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A Mössbauer Investigation of Natural Troilite from the Agpalilik Meteorite

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Abstract. Troilite close to FeS, with 0.17 weight percent Cr as main impurity, was obtained from the Agpalilik meteorite. Powder Mössbauer spectroscopy was made in the temperature range 77–645 K. The full Hamiltonian was applied in the fittings. Assuming the asymmetry parameter η to be constant on passing from the high-temperature NiAs-type structure to the medium-temperature MnP-type structure yields a quadrupole splitting ($dq=0.5e^2qQ(1+(\eta^2)/3)^{1/2}$) value of $-0.25(2)$ mm/s for these phases. In low-temperature troilite $|dq|=0.85$ mm/s at room temperature. The combinations of (η, θ, ϕ) in troilite giving identical spectra range from (0, 49°, –) to (1, 45°, 50°) for negative $\mathbf{V}_{zz}$ or from (0.3, 57°, 78°) to (1, 58°, 54°) for positive $\mathbf{V}_{zz}$. Assuming a negative $\mathbf{V}_{zz}$ and $\mathbf{B}\|\mathbf{c}$ gives a θ value in agreement with the shortest Fe-S join being the $\mathbf{V}_{zz}$ orientation. The magnetic spin flip of 90° is proposed to occur in the MnP-phase only. The MnP phase-troilite transition occurs at lower temperatures and is more sluggish than in pure FeS.

Introduction

Troilite has a composition close to FeS. Below 413 K there is a miscibility gap to pyrrhotite, $Fe_{1-x}S$, where $x \geq 0.076$ at room temperature (rt) (Yund and Hall 1968). FeS exhibits different structures depending on temperature and has been the subject of many investigations (e.g. Horwood et al. 1976, Gosselin et al. 1976, Andresen and Torbo 1967). The results on e.g. magnetic behaviour are, however, somewhat contradictory. This might be due to non-equilibrated synthetic samples; in this study we have therefore used meteoritic troilite.

Structures of FeS

Above ~483 K FeS crystallizes in the hexagonal NiAs-structure ($P\,6_3/mmc$; Töpel-Schadt and Müller 1982) with axes $a=3.44$ Å and $c=5.88$ Å at rt (calculated from Evans 1970). The Fe atoms are stacked along the **c**-axis, each atom surrounded by two staggered S triangles, one above and one below (Fig. 1a). This leads to a threefold rotation axis passing through the Fe atoms. Thus, the main component of the electric field gradient tensor, $\mathbf{V}_{zz}$, is $\|\mathbf{c}$ and the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz})$ equals zero.

On lowering the temperature FeS transforms into the orthorhombic MnP-structure (*Pnma*; King and Prewitt 1982). The linear arrangement of Fe atoms is replaced by a zig-zag chain (Fig. 1b). If the former **c**-axis is denoted **c*** in the MnP-structure, the Fe-Fe joins make an angle of 3.5° with **c*** at ~463 K (calculated from King and Prewitt 1982). Thus, neither the $\mathbf{V}_{zz}$-orientation nor the η-value are given by symmetry considerations.

At high temperatures the magnetic spins in the MnP phase are perpendicular to **c*** ($\theta=90°$) and at lower temperatures parallel to it (Horwood et al. 1976). Various values for the spin flip or spin rotation temperature, T_s, have been reported; e.g. 445 K (Horwood et al. 1976), and 458 K (Andresen and Torbo 1967).

Below T_α (~413 K) FeS transforms into hexagonal troilite ($P\bar{6}2c$; Evans 1970). Every second Fe-Fe join is $\|\mathbf{c}$ and the others make an angle of 11° to it at rt (calculated from Evans 1970), see Figure 1c. The three-fold rotation axis (**c**-axis) passes through S atoms but not through Fe atoms. Thus, neither the orientation of $\mathbf{V}_{zz}$ nor the value of η can be inferred directly.

Experimental Details

Samples were obtained from a piece of the Agpalilik iron meteorite (Cape York shower), found by Buchwald near Thule, Greenland in 1963, and described by him and others (e.g. Buchwald 1964, Kracher et al. 1977). Small grains were picked out from a cm-sized troilite inclusion under stereomicroscope. Care was taken to remove oxidized parts.

Among possible trace elements only Cr (0.17 wt%) was detected using electron microprobe analysis. Kracher et al. (1977) reported ~0.13 wt% Cr for Agpalilik troilite and less than 0.02 weight percent each for all other elements. Jochum et al. (1975) investigated a single Agpalilik troilite inclusion and reported a Cr content of ~0.12 weight percent, Ni ~440 ppm, Mn ~220 ppm, Cu ~90 ppm, Se ~50 ppm, Co ~40 ppm and lower concentrations of 14 other elements. Cr was evenly distributed in the troilite and the authors suggest solid solution as a possibility. Buchwald (1977) suggested a maximum solid solution of Cr, Mn, Zn, Ni, Cu, and Co of 1 percent in total in natural troilites. X-ray analyses at rt (296 K) on an untreated sample and after high temperature runs ($T_{max}=435$ K, $T>400$ K for five weeks) showed d_{102} values of 2.0939 and 2.0938 Å, respectively, which agree with 50.0 at percent Fe in $Fe_{1-x}S$ (Yund and Hall 1969); $a=5.968(1)$, $c=11.766(3)$ and $a=5.968(1)$, $c=11.764(2)$ Å, respectively.

The powdered samples, containing ~5 mg Fe/cm², were spread out on a horizontal disc in a vacuum furnace for

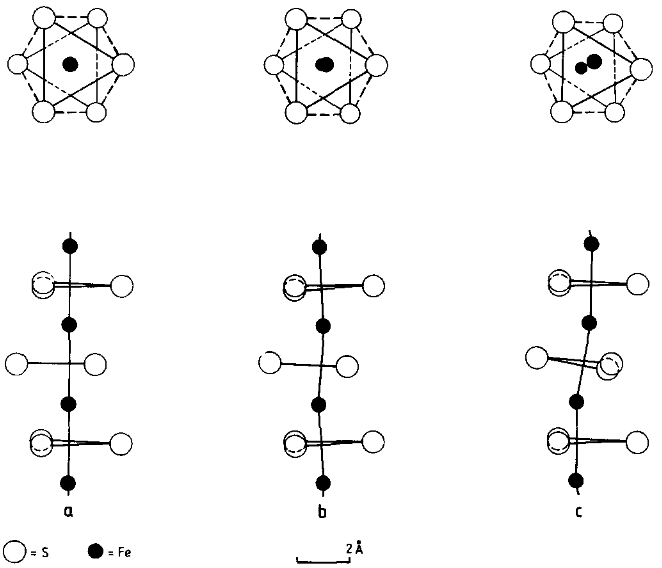

Fig. 1a–c. Structures of FeS. **(a)** NiAs-type, **(b)** MnP-type at ~463 K, **(c)** troilite. Top: octahedral iron sites viewed from above. Bottom: side view through the mid-point between the two middle Fe atoms

Mössbauer runs. The absorber temperature was controlled within ±0.5 K with an accuracy of ±2 K. An iron foil was used to calibrate the velocity scale at rt. Final analysis was made on folded spectra (256 channels each). Due to thin absorbers, Lorentzian lines could be used without any thickness correction.

Analysis and Results

High Temperature ($T > T_\alpha$)

FeS transforms from antiferromagnetic to paramagnetic behaviour at 600 K (Horwood et al. 1976). A spectrum recorded at 645 K (Fig. 2a) shows a symmetric doublet with $cs = 0.53$ mm/s and $|dq| = 0.25$ mm/s, where cs is the centroid shift relative natural iron at rt and the magnitude of the paramagnetic quadrupole splitting, $|dq|$, is defined as the peak separation. Above 600 K no temperature dependence was observed for $|dq|$. As the relation between dq and the quadrupole interaction, $0.5\, V_{zz}e\mathrm{Q}$, is given by:

$$dq = 0.5\, V_{zz}e\mathrm{Q}(1 + (\eta^2)/3)^{1/2}$$

where $\eta = 0$ in the NiAs phase, the sign of $\mathbf{V}_{zz}$ is not given by the peak separation alone.

Below 600 K the NiAs phase shows a sextet (Fig. 2b). In general it is not possible to obtain unique values of the parameters η, θ, ϕ from such a spectrum, ϕ being the angle between $\mathbf{V}_{xx}$ and the projection of $\mathbf{B}$ onto the $\mathbf{V}_{xx} - \mathbf{V}_{yy}$ plane. Instead, unique values of cs, $|dq|$, and B can be obtained according to Karyagin (1966), and van Dongen et al. (1975). Applying the notation in Figure 3 and the equation

$$a_2 = \sum_{i<j} E_i E_j$$

it follows that

$$a_2 = -0.5((dq)^2 + 1.6308\, B_g^2).$$

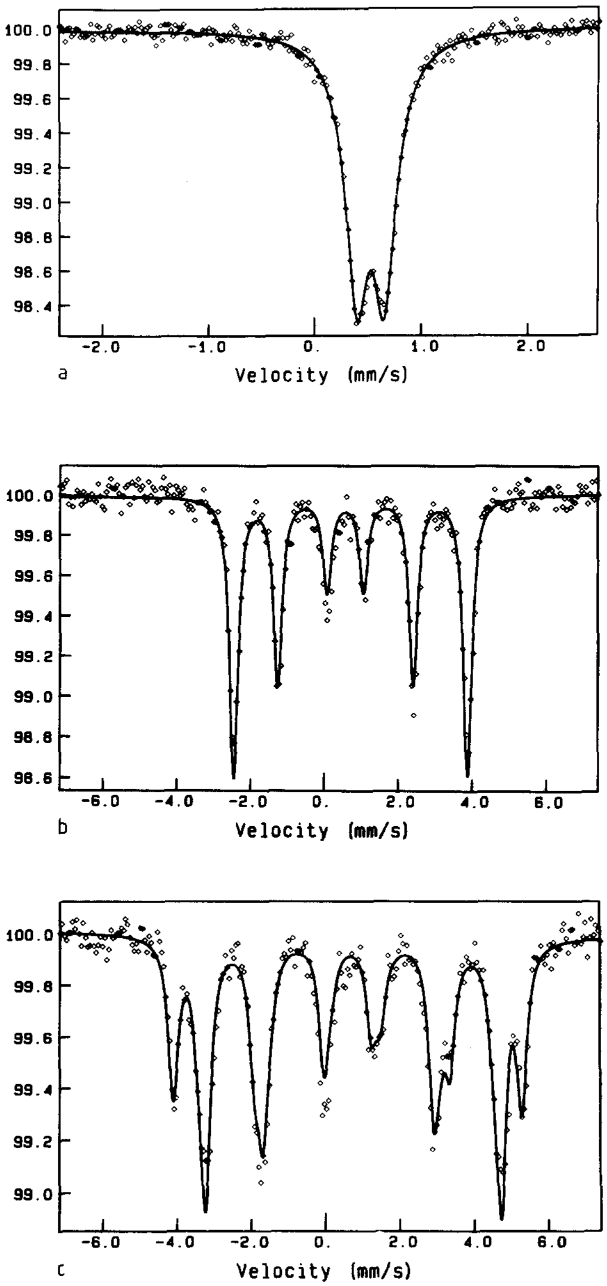

Fig. 2a–c. Transmission Mössbauer spectra (y-axis in %) and fitted functions for FeS recorded at different temperatures. **(a)** paramagnetic doublet at 645 K. **(b)** sixline pattern at 499 K (NiAs phase). **(c)** three sixline patterns at 409 K, due to troilite iron (broadest), and to MnP phase iron with $\theta = 0°$ and $90°$ respectively

I.e., a four doublet (eight line fit) model is the result, with B_g as the splitting of all doublets. The uncertainties in a_2 can be estimated to < 0.1 mm^2/s^2 and in B_g to 0.01 mm/s and hence the uncertainty in $|dq|$ is 0.2 mm/s when $|dq| =$ 0.25 mm/s. Thus, it is more reasonable to apply the full Hamiltonian, *i.e.* the electric interaction is not treated as a perturbation on the magnetic interaction. Our approach was that of Jernberg and Sundqvist (1983), assuming $\eta = 0$. From the output of the fittings E_1, E_2, E_3, E_4, and B_g were calculated and then the η, θ, ϕ intervals could be computed as above. As $\theta = 90°$ at high temperatures, the only relevant solution here gives a negative dq.

No values of η and V_{zz} can be predicted for the MnP phase. No significant changes in cs, dq, or B occur at the

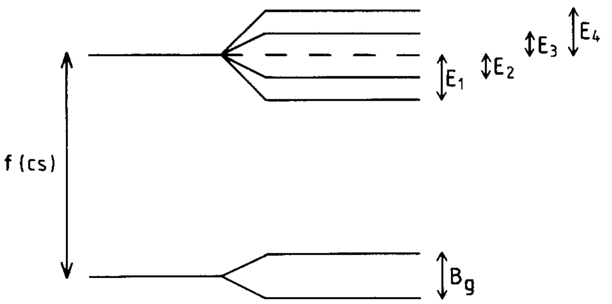

Fig. 3. Definition of the parameters E_1, E_2, E_3, E_4, and B_g used in the calculations of *cs*, *dq*, and *B*

Table 1. Mössbauer parameters for troilite, calculated according to van Dongen et al. (1975)

T K	*dq* mm/s	$\eta_1-\eta_2$	$\theta_1-\theta_2$	$\phi_1-\phi_2$
77	−0.96	0−1	49−47	(48)−49[a]
	+0.96	0.3−1	57	78−54
295	−0.85	0−1	48−45	(44)−49
	+0.85	0.4−1	57−58	74−56
327	−0.83	0−1	48−45	(46)−50
	+0.83	0.4−1	57	77−57
392	−0.76	0−1	47−45	(44)−49
	+0.76	0.4−1	57−58	77−57
409	−0.73	0−1	48−45	(44)−49
	+0.73	0.4−1	57−58	77−57

[a] η is varied in steps of 0.1. Values in parentheses correspond to $\eta=0.1$, as ϕ is not defined for $\eta=0$

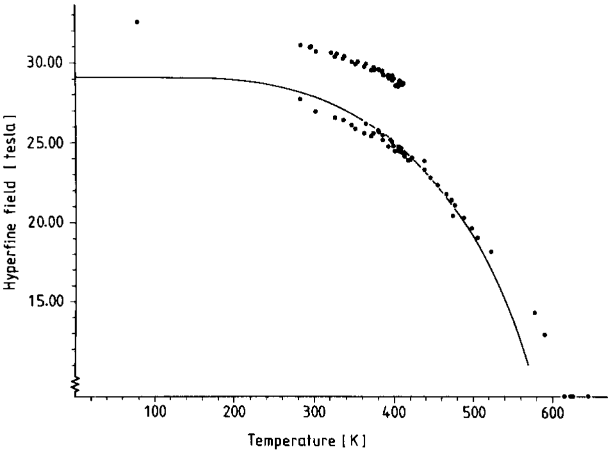

Fig. 4. The hyperfine field *versus* temperature. The two branches are due to troilite and MnP/NiAs-phases, respectively. The solid line is the Brillouin function for $S=1/2$ with $T_N=600$ K, passing through an experimental point at 420 K

NiAs-MnP phase transition, which is reasonable due to its second order nature (King and Prewitt 1982). Therefore, we assumed $\eta=0$ and $\mathbf{V}_{zz}\|\mathbf{c}^*$ for the MnP phase.

Low Temperature ($T<T_\alpha$)

In fitting troilite spectra η was varied in order to yield the smallest least square sum. Parameter values (Table 1) were then obtained according to van Dongen et al. (1975).

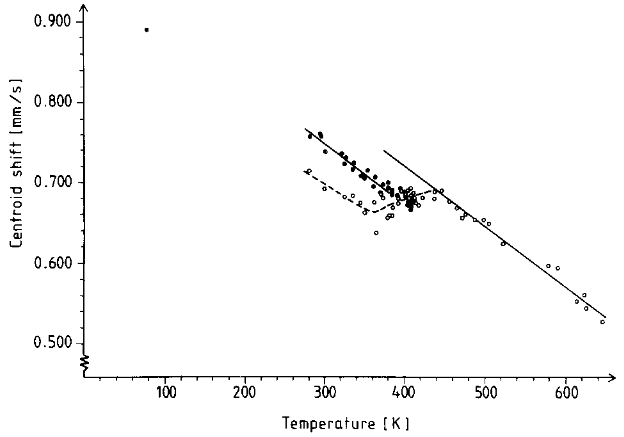

Fig. 5. The centroid shift (relative α-Fe at rt) *versus* temperature. Open and filled circles represent MnP/NiAs and troilite measurements, respectively

Table 2. Compilation of Mössbauer parameters for the MnP and NiAs phases at increasing temperatures. Below 413 K, a third pattern representing the troilite phase has also been fitted

T K	*I* %	*w* mm/s	*cs* mm/s	*B* T	*dq* mm/s	θ°
409	25	0.32+	0.68+	24.39+	−0.25!	0!
	24	0.32+	0.68+	24.39+	−0.25!	90!
410	36	0.35+	0.68+	24.44+	−0.25+	0!
	42	0.35+	0.68+	24.44+	−0.25+	90!
412	42	0.33+	0.68+	24.39+	−0.23+	0!
	46	0.33+	0.68+	24.39+	−0.23+	90!
413	41	0.37+	0.68+	24.27+	−0.23+	0!
	59	0.37+	0.68+	24.27+	−0.23+	90!
415	37	0.39+	0.68+	24.11+	−0.25+	0!
	63	0.39+	0.68+	24.11+	−0.25+	90!
422	18	0.43+	0.67+	23.58+	−0.25+	0!
	82	0.43+	0.67+	23.58+	−0.25+	90!
442	4	0.39+	0.66+	22.54+	−0.27+	0!
	96	0.39+	0.66+	22.54+	−0.27+	90!
473	18	0.31+	0.65+	21.39+	−0.23+	0!
	82	0.31+	0.65+	21.39+	−0.23+	90!
523	100	0.34	0.62	18.12	−0.26	90!
578	100	0.37	0.60	14.27	−0.26	90!
626	100	0.26	0.54	0	+ −0.25	90!
645	100	0.26	0.53	0	+ −0.25	90!

Intensities (*I*) are given for $\theta=0°$ and 90° in each run. The sign + indicates that the two values of a parameter are constrained to be the same. "!" indicates a value to be fixed in the fitting. *w* = full width at half maximum

The MnP phase-troilite transition is marked by an increase in *B* of 4 T (Figs. 2c and 4). The extrapolated value at 0 K is 33 T, in good agreement with Ono et al. (1962) and Hafner and Kalvius (1966). $|dq|$ shows a clear change too, being ~3 times larger in troilite. $|dq|=0.85$ mm/s at rt and d $|dq|/\mathrm{d}T=7*10^{-4}$ mm/sK in the interval 77 K − T_α. The *cs* (Fig. 5) has no clear discontinuity at T_α. Troilite and the NiAs-MnP phases show similar $\mathrm{d}cs/\mathrm{d}T$ values ($-8*10^{-4}$ mm/sK). In the vicinity of T_α the linear depen-

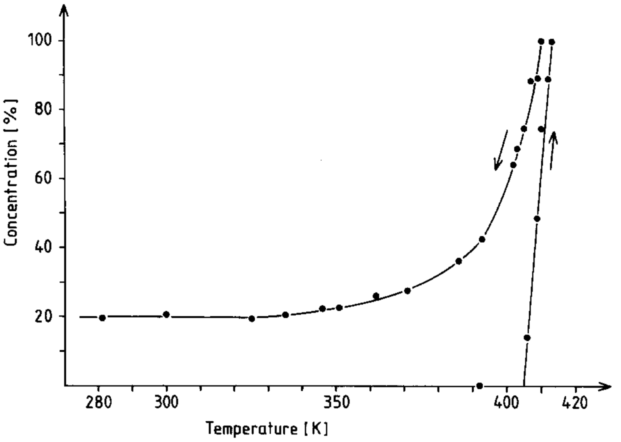

Fig. 6. Concentration of MnP phase *versus* temperature for increasing and decreasing temperatures. The sample was kept at each temperature for one day

dence of the latter is replaced by a cross-over; at low temperatures troilite shows higher *cs* values.

On relatively rapid heating, the troilite-MnP phase transition is fairly sharp, being completed at 413 K. However, the reverse transition starts at 410 K. The MnP phase partly survives down to low temperatures (Fig. 6). The detailed behaviour depends on sample treatment.

Discussion

Spin Directions

We found spin direction changes from ~410 to ~470 K on heating and from ~450 to ~360 K on cooling. The detailed behaviour depends on sample treatment. According to Töpel-Schadt and Müller (1982), the MnP-NiAs phase transition occurs at ~483 K. We found $\theta = 90°$ above that temperature, i.e. in the NiAs phase. Also in troilite we found a unique θ(~47° for $V_{zz} < 0$ or ~57° for $V_{zz} > 0$, Table 1). Thus, the changes in θ seem to occur in the MnP phase only. Two models are plausible here:

a) The spins rotate in a temperature interval. The angle at a particular temperature depends on local composition.

b) The spins flip at a definite temperature, T_s, dependent on local composition. Inhomogeneous samples result in coexistence of the two spin directions in a temperature interval.

Andresen (1960) and Sparks et al. (1962) discussed a) and the latter authors found the interval 458-433 K with $\theta = 20°$ at 433 K for $Fe_{0.996}S$. Horwood et al. (1976) favoured b) and found $T_s = 445$ K for FeS.

a) requires fitting of at least one sextet for the MnP phase. b) requires two sextets since the MnP phase contains components with $\theta = 0°$ and 90°. Applying a) with one sextet yields transition region half-widths >0.1 mm/s broader than for troilite and NiAs phase spectra. Thus, if a) is true, this indicates a distribution of θ -values at a given temperature. b) yields half-widths like those of the other phases.

In b), the broadened peaks could be due to internal shoulders, while a) with only one local maximum in the θ-distribution should give asymmetric profiles without shoulders. Many of our spectra do show indications of such a shoulder, especially in peak number five. Thus, b) is favoured but the resolution is not good enough for excluding a).

Susceptibility studies by Horwood et al. (1976) showed the spins to flip locally. Mössbauer studies by Baek (1986) showed T_s to be heavily influenced by V and Co doping; still, the temperature interval was narrow, supporting b). Since b) also is the simpler model, we applied it in our fittings.

The Centroid Shifts

According to King and Prewitt (1982) the MnP phase density at ~463 K is 4.82 g/cm^3 with an average nearest Fe-S distance of 2.477 Å. In troilite at ~393 K the corresponding values are 4.80 g/cm^3 and 2.494 Å. Thus, the MnP phase is more compact than troilite.

Increased pressure normally results in compression of the *4s* orbital and increased covalency of the *3d* electrons (Williamson 1978), giving a decrease in the isomer shift (for *3d* electrons as a result of reduced shielding).

However, the *cs* for the MnP-NiAs phases is 0.048 mm/s larger than for troilite at the same temperature (Fig. 5, extrapolated values). Thus, the *cs* change does not seem to be related to the volume changes but more likely to an electron transfer process. Furthermore, the dcs/dT values in the troilite and MnP-NiAs phases both agree within experimental error with the second order Doppler shift slope of $-7.3*10^{-4}$ mm/sK (Cohen 1976). This also indicates that the volume changes do not significantly influence the *cs*. An electron transfer model is further supported by the change in electric conductivity along the **c**-axis being ~10^3 times larger above T_α than below (Ward 1970).

The Hyperfine Field

We obtained $T_N = 600 \pm 10$ K, in agreement with e.g. Horwood et al. (1976). Figure 4 describes a Brillouin function with $T_N = 600$ K, $S = 1/2$, and $B_{hf} = 24.1$ T at 420 K. The experimental B_{hf} values lie over the curve above 500 K, in agreement with Horita and Hirahara (1971), who applied the $S = 2$ curve. As the $S = 1/2$ curve is the most threshold shaped one, the statement holds for all Brillouin curves.

B is 4.2 T larger in troilite than in the MnP phase at 410 K. The temperature dependence of the latter changes at 380 K. These findings resemble the variation in *cs* (Fig. 5) and should then be attributed to the earlier mentioned electron transfer. The high B_{hf} value for troilite might be due to an increased Fermi contact field as a result of an increased *4s* electron density.

The Quadrupole Interaction

At 409 K the obtained $|dq|$ for troilite is 0.73 mm/s, which is ~3 times larger in magnitude than for the MnP phase. Thiel and van den Berg (1968), Horita and Hirahara (1971), and Baek et al. (1984) applied a first order perturbation theory and defined the quadrupole splitting

$$qs = 0.5((v_6 - v_5) - (v_2 - v_1))$$

or similarly (v_i etc. are the peak positions with increasing velocity in the sextet). According to this model, the *qs* change over the MnP phase-troilite transition is very small, which may give the erroneous impression that the quadrupole interaction strength *eq* does not vary.

Hafner and Kalvius (1966) compared troilite spectra with simulated full Hamiltonian ones, assuming $\eta = 0$. A possible solution was $0.5e^2qQ = -0.88$ mm/s and $\theta = 48°$

(or +0.9 mm/s and 62° "in an appreciably poorer fit") for $T<295$ K, in rather good agreement with our full Hamiltonian results. However, it is not possible to judge between the different η, θ, ϕ solutions in Table 1 as all result in identical spectra.

In the MnP-NiAs phases we found $|dq|=0.25(2)$ mm/s, where the negative solution most probably is the relevant one.

The Orientation of $\mathbf{V}_{zz}$

In the NiAs phase, and probably in the MnP phase, $\mathbf{V}_{zz} \| \mathbf{c}$ (or $\mathbf{c}^*$). For troilite at rt, two possible solutions were obtained: $dq=-0.85$ mm/s and $\theta=47°$ or $dq=+0.85$ mm/s and $\theta=57°$. Varying η yields a variation in θ-values within ~3°. The magnetic moments of the Fe-atoms are $\|\mathbf{c}$ (Horwood et al. 1976). The shortest Fe-S join is 2.36 Å at rt, making an angle of 50.8° with $\mathbf{c}$ (at ~393 K: 2.37 Å, 51.1°). This is shorter than the corresponding distance in the MnP phase, 2.46 Å at ~463 K (calculated from King and Prewitt 1982). However, the shortest Fe-Fe distances are almost equal (2.93 Å in troilite at ~393 K and 2.92 Å in MnP phase at ~463 K; King and Prewitt 1982). Thus, we find indications for a $\mathbf{V}_{zz}$ change from $\|\mathbf{c}^*$ in the MnP phase to $\|$ the shortest Fe-S join in troilite, giving $dq=-0.85$ mm/s (at 295 K) as the real solution.

Transition Temperatures vs. Composition

Both T_α and T_s are sensitive to impurities and vacancies. Baek (1986) found $T_\alpha=400$ K and $T_s=486$ K for $Fe_{0.975}V_{0.025}S$ and $T_s=200$ K for $Fe_{0.975}Co_{0.025}S$.

Horwood et al. (1976) showed T_s to be lowered with 40 K in average for every percent of Fe vacancies; T_α was also somewhat lowered. In our samples, T_α is not higher than in pure FeS (Fig. 6, heating). The cooling curve indicates T_α to be lowered due to the trace element substitution, and the transition to occur in a temperature interval due to inhomogenities. Compared to the narrow interval reported for pure FeS (Horwood et al. 1976), the presence of MnP phase at low temperatures indicates the substitution to retard the transition.

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