

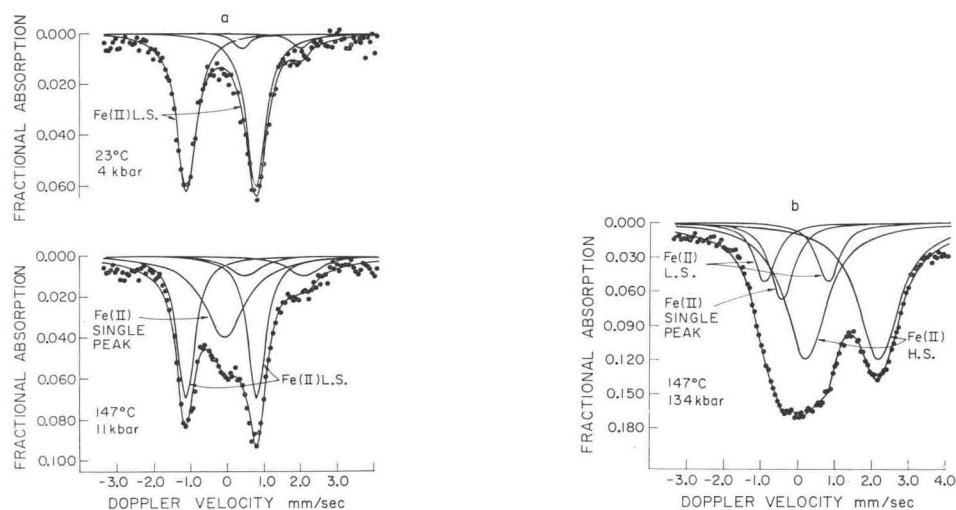


FIG. 13. (a) Spectra of $\text{Fe}^{57}\text{Fe}(\text{CN})_5\text{NO}$. (b) Spectra of $\text{Fe}^{57}\text{Fe}(\text{CN})_5\text{NO}$ continued.

$^{57}\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}]$ only a moderate decrease in isomer shift and increase of quadrupole splitting typical for ionic ferrous ions. This is further evidence that the change of spin state of ferrocyanides is not due to isomerization.

As indicated earlier, the low-spin ferrous ion coordinated to the carbon of the cyanide and to the nitrogen of the NO, exhibits a very low-isomer shift, indicating that the delocalization of the 3d electrons to the NO is even stronger than that to the cyanides. There is a large quadrupole splitting because of the distortion from octahedral symmetry. As the spectra in Fig. 13a and b show, the $[\text{Fe}^{57}\text{Fe}(\text{CN})_5\text{NO}]^{-2}$ ion exhibits two phenomena as a function of pressure. At modest pressure and high temperature, a single peak appears with essentially the same isomer shift as the quadrupole split low-spin pair. It grows with

pressure at first, then decreases in intensity along with the original pair as the conversion to high spin $\text{Fe}(\text{II})$ begins to dominate. Figure 14 exhibits the amount of the single peak low-spin material as a function of temperature and pressure for $\text{Fe}^{57}\text{Fe}(\text{CN})_5\text{NO}$. Figure 15 shows the conversion to high spin $\text{Fe}(\text{II})$ for the same compound. We were able to quench in partially converted samples and obtain its spectra on them. In Fig. 16 are represented three spectra in the region of the CN^- and NO stretching vibrations; one at atmospheric pressure, one from 35 kbar and 147°C, where there is a maximum amount of the single low-spin peak, and one from 160 kbar and 110°C where the main conversion is to high-spin $\text{Fe}(\text{II})$. At one atmosphere, both peaks are at lower energy than that of the corresponding free ion, as the intraionic bonding is weakened by the strong bond to the metal. At 147°C and 35 kbar, a peak grows on the high energy

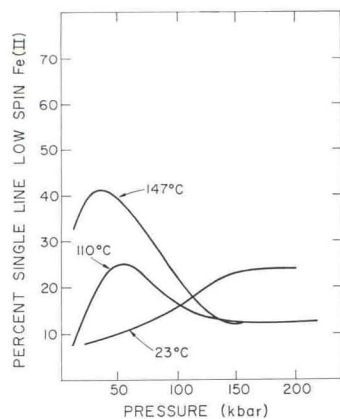


FIG. 14. Percent single peak $\text{Fe}(\text{II})$ low spin versus pressure— $\text{Fe}^{57}\text{Fe}(\text{CN})_5\text{NO}$.

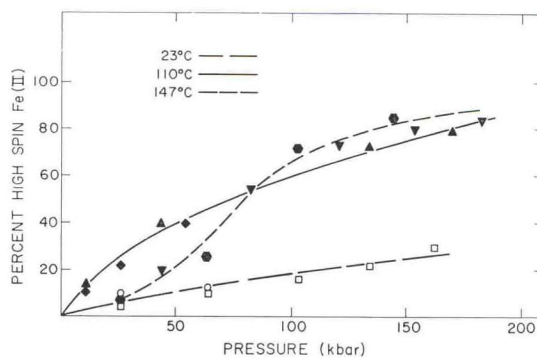


FIG. 15. Percent high-spin $\text{Fe}(\text{II})$ versus pressure— $\text{Fe}^{57}\text{Fe}(\text{CN})_5\text{NO}$.

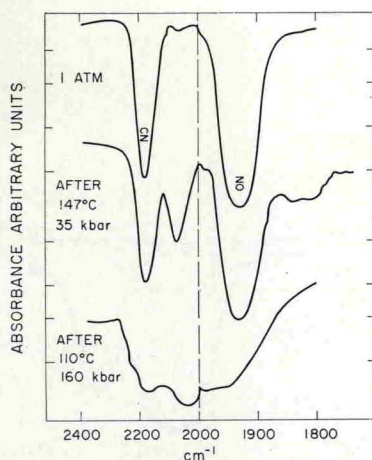


FIG. 16. IR Spectrum of $\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}]$.

side of the NO stretch, near the free ion value. This corresponds to those sites where the metal to NO bond is weakened, giving a more symmetric spectrum and a single Mössbauer peak. At high pressure, the new NO stretching peak is very strong, and a shoulder appears on the high energy side of the CN stretching peak. This situation corresponds to reduced metal to ligand bonding, giving rise to the high spin Fe(II).

In summary, with increasing pressure, there is a relative lowering of the energy of the iron 3d orbitals vis-à-vis the ligand orbitals. This has important effects on both the oxidation state and

spin state of iron. An understanding of this behavior has significant consequences in the chemistry and physics of iron, and possibly also for understanding its biological activity and geophysical behavior.

References

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