

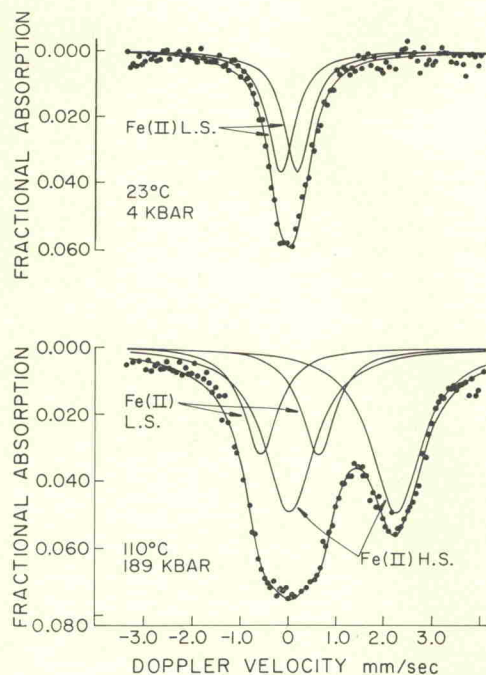


FIG. 3. Mössbauer spectra of copper ferrocyanide.

a maximum in the isomer shift at about 30 kbar. The significance of these differences will be clear a little later. Table II shows the change of quadrupole splitting with pressure. [With the techniques available to us in 1967 it was not possible to resolve the quadrupole splitting for $K_4Fe(CN)_6$.]

At high pressure and at temperatures above 100°C an unexpected phenomenon occurs. A new pair of peaks

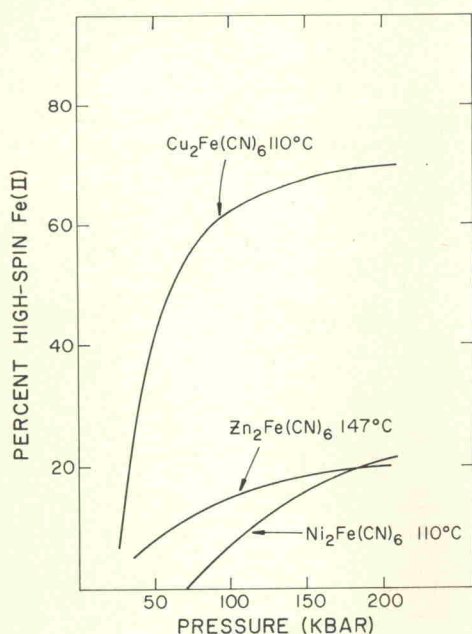


FIG. 4. Conversion to high-spin Fe(II) vs pressure—ferrocyanides.

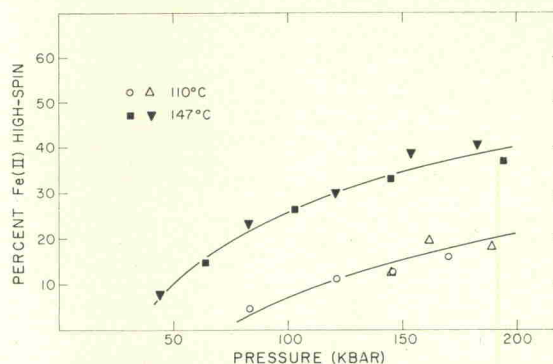


FIG. 5. Conversion to high-spin Fe(I) vs pressure at 110°C and 147°C—nickel ferrocyanide.

appears in the spectrum and increases in amount with pressure at the expense of the original spectrum. Figure 3 shows typical spectra for $Cu_2Fe(CN)_6$. The new peaks have a center of gravity of 1.00–1.20 mm/sec and a quadrupole splitting of ~ 2.0 mm/sec. The isomer shift decreases with increasing pressure (about 0.1 mm/sec in 100 kilobars). The quadrupole splittings are tabulated in Table II. In Fig. 4 conversions are shown as a function of pressure for the copper and nickel salts at 110°C and the zinc salt at 147°C. There was only a small conversion for zinc at 110°C; on the other hand, the copper salt showed measurable conversion at 23°C at the highest pressures. Figure 5 demonstrates the effect of temperature on conversion for $Ni_2Fe(CN)_6$. (All conversions were obtained from the areas under Lorentzian peaks fit to the data. They are nominal in the sense that there may be a difference in f number at the different sites.) The process is reversible, but quite

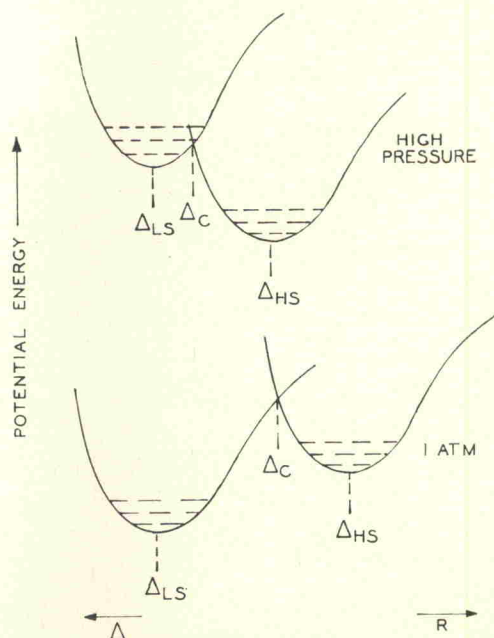


FIG. 6. Schematic potential-energy diagram.

TABLE III. Isomer shifts (I.S.) for ferricyanides and prussian blue at 4 kbar and 23°C (relative to Fe metal).

Compound	I.S. (mm/sec)	
$\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$	-0.076	(+0.28 at 147°C and 11 kbar)
$\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$	-0.112	
$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	-0.074	
$\text{Na}_3\text{Fe}(\text{CN})_6$	-0.061	
$\text{K}_3\text{Fe}(\text{CN})_6$	-0.093	
$\text{Fe}_4[^{57}\text{Fe}(\text{CN})_6]_3$	-0.169	
$^{57}\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	+0.384	

sluggishly so. When the sample was powdered by grinding, it returned completely to the low-spin Fe(II) state.

There appear to be two possible explanations for the observed phenomenon. Either low-spin Fe(I) or high-spin Fe(II) is being formed. It is known that $(\text{CN})^-$ is a ligand with some tendency to stabilize low oxidation states, and one would expect an increase in isomer shift due to increased shielding of the 3s electrons, as well as a large quadrupole splitting with Fe(I). On the other hand, it is difficult to see how there would be energy available to transfer an electron from the ligands to the e_g levels, and the t_{2g} levels are full in low-spin Fe(II).

There is a considerable body of evidence that indicates the formation of high-spin Fe(II). The isomer shift is a little low, but not unlike some high-spin ferrous-phenanthroline complexes. The quadrupole splitting is in the usual range except possibly for zinc. As indicated above, there is considerable hysteresis on release of pressure. Using an apparatus developed to study organic reactions at high pressure, we quenched a sample from 200 kbar and 110°C, obtaining 5.1 mg of product containing 18% of the "high-spin" material according to its Mössbauer spectrum.

A very sensitive Faraday balance indicated that this material had a susceptibility 1.75 times that of unpressed material. This would indicate 15%-21% of high-spin Fe(II) depending whether one calculates on a "spin-only" basis or ratios between susceptibilities of known high- and low-spin ferrous materials. It was possible to get reasonable ir, visible, and uv spectra in a KBr pellet. The cyanide stretching frequency is at

TABLE IV. Quadrupole splittings high spin Fe(II) formed under pressure from ferricyanides.

Original compound	Pressure (kbar)				
	50	100	150	200	
$\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$	2.14	2.22	2.28	2.31	(110°C)
$\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$	...	2.32	2.32	2.34	(110°C)
$\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	1.60	1.43	1.30	1.21	(110°C)
$\text{K}_3\text{Fe}(\text{CN})_6$	1.80	1.88	1.84	1.81	(110°C)
$\text{Na}_3\text{Fe}(\text{CN})_6$	2.50	2.70	2.85	2.95	(110°C)

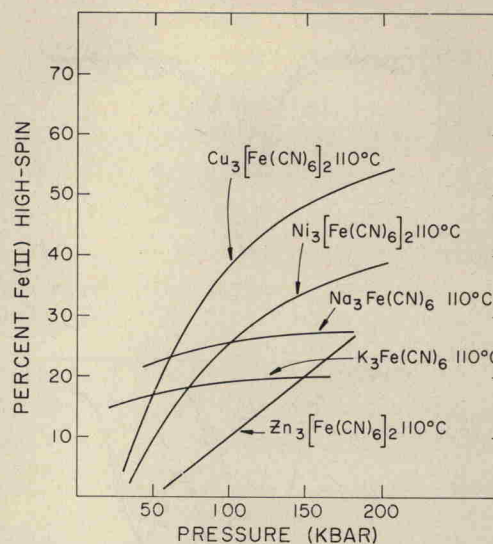


FIG. 7. Conversion of ferrocyanides made by reducing ferricyanides to high-spin Fe(II) vs pressure.

2090 cm^{-1} in ferrocyanides, which is considerably lower in energy than the free-cyanide value. This material exhibited a shoulder on the high-energy side at 2180 cm^{-1} . This would be consistent with reduced Fe-C binding. The Fe-C stretching frequency at 494 cm^{-1} had lost intensity and a new peak appeared at 467 cm^{-1} , again consistent with reduced Fe-C binding. A weak peak appeared in the near-ir at 11 800 cm^{-1} . This is a reasonable position for the $^5T_{2g} \rightarrow ^5E_g$ transition measuring the crystal-field parameter Δ in a high-spin Fe(II) compound. The uv spectra were of poor quality but it

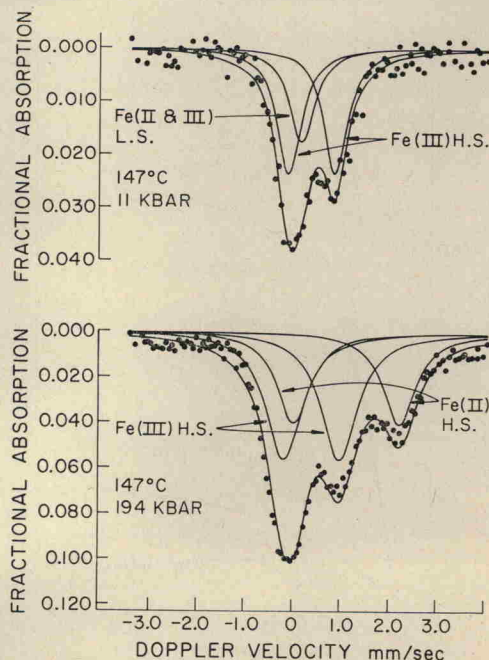


FIG. 8. Mössbauer spectra of copper ferricyanide.