By accepting a value of 17.1 for pK_{a_2} of H_2S the ionization ratio $[S^{2-}]/[SH^-]$ as determined in the present work may be used to derive additional values for H_-. As shown in Figure 7 they are within ±0.1 unit of those given by Yagil and thus support the approximately linear dependence of H_- on $[OH^-]$ for $[OH^-] > 8\ M$. This result is surprising considering the large difference in the "indicators" used and may only be a chance coincidence. However, it could suggest that the H_- acidity function, after all,[19] is largely independent of the class of indicators used and thus is generally applicable to highly concentrated alkali hydroxide solutions.

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The Effect of Pressure on the Spin State of Iron(II) in Manganese(IV) Sulfide[1a]

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Mössbauer resonance studies as a function of pressure on iron as a dilute substitutional impurity in MnS_2 have revealed a high-spin to low-spin transition which initiates near 40 kbars and is complete by about 120 kbars. MnS_2 has the cubic structure of pyrites (FeS_2). The iron in FeS_2 is low spin at all pressures. Since FeS_2 has a smaller lattice parameter than MnS_2, the difference in spin states at 1 atm and the transition from iron in MnS_2 are qualitatively consistent with theory.

The effect of pressure to 165 kbars has been measured on the spin state of ^{57}Fe, presumably as a substitutional impurity in MnS_2, using Mössbauer resonance. The high-pressure Mössbauer apparatus has been described elsewhere.[2] The pressures are accurate at least to ±10%. It took 6–36 hr to accumulate sufficient counts at each pressure. Consecutive spectra taken at a given pressure showed no differences, so that no time-dependent phenomenon is involved. The MnS_2 was prepared by a hydrothermal method.[3] The iron, enriched to 90% in ^{57}Fe, was incorporated by adding the appropriate amount of ^{57}Fe solution to the manganese sulfate solution before precipitation by the polysulfide. MnS_2 has the pyrite structure with a lattice constant $a = 6.102$ Å.[4] It becomes antiferromagnetic at 47.93°K.[5] Most of the data were obtained on a sample containing 2% ^{57}Fe. (Three different high-pressure runs were made at this concentration.) One high-pressure run was also made on a sample containing 0.5% ^{57}Fe, and an atmospheric pressure spectrum was obtained on a sample containing traces of ^{57}Co. The atmospheric pressure values of the isomer shift and quadrupole splitting appear in Table I. At 1 atm the samples were predominantly high spin. The samples containing 2% ^{57}Fe exhibited about 10% low spin, as indicated by the relative areas under the curves obtained by fitting the data with Lorentzian peaks. The samples with lower concentrations of iron showed slightly less low spin (5–6% for the sample containing traces of ^{57}Co). It should be noted that the isomer shift for the high-spin iron is somewhat lower than that for the normal ferrous iron (~1.3 mm sec) but comparable to that for ferrous iron in FeS[5] and similar compounds.

The primary effect of pressure was the conversion of Fe(II) from the high-spin to the low-spin state. A change in the amount of high spin first becomes measurable at about 40 kbars, and by 120–130 kbars the conversion is complete. Typical spectra appear in Figure 1. Figure 2 shows conversion as a function of pressure. While it was more difficult to get a quantitative fit for the 0.5% sample under pressure, the pressure-induced conversion clearly initiates near 35–40 kbars and was again complete at 120–130 kbars; *i.e.*, the behavior under pressure was essentially identical with that of the 2% sample. The spin conversion was quite reversible with only a modest hysteresis, almost certainly due to residual strain in the sample. There was a modest decrease in isomer shift with increasing pressure for both spin states and an increase in quadrupole splitting, especially for the high-spin component. These effects are similar to our observations on a wide variety of compounds[6] and will not be discussed here.

In an earlier paper[7] Mössbauer resonance studies at high pressure were made on FeS_2 in the pyrite structure. The 1-atm lattice parameter is 5.504 Å, and this material is low spin at 1 atm. The initial isomer shift (relative to iron metal) and the quadrupole splitting are 0.30 and 0.61 mm/sec, respectively, and these values are reasonably close to the 1-atm values for the low-spin component in MnS_2, especially when one considers the problems in accurately characterizing a 10%

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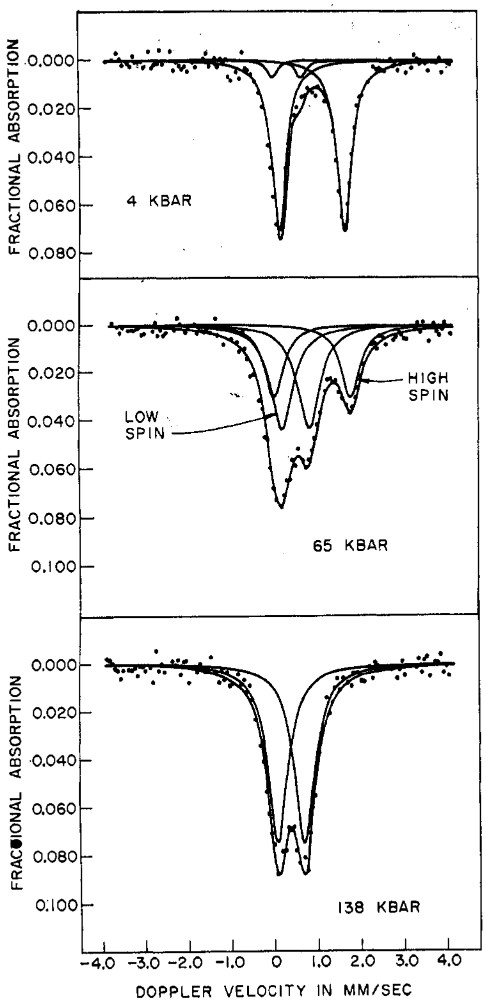

Figure 1.—Fractional absorption *vs.* Doppler velocity for MnS_2-(^{57}Fe).

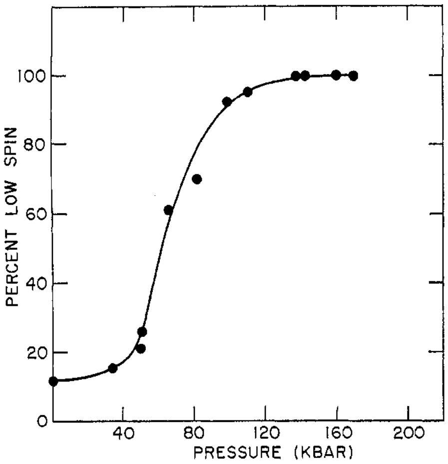

Figure 2.—Conversion to low spin for MnS_2(^{57}Fe).

low-spin concentration. The fact that ^{57}Fe in high dilution in MnS_2 is almost entirely high spin is associated with the larger lattice parameter in the MnS_2 lattice and the correspondingly smaller crystal field at the Fe site.

The high-spin state is the normal state of the ferrous ion in ionic compounds according to Hund's rule. As the crystal field increases, the balance between kinetic and potential energy may favor a high-spin to low-spin transformation. A simple point-charge model would predict that the crystal field would vary as R^{-5}, where R is the ion–ligand distance. Although the point-charge model is quite inadequate to calculate quantitatively the crystal field even in ionic compounds, the R^{-5} rule describes the volume dependence of the crystal field remarkably well for NiO[8] and for impurity ions in Al_2O_3.[9] The situation in MnS_2 is complicated by the probability of covalent bonding and a somewhat complex local geometry, so that even semiquantitative calculations are not feasible, but the ligand field certainly increases with compression.

A few data were also obtained for iron as a dilute impurity in $MnSe_2$ and $MnTe_2$. The $MnSe_2$ was prepared by the same technique as that used for MnS_2. $MnTe_2$ was prepared by direct synthesis from the elements.[10] At 1 atm the iron is predominantly in the high-spin state as it was in MnS_2. The atmospheric values for the Mössbauer parameters appear in Table I.

Table I

Isomer Shift and Quadrupole Splitting at 1 Atm for ^{57}Fe in MnS_2–$MnSe_2$–$MnTe_2$

Compd[a]	Quadrupole splitting[b] High spin	Low spin	Isomer shift[c] High spin	Low spin
MnS_2	1.50	0.60	0.84	0.35
$MnSe_2$	1.51	0.54	0.81	0.48
$MnTe_2$	1.35	0.48	0.77	0.51

[a] Containing 2% ^{57}Fe. [b] In mm/sec. [c] In mm/sec relative to metallic iron.

In both cases the amount of low spin increased with pressure starting at 35–40 kbars. The conversion was complete by 130 kbars. It was difficult to obtain quantitative results because of scattering by the heavy atoms. The selenide and telluride have larger lattice parameters than does the sulfide, but the space available for the iron may not be larger. Furthermore, there may be local relaxation near the iron, so that the local lattice parameters may differ from the bulk values.

Strens[11] has published a note giving optical evidence for a high-pressure spin transformation in the mineral gillespite ($BaFe^{II}Si_4O_{10}$). However, the present work represents the first really clear-cut measurement of a high- to low-spin conversion as a function of pressure.

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