibit up to 60% conversion. The process is reversible, with hysteresis.

Complexes also form with two molecules of phenanthroline and two other ligands. These bis complexes are usually high spin at one atmosphere. At a modest pressure they convert partially or even completely to low spin, but above about 40–50 kbars the amount of high spin again increases^[9, 29, 30].



[A 978.7]

Fig. 7. Mössbauer spectra of Fe^{II} in MnS_2 at 4 kbar, 65 kbar, and 138 kbar.

The LS $\rightarrow$ HS transition seems paradoxical at first on both thermodynamic and electronic grounds. One must remember that it is the volume of the system as a whole which must decrease with increasing conversion at constant T and p . This volume decrease may involve changes in intermolecular forces as well as bond lengths. It is not, of course, necessary that any particular bond must shorten.

The back donation which provides the large ligand field depends on the availability of the ligand π^* orbitals. As already shown (Fig. 3), the π - π^* energy difference decreases rapidly with pressure. If there is significant mixing of the π and π^* orbitals they will become less available for back donation from the iron. In Table 1 a calculation for phenanthroline is given using Eq. (1). At one atmosphere the π orbital is stable by about 1.35 eV. Above 50 kbars the energy difference is such that there could be considerable thermal π - π^* transfer and hybridization inhibiting back donation. The calculation is very crude, but it illustrates that the hypothesis is feasible. This could be called an induced electronic transition, since a transformation on the ligand changes the bonding to the iron and thus its spin state.

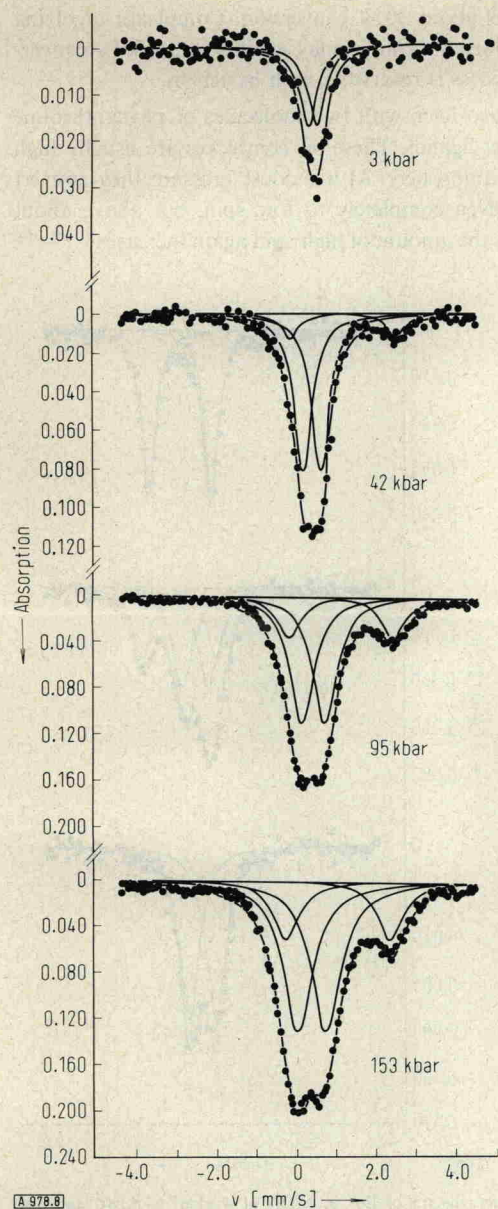


Fig. 8. Mössbauer spectra of Fe^{II} in $\text{Fe}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ at various pressures.

Table 1. Comparison of the energies associated with thermal and optical excitation: $\pi \rightarrow \pi^*$ transition in 1,10-phenanthroline.

p (kbar)	$h\nu_{\text{max}}$ [eV]	$\delta E_{1/2}$ [eV]	E_{th} [eV]
0	4.6	0.95	+1.35
50	4.45	1.05	+0.45
100	4.30	1.14	-0.40
150	4.20	1.20	-0.98

One would expect that, at any pressure, the amount of low spin present for a series of related compounds would depend on the size of the ligand field. Δ is difficult to measure directly for these complexes, but it has been shown^[31] that there is a good correlation between the $\text{Fe}^{\text{II}}_{\text{LS}}$ isomer shift and Δ ; the smaller the isomer shift (*i.e.* the larger the back donation) the larger is Δ . Figure 9 shows the relative amounts of $\text{Fe}^{\text{II}}_{\text{HS}}$ and $\text{Fe}^{\text{II}}_{\text{LS}}$ at 100 kbars for a series of substituted phenanthrolines. It can be seen that the correlation with the isomer shift of $\text{Fe}^{\text{II}}_{\text{LS}}$ is, indeed, very good.

An increase in spin multiplicity with pressure has also been observed in other iron compounds. The ferrocyanides are

low spin compounds with relatively large ligand fields. At room temperature they remain low spin to 200 kbars, at least. However, at 100 °C and 150 kbars $\text{Cu}_2\text{Fe}(\text{CN})_6$ exhibits

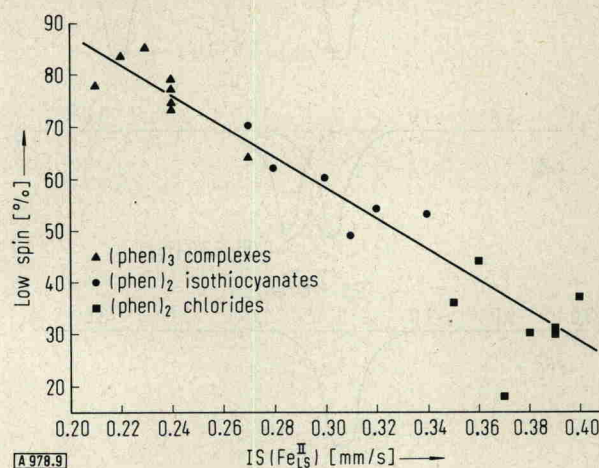


Fig. 9. Percent low spin Fe^{II} vs $\text{Fe}^{\text{II}}_{\text{LS}}$ isomer shift in phenanthroline complexes.

65% high spin ferrous ion and $\text{Ni}_2\text{Fe}(\text{CN})_6 \sim 18\text{--}20\%$. $\text{Zn}_2\text{Fe}(\text{CN})_6$, which is isomorphous, shows no conversion. Neither do the sodium nor potassium salts with slightly different structure. At 150 °C and 150 kbars the zinc salt shows $\sim 25\%$ conversion and the sodium and potassium salts only small traces thereof. Apparently cation electrons also interact with the ligand orbitals in these compounds.

One also observes an increase in spin state with pressure in some substituted ferrous phthalocyanines^[9, 32]. This planar molecule involves four pyrrole rings bridged by nitrogens with the iron in a site of D_{4h} symmetry. The iron is in an intermediate spin state. When pyridines or picolines are coordinated axially to the iron a low spin $\text{Fe}(\text{II})$ ($\text{S}=\text{O}$) state results, primarily because of back donation to the nitrogens on the axial ligands. At high pressure a partial conversion of low spin to intermediate spin iron is observed as the back donation is reduced.

3.1.2. Reduction of $\text{Fe}(\text{III})$ and $\text{Cu}(\text{II})$

The third electronic transition of interest here is the reduction of $\text{Fe}^{\text{III}}_{\text{HS}}$ to $\text{Fe}^{\text{II}}_{\text{HS}}$ with pressure. Recent studies on $\text{Cu}(\text{II})$ are also discussed briefly. Once again Mössbauer spectra are presented as primary evidence. In Figure 10 we show an $\text{Fe}(\text{III})$ spectrum at low pressure, the continuing increase in the amount of $\text{Fe}^{\text{II}}_{\text{HS}}$ with pressure, and the reversibility (with hysteresis) upon release of pressure. The reduction takes place by transfer of a ligand electron (probably from a nonbonding orbital) to the metal 3d orbital. The electron and the hole on the ligand probably remain closely associated. There should be a definite relationship between the amount of reduction (*i.e.* the fraction of ferric sites still present) and the area under a ligand-metal charge transfer peak in the optical spectrum. Figure 11 exhibits such a relationship for two hydroxamate-iron complexes (AHA=acetohydroxamic acid, SHA=salicylhydroxamic acid) and a protein (FA=ferrichrome A) which complexes to $\text{Fe}(\text{III})$ through three hydroxamate groups. The solid line shows the conversion obtained from Mössbauer measurements while the points represent relative area under the optical absorption peak. The agreement is good.