On the Phase Relations of Synthetic and Natural Pyrrhotites (Fe$_{1-x}$S)

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Natural and synthetic pyrrhotites (Fe$_{1-x}$S) are distinguished by a rather large variation of the iron to sulfur ratio. Hägg and Sucksdorff[1] found that the sulfur excess causes vacant iron positions in the B-8 (NiAs) structure rather than substitution of sulfur for iron. They also found the existence of a superstructure from the stoichiometric composition FeS to Fe$_{0.953}$S (51.2 atomic per cent S). In preparations quenched from 650° C the phase of the B-8 (NiAs) structure type was observed to exist in the composition range Fe$_{0.938}$S-Fe$_{0.802}$S (51.6 to 55.5 atomic per cent S). Later, synthetic pyrrhotites have been subjected by Roberts[2] to thermal analysis and by Haraldsen[3-5] to X-ray and magnetic studies. Neither Hägg and Sucksdorff[1] nor Haraldsen[4,5] found any phases with other structures than the superstructure (B-8 like) and the ordinary B-8 structure. Roberts[2] mentioned, however, that he observed signs of slow structural changes from his exploratory X-ray photographs.

According to Haraldsen[5], a survey diagram as shown on Fig. 1 can be drawn concerning the transformations in pyrrhotites. The heavy lines indicate the temperatures where abrupt changes in the lattice constants and magnetic susceptibility take place. The β-transformation at 325° C is common to all pyrrhotites and likewise the α-transformation which takes place at 138° C in FeS. The α-transformation temperature is lowered with increasing sulfur content and the transformation finally becomes very sluggish. In addition, two other lines are drawn indicating transformations which vary with the sulfur content. The line starting at 150° C and 51.5 atomic per cent sulfur indicates the γ-maximum of a sudden increase in magnetic susceptibility. The preparations on the right side of the dotted line at 52.4 atomic per cent sulfur are ferromagnetic. Roberts[2] expressed the opinion that an additional transformation takes place in synthetic pyrrhotites between 325° and 550° C.
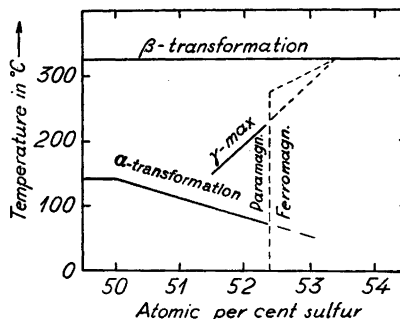
Fig. 1. Temperatures where magnetic effects
    take place in synthetic pyrrhotites.

Byström [6] investigated Swedish pyrrhotites by means of X-rays with the interesting result that many of them displayed a monoclinic structure while only a few of them had hexagonal structure. Others again contained a mixture of these two structures. Chemical analyses gave no connection between the sulfur content and the symmetry, and Byström suggested that the change in structure was due to a polymorphous transformation.

Buerger [7] investigated single crystals of ferromagnetic pyrrhotites from two different localities by the precession method [8]. Both crystals revealed the same hexagonal superstructure characteristics and the one from Schneeberg, Saxony, was found to have the following cell dimensions *:

$$A = 2a = 6.87 \text{ Å} \qquad\qquad C = 4c = 22.7 \text{ Å}$$

The a-axes are two, the c-axis four times greater than of pyrrhotites having the ordinary B-8 structure. The cell dimensions of this superstructure have no connection with those observed by Hägg and Sucksdorff and the phase is furthermore ferromagnetic instead of paramagnetic. Buerger states, however, that there are also some indications present that the two pyrrhotites possess either a lower hexagonal symmetry or even an orthorhombic or monoclinic symmetry. The latter possibility would agree with the results obtained by Byström.

Another new superstructure with $A' = 3a$ and $C' = 2c$ has been found by Graham [9] in single crystals of paramagnetic pyrrhotites which were formed by the action of a sodium sulfide solution on the walls of a steel bomb held at 400° C and about 1 200 bars.

Our investigation was performed in order to find out if the phases with monoclinic structure and superstructures reported to exist in natural pyrrhotites also had ranges of stability in pyrrhotites synthesized by dry methods. In addition, some Norwegian pyrrhotites were studied.

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* Lattice constants taken from earlier investigations have been transformed from kX units to Å units by multiplication with the factor 1.00202.

The present investigation has confirmed many of the results obtained earlier. Thanks to the good X-ray equipment now at our disposal, the range of existence of the superstructure, detected by Hägg and Sucksdorff, and of the B-8 structure, could be determined more accurately. Furthermore, it was possible to ascertain that the iron sulfide phase with monoclinic structure is stable at temperatures below 325° C and has a higher sulfur content than the phase with B-8 structure which is stable in the same temperature region.

PREPARATION OF THE ALLOYS

The iron used for making the alloys was prepared from Fe_2O_3, Merck "Ferrum oxyda-tum sec. L. Brandt" by reduction with dry, purified hydrogen gas. The sulfur used had been prepared by Haraldsen[3] from sulfur c.p. by repeated vacuum distillations. The pyrrhotites were synthesized by weighing the amounts of iron and sulfur calculated for the different compositions into silica tubes which were then evacuated and sealed off. Each sample weighed approximately one gram.

After being heated at 1 000° C for 24 hours, the preparations were slowly cooled down in the furnace, then ground and homogenized at 290° C. This temperature was chosen in order to be well below the 325° C transformation. A regulator kept the furnace tempera-ture constant to ± 3° C. After annealing for 40 days, the preparations were quenched by dropping them into ice water.

INVESTIGATION OF THE PYRRHOTITES

A. X-r a y   t e c h n i q u e

X-ray photographs of the synthetic pyrrhotites were taken in a Unicam 19 cm dia-meter high temperature camera using an air-cooled X-ray tube with Fe anode of a Philips Geiger Counter Spectrometer. The exposure time was 20 hours at 36 kVp and 6 mA. The derived lattice constants are expressed in Å units using $\lambda = 1.935\ 97$ Å as the wavelength of $FeK\alpha_1$ radiation. The absolute errors in our lattice dimensions are less than ± 0.001 Å for values given to the fourth decimal and less than one part in two thousand when three decimals are given.

A series of room photographs were also taken of freshly annealed parts of the sample earlier prepared by Haraldsen. A cylindrical 11.4 cm diameter powder camera was used, and with the Fe-K radiation from a Siemens tube, the exposure time was 3 hours at 37 kVp and 8 mA. Powder photographs of the pyrrhotite minerals were taken in a Philips 11.48_3 cm camera utilizing the Straumanis technique of film mounting.

B. S y n t h e t i c   p y r r h o t i t e s

The composition and lattice constants of the new preparations, investigated at room temperature (15—20° C) in the Unicam camera, are listed in Table 1. The lattice constant values in parentheses are arranged to bring out the orthohexagonal cell dimensions.

Table 1. Lattice constants in Å units of synthetic pyrrhotites at room temperature.

Composition	$a, (b\sqrt{3})$	$b, \left(\dfrac{a}{3}\sqrt{3}\right)$	c	β
$Fe_{1.020}S$	5.963_6	(3.443_1)	$2 \times 5.874_5$	
$Fe_{1.000}S$	5.965_9	(3.444_4)	$2 \times 5.879_1$	
$Fe_{0.971}S$	$\begin{cases} 5.969_7 \\ (5.969_7) \end{cases}$	$\begin{matrix}(3.446_6) \\ 3.446_6\end{matrix}$	$\begin{matrix}2 \times 5.882_3 \\ 6.761_2\end{matrix}$	
$Fe_{0.943}S$	(5.972_5)	3.448_2	5.760_4	
$Fe_{0.926}S$	(5.975_2)	3.449_8	5.751_4	
$Fe_{0.909}S$	(5.969_0)	3.446_2	5.736_9	
$Fe_{0.893}S$	(5.959_8)	3.440_9	5.720_2	
$Fe_{0.877}S$	5.952	3.433	5.690	90.4
$Fe_{0.833}S$	5.951	3.435	5.692	90.4

$Fe_{1.000}S$. In accordance with earlier results, the X-ray photograph of this preparation shows "superstructure" interferences. Hägg and Sucksdorff[1] derived the superstructure from the B-8 (NiAs) structure by 90° rotation in the basal plane, multiplication of the a-axis by $\sqrt{3}$, and doubling of the c-axis. Our values for the lattice constants are in good accord both with the results of Hägg and Sucksdorff[1], ($a = 5.958$ Å, $c = 11.74$ Å) and with those of Haraldsen[4], (mean values: $a = 5.97$ Å, $c = 11.76$ Å).

$Fe_{0.971}S$. This composition should lie in the range between that of the superstructure and the B-8 structure. Hägg and Sucksdorff were of the opinion that the transition between these structures was continuous while Haraldsen observed a sharp break in the lattice dimension curves at $Fe_{0.962}S$ (51.0 atomic per cent S) and therefore concluded a two phase transition. The photograph of our annealed $Fe_{0.971}S$ preparation, clearly reveals that two phases are present, the superstructure phase and a phase richer in sulfur with B-8 structure. The $Fe_{0.971}S$ preparation contains considerable amounts of the phase with B-8 structure. On the other hand Haraldsen[3,4] found that the preparations $Fe_{1.020}S$ and $Fe_{1.010}S$ belong to the two phase region iron/FeS. Thus the existence of the superstructure phase is evidently connected with the stoichiometric composition FeS.

$Fe_{0.943}S$. This preparation gives the interferences from a structure of the B-8 (NiAs) type. In addition the two strongest interferences from the superstructure phase are observed, and $Fe_{0.943}S$ is therefore a two phase preparation just as $Fe_{0.971}S$. In accordance with this, the lattice constants of $Fe_{0.971}S$ and $Fe_{0.943}S$ are found practically unchanged.

$Fe_{0.926}S$ to $Fe_{0.893}S$. In this concentration range the lattice constants show a considerable variation and a range of homogeneity no doubt exists. The

preparation $Fe_{0.893}S$ seems, however, to lie in a two phase region as it contains the strongest interferences of the preparation $Fe_{0.877}S$ richer in sulfur. The phase with B-8 structure should accordingly have a range of homogeneity between say $Fe_{0.935}S$ and $Fe_{0.900}S$ (51.7 to 52.6 atomic per cent S) *.

$Fe_{0.877}S$ to $Fe_{0.833}S$. At the composition $Fe_{0.877}S$ a marked change is observed on the photographs. Some previous interferences are split up into two or more components in a manner which is characteristic of a change to lower symmetry. It was a deformation just of this kind which Byström[6] observed on some pyrrhotite minerals. Such a low symmetric — possibly monoclinic — pyrrhotite structure has, however, not earlier been found in synthetic preparations and we suppose that annealing below the 325° C transformation temperature is essential for its formation.

Phases with B-8 like structures of low symmetry have been observed in many of the systems of transition elements with the chalcogens (S, Se, Te). In the system iron-selenium ** Hägg and Kindström[10] suggested a monoclinic indexing of the low symmetric structure. Until single crystal studies can be made on synthetic pyrrhotites we follow the scheme of Hägg and Kindström when indexing the interferences from the low symmetric structure.

No differences in the lattice constants are found which indicate a range of homogeneity between $Fe_{0.877}S$ and $Fe_{0.833}S$. In addition, FeS_2 (pyrite) interferences also show up on the $Fe_{0.833}S$ preparation. The monoclinic phase should therefore have a composition close to $Fe_{0.877}S$ and the phase can be designated as Fe_7S_8.

As already mentioned, a series of synthetic pyrrhotites, previously prepared by one of us, were studied at room temperature with X-rays. The composition, heat treatment and lattice constants of these preparations are listed in Table 2. By comparing the results in Tables 1 and 2, the agreement is seen to be very good. It is of special interest to note that also the 16 year old $Fe_{0.971}S$ preparation is found to consist of two phases after annealing. Furthermore, the deformation into lower symmetry has taken place in the $Fe_{0.870}S$ and the $Fe_{0.833}S$ preparations.

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* Whether or not a range of homogeneity exists at room temperature it cannot be concluded from the quenched preparations.

** Hägg and Kindström found that the phase with B-8 like structure has a range of homogeneity between $Fe_{1.000}Se$ and $Fe_{0.739}Se$. According to our results, not yet published, this is only the case at higher temperatures. At lower temperatures there exist two separate phases with low symmetric B-8 like structures, one at the composition $Fe_{0.870}S$ with no appreciable range of homogeneity, the other with a composition between $Fe_{0.800}Se$ and $Fe_{0.750}Se$. The structure of the former phase is very similar to that of $Fe_{0.877}S$. A phase with ordinary B-8 structure does not exist at room temperature in the system iron-selenium.

Table 2. Lattice constants in Å units of the previous preparations after annealing.

| Composition | Heat-treatment | | $a, (b\sqrt{3})$ | $b, \left(\dfrac{a}{3}\sqrt{3}\right)$ | c | β |
	C°	days				
$Fe_{1.000}S$	300	30	5.967	(3.445)	2×5.873	
$Fe_{0.971}S$	290	40	{ 5.967 (5.967)	(3.445) 3.445	2×5.871 5.752	
$Fe_{0.952}S$	300	30	(5.974)	3.449	5.780	
$Fe_{0.926}S$	290	40	(5.977)	3.451	5.760	
$Fe_{0.909}S$	300	30	(5.970)	3.447	5.738	
$Fe_{0.893}S$	290	40	(5.960)	3.441	5.721	
$Fe_{0.870}S$	300	30	5.962	3.442	5.714	90.3°
$Fe_{0.833}S$	290	40	5.953	3.438	5.702	90.4°

The existence of the phase with ordinary B-8 structure is by the present investigation found to be restricted to the narrow composition range between $Fe_{0.935}S$ and $Fe_{0.900}S$. High temperature thermal analysis carried out by Jensen [11] showed that congruent melting took place only in synthetic pyrrhotites at the composition $Fe_{0.926}S$, while FeS was found to melt over a temperature range of nearly 100° C. The only solid pyrrhotite with a definite melting point therefore has a composition within the range of homogeneity of the phase with plain B-8 structure at low temperature.

As a result of our X-ray investigation of annealed, synthetic pyrrhotites these phases were found:

1. A phase with superstructure (B-8 like) at the stoichiometric composition $Fe_{1.000}S$.
2. A phase with B-8 structure in the composition range $Fe_{0.935}S$ to $Fe_{0.900}S$.
3. A phase with structure of low symmetry and a composition close to $Fe_{0.877}S$ or Fe_7S_8.

C. Natural pyrrhotites

The pyrrhotites found in nature are of terrestrial and meteoritic origin. The terrestrial pyrrhotites generally have sulfur in excess of the stoichiometric composition and also ferromagnetic properties. Most formulas range between $Fe_{16}S_{17}$ and Fe_5S_6 (51.52 to 54.55 atomic per cent S), see *e.g.* Henglein [12]. The meteoritic types are designated as troilite and have usually compositions close to the stoichiometric ratio. Terrestrial pyrrhotites are, however, not always richer in sulfur than the meteoritic. Eakle [13] analyzed a terrestrial pyrrhotite from Del Norte County in California and reported stoichiometric

composition. On the other hand, a compilation of 31 "troilite" analyses by Buddhue [14] showed that 7—8 % of the meteoritic pyrrhotites had a sulfur excess corresponding to that of ordinary terrestrial pyrrhotites.

Norwegian pyrrhotites were placed at our disposal by the Mineralogical-Geological Museum of the University in Oslo and we should like to express our appreciation to Professor Ivar Oftedal for careful selection of the specimens. Chemical analyses were carried out on four of these pyrrhotites. The sulfur was determined by weight as $BaSO_4$, the iron as Fe_2O_3. Cobalt and nickel, if present, were precipitated and ignited with the iron. Our best thanks are due to mag. scient. Astri Tønsager for carrying out the analyses. The results are listed in Table 3 together with a spectrographic search for other elements,

Table 3. Analyses of four Norwegian pyrrhotites.

Locality	Bø, Valle Setesdal	Setregruben Østfold	Åmdal Froland	Herzog Friedrich Grube, Kongsberg
Fe	61.79 61.90	61.60 61.54	61.02 60.75	59.84 59.82
S	38.43 38.06	38.64 38.41	39.11 39.14	39.50 39.59
Insol. (Ag)	—	—	—	0.55
Sum	100.22 99.96	100.24 99.95	100.13 99.89	99.89 99.96
Formula	$Fe_{0.928}S$	$Fe_{0.916}S$	$Fe_{0.893}S$	$Fe_{0.869}S$
Ferromagnetic properties	V. weak	Weak	Medium	Strong
Spectrographic analysis	0.1 Ni 0.1 Cu	0.1 Co 0.1 Ni 0.1 Cu	0.2—0.3 Co 0.1 Ni 0.2—0.3 Cu	0.2 Co <0.1 Ni <0.5 Cu

kindly carried out by Ing. S. Rutlin, Statens Råstofflaboratorium, Oslo. By a qualitative magnetic test the ferromagnetic properties of the minerals were found to increase with increasing sulfur content. This is in accordance with the results of Haraldsen [3] on synthetic preparations, and those of Juza and Biltz [15] on decomposed pyrite.

The following pyrrhotites were investigated by X-rays and the lattice constants found are listed in Table 4.

1. *Bø, Valle in Setesdal.* The X-ray photograph of this specimen contains interferences from the hexagonal B-8 structure only.

2. *Setregruben, Østfold.* A slight decrease in lattice constants is observed and the specimen is distinctly more ferromagnetic than No. 1.

3. *Åmdal, Froland.* In addition to the interferences caused by the hexagonal structure, the photograph also contains interferences from the low symmetric structure. The presence of a phase with this structure makes the mineral more magnetic than No. 2.

4. *Kongens Grube, Kongsberg.* A powdered crystal, of which we have no analysis, gave a photograph showing the presence of both the hexagonal phase and that of low symmetry.

5. *Herzog Friedrich Grube, Kongsberg.* The hexagonal phase has disappeared and only interferences from the monoclinic phase are visible on the photographs. This mineral has the highest sulfur content and has also the strongest ferromagnetic properties.

Weissenberg photographs have been taken of some small pyrrhotite crystals from Kongsberg, deposited on silver threads. The crystals were hexagonal and showed no superstructure interferences that could indicate a larger elementary cell than that found for the B-8 type.

The lattice constants found for the Norwegian pyrrhotites agree very well with those found for the synthetic preparations. By comparing the values in Tables 1 and 4 for the B-8 structure, the c-axis is, however, seen to vary less with the sulfur content for the minerals than for the synthetic samples. The homogeneity range of the hexagonal pyrrhotite minerals therefore seems to be narrower than found for the synthetic preparations. Disregarding the differences in formation between the natural and the synthetic pyrrhotites, this might be explained by the fact that the minerals are probably closer to thermodynamic equilibrium at "room temperature" than the synthetic preparations.

Table 4. *Lattice constants in Å units of some Norwegian pyrrhotites.*

Locality	$a, (b \sqrt{3})$	b	c	β
Bø, Valle Setesdal	(5.967_4)	3.445_3	5.735_9	$(90°)$
Setregruben, Østfold	(5.964_8)	3.443_8	5.733_9	$(90°)$
Åmdal, Froland	(5.963)	3.443	5.729	$(90°)$
	5.951	3.436	5.695	$90.4°$
Kongens Grube, Kongsberg	(5.963)	3.443	5.732	$(90°)$
	5.952	3.437	5.699	$90.4°$
Herzog F. Grube, Kongsberg	5.953	3.429	5.680	$90.4°$

Of the analyzed pyrrhotites the sample richest in sulfur has the monoclinic structure. The sample from Åmdal, Froland with somewhat less sulfur is a mixture of the phase with the monoclinic structure and the phase with the hexagonal structure, whereas the two samples poorest in sulfur are pyrrhotites with hexagonal structure. This investigation of Norwegian pyrrhotites thus also supports the conclusion drawn from studying synthetic preparations that the monoclinic phase has a greater sulfur content than the hexagonal phase.

Minerals which contain the superstructure phase — troilite — and the hexagonal pyrrhotite phase intermixed are not yet known. Their existence, however, seems probable and we have in progress an X-ray study of the iron rich, natural pyrrhotites.

D. Comparison with previous results

If we compare our results with those of Byström [6], the agreement between the lattice constant determinations is very good. The lattice constants found by him for Swedish pyrrhotites vary within these limits:

Hexagonal structure $a = 3.438 - 3.445$ Å
$c = 5.724 - 5.740$ Å
Monoclinic structure $a = 5.945 - 5.954$ Å $b = 3.432 - 3.438$ Å
$c = 5.689 - 5.701$ Å $\beta = 89.45° - 89.66°$
$(90.34° - 90.55°)$

As well from Byström's results as from ours it can be seen that there is a marked difference in the length of the c-axis of the hexagonal and the monoclinic structure.

The analyses in Byström's study of pyrrhotites gave no indications that the hexagonal and the monoclinic phase differ with respect to their sulfur content. From the high temperature study of synthetic pyrrhotites by Haraldsen [5] it was known that the c-axis of pyrrhotites contracts with increasing temperature, especially at the 325° C transformation (β-transformation). Byström made the assumption that the pyrrhotites should display monoclinic structure *above* the 325° C transformation temperature and sometimes have been cooled down to their present temperature without change into the hexagonal structure. He pointed out that this assumption was in accordance with the temperature variations of the length of the c-axis. In order to test his explanation the monoclinic pyrrhotite from Herzog Friedrich Grube, Kongsberg was annealed at 350° C for 7 days and quenched. The X-ray photograph of this preparation showed that the monoclinic deformation had disappeared and that the structure was of the ordinary B-8 type with lattice constants:

$a = 3.435$ Å $c = 5.692$ Å

This result is in agreement with our X-ray high temperature investigation (see later) as we found no signs that a monoclinic deformation exists above the 325° C transformation. It therefore seems impossible to maintain the assumption made by Byström that the monoclinic pyrrhotite is a β-transformed, high temperature modification in the system iron sulfur.

Allen, Crenshaw, Johnston and Larsen[16] found that hydrothermal syntheses at 200° C gave orthorhombic pyrrhotites while syntheses at 80° C gave hexagonal pyrrhotites. Byström found very good agreement between the axial ratios of his monoclinic pyrrhotites, determined by means of X-rays, and those found goniometrically by Larsen for the hydrothermally prepared orthorhombic pyrrhotites. He therefore pointed out that the small angular deformation might have been overlooked by Larsen and that the orthorhombic crystals in reality were monoclinic. Applying this explanation to the apparently orthorhombic pyrrhotites found in nature we arrive at the conclusion that the pyrrhotites are either hexagonal or monoclinic, with or without superstructures, and that no orthorhombic pyrrhotites seem to exist.

Allen et al.[16] could give no proof that the hexagonal and the "orthorhombic" crystals prepared by them had the same composition and if we suppose that the "orthorhombic" (monoclinic) pyrrhotites which had been formed at 200° C had higher sulfur content than those formed at 80° C there seems to be no objection against the assumption that both the hexagonal and the low symmetric phase can exist as stable phases at room temperature.

The pyrrhotites which display the low symmetric (monoclinic) structure are richest in sulfur, having a composition close to Fe_7S_8. They also have ferromagnetic properties and have either been formed at low temperatures or have been cooled down slowly so that the transformation from the B-8 structure, stable at higher temperatures, to the low symmetric structure has taken place. The hexagonal pyrrhotites are poorer in sulfur and have paramagnetic or weak ferromagnetic properties. If their sulfur content equals that of the monoclinic pyrrhotites they must have been formed at comparatively high temperatures and have cooled down so rapidly that a transformation to the monoclinic structure did not take place.

Results obtained by Kiskyras[17] who investigated the magnetic properties of a large number of natural pyrrhotites fit into this picture. He concluded the existence of two types of pyrrhotites: one of hydrothermal origin which is ferromagnetic and rich in sulfur (52.8 atomic per cent S) and another from high temperature deposits (pegmatic or contact metamorphic) which is poorer in sulfur (52.5 atomic per cent S) and has weak magnetic properties. As Kiskyras reasons in terms of the results of Allen et al.[16], he incorrectly supposes

that the sulfur rich ferromagnetic pyrrhotites have the higher symmetry instead of the lower of the two types.*

HIGH TEMPERATURE X-RAY INVESTIGATION

X-ray studies of synthetic pyrrhotites at higher temperatures have been performed by Haraldsen [5] in order to investigate if the observed changes in magnetic properties were connected with special structures or structural changes. The present study is especially concerned with the ranges of homogeneity of the synthetic pyrrhotite phases at higher temperatures. It also seemed of interest to see if the orthorhombic pyrrhotite reported by Allen et al.[16] could be found at higher temperatures in the pyrrhotites synthesized by dry methods.

A series of X-ray photographs were taken at $185-190°$ C. This temperature was chosen in order to be in the middle of the stability range of the α-transformed pyrrhotites. The preparations were the same as those used for the room temperature investigation and had been annealed at $290°$ C for 40 days. In Table 5 are listed the composition of the preparations and the lattice constants found at $185-190°$ C. The temperature of the X-ray camera was maintained constant to $\pm 3°$ C.

Table 5. Lattice constants in $\overset{\circ}{A}$ units of synthetic pyrrhotites at $185-190°$ C.

Composition	°C	a, (b $\sqrt{3}$)	b	c	β	Hexagonal axial ratio
$Fe_{1.020}S$	190	(6.063_9)	3.501_0	5.807_7	$(90°)$	1.659
$Fe_{1.000}S$	190	(6.064_6)	3.501_4	5.807_2	$(90°)$	1.659
$Fe_{0.971}S$	185	(6.051_8)	3.494_0	5.788_0	$(90°)$	1.657
$Fe_{0.943}S$	185	(6.036_7)	3.485_3	5.769_4	$(90°)$	1.655
$Fe_{0.926}S$	190	(6.030_0)	3.481_4	5.752_6	$(90°)$	1.653
$Fe_{0.893}S$	190	(6.009_3)	3.469_5	5.720_5	$(90°)$	1.649
$Fe_{0.877}S$	190	5.994	3.460	5.697	90.4°	
$Fe_{0.833}S$	190	5.994	3.460	5.697	90.4°	

Fe$_{1.000}$S. Haraldsen [5] connected the appearance and disappearance of the superstructure interferences in FeS with the α-transformation at $138°$ C.

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* After this paper was written, S. V. Lipin, Zapiski Vsesoyuz. *Mineral. Obshchestva (Mém. soc. russe minéral.)* **80** (1951) 258, *Ch. A.* **46** (1952) 3342 discusses the magnetic properties of pyrrhotite. Minerals heated to above 280° C show an approximate proportionality between magnetic susceptibility and sulfur content while this is not the case for unheated natural pyrrhotites. His results on the latter point are thus in disaccord with those of Kiskyras [17].

Confirming this, $Fe_{1.000}S$ exhibits no superstructure interferences at 190° C. The interferences can be indexed assuming an ordinary B-8 structure. Results of the film measurements and intensity calculations are listed in Table 6. The agreement between observed and calculated intensities is not as good as could be expected from a parameter free B-8 structure, and the deviations are most likely due to slight changes in the positions of the atoms.

Table 6.   Powder photograph of FeS at 190° C.   FeK radiation.   Intensity refers to a doublets, a_2 and β interferences are omitted.

Θ	$\sin^2 \Theta \cdot 10^4$		$h\,k\,i\,l$	Intensity	
	obs.	calc.		obs.	calc.
18.63	1021	1020	$a_1a_2 10\bar{1}0$	5	4.9
19.20	1082	—	?	2	—
19.50	1114	1113	$a_1a_2 0002$	1	0.5
21.11	1297	1299	$a_1a_2 10\bar{1}1$	5	3.6
27.51	2133	2133	$a_1a_2 10\bar{1}2$	20	16
33.58	3059	3057	$a_1 11\bar{2}0$	10	10
36.39	3519	3520	$a_1 10\bar{1}3$	3	1.8
39.69	4078	4076	$a_1 20\bar{2}0$	2	1.7
40.25	4175	4168	$a_1 11\bar{2}2$	1	1.1
41.31	4358	4354	$a_1 20\bar{2}1$	4	1.6
41.82	4446	4446	$a_1 00\bar{0}4$	3	2.6
46.06	5185	5187	$a_1 20\bar{2}2$	12	11
47.66	5464	5465	$a_1 10\bar{1}4$	3	3.3
54.16	6572	6577	$a_1 20\bar{2}3$	4	1.7
57.63	7134	7134	$a_1 21\bar{3}0$	1	4.1
59.43	7414	7412	$a_1 21\bar{3}1$	6	5.1
60.02	7503	7503	$a_1 11\bar{2}4$	20	25
63.18	7964	7966	$a_1 10\bar{1}5$	4	2.9
65.22	8244	8245	$a_1 21\bar{3}2$	30	41
67.40	8523	8522	$a_1 20\bar{2}4$	4	5.8
72.32	9078	—	?	6	—
73.28	9172	9172	$a_1 30\bar{3}0$	20	26
78.99	9635	9635	$a_1 21\bar{3}3$	20	21

$Fe_{0.971}S$ to $Fe_{0.926}S$. Between the composition $Fe_{1.000}S$ and $Fe_{0.971}S$ a pronounced shift in the interference positions is observed. This continues until the composition $Fe_{0.877}S$ is reached, indicating that an extended range of homogeneity exists. Contrary to what was observed on $Fe_{1.000}S$, weak additional interferences are found on our $Fe_{0.971}S$, $Fe_{0.943}S$ and $Fe_{0.926}S$ preparations. In Table 7 are listed the additional low angle interferences occuring on

a $Fe_{0.971}S$ photograph. The cell dimensions and atomic positions of the super-structure cell cannot be determined with any certainty by the powder method and we will therefore not discuss the various ways in which these additional interferences might be explained.

Table 7. Additional low angle interferences observed on $Fe_{0.971}S$ at 185° C.
FeK Radiation

Int.	w	w	w	vw	vw	m	w.—	vw	w —
$\sin^2 \Theta \cdot 10^4$	534	560	576	612	650	678	913	949	1589

$Fe_{0.893}S$. A decrease in cell dimensions from the composition $Fe_{0.926}S$ is observed. However, the weak additional interferences have disappeared.

$Fe_{0.877}S$ to $Fe_{0.833}S$. At the composition $Fe_{0.877}S$, a structural deformation is found. The assumptions used to derive the lattice constants at 190° C were the same as for the room temperature photograph. At the composition $Fe_{0.833}S$ interferences from the FeS_2-pyrite-phase are observed and there are no appreciable changes in lattice constants from $Fe_{0.877}S$ to $Fe_{0.833}S$.

In Fig. 2 the dimensions of the b-and c-axes are plotted as function of the composition. No break is observed at the transition from hexagonal to monoclinic structure. At 190° C therefore, a homogeneity range apparently exists all the way from $Fe_{1.000}S$ to $Fe_{0.877}S$.

Another series of high temperature photographs were taken at 360° C i.e. just above the β-transformation temperature. The derived lattice constants are listed in Table 8. Neither superstructure interferences nor interferences

Table 8. Lattice constants in Å units of synthetic pyrrhotites at 360° C.

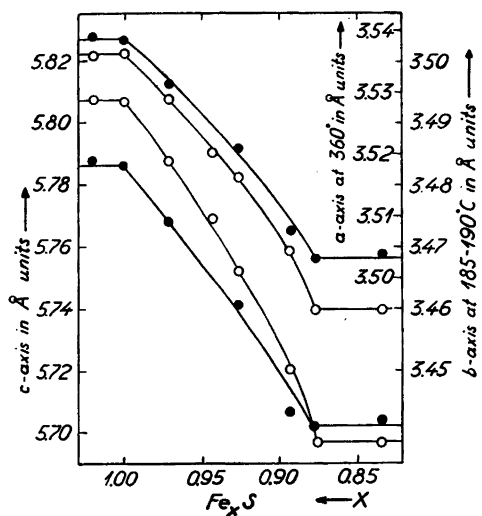| Composition	a	c	c/a
$Fe_{1.020}S$	3.539	5.788	1.635
$Fe_{1.000}S$	3.538_6	5.786_5	1.635
$Fe_{0.971}S$	3.531_2	5.768_1	1.633
$Fe_{0.926}S$	3.520_9	5.741_5	1.631
$Fe_{0.893}S$	3.507_5	5.706_5	1.627
$Fe_{0.877}S$	3.503	5.702	1.628
$Fe_{0.833}S$	3.503_8	5.703_9	1.628

Fig. 2. Lattice constants of synthetic pyr-
rhotites at 185—190° C (— ○ —) and 360° C
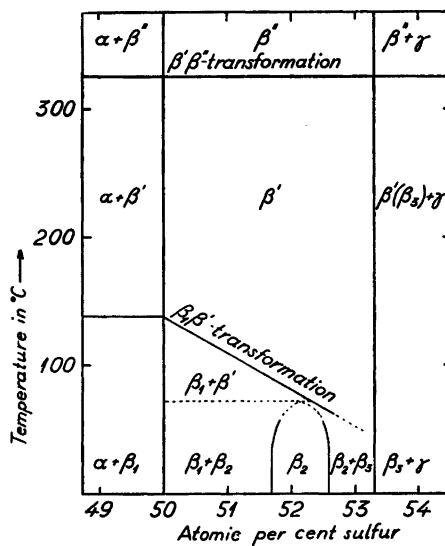(— ● —).

Fig. 3. Tentative phase diagram for syn-
thetic pyrrhotites.

indicating lower symmetry are observed and the lattice constants decrease in an orderly manner. It appears from Fig. 2 that the pyrrhotite phase at this higher temperature has a range of homogeneity between the limits $Fe_{1.00}S$ and $Fe_{0.88}S$. It can be mentioned that Coughlin [18] in a study of the high temperature heat content of iron sulfides found $Fe_{1.030}S$ (49.26 atomic per cent S) to be a single phase preparation at higher temperatures. Although our results are not conclusive at this point, a slight extension of the range of homogeneity on the iron rich side seems to have taken place at 360° C.

In a few cases the sealing of the thin walled quartz capillaries was unsatisfactory, which caused a slight oxidation of the sample to take place. X-ray photographs then showed a decrease in cell dimensions of the pyrrhotite phase. Later on, pyrite and iron oxide interferences were observed. This has some connection with results found by Kiskyras [19]. He observed that the weathering process made pyrrhotite ores and rocks more ferromagnetic and connected that with an increase in sulfur content. The results of our X-ray study show that the pyrrhotite diminishes its cell dimensions during the oxidation process and this is most likely due to increased sulfur content.

When we took X-ray photographs of the synthetic pyrrhotites after they had been cooled down from 360° C to room temperature, no monoclinic defor-

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mation could be observed on the $Fe_{0.877}S$ and the $Fe_{0.833}S$ preparations. Furthermore, the $Fe_{0.971}S$ sample was not found to split into the two phases which are stable at room temperature (see page 1455). This explains the results which were found both by Hägg and Sucksdorff [2] and by Haraldsen [4], namely that a single phase with hexagonal structure is the only existing pyrrhotite phase. Evidently the phase relations as given by their preparations correspond to equilibrium approach at higher temperature than those given by our preparations annealed at 290° C.

The sulfur rich limit for the homogeneity range of pyrrhotites at 20°, 185° and 360° C is found close to the composition Fe_7S_8. This is in perfect accord with the results of Roberts [2] and Haraldsen [4] whereas Juza and Biltz [15] report the somewhat lower value 52.8 atomic per cent sulfur as the sulfur rich limit of the homogeneity range of the pyrrhotite phase. Recently, Lukes, Prutton and Turnbull [20] studied the reaction between $FeCl_2$ and H_2S gas, and found that the amount of H_2 gas formed during the reaction corresponded to the formation of $Fe_{0.877}S$ (53.27 atomic per cent S). The experiments were carried out at various temperatures between 343.7° C and 455.6° C. At the highest temperature an increase in the H_2 gas formation took place, indicating a higher sulfur content, but the authors pointed out that this might be due to incidental errors.

Our exploratory X-ray photographs of pyrrhotites at 550° C did not reveal any extension of the homogeneity range beyond the composition $Fe_{0.87}S$. On the other hand Allen et al.[16] determined the sulfur rich limit at 565° C to be $Fe_{0.833}S$ (54.55 atomic per cent S). Later, Merwin and Lombard [21] found that pyrrhotite had a composition between $Fe_{0.846}S$ and $Fe_{0.835}S$ (54.17 and 54.50 atomic per cent S) in equilibrium with pyrite and sulfur vapor at 678° C (pS = 455 mmHg). The value $Fe_{0.80}S$ (55.5 atomic per cent S) found by Hägg and Sucksdorff [2] as the solubility limit for sulfur in pyrrhotite at 650° C seems to be somewhat high.

SOME CONSIDERATIONS REGARDING THE TRANSFORMATIONS

Figure 3 gives the phase relations of the pyrrhotites as they appear from the present investigation. Below the $\beta_1\beta'$-transformation temperature there exist three phases — β_1, β_2 and β_3 — separated by two phase regions.

The β_1 phase exists at the stoichiometric composition at room temperature and is stable up to 138° C. The atomic arrangement within its superstructure cell has not yet been worked out.

As the sulfur content is increased above the stoichiometric composition, a two phase region between the β_1 and the β_2 phase appears, and the $\beta_1\beta'$-trans-

formation temperature decreases. On further increase in sulfur, the homogeneity range of the β_2-phase follows and then a narrow two phase region between the β_2 and β_3 phases. The pyrrhotite phase richest in sulfur, the β_3 phase, has no appreciable range of homogeneity.

Some doubt arises as to the existence of the $\beta_1\beta'$-transformation in the sulfur rich preparations. The transformation was observed by Roberts [2] as well as by Haraldsen [3] at the composition $Fe_{0.909}S$ (52.40 atomic per cent S). On Roberts' transformation diagram, a point is also drawn at 40° C and the composition $Fe_{0.885}S$ (53.05 atomic per cent S) but this transformation point is not discussed in the text. Not enough information is present either to ascertain the presence of a transformation in the pure β_3 phase on change into the β' phase or the limits of the $\beta_1 + \beta_2$, and $\beta_2 + \beta_3$ regions.

In the temperature range between the $\beta_1\beta'$- and the $\beta'\beta''$-transformation, we have found no definite proof of two phase regions. The structural relationship in this range which we have designated by β', is, however, rather complicated. The following features are characteristic of the β' phase:

1. Superstructure interferences are found at the intermediate compositions.
2. A structural deformation is observed at the sulfur rich limit.
3. The axial ratio is above the ideal value 1.633.
4. The intensity ratios of the interferences differ from those at 360° C in some preparations.

Much additional work is required to assure whether or not the transition between the structures occuring in the β' region is continuous under equilibrium conditions.

At 360° C a single pyrrhotite phase exists between the limits $Fe_{1.00}S$ and $Fe_{0.88}S$. As the sulfur content increases from $Fe_{1.000}S$ a proportional part of the iron atoms is missing in the structure. If this loss of atoms only affects every second layer in the c-direction, a transition from a B-8 (NiAs) to a C-6 $Cd(OH)_2$ structure type can be said to occur. In the system $CoTe-CoTe_2$, Tengnér [22] supposed that a statistical deficiency existed only as long as the metal deficit is small. Since but a relatively small part of the iron can be missing in the pyrrhotite phase, the vacant lattice sites are probably distributed at random on the positions $000; \, 00\frac{1}{2}$. A preferential deficiency of iron atoms in say $00\frac{1}{2}$ would cause intensity changes and the occurrence of additional interferences. We have not been able to observe that, and furthermore, the close to ideal axial ratio in the pyrrhotites at 360° C may be an indication of a statistical missing of the iron atoms. The pyrrhotite phase on Fig. 3 designated with β'' is therefore supposed to have an ordinary B-8 structure with iron atoms missing at random when the sulfur content exceeds the stoichiometric ratio.

SUMMARY

1. X-ray studies of synthetic pyrrhotite samples annealed at 290° C and quenched, reveal the existence of three phases with different compositions. The β_1-phase exists at the stoichiometric composition $Fe_{1.000}S$ with a B-8 like superstructure and the lattice constants

$$a = 5.965_9 \text{ Å} \qquad\qquad c = 11.758_2 \text{ Å}$$

The β_2-phase with B-8 structure has a range of homogeneity between $Fe_{0.935}S$ and $Fe_{0.900}S$ (51.69 to 52.60 atomic per cent S). The lattice constants at the iron rich limit are

$$a = 3.448_2 \text{ Å} \qquad\qquad c = 5.760_4 \text{ Å}$$

and at the sulfur rich limit:

$$a = 3.440_9 \text{ Å} \qquad\qquad c = 5.720_2 \text{ Å}$$

The β_3-phase has a low symmetric structure and a composition close to $Fe_{0.877}S$ (53.27 atomic per cent S). These monoclinic lattice constants were computed:

$$a = 5.952 \text{ Å}, \qquad b = 3.433 \text{ Å}, \qquad c = 5.690 \text{ Å}$$
$$\text{and } \beta = 90.4°$$

Preparations rapidly cooled from above the 325° C transformation temperature do not reveal the monoclinic deformation and the two phase regions.

2. The lattice constants found for pyrrhotite minerals agree very well with those found for the β_2 and β_3 phases. Chemical analyses confirm that the sulfur content of the low symmetric β_3 phase is higher than the sulfur content of the β_2 phase in the pyrrhotite minerals. Distinct ferromagnetic properties are connected with the low symmetric structure.

3. X-ray high temperature studies on synthetic pyrrhotites were performed at 185—190° C and at 360° C. At the former temperature probably a single phase, the β' phase, exists between the limits $Fe_{1.000}S$ and $Fe_{0.877}S$ (50 to 53.27 atomic per cent S). At the sulfur rich limit the monoclinic deformation still exists.

$$Fe_{1.000}S: \qquad a = 3.501_4 \text{ Å}, \qquad c = 5.807_2 \text{ Å}$$
$$Fe_{0.877}S: \qquad a = 5.994 \text{ Å}, \qquad b = 3.460 \text{ Å}$$
$$c = 5.697 \text{ Å} \quad \text{and} \quad \beta = 90.4°$$

By raising the temperature to 360° C the monoclinic deformation disappears and the lattice constants vary within these limits:

$$Fe_{1.000}S: \qquad a = 3.538_6 \text{ Å}, \qquad c = 5.786_5 \text{ Å}$$
$$Fe_{0.877}S: \qquad a = 3.503 \text{ Å}, \qquad c = 5.702 \text{ Å}$$

No extension of the range of homogeneity is observed at 550° C.

REFERENCES

1. Hägg, G., and Sucksdorff, I. *Z. phys. Chem.* **B 22** (1933) 444.
2. Roberts, H. S. *J. Am. Chem. Soc.* **57** (1935) 1034.
3. Haraldsen, H. *Z. anorg. u. allgem. Chem.* **231** (1937) 78.
4. Haraldsen, H. *Z. anorg. u. allgem. Chem.* **246** (1941) 169.
5. Haraldsen, H. *Z. anorg. u. allgem. Chem.* **246** (1941) 195.
6. Byström, A. *Arkiv Kemi, Mineral. Geol.* **19 B** (1945) no. 8, see also Lindroth, G. T. *Jernkontorets Ann.* **130** (1946) 27.
7. Buerger, M. J. *Am. Mineral.* **32** (1947) 411.
8. Buerger, M. J. *A S X R E D Monograph No. 1* (1944).
9. Graham, A. R. *Am. Mineral.* **34** (1949) 462.
10. Hägg, G., and Kindström, A. L. *Z. phys. Chem.* **B 22** (1933) 453.
11. Jensen, E. *Am. J. Sci.* **240** (1942) 695; *Trans. Am. Geophys. Union* (1942 : II) 347.
12. Henglein, M. in Doelter, C., and Leitmeier, H. *Handbuch der Mineralchemie* **IV 1** (1926) 499.
13. Eakle, A. S. *Am. Mineral.* **7** (1922) 77.
14. Buddhue, J. B. *Popular Astronomy* **45** (1937) 386.
15. Juza, R., and Biltz, W. *Z. anorg. u. allgem. Chem.* **205** (1932) 273.
16. Allen, E. T., Crenshaw, J. L., Johnston, J., and Larsen, E. S. *Z. anorg. Chem.* **76** (1912) 201; *Am. J. Sci.* **33** (1912) 169.
17. Kiskyras, D. A. *Neues Jahrb. Mineral. Geol. Pal. Beilage* **80 A** (1950) 297.
18. Coughlin, J. P. *J. Am. Chem. Soc.* **72** (1950) 5445.
19. Kiskyras, D. A. *Beitr. angew. Geophys.* **10** (1943) 308.
20. Lukes, J. J., Prutton, C. F., and Turnbull, D. *J. Am. Chem. Soc.* **67** (1945) 697.
21. Merwin, H. E., and Lombard, R. H. *Econ. Geol.* **32** (1937) 203.
22. Tengnér, S. *Z. anorg. u. allgem. Chem.* **239** (1938) 126.