Phase transitions and kinetics in natural FeS measured by X-ray diffraction and Mössbauer spectroscopy at elevated temperatures

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Abstract

The effects of temperature and time on phase transitions in FeS were investigated by X-ray diffraction in the temperature range 296–573 K and by Mössbauer spectroscopy in the range 285–475 K. Natural troilite from the Agpalilik meteorite (Cape York shower), containing $\sim$0.17 wt% Cr, was used in the study. The α transition from troilite ($P\bar{6}2c$) to MnP structure ($Pnma$) occurs in an interval of at least 40 K and is complete at 413 K. No change of the NiAs-type ($P6_3/mmc$) subcell volume due to the transition could be detected. Magnetic spin flip in the MnP-type phase is time dependent, requiring several weeks at 429 K. The transition from the MnP-type phase to troilite is sluggish. The relative concentrations of the phases simultaneously present below 413 K depend on both the ambient temperature and the thermal history. Below 413 K, the transition is hampered by differing subcell volumes, causing structural incoherence that increases with the degree of undercooling. In addition, the magnetic spins in the MnP-type phase are preferentially oriented perpendicular to the necessary configuration for the transition. The two phases constitute an unstable assemblage at room temperature. The metal-metal bond strength is anisotropic and increases as temperature decreases. This may be an important factor in the crystallographic and magnetic transitions of FeS. The troilite structure probably forms along different reaction paths depending on cooling rate.

Introduction

FeS assumes different, related, temperature-dependent crystallographic and magnetic structures in which the Fe atoms occupy octahedral positions with varying degrees of distortion. At low temperatures, hexagonal troilite with space group $P\bar{6}2c$ (Evans, 1970) is stable. In this structure, which has been reported only for FeS (King and Prewitt, 1982), all Fe atoms are contained in triangular clusters of three atoms in planes perpendicular to **c**. These clusters are stacked so that half of the Fe-Fe joins along **c** are parallel and half are inclined to the **c** axis. The S atoms may be regarded as forming triangles about these Fe-Fe joins. The normals to the planes of these triangles tend to align with the Fe-Fe joins; thus, half of the planes are perpendicular to **c**, half are tilted. The structure can be derived from the NiAs structure; based on the NiAs subcell axes A and C, the troilite supercell axes are given as $a = \sqrt{3}A$ and $c = 2C$ (Hägg and Sucksdorff, 1933).

The troilite structure, including its clusters, breaks down at the α transition. On heating through T_α, troilite transforms into the orthorhombic MnP-type structure with space group $Pnma$ (King and Prewitt, 1982). Here, the Fe-Fe joins form zigzag chains and all S triangles are tilted. Various values of T_α have been given for ambient pressures: 413 K, based on electrical resistivity measurements on synthetic FeS (Ozawa and Anzai, 1966); 425

K, based on DTA of synthetic samples (Moldenhauer and Brückner, 1976); and 388–423 K, based on TEM of meteoritic troilite (Töpel-Schadt and Müller, 1982). However, Haraldsen (1941) found X-ray supercell reflections of synthetic samples to be weaker at 375 K than at 293 K. Thus, the α transition is indicated to be gradual with an onset detectable at 375 K. Using Mössbauer spectroscopy with meteoritic troilite, Kruse and Ericsson (1988) obtained a completed transition at 413 K on heating. The reverse transition started at 410 K and was not completed even after 15 d of slow cooling to 280 K, where 20% of the Fe still was included in the MnP-type structure.

Susceptibility measurements on a synthetic $Fe_{0.996}S$ single crystal (Horwood et al., 1976) showed that antiferromagnetically coupled spins of the Fe atoms point along the **c** axis of the NiAs subcell (c_{NiAs}) below the spin-flip temperature ($T_s \approx 445$ K), where the spins flipped reversibly by 90°. Values for T_s include 458 K for synthetic FeS using neutron diffraction (Andresen and Torbo, 1967) and the intervals $\sim$410–470 K (heating) and $\sim$450–360 K (cooling) for meteoritic troilite (Kruse and Ericsson, 1988); the detailed behavior depended on sample treatment.

FeS transforms into the NiAs-type structure with space group $P6_3/mmc$ at $\sim$483 K on heating (Töpel-Schadt and Müller, 1982). In that structure, the Fe-Fe joins form a straight line along **c**; all S triangle planes are perpendicular to **c**. The antiferromagnetic order in FeS breaks down into paramagnetism at $T_N \approx 600$ K (Horwood et al., 1976).

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Despite the voluminous literature on iron sulfides, quantitative information on FeS properties above room temperature is often insufficient to explain either phase stabilities or the transition mechanisms. The purpose of the present work was to investigate the effect of temperature and time on the stabilities of the different FeS phases. To ensure room-temperature equilibrium conditions in the starting material, meteoritic troilite was used.

EXPERIMENTAL DATA

Troilite was obtained from the iron meteorite Agpalilik (Cape York shower), which was discovered and collected in 1963 by Buchwald near Thule, Greenland (Buchwald, 1964). Samples were taken from a centimeter-sized troilite inclusion; oxidized parts of the small grains were carefully removed under a stereomicroscope. This same inclusion was used in a previous study (Kruse and Ericsson, 1988).

Electron microprobe analysis showed only Cr (0.17 wt%) of the probable trace elements. This is in good agreement with Kracher et al. (1977), who found ~0.13 wt% Cr and less than 0.02 wt% each of all other trace elements. Jochum et al. (1975) found Cr (~0.12 wt%), Ni (~440 ppm), and Mn (~220 ppm) in a single troilite inclusion from Agpalilik, and the average concentrations of 17 other elements were each lower than 100 ppm. The even distribution of Cr in troilite implied solid solution rather than a separate Cr-rich phase. An approximate formula for the samples used in this study is therefore $Fe_{0.997}Cr_{0.003}S$.

Cell parameters were determined by X-ray powder diffractometry in vacuum using Ni-filtered Cu radiation. The sample was ground under acetone and mixed with KCl standard; a slurry was then made with Zapon lacquer and mounted onto an electrically heated Pt sample holder fitted with a thermocouple on its bottom side. The accuracy of the temperature measurements was estimated to be ±2 K. Two X-ray scans, toward higher and lower angles, were made at each measuring temperature at a speed of $2\theta = 0.125°$/min. Peak positions were corrected using a second-degree polynomial computed for each diffractometer pattern from the expected positions of four KCl peaks (computed from Pies and Weiss, 1973).

The sample was successively heated and analyzed from 296 K to 423 K, where T_α was presumably exceeded. Cooling behavior was investigated by experiments at 403, 383, and 296 K. The sample was then kept under vacuum at 296 K for approximately one month and analyzed once more. Heating experiments were then restarted at 433 K. After the last heating experiment, at 573 K, the sample was rapidly cooled (from 573 to 296 K in 130 s) and analyzed again. No influence of oxidation was noticed during or after heating experiments.

Quantitative analyses of relative concentrations of FeS structure types and spin configurations were made using Mössbauer spectroscopy in the temperature range 285–475 K, following Kruse and Ericsson (1988). Spectra were analyzed using a computer program written by Jernberg and Sundqvist (1983). In order to monitor phase stabilities and reaction kinetics related to the α transition and spin flip, samples were kept at constant temperature and data were collected daily.

RESULTS AND DISCUSSION

Diffractometry

The untreated sample showed only troilite peaks. Beginning at 373 K, additional broad MnP-type structure reflections close to those of troilite could be observed. On continued heating, the relative intensities of the MnP peaks successively increased until, at 413 K, no troilite could be detected. After slow cooling to 296 K, both sets of reflections showed approximately equal intensities, indicating two phases in the sample. However, after rapid cooling from 573 to 296 K, the X-ray pattern was dominated by troilite peaks; MnP- or NiAs-type peaks were weak and no numerical values could be obtained. No discontinuous change in cell parameters was observed between 423 and 433 K; thus, maintaining the sample at 296 K for about one month between these two heating experiments was assumed not to have affected the results.

In the heating interval 296–393 K, only troilite peak positions were measured. MnP- and NiAs-type peaks were measured in the interval 413–573 K. For these intervals, axes determinations were made using five NiAs subcell peaks (100, 101, 102, 110, and 103). In the interval 398–409 K, strong reflections occurred for both troilite and the MnP-type phase, but owing to overlap and poor resolution, only three peaks of each phase could be measured. During cooling experiments, the 103 peak was of poor quality in some diffraction patterns, so this peak was excluded and data for only four peaks were measured.

Heating: The α transition. Heating results are compiled in Table 1. The variations of subcell dimensions a and c vs. temperature are given in Figures 1a and 1b for the temperature intervals 296–393 K and 413–573 K, respectively. A common feature for both subcell axes is a discontinuity at the α transition, with a 0.6% increase in a and a 1.2% decrease in c. Sparks et al. (1962) reported similar results (0.5% for a and 1% for c) for cooling experiments on synthetic ~FeS using neutron diffraction. The small positive slope of c vs. T in the interval 296–393 K contrasts with the X-ray investigations of Taylor (1970) and King and Prewitt (1982), who noticed a decrease in c. Taylor (1970) presented data obtained at 298 and 398 K; King and Prewitt (1982) listed cell parameters for 294 and 393 K. The higher temperatures in both studies are clearly within the range of appearance of the MnP phase. Contributions in new but overlapping reflections may therefore have been interpreted simply as shifts in the positions of the troilite peaks, thus resulting in a lower c value.

The Fe atoms in the troilite structure (Bertaut, 1956; Evans, 1970; King and Prewitt, 1982) form triangular clusters. These are due to 3d electrons forming Fe-Fe bonds when the separation between the Fe atoms is less than a critical value (Goodenough, 1962). The clustering
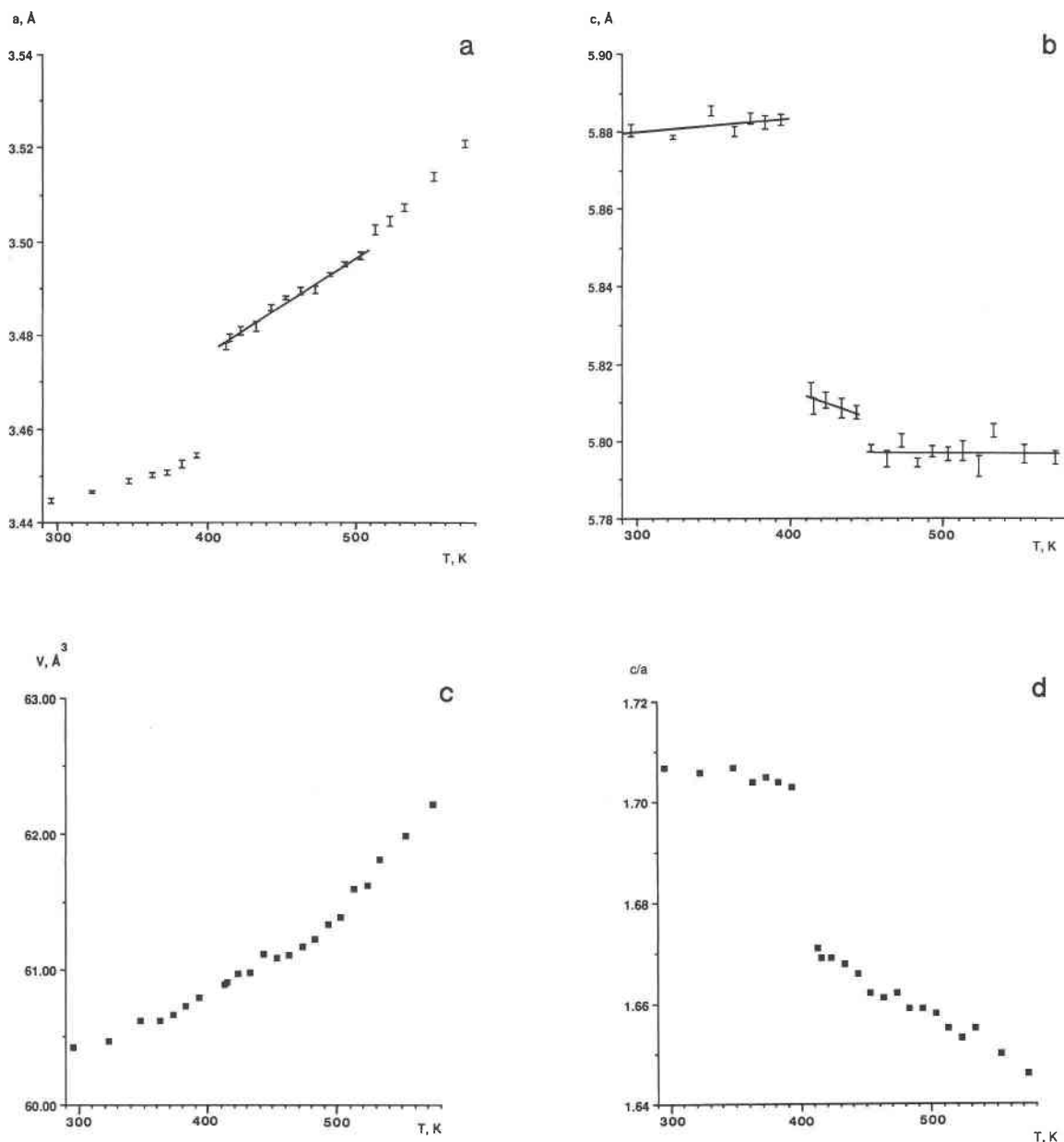
Fig. 1. Cell parameter data from heating experiments, computed from NiAs-type subcell peaks 100, 101, 102, 110, and 103. (a) Length of the a_{NiAs} axis vs. temperature. A linear least-squares fit for the interval $413 \leq T \leq 503$ K is shown ($a = 2.0448 \cdot 10^{-4} T + 3.3943$ Å). (b) Length of the c_{NiAs} axis vs. temperature. Three different linear trends are indicated. (c) Cell volume V_{NiAs} vs. temperature. (d) Axis ratio c_{NiAs}/a_{NiAs} vs. temperature.

corresponds to a contraction in planes perpendicular to **c**, i.e., along the **a** axes. Clusters break down at the α transition, and the resultant outward movement of Fe atoms is expressed in the discontinuous expansion of the **a** axis, which enables the **c** axis to contract simultaneously. According to Taylor (1970), the NiAs-type cell volume (V_{NiAs}) abruptly increases by 0.43 Å³ on heating through T_α. King and Prewitt (1982) reported a decrease in V_{NiAs} values on heating, from 60.83 Å³ at 393 K to

60.60 Å³ at 463 K. In the present investigation, no difference in V_{NiAs} due to the transition could be observed (Fig. 1c). The axis lengths of the present study and the positional parameters of King and Prewitt (troilite structure at 294 K) give a critical Fe-Fe distance of ~2.93 Å (at 393 K) for the rupture of clusters.

The MnP-NiAs type structure transition. The near-linear *a* vs. *T* distribution between 413 and 503 K is separated by a small discontinuity from a nonlinear relation-
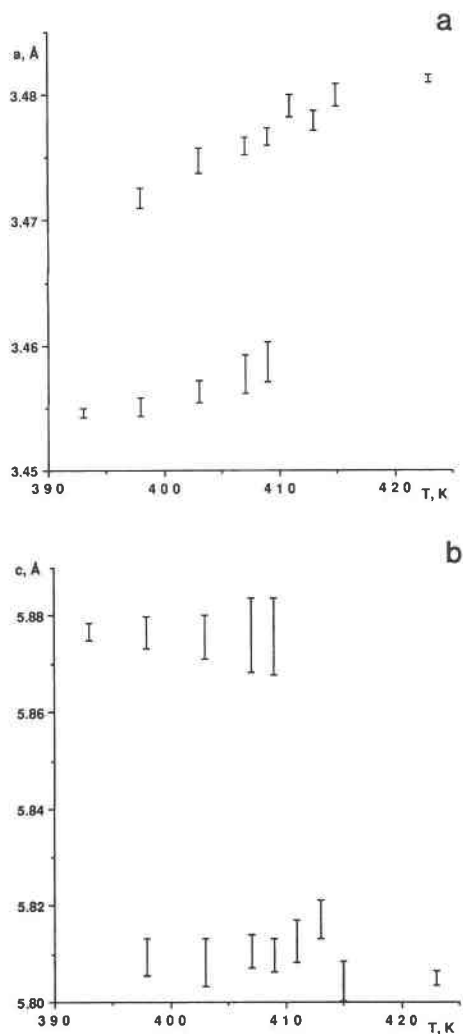
Fig. 2. Cell parameters for troilite and the MnP-type phase simultaneously present in the sample. Computed from heating experiments using NiAs-type subcell peaks 100, 102, and 110. (a) Lengths of a_{NiAs} vs. temperature; smaller values represent troilite. (b) Lengths of c_{NiAs} vs. temperature; larger values represent troilite.

TABLE 1. Compilation of heating experiment measurements

Temperature (K)	a (Å)	c (Å)	V (Å^3)	c/a
296	3.4447(6)	5.8804(16)	60.427	1.707
323	3.4465(2)	5.8785(5)	60.471	1.706
348	3.4488(5)	5.8854(13)	60.623	1.707
363	3.4503(5)	5.8800(12)	60.622	1.704
373	3.4507(6)	5.8834(15)	60.671	1.705
383	3.4526(7)	5.8825(18)	60.728	1.704
393	3.4543(5)	5.8830(14)	60.793	1.703
413	3.4778(8)	5.8131(19)	60.890	1.671
415	3.4795(8)	5.8089(20)	60.906	1.669
423	3.4809(9)	5.8105(21)	60.971	1.669
433	3.4819(10)	5.8085(24)	60.985	1.668
443	3.4859(7)	5.8073(18)	61.115	1.666
453	3.4880(4)	5.7981(9)	61.091	1.662
463	3.4894(8)	5.7953(20)	61.109	1.661
473	3.4897(7)	5.8002(17)	61.172	1.662
483	3.4929(4)	5.7944(10)	61.221	1.659
493	3.4952(6)	5.7973(15)	61.333	1.659
503	3.4970(8)	5.7966(18)	61.388	1.658
513	3.5026(11)	5.7975(26)	61.595	1.655
523	3.5044(11)	5.7935(26)	61.618	1.653
533	3.5072(8)	5.8027(18)	61.814	1.655
553	3.5140(10)	5.7966(23)	61.988	1.650
573	3.5209(8)	5.7957(18)	62.224	1.646

Note: Cell parameters are given for the NiAs-type subcell. Peaks 100, 101, 102, 110, and 103 were measured twice at each temperature.

ship at higher temperatures. Horita and Hirahara (1971) conducted Mössbauer spectroscopy on single-crystal synthetic FeS and reported deviations of the measured hyperfine magnetic field, B_{hf}, from an associated Brillouin function above 500 K. Kruse and Ericsson (1988) reported similar results. Andresen (1960), using neutron diffraction and synthetic FeS, showed a corresponding deviation below 500 K. These deviations may indicate a phase transition close to 500 K. The MnP-NiAs type structure transition temperature of 483 K reported by Töpel-Schadt and Müller (1982) was described as imprecise. King and Prewitt (1982) reported an MnP-NiAs type transition temperature of 490 ± 20 K. The small discontinuity at ~508 K (Fig. 1a) is therefore inferred to represent a first-order MnP-NiAs type transition. King and

Prewitt (1982) proposed that it is second order; however, since the discontinuity is small, it could escape detection. This suggests that claims of the second-order nature of the MnP-NiAs type transition for several substances based on sparse data (Selte and Kjekshus, 1973) may be in error.

Spin orientation and c. A discontinuity at ~450 K separates two linear trends of c vs. T (Fig. 1b). Sparks et al. (1962) reported spin flips in the interval 458–433 K on cooling and a c vs. T plot similar to Figure 1b. In the range 413–443 K, where the c vs. T slope is negative, Kruse and Ericsson (1988) noticed spin flips on heating. Thus, the spin reorientation is implied to be coupled to changes in c. The repulsion along c_{NiAs} between the antiferromagnetically coupled Fe atoms, due to the spin orientation parallel to c_{NiAs}, is lost as the spins flip 90° on heating. The gradual increase in concentration of spins perpendicular to c_{NiAs} would correspond to a decrease in c. In a series of measurements with a rate of temperature increase approximately the same as in the present investigation, ~97% of the spins had flipped at 450 K (Kruse and Ericsson, unpublished data). The discontinuity in c vs. T at ~450 K and the saturation behavior on further heating can therefore be assumed to mark the completion of the magnetic rearrangement. The coupling between magnetic ordering and c for NiAs-related compounds has also been mentioned by Kamimura (1988).

Bond relations. The behavior of V_{NiAs} with temperature differs considerably for the different phases involved (Fig. 1c). Troilite and the MnP-type phase expand at a much lower rate during heating compared with the NiAs-type phase. The larger influence of metal-metal bonding in
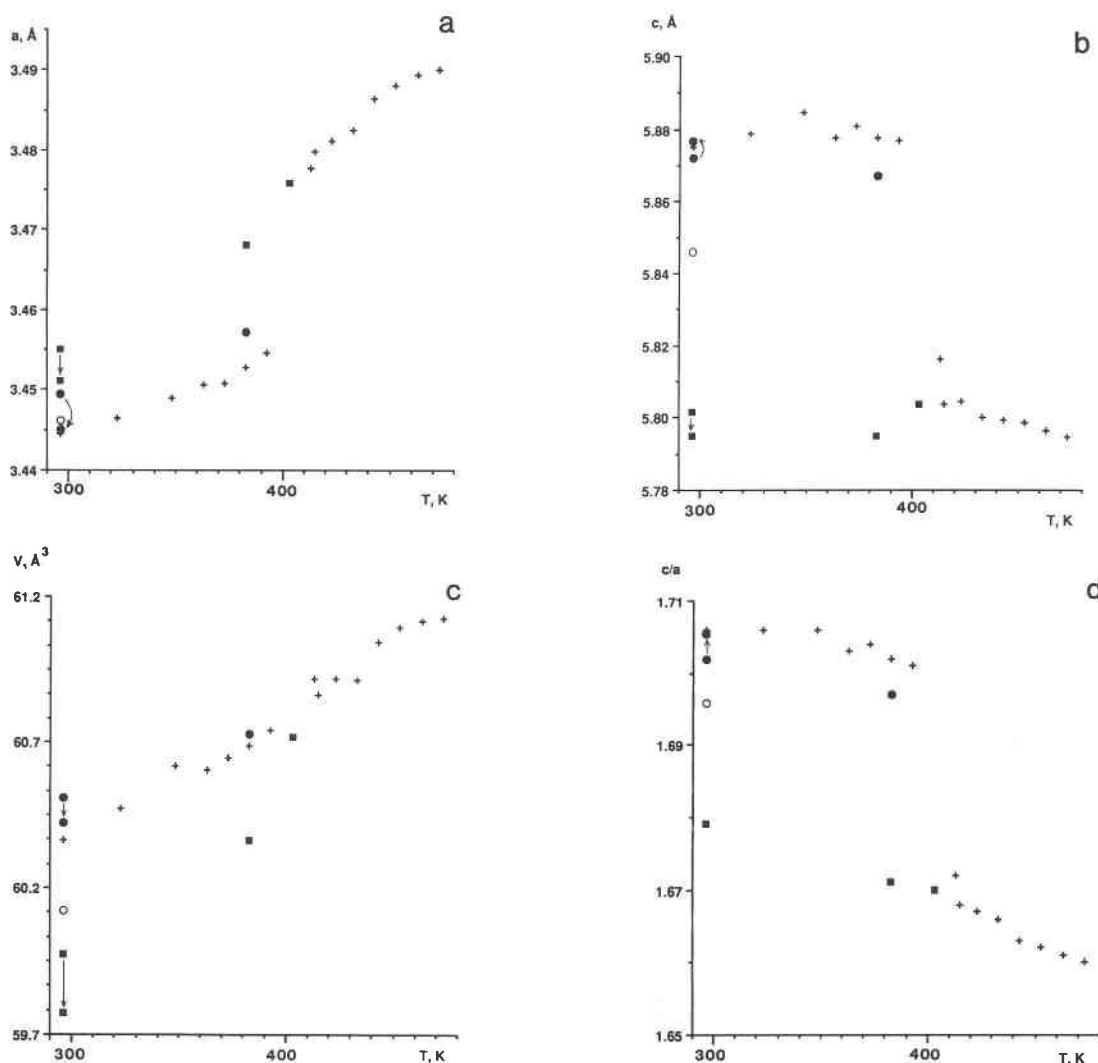
Fig. 3. Effect of sample treatment on cell parameters. Heating experiments = crosses; MnP-type phase during slow cooling and storing at 296 K = closed squares; troilite during slow cooling and storing at 296 K = closed circles; troilite after rapid cooling = open circles. Arrows indicate changes during about one month at 296 K. Computed from NiAs-type subcell peaks 100, 101, 102, and 110. (a) Length of a_{NiAs} vs. temperature. (b) Length of c_{NiAs} vs. temperature. (c) Cell volumes V_{NiAs} vs. temperature. (d) Axis ratio c_{NiAs}/a_{NiAs} vs. temperature.

MnP-type vs. NiAs-type phases (Selte and Kjekshus, 1973) and the strong cluster bonding in troilite thus appear to dampen the thermal expansion. Toward lower temperatures, the c/a ratio (Fig. 1d) shows a successively larger deviation from the value 1.63, which represents an unstrained symmetrical octahedral site. This implies an overall increase in the Fe-Fe bond strength in planes perpendicular to c_{NiAs}, thus forcing c_{NiAs} to expand. Spin alignment along c_{NiAs} during cooling may also result from contraction in the **a-a** plane. Vacancies in Fe positions would weaken the overall Fe-Fe bonding strength, and therefore lower temperatures would be required to achieve the bond strengths needed for spin flips and the α transition. This is consistent with the results of Horwood et al. (1976), for example.

Simultaneous measurements on both troilite and the MnP-type phase during heating in the interval 393–423 K confirm the discontinuous nature of changes in a and c at the α transition (Fig. 2). Between 296 and 409 K the thermal expansion of a in troilite increases with temperature, indicating a successive weakening of the Fe-Fe bonds (Figs. 1a, 2a), whereas c is almost constant (Figs. 1b, 2b).

Cooling: Phase behavior. Cell parameters during heating, slow cooling, and rapid cooling in the interval 296–473 K are compared in Figures 3a–3d. Measurements for troilite that was slowly cooled to 296 K gave an a value somewhat larger than that of the untreated sample. During about one month at 296 K, this value decreased and approached the starting value, whereas c showed a small
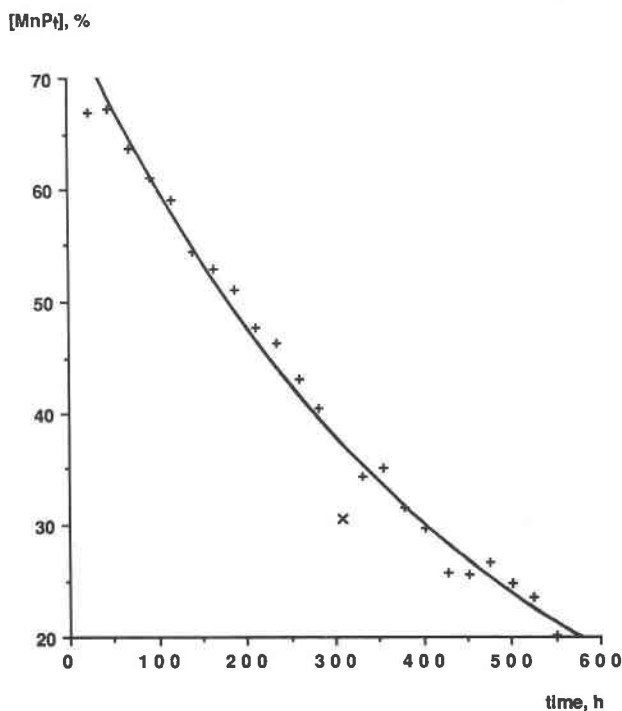
[MnP↑], %

Fig. 4. Concentration of the MnP-type phase with $\mathbf{B}_{hf} \parallel \mathbf{c}_{NiAs}$ ([MnP↑]) vs. time at 429 K. An exponential best fit, [MnP↑] = 75.7 $e^{-0.0023t}$, has a correlation coefficient $R = 0.99$. X indicates a datum not included in the best fit.

TABLE 2. Heating histories and relative intensities of subspectra for three Mössbauer experiment series

T (K)	T_p (K)	t, T_p (h)	[tr] (%)	[MnP↑] (%)	[MnP→] (%)
296			100	0	0
~408			92	3	5[A]
410	417	~0.2	89	6	5
298	429	550	82	5	13
424			0	65	35[B]
401	424	23	90	5	6[C]
434			0	43	57[D]
400	434	168	74	~6	~20[E]
285	400	471	90	3	7[F]
421			0	66	34[G]
407	422	116	72	17	11[H]
475			0	0	100[I]
407	475	45	5	67	27
407	475	45	6	67	27
407	475	45	10	63	27
397	~473	~10	84	10	6
399	~473	~10	87	8	6
375	~473	~3	95	2	3[J]

Note: Elapsed time increases downward within each series. Abbreviations: T = measuring temperature; T_p = previous higher heating temperature; t, T_p = time spent by the sample at T_p; [tr] = concentration of troilite; [MnP↑] = concentration of MnP-type phase with magnetic spins $\parallel \mathbf{c}_{NiAs}$; [MnP→] = concentration of MnP phase with spins $\perp \mathbf{c}_{NiAs}$.
[A] Stable during 138 h (six spectra).
[B] After 23 h.
[C] Stable during 146 h (five spectra).
[D] After 168 h.
[E] Concentration of troilite stable during 471 h (14 spectra), small decrease in [MnP↑].
[F] Stable during 212 h (four spectra).
[G] After 116 h.
[H] Stable during 69 h (three spectra).
[I] After 22 h.
[J] Stable during 117 h (four spectra).

increase. The value of V_{NiAs} decreased, approaching the starting value. The slowly cooled troilite phase was therefore not equilibrated, with bonds in the **a-a** plane still being formed or strengthened, forcing the **c**-axis to expand.

During slow cooling and subsequent maintenance of the sample at 296 K, the a value of the MnP-type phase approached that of troilite, whereas c remained close to the value present above T_α. The value of V_{NiAs} is thus smaller for the MnP-type phase than for troilite below 413 K and continues to decrease at 296 K. The value of ΔV_{NiAs} between the phases may induce a structural misfit, making the transition from the MnP-type phase to troilite successively more difficult as the temperature decreases.

The paradox of a larger concentration of troilite after rapid cooling than after slow cooling indicates a direct NiAs-type phase → troilite transition mechanism in addition to the NiAs → MnP → troilite path. An NiAs → MnP-type transition requires the tilting of every S triangle and Fe-Fe join along **c**, whereas an NiAs → troilite transition only requires tilting of every second S triangle and every second Fe-Fe join along **c**. FeS rapidly cooled into the troilite stability range would therefore avoid the intermediate MnP-type phase.

Mössbauer spectroscopy

Spin-flip kinetics. The reorientation of spins from parallel to perpendicular to $\mathbf{c}_{NiAs}$ (i.e., the MnP↑ and MnP→ configurations, respectively) could be observed as a shift in intensities of subspectra within the MnP-type spectrum above 413 K. In fitting spectra, intensities were free parameters; half-widths, centroid shifts, and B_{hf} were constrained to the same values for both subspectra. The quadrupole splitting values were fixed to -0.25 mm/s, following Kruse and Ericsson (1988), and θ (i.e., here the angle between B_{hf} and $\mathbf{c}_{NiAs}$) to 0° and 90° (Horwood et al., 1976). The intensity of the MnP↑ subspectrum (i.e., [MnP↑]) with time over 550 h (22 spectra) at ~429 K is given in Figure 4. An exponential best fit with a correlation coefficient $R = 0.99$ was obtained. Using a second isothermal series (five spectra, 434 K, 168 h, $R = 0.97$), the rate coefficients k (given by [MnP↑] = [MnP↑]$_0$ e^{-kt}, where [MnP↑]$_0$ is the initial concentration) were used to compute the preexponent A and the activation energy E_a in the Arrhenius equation $k = A\, e^{-E_a/RT}$. Values of $A = 0.004$/h and $E_a = 2$ kJ/mol were calculated.

Troilite-MnP type phase transitions. Troilite and the MnP-type phases exhibit distinctly different Mössbauer subspectra. As the troilite structure is not present above 413 K for the Agpalilik sample, phase transitions had to be studied below 413 K. Table 2 lists relative intensities of subspectra for different heating histories.

The original samples do not show any signs of the MnP-type phase at room temperature. At higher temperatures

but below 413 K, the MnP-type phase appears in apparently stable concentrations (e.g., 408-K experiment, top series in Table 2). Samples heated above 413 K and subsequently used in measurements below this temperature contain varying concentrations of the MnP-type phase depending on the previous heating temperature. The ~400-K experiments (middle series) show considerably higher contents of the MnP-type phase after heating at 434 K than after heating at 424 K (26% vs. 11%). Corresponding values for the 407-K experiments (bottom series) are 94% vs. 28% for preheating at 475 and 422 K, respectively. As troilite is not present at these temperatures, the differences must be due to some process affecting the the MnP-type phase only.

A comparison of the intensity of the MnP→ subspectra with that of troilite subspectra measured at lower temperatures shows that a higher MnP→ value decreases the subsequent troilite intensity. For example, 90% of troilite follows 35% of MnP→ in the 401-K experiment (middle series), 74% follows 57% in the 400-K experiment (middle series), 72% follows 34% in the 407-K experiment after preheating at 422 K (bottom series), and 5% follows 100% (407-K experiment after 475 K, bottom series). Because spins remain parallel to c_{NiAs} during the troilite → MnP-type phase transition (Horwood et al., 1976), it is likely that the reverse transition requires this spin orientation. Any transition between MnP→ and troilite would hence have to go through MnP↑. A decrease in [MnP↑] with time can be detected at 400 K (middle series) and at 407 and 397–399 K (bottom series), here simultaneously with an increase in troilite concentration. The spin flip begins below 413 K (408-K experiment; top series), the MnP→ configuration probably being energetically more favorable (see preceding section). This configuration would therefore act as a sink, retarding the transition from the MnP-type phase to troilite. The lack of reversibility may partly explain the hysteresis effect at the α transition as shown by (for example) the higher troilite concentration at 408 K on heating (top series) compared with the lower troilite concentration at 400 K on cooling (middle series), despite the lower temperature in the latter case.

The decrease in c for the MnP-type phase between 403 and 383 K (Fig. 3b) is consistent with a relative decrease in [MnP↑]. If this spin orientation is required for the transition to troilite, the relative [MnP→] would increase during the transition and result in a smaller value of c. The apparently stable troilite concentration at 400 K (74%, middle series) and the differing troilite concentration at 407 K (5–10%) and 397 K (84%) after preheating to ~474 K in both cases (lower series) indicate that a certain degree of undercooling is needed for the transition of the MnP-type phase to troilite.

Comparison of troilite and the MnP-type phase. The Mössbauer isomer shift (IS) of the MnP-type phase is larger than that of troilite above T_α but smaller when the phases are simultaneously present in a sample at lower temperatures (Kruse and Ericsson, 1988); the authors proposed an electron transfer process to account for this difference. The absence of a ΔV_{NiAs} due to the α transition

supports this proposal. On formation of troilite type clusters in FeS, one paired 3d electron per Fe atom is delocalized (Goodenough, 1978). The reduction in 3d electron density would reduce shielding of 3s electrons and decrease the IS at the MnP-type phase–troilite transition. The higher d electron density in the MnP-type phase may facilitate bonding interaction along c_{NiAs} and account for its smaller length. The smaller V_{NiAs} for the MnP-type phase would thus lead to a lower IS than for troilite. The small V_{NiAs} decrease in troilite at 296 K after slow cooling is accompanied by a small increase in c/a, whereas the MnP-type phase shows a larger V_{NiAs} decrease but no c/a variation. The bond strength in the MnP-type phase thus appears to be more isotropic than in troilite.

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