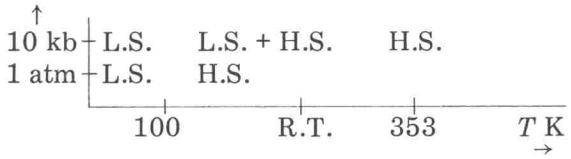
have been reported by Drickamer and Frank [27]. In these cases Mössbauer or absorption spectroscopy was used as the diagnostic tool to observe the changes. For changes in solutions, see Sinn [26].

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.



The $Fe(phen)_2X_2$ and $Fe(bipy)_2X_2$ complexes, where phen = 1,10-phenanthroline, bipy = 2,2′-bipyridine and X = Cl^-, Br^-, N_3^-, 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.

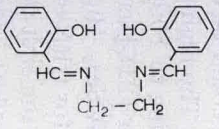
The results of the low temperature conversion to low spin may be explained in terms of a strengthening of the Fe—N (phen or bipy) and Fe—N (NCS and NCSe) bonds due to back-donation of the t_{2g} electrons of the metal to the π^* orbitals of the organic ligand and NCSe. This mechanism may also be present 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]

	Central atom C.N.	High spin (No. of unpaired e's)		Conversion pressure (kbar)	Exp
	5	3	High Spin → Low Spin	21	NO
)	6	2	High Spin → Low Spin	18	Ske
^{6})	6	2	High Spin → Low Spin	8—10	Ske
)	6	2	High Spin → Low Spin	15	Ske
	5	3	High Spin → Low Spin	4	Ske
	4	2	High Spin → Low Spin [a]	12	Ske
	6	5	High Spin → Low Spin	35	Ske

on also occurs.

= phenanthroline; bipy = bipyridyl; nnp = $Et_2N{-}(CH_2)_2{-}\overset{H}{\underset{|}{N}}{-}(CH_2)_2P\phi_2$; Bz = benzy

ine) = 

; EPDTC = N-ethyl-N-phenyldithiocarbamato.