have been reported by Drickamer and Frank [27]. In these cases Mössbauer or absorption spectroscopy was used as the diagnostic tool to observe the changes. For changes in solutions, see Sinn [26].

Recently, several systems have been examined using vibrational spectroscopy as the diagnostic tool to identify spin-state equilibria in the solid state. In these examples the far IR region, and in particular, the metal—ligand vibration was followed with pressure to determine a change from a high-spin to a low-spin state. The high-spin, metal—ligand vibration occurs at lower energy than the low-spin, metal—ligand vibration. In some instances low temperatures are used with pressure to facilitate the conversion.

The complex $NiBr_2(Bz\phi_2P)_2$ was converted at 12 kbar from a high-spin, distorted tetrahedral molecule to a low-spin, square-planar configuration [213]. In this complex a structural change as well as a spin-state conversion occurred. $Co(nnp)(NCS)_2$, where nnp = $Et_2N-(CH_2)_2-NH-(CH_2)_2P\phi_2$, was converted at 10 kbar and 150 K from the high-spin to low-spin state [214]. The relationship of the equilibria with temperature and pressure is shown below.

10 kb- 1 atm-	L.S. L.S. L.S. H.S		+ H.S.	H.S.	
	100)	R.T.	353	TK

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The Fe(phen)₂X₂ and Fe(bipy)₂X₂ complexes, where phen = 1,10-phenanthroline, bipy = 2,2'-bipyridine and X = Cl⁻, Br⁻, N₃⁻, NCO⁻, OAc⁻, HCOO⁻ exist in high-spin states [215]. The complexes Fe(phen)₂(NCS)₂, Fe(phen)₂-(NCSe)₂ and Fe(bipy)₂(NCS)₂ were studied at high pressures and/or low temperature [215]. Complete conversion with pressure to low spin did not occur. However, the mixtures of high-spin and low-spin forms maintained at high pressures, could be converted to the low-spin state if the sample was cooled to 100 K. The high-spin state can be converted to the low-spin state directly with cooling to 100 K. The results parallel those obtained by Fisher and Drickamer [216] using Mössbauer techniques for Fe(phen)₂(NCS)₂ and Fe-(phen)₂(NCSe)₂. High-spin—low-spin crossovers with pressure have also been observed for tri(N-ethyl-N-phenyldithiocarbamato)iron(III) [217,218], and represent the first pressure conversions of Fe(III) to low-spin. These results may have some consequences in problems relating to the earth's mantle.

The results of the low temperature conversion to low spin may be explained in terms of a strengthening of the Fe—N (phen or bipy) and Fe—N (NCS and NCSe) bonds due to back-donation of the t_{2g} electrons of the metal to the π^* orbitals of the organic ligand and NCSe. This mechanism may also be present at the outset of pressure applications, but the back-donation of the metal is reduced with increasing pressure by the accessibility of the π electrons from the ligand to the ligand π^* orbitals [27]. Table 22 summarizes high-pressure spin-state conversions.

pin	interconversions	[215-218
pm	merconversions	1410 410

the second s					
	Central atom C.N.	High spin (No. of unpaired e's)		Conversion pressure (kbar)	Ex
	5	3	High Spin \rightarrow Low Spin	21	NC
)	6	2	High Spin \rightarrow Low Spin	18	Ske
⁶)	6	2	High Spin \rightarrow Low Spin	8-10	Ske
)	6	2	High Spin \rightarrow Low Spin	15	Ske
	5	3	High Spin \rightarrow Low Spin	4	Ske
	4	2	High Spin \rightarrow Low Spin ^a	12	Ske
	6	5	High Spin \rightarrow Low Spin	35	Ske
			The second se	the second s	

on also occurs. = phenanthroline; bipy = bipyridyl; nnp = $Et_2N-(CH_2)_2-N-(CH_2)_2P\phi_2$; Bz = benzy ine) = , HO-(N); EPDTC = N-ethyl-N-phenyldithiocarbamato. 6

