

The Crystal Chemistry and Magnetic Properties of Iron in the Monosulfide Solid Solution of the Fe-Ni-S System

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Abstract

Compositions of varying iron:nickel and metal:sulfur ratios occurring within the monosulfide solid solution (Mss) of the Fe-Ni-S system have been synthesized at 600°C. The samples were characterized by X-ray diffraction and electron microprobe analysis, and the crystal chemistry and magnetic properties of iron in the samples studied by Mössbauer spectroscopy. Compositions close to the FeS corner of the Mss have a six-peak Mössbauer spectrum indicating antiferromagnetically ordered iron in one distinct site. Compositions across the center of the Mss ((Fe, Ni)_{0.998}S) exhibit similar six-peak spectra until \lesssim 25 wt percent iron when a magnetic order \rightleftharpoons disorder transition occurs. Samples with $<$ 20 wt percent iron exhibit simple doublet spectra with very small isomer shifts (\sim 0.50 mm/sec) and quadrupole splittings (\sim 0.40 mm/sec) for Fe²⁺ in octahedral sites. These low values probably are due to electron delocalization and metallic behavior at the Ni-rich end of the Mss. Samples having still lower metal content (\sim M_{0.91-0.95}S) exhibit the order \rightleftharpoons disorder transition at \sim 35 wt percent iron, and have more complex magnetic spectra due to vacancy ordering. The magnetic order \rightleftharpoons disorder transition occurs in regions of the Mss where it breaks on cooling. Discontinuities occur in *d*(102) and *c* vs composition plots in these regions and have been used to support a previous proposal of a “modulated structure” in these regions.

Introduction

The mineral phases occurring in the Fe-Ni-S system are both geologically widespread and economically important. Pentlandite, the major source of nickel, occurs in many deposits as discrete grains, veinlets, and “flames” in pyrrhotite. Numerous studies have established that the pentlandite forms on cooling, long after ore emplacement, as an exsolution product from a nickeliferous pyrrhotite solid solution, the so-called monosulfide solid solution (Fe_{1-x}S-Ni_{1-x}S, designated Mss) which spans the Fe-Ni-S system from above 900° to below 300°C (Fig. 1).

The considerable literature on the Fe-Ni-S system has been reviewed in the recent publications of Naldrett, Craig, and Kullerud (1967); Shewman

and Clark (1970); Misra and Fleet (1973a), and Craig (1973). The present work is concerned only with Mss compositions within the limits defined between 600 and 300°C by Naldrett, Craig, and Kullerud (1967).

The Ni_{1-x}S end member of the Mss occurs in two forms. The high temperature or α -form is hexagonal, and has the true NiAs-type structure. The low temperature form is rhombohedral, and has the millerite structure (Kullerud and Yund, 1962). At 600°C, the α -form extends from 35.33 wt percent sulfur (stoichiometric NiS) to 37.8 wt percent sulfur; whereas, at 370°C, the compositional range is reduced to 35.33–37.0 wt percent sulfur. Although stoichiometric NiS inverts to the millerite form below 370°C, more sulfur-rich compositions persist in the high-temperature form down to 282°C, and then break down eutectoidally into NiS (millerite) and Ni₃S₄ (polydymite).

At the Fe_{1-x}S end of the solid solution, phase re-

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lations are more complex and are yet being evaluated. Above 325°C, phase studies in the Fe-S system (Arnold, 1959; Toulmin and Barton, 1964) have shown that the high temperature pyrrhotite phase with the NiAs-structure extends from stoichiometric FeS (36.47 wt percent sulfur) to a maximum of 41.3 wt percent sulfur at 743°C. At 600°C the solid solution extends from 36.47 wt percent sulfur to 40.3 wt percent; but at 350°C, the pyrrhotite in equilibrium with pyrite has 39.2 wt percent sulfur. Below 248°C (Kissin and Scott, 1972) monoclinic pyrrhotite, Fe₇S₈, becomes stable and coexists with pyrite. The so-called "intermediate hexagonal pyrrhotite" field, a low temperature extension of the high temperature pyrrhotite phase, is stable between 37.7 and 39.0 wt percent sulfur at 100°C (Nakazawa and Morimoto, 1970). This region is characterized by several superstructure types whose stability relations are as yet unclear (Arnold, 1959; Yund and Hall, 1969; Taylor, 1970; Nakazawa and Morimoto, 1970; Kissin and Scott, 1972). The interesting magnetic properties of the structural types in this region have been reviewed by Ward (1970).

Thus, the crystal chemistry of the Ni_{1-x}S end member is fairly well characterized, and in part, so is that of the Fe_{1-x}S compositions. Very little is known of the behavior of iron and nickel in the inter-

mediate compositions of the Mss. In the present study, a series of compositions across the Mss at various Fe:Ni ratios and sulfur contents have been synthesized and quenched from 600°C. The Mössbauer spectra of iron in these phases have been examined in an attempt to understand further the crystal chemistry of the monosulfide solid solution.

Experimental Techniques

Mss compositions (shown in Fig. 1) were prepared by conventional evacuated silica tube techniques, using 99.999+ percent pure materials (as indicated by the supplier's, ASARCO'S, analyses). Iron and nickel were reduced in a stream of hydrogen at 700°C for 6 hours prior to use. Samples were synthesized at 600°C by initial reaction of the elements for one day, grinding under ethyl alcohol, and reannealing for six to ten days. Samples were rapidly cooled in ice water at the termination of each experiment. Homogeneity of the synthesized Mss was checked by X-ray powder diffraction, using monochromatized CuK_{α1} radiation, and by electron microprobe analysis.

Mössbauer spectra were obtained using an Austin Science Associates drive unit with a source of ⁵⁷Co in Pd. The spectra were accumulated using a Nuclear Data multichannel analyzer, and interpreted with the

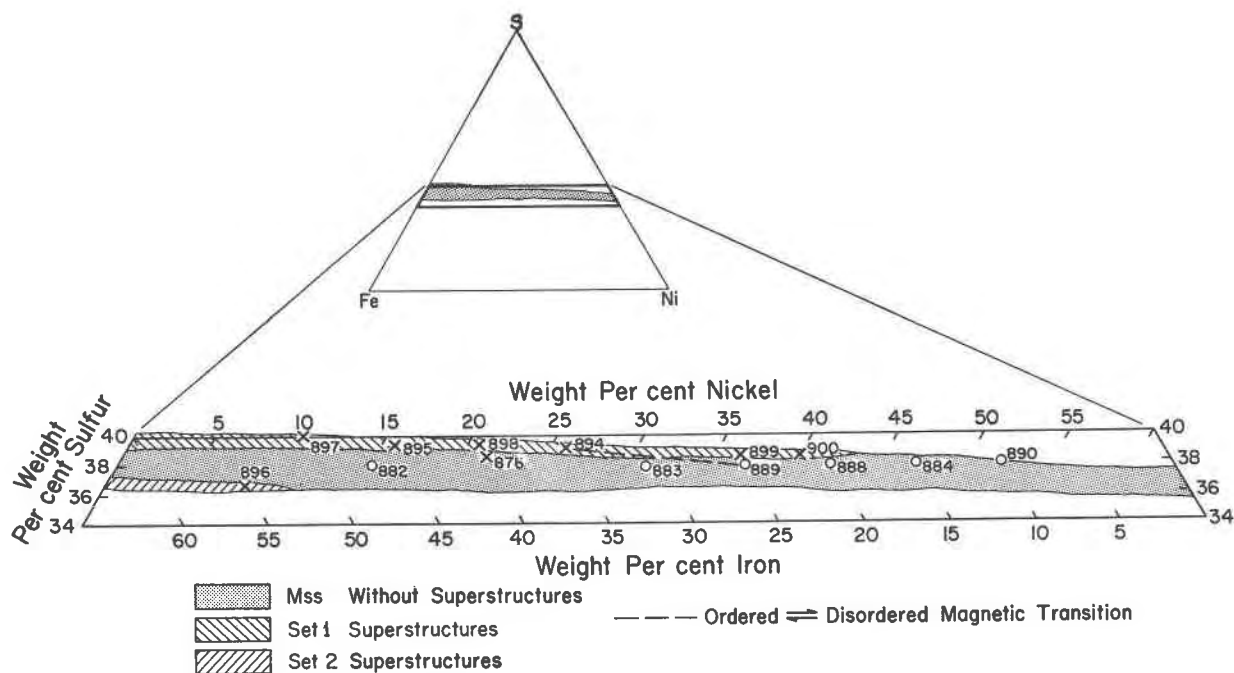


FIG. 1. Part of the Fe-Ni-S system at 600°C showing the compositional limits of the Mss (after Naldrett *et al.*, 1967) and the compositions synthesized and studied in this work. Three digit numbers with X's and O's give numbers of synthesized samples.

TABLE 1. Compositions and Mössbauer Parameters of Mss Samples

Sample	Composition			Approx. Formula	Mössbauer Parameters*		
	weight Fe	percent Ni	S		H _{loc} (Kgauss)	δ (mm/sec)	Δ or Δs (mm/sec)
(a) "series 1" samples							
882	47	15	38	M _{0.966} S	289	0.70	+0.13
882	31	31	38	M _{0.966} S	289	0.67	-0.11
889	25	37	38	M _{0.966} S	289 0	0.69	+0.06 +0.42
888	20	42	38	M _{0.966} S	0	0.56	0.41
884	15	47	38	M _{0.966} S	0	0.53	0.43
890	10	52	38	M _{0.966} S	0	0.49	0.48
(b) "series 2" samples							
878	40	21.5	38.5	M _{0.950} S	301 256	0.64 0.60	+0.06 0
899	25	36.5	38.5	M _{0.950} S	0	0.52	0.40
900	21.5	40	38.5	M _{0.950} S	0	0.54	0.42
897	50	10	40	M _{0.910} S	281 230	0.61 0.62	+0.03 0
895	45	15.7	39.3	M _{0.928} S	268 228	0.60 0.59	-0.03 -0.12
898	40	20.5	39.5	M _{0.924} S	175	0.50	-0.15
894	35	25.9	39.1	M _{0.934} S	?	?	?
899	25	36.5	38.5	M _{0.950} S	0	0.52	0.40
900	21.5	40	38.5	M _{0.950} S	0	0.54	0.42
896	55	8.5	36.5	M _{1.0} S	304	0.71	-0.34

*Symbols:
H_{loc} = magnetic field at the Fe nucleus
δ = isomer shift relative to Fe foil
Δ or Δs = quadrupole splitting or difference in separation of the two outermost lines on left and right hand sides of the magnetic subspectra (also given the symbol ε by some authors).

aid of a least-squares computer program written by Dr. A. J. Stone of Cambridge University. Determinations were made chiefly at room temperature (~300 K), and with some additional measurements at liquid nitrogen temperature (~77 K). Iron foil was used to calibrate the spectrometer, and all isomer shifts are quoted relative to the center of gravity of an iron foil spectrum as zero.

Results

Figure 1 shows the (Fe,Ni)_{1-x}S compositions synthesized at 600°C and studied in this work. The compositional limits of the Mss shown are taken from the paper by Naldrett *et al* (1967). Hatched areas on this figure indicate the compositional regions where those authors observed what they termed "set 1" and "set 2" superstructure lines.

The compositions examined in this work can be considered to represent: (1) a main series extending across the Mss at different Ni:Fe ratios, but at constant sulfur content (38 wt percent sulfur); (2) a

second series of compositions in the area of the "set 2" superstructure lines; and (3) a single composition in the "set 1" superstructure region. The main series (termed "series 1" in this paper) is discussed first, and the "set 2" superstructure group ("series 2") and other compositions are discussed later.

Series 1

All of the samples in this series contain 38 wt percent sulfur. They are numbered 882, 883, 889, 888, 884, and 890, and their compositions are shown on Figure 1 and in Table 1(a). Superstructure reflections were not observed for phases of these compositions by Naldrett *et al* (1967), but Shewman and Clark (1970) observed superstructure reflections in a region near 18.8 wt percent iron, 43.8 nickel, and 37.4 sulfur, and Misra and Fleet (1973a) report superstructure lines in all portions of the Mss. Representative Mössbauer spectra, obtained at room temperature from these samples, are shown in Figure 2. The Mössbauer parameters are presented in Table 1(a).

The spectrum for sample 882 (47 wt percent iron) is a simple six-peak hyperfine spectrum, arising from antiferromagnetically ordered iron. The spectrum shows no evidence of iron occupying more than one distinct site, although the peaks are somewhat broad, and the reduced intensity of the outermost peaks suggests some variation in the local magnetic fields over the iron sites. The spectrum (Fig. 2) does not suggest any distinct ordering of vacancies or nickel atoms.

Sample 883 (31 wt percent iron) is also magnetically ordered and the internal field and isomer shift are very slightly reduced. The asymmetry of the inside limbs of the main peaks suggests a contribution from iron in a second type of local environment in the structure. This should not be due to the vacancies (the vacancy concentration is the same as in 882), but to the additional nickel atoms.

Sample 889 shows a great reduction in the intensity of the magnetic hyperfine spectrum, and the appearance of an intense central doublet with a fairly low isomer shift and quadrupole splitting (Figure 2). This type of behavior is observed in antiferromagnetic materials on approaching the Néel temperature, and shows partial breakdown of the long range magnetic order. When the iron concentration is further reduced to 20 wt percent (888), the magnetic ordering disappears completely, and only a single quadrupole doublet remains. The spectra for the

samples containing 20, 15, and 10 wt percent iron are very similar. The spectrum for 884 (15 wt percent iron) is shown in Figure 2. The narrow linewidth and evidence of only one distinct site in these spectra are interesting; so are the small values of the isomer shift and quadrupole splitting, which are closer to those observed for Fe^{2+} in tetrahedral sites in sulfides. The possible occupancy of the ordinarily empty tetrahedral sites in the NiAs-type structure, thus enabling development of phases with excess metal, has been indicated by Goodenough (1963). However, the absence of known phases with excess metal suggests this to be very minor.

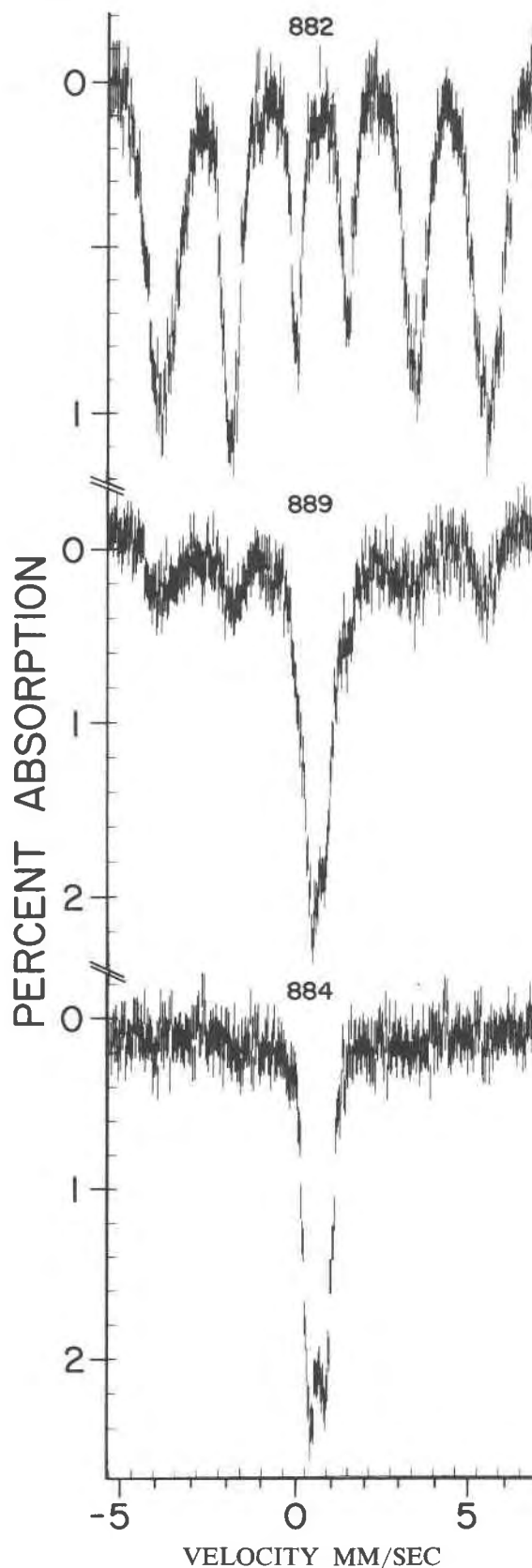
The variations in Mössbauer spectral parameters as a function of composition in the "series 1" samples are shown graphically in Figure 3. The internal magnetic fields decrease very slightly with decreasing iron content to the point at which magnetic order breaks down (~ 25 wt percent iron). The average value of the isomer shift shows a systematic decrease with decreasing iron content, although there is a sharp drop at the order \rightarrow disorder magnetic transition which will be discussed later. The quadrupole splitting of the magnetically disordered compositions exhibits a systematic increase with decreasing iron content, but the splittings of the magnetic spectra are too small to be considered reliable.

Series 2

After study of the series 1 compositions, the effects of greater metal deficiency on the crystal chemistry of the Mss were examined. In particular, it was decided to examine compositions exhibiting the "set 2" superstructure lines described by Naldrett *et al* (1967). Such superstructures are probably the result of ordering or partial ordering of vacancies on quenching.

It is not possible to examine a section at constant sulfur content in the compositional region of "set 2" superstructure lines, because the field slopes towards lower sulfur with increasing nickel content. Three compositions containing 38.5 wt percent sulfur (878, 899, 900), one of which (878) is outside the "set 2" field, have been studied. The samples 899 and 900, together with a series of phases of varying sulfur content (897, 895, 898, 894), form a complete series across the field.

FIG. 2. Mössbauer spectra (at 300 K) of Mss compositions 882, 889, and 884 of the "series 1" samples (38 wt percent S).



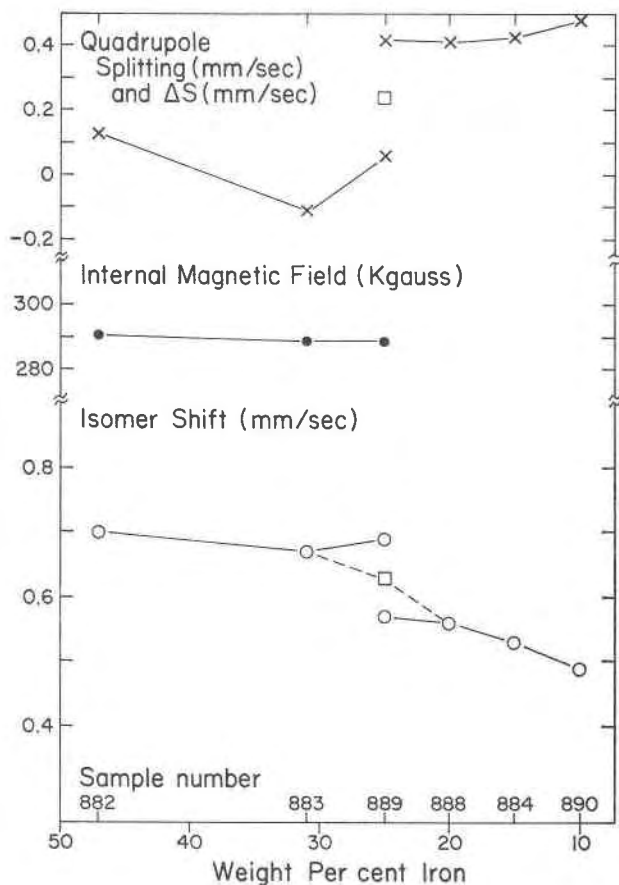


FIG. 3. Variation of the Mössbauer isomer shift, quadrupole splitting (or Δs), and local magnetic field at the iron nucleus as a function of composition in the "series 1" samples. (\square represents a mean value).

The compositions in this series all exhibit the "set 2" superstructure X-ray powder lines (Naldrett *et al* (1967), Table 2, p. 836). An attempt was made to assign tentatively a structure type and to index this pattern, using a procedure discussed by Schwarz and Vaughan (1972). Best agreement was found using a 2A, 4C hexagonal superstructure of the type described by Fleet (1968), although it is probably an oversimplification to ascribe only one superstructure type to this series.

The Mössbauer parameters for these samples are given in Table 1 (b). In this table, the samples 878, 899, and 900 are grouped in a series for comparison and are also repeated in the complete series 897, 895, 898, 894, 899, and 900.

In the series 878, 899, and 900, the transition from a magnetically ordered to a paramagnetic state takes place at an iron concentration greater than

25 wt percent. The spectrum of sample 878 (40 wt percent iron) resembles 833 in its appearance, and broadening of the outermost peaks enables additional peaks to be fitted to this spectrum, defining a second hyperfine sub-spectrum. This suggests more than one type of environment for iron atoms, even though this sample is not in the region of "set 2" superstructure lines. Sample 899 exhibits a broadened doublet; but in sample 900, which contains 21.5 wt percent iron, the spectrum is sharper.

The spectrum of sample 897 is considerably more complex than any described so far (Fig. 4). It has been fitted to two separate magnetic subspectra indicating two (at least) distinct positions for iron in the superstructure. Two sets of six-peak magnetic subspectra can also be fitted to sample 895. Mössbauer parameters for the compositions 897, 895, and 898 at 300 K are given in Table 1 (b). The spectrum of 898 shows a partial collapse of the magnetic hyperfine fields into a broad, highly distorted spectrum (Fig. 4) best represented by the parameters given in Table 1(b). It is probably a six-peak hyperfine spectrum superimposed on a broad peak like that observed in sample 894. The spectrum of sample 894 (Fig. 4) is so distorted that reasonable parameters could not be obtained, whereas 899 and 900 are doublets much like 884 of series 1 (Fig. 2). As in the series 1 samples, the general trends are toward reduced internal magnetic fields and isomer shifts, and increased quadrupole splittings with increasing nickel content. At 300 K, the transition between the ordered and paramagnetic phases now occurs at close to 35 wt percent iron for a sample with 39.12 wt percent sulfur.

Finally, one sample exhibiting the "set 1" superstructure lines described by Naldrett *et al* (1967) has been examined (sample 896). The close relationship between X-ray powder patterns of "set 1" type and those of troilite has been already pointed out by these authors. Sample 896 is nearly stoichiometric in composition, and contains 8.5 wt percent nickel. Both the internal fields and isomer shifts for this sample are somewhat reduced relative to troilite, but the single six-peak spectrum is that expected for a troilite-type phase (Table 1(b)).

The effect of cooling the sample to liquid nitrogen temperature (~ 77 K) was examined in several series 1 and series 2 samples. In general, for a particular sample, a minor increase in the internal magnetic field at the nucleus (H_{loc}) and the isomer shift (δ) occurred on cooling, and the position of the order \rightleftharpoons

disorder magnetic transition moved towards the Ni_{1-x}S end of the Mss by ~ 5 –10 wt percent.

Discussion

The major change in the Mössbauer spectra of the Mss as a function of composition is the breakdown of magnetic order shown by the transition from six-peak hyperfine spectra to doublets. At 300 K and 38 wt percent sulfur, this occurs at ~ 25 wt percent iron. When the total metal content is decreased (with formation of vacancies), the breakdown occurs at more iron-rich compositions. In a sample containing 39.12 wt percent sulfur (sample 894) it may be estimated as close to 35 wt percent iron at 300 K. The magnetic order, like the c dimension of the unit cell, is therefore very strongly dependent on the M:S ratio; the approximate position of the transition is shown in Figure 1. The transition also occurs at a more iron-deficient composition when the spectra are studied at 77 K.

It may or may not be significant that this breakdown in magnetic order occurs in regions of the Mss where it separates into two distinct phases on cooling. Craig (1973) reports breaks in the Mss at 27 percent Fe, 35 percent Ni, and 38 percent S (by weight), and at 36 percent Fe, 25 percent Ni, and 39 percent S occurring at $\sim 255^\circ\text{C}$ and $\sim 263^\circ\text{C}$ respectively. These breaks follow the shallow slope of the order \rightleftharpoons disorder transition (Fig. 1). Since a number of other variables are involved, further studies of the magnetic properties will be required to determine if this correlation is meaningful. Discontinuities in plots of $d(102)$ and of c parameters against composition have also been reported in the same regions of the Mss (Shewman and Clark, 1970; Misra and Fleet, 1973b). All of these phenomena could be related to clustering of nickel atoms in the structure or to formation of a "modulated structure" (Taylor, 1961). The latter suggestion involves an intermediate stage in the separation of two phases of different composition but nearly equal lattice parameters, and has since been proposed by Shewman and Clark (1970). These authors observed superstructure reflections in the Mss at 18.8 wt percent iron, 43.8 wt percent nickel, and 37.4 wt percent sulfur, this composition lying close to the region of the order \rightleftharpoons disorder transition. The present authors have observed "side bands" in X-ray powder

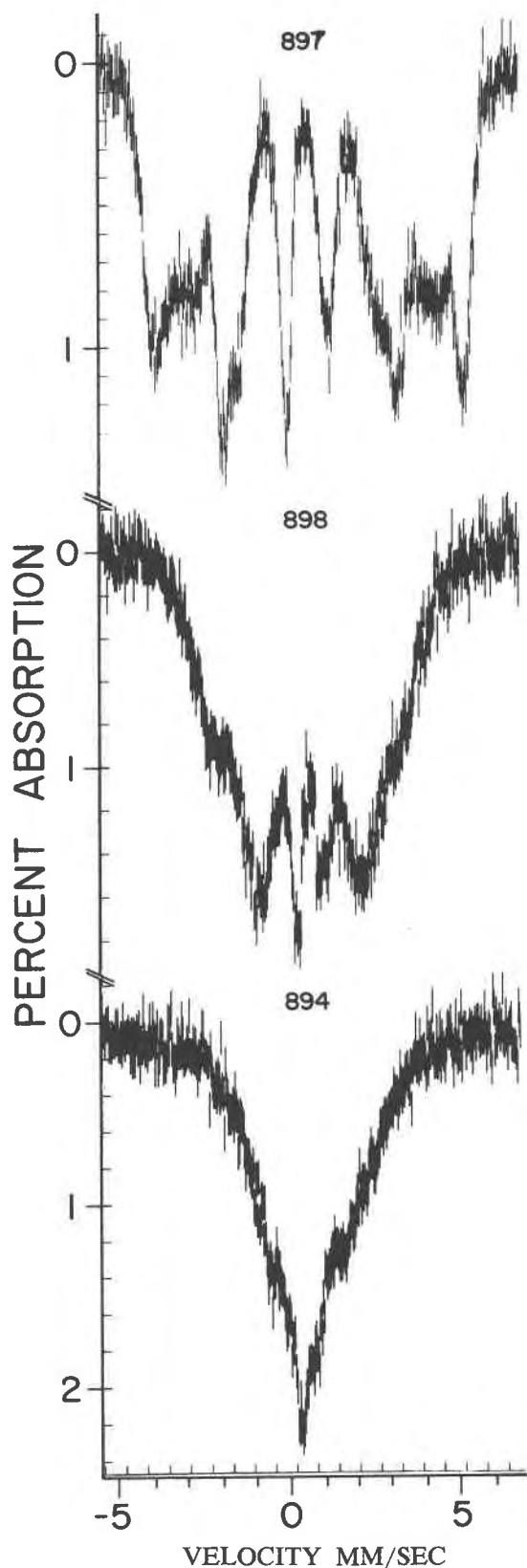


FIG. 4. Mössbauer spectra (at 300 K) of Mss compositions 897, 898, and 894 of the "series 2" samples.

diffraction photographs taken of sample 889, which lies on the order \rightleftharpoons disorder transition boundary. They are virtually identical to those described by Taylor (1961) for modulated structures, and are absent in photographs of the samples away from the transition. The appearance of side bands in the X-ray pattern at this composition indicates that significant atomic rearrangement proceeds even on rapid cooling. The rearrangement observed likely heralds the separation of the Mss into two distinct and recognizable phases at lower temperatures.

The variations in the isomer shift and quadrupole splitting across the Mss (shown in Figure 3 and Table 1) are also interesting. The Mössbauer isomer shift is chiefly influenced by the s electron density at the iron nucleus (Wertheim, 1964), with greater s electron density producing a lower isomer shift. It is, therefore, affected by the degree of delocalization of the Fe 3d electrons, which can shield some of the s electron density from the nucleus. Hence, in sulfides, where the Fe 3d electrons are more delocalized than in oxides and silicates, the s electron density at the nucleus is greater and the isomer shift lower. M-S interatomic distances, which are themselves an indication of electron delocalization (or "covalence"), also correlate with changes in the isomer shift. The reduction in isomer shift towards the Ni_{1-x}S end of the Mss follows the reduction in cell dimensions (end-member values, from Misra and Fleet, 1973b, are $a = 3.4436 \text{ \AA}$, $c = 5.8759 \text{ \AA}$, for FeS; and $a = 3.4345 \text{ \AA}$, $c = 5.3439 \text{ \AA}$ for NiS). Nevertheless, the isomer shifts of such compositions as 884, 890, and 899 are low for octahedrally coordinated Fe²⁺, perhaps reflecting considerable electron delocalization.

The variations in the ΔS values of the magnetic spectra are too small to be considered experimentally reliable. However, an increase in quadrupole splitting of the non-magnetic compositions with increasing nickel content is clearly observed in both the series 1 and 2 samples. The quadrupole splittings for all the samples are small compared to those for octahedral Fe²⁺ in oxides and silicates. This is probably a consequence of delocalization of the sixth 3-d-electron.

Paramagnetic two-peak spectra with unusually low isomer shifts for octahedral Fe²⁺ have been observed by Vaughan and Tossell (1973) and by Coey, Roux Buisson, and Chamberod (1973). The former were for an order \rightleftharpoons disorder magnetic transition in Fe₇S₈ at high pressure, and the latter for a temperature-

dependent but similar transition in α -NiS doped with one percent iron, occurring at $\sim 260 \text{ K}$ (at 1 atm). In both cases, a strong parallel may be drawn with the present study, and the low isomer shifts attributed to the virtual absence of a magnetic moment on the iron atom. The iron could be described as "low-spin," although a distinction between high- and low-spin in this case is probably meaningless. Beyond the order \rightarrow disorder transition in the Mss, compositions may exhibit weak temperature independent Pauli paramagnetism and metallic conductivity (as observed in pure α -NiS above the non-metal \rightarrow metal transition at $\sim 260 \text{ K}$).

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References

- ARNOLD, R. G. (1969) Pyrrhotite phase relations below $304 \pm 6^\circ\text{C}$ at $<1 \text{ atm. total pressure}$. *Econ. Geol.* **64**, 405-419.
- COEY, J. M. D., H. ROUX BUISSON, AND A. CHAMBEROD (1973) The metal-nonmetal transition in NiS studied by the Mössbauer effect of ⁵⁷Fe. *Solid State Commun.* **13**, 43-45.
- CRAIG, J. R. (1973) Pyrite-pentlandite assemblages and other low temperature relations in the Fe-Ni-S system. *Am. J. Sci.* **273-A**, 496-510.
- FLEET, M. E. (1968) On the lattice parameters and superstructures of pyrrhotites. *Am. Mineral.* **53**, 1846-1855.
- GOODENOUGH, J. B. (1963) *Magnetism and the Chemical Bond*. Interscience, New York.
- KISSIN, S. A., AND S. D. SCOTT (1972) Phase relations of intermediate pyrrhotites. *Geol. Soc. Am. Abstr. Programs*, **4**, 562.
- KULLERUD, G., AND R. A. YUND (1962) The Ni-S system and related minerals. *J. Petrol.* **3**, 126-175.
- MISRA, K. C., AND M. E. FLEET (1973a) The chemical compositions of synthetic and natural pentlandite assemblages. *Econ. Geol.* **68**, 518-539.
- , AND ——— (1973b) Unit cell parameters of monosulfide, pentlandite and taenite solid solutions within the Fe-Ni-S system. *Mat. Res. Bull.* **8**, 669-683.
- NAKAZAWA, H., AND N. MORIMOTO (1970) Pyrrhotite phase relations below 320°C . *Proc. Japan Acad.* **46**, 678-683.
- NALDRETT, A. J., J. R. CRAIG, AND G. KULLERUD (1967) The central portion of the Fe-Ni-S system and its bearing on pentlandite exsolution in iron-nickel sulfide ores. *Econ. Geol.* **62**, 826-847.
- SCHWARZ, E. J., AND D. J. VAUGHAN (1972) Magnetic phase relations of pyrrhotite. *J. Geomag. Geoelec.* **24**, 441-458.
- SHEWMAN, R. W., AND L. A. CLARK (1970) Pentlandite phase relations in the Fe-Ni-S system and notes on the

- monosulfide solid solutions. *Can. J. Earth Sci.* **7**, 67–85.
- TAYLOR, A. (1961) *X-ray Metallography*. John Wiley, New York.
- TAYLOR, L. A. (1970) Low temperature phase relations in the Fe-S system. *Carnegie Inst. Wash Year Book*, **68**, 259–270.
- TOULMIN, P., AND P. B. BARTON (1964) A thermodynamic study of pyrite and pyrrhotite. *Geochim. Cosmochim. Acta*, **28**, 641–671.
- VAUGHAN, D. J., AND J. A. TOSSELL (1973) Magnetic transitions observed in sulfide minerals at elevated pressures and their geophysical significance. *Science*, **179**, 375–377.
- WARD, J. D. (1970) The structure and properties of some iron sulfides. *Rev. Pure Appl. Chem.* **20**, 175–206.
- WERTHEIM, G. K. (1964) *Mössbauer Effect: Principles and Applications*. Academic Press, New York.
- YUND, R. A., AND H. T. HALL (1969) Hexagonal and monoclinic pyrrhotites. *Econ. Geol.* **64**, 420–423.

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