Phase and Structural Relations in the System

Iron Tellurium

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Only a few investigations have dealt with the reaction between iron and tellurium and the formation of iron tellurides. Tammann and Schaar-wächter [1] subjected a mixture of equivalent amounts of iron and tellurium to thermal analysis and examined the reaction product. It was found to consist of an iron tellurium compound surrounded by tellurium, indicating the existence of an iron subtelluride. Moser and Ertl [2], as well as Oftedal [3], also only obtained heterogeneous preparations. Oftedal was, nevertheless, able to demonstrate by X-ray methods that his quenched preparations contained a phase Fe_xTe_y of the B8 (NiAs) structure type, having a composition which most likely deviated from the simple stoichiometric formula FeTe. Brukl [4] on the other hand, reported the existence of an iron monotelluride with stoichiometric composition formed by the action of hydrogen telluride on ferrous salt solutions.

Tengnér [5] prepared iron ditelluride, $FeTe_2$, and determined its crystal structure to be of the C18 (marcasite) type. $FeTe_2$ was later found in nature by Thompson [6], who gave it the name Frohbergite.

Our study of the system iron tellurium was started several years ago, and only a short note [7] in Norwegian giving some preliminary results has thus far been published.

PREPARATION OF THE ALLOYS

The *iron* used was prepared from Fe_2O_3, Merck "Ferrum oxydatum sec. L. Brandt", by reduction with dry, purified hydrogen gas, first for 4 hours at 400°—600° C and then for 2 hours at 1 000° C. Heating at the latter temperature was prolonged until constant weight was obtained.

One part of the *tellurium* used was "Tellurium, reinst in Stangen" from Kahlbaum. Another part was prepared by dissolving tellurium metal in nitric acid $(d = 1.25)$ at 70° C and recrystallizing the basic nitrate. The nitrate was dissolved in nitric acid and hydrated tellurium oxide precipitated by hydrolysis. The oxide was washed and heated to 600° C and then dissolved in hydrochloric acid. From this solution tellurium was precipitated, partly with hydrazine hydrate and partly with sodium hypophosphite. Finally, the tellurium was subjected to repeated vacuum distillations in silica vessels. A spectro-

graphic analysis, kindly carried out by sivilingeniør S. Rutlin, Statens Råstofflaboratorium, Oslo, revealed no impurities *, and this material was used for the determination of the lattice constants and the composition of the phases.

The alloys were prepared by heating calculated amounts of iron and tellurium in evacuated and sealed silica tubes. The heating of the preparations was done in various ways, but the preparations used for phase analysis were first heated at 900° C for 24 hours. At this temperature all preparations with more than 44.5 atomic % tellurium were molten. After they had been cooled, the grey, metallic reguli were finely ground and parts of each regulus were annealed, respectively, at 300° C, 600° C and 750° C for 24 hours in evacuated and sealed silica tubes. The samples were quenched from these temperatures in ice water.

Tellurium-rich preparations, which were made in order to determine the composition of the iron ditelluride, were annealed for 14 days at 425° C and slowly cooled to room temperature. Single crystals of one of the iron telluride phases (the β-phase) were obtained by heating $FeTe_{0.5}$ and $FeTe_{0.67}$ for 34 days at 800° C. In all, iron tellurium alloys with 29 different compositions were made in the range $FeTe_{0.5}$ to $FeTe_3$.

Some FeTe alloys were prepared at 1 000° C. In that case the walls of the silica tubes got covered with a thin black film, and a small condensate was found in the top of the tube. This black coating was avoided by holding the temperature at 900° C, and the distillation process was avoided by keeping the top part of the silica tube slightly hotter than the bottom.

PHASE INVESTIGATION BY X-RAY DIFFRACTION

All the alloys prepared were examined by the X-ray powder method. Cameras with 5.75 cm diameter were used for phase identification and a Philips 11.48_3 cm diameter camera, with Straumanis asymmetric film mounting, was used for lattice constant determinations. $FeK\alpha$ radiation was employed and all the lattice constants are expressed in Å units ($\lambda\ FeK\alpha_1 = 1.93597$ Å). The error in the lattice dimensions is 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, unless otherwise stated. Lattice constants from earlier investigations have been transformed from kX to Å units by multiplication by the factor 1.00202.

The iron used was found to have the lattice constant $a = 2.8663 \pm 0.0002$ Å at room temperature (20 $\pm$ 2° C). This value is in perfect agreement with the precision value $a = 2.86635$ Å recently reported by Thomas [8]. The lattice constant found for iron in equilibrium with the first intermediate iron telluride phase was $a = 2.8669 \pm 0.0002$ Å in the preparation $FeTe_{0.60}$ quenched from 900° C. The slight difference between the two values indicates the range of homogeneity of the α-phase in the system iron tellurium to be very narrow.

a. Phase relations below 425° C

Phase analysis of preparations quenched from 300° C led to the conclusion that the intermediate iron telluride phase richest in iron exists in the composition range $FeTe_{0.8}$ to $FeTe_{0.9}$. X-ray powder photographs of this phase — *the β-phase* — could be indexed assuming a tetragonal unit cell. For a preparation

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* Some tellurium of another origin (Tellurium lump, B.D.H.) was distilled without chemical purification. In this case the spectrographic analysis showed the presence of some Fe and traces of Mg and Pb.
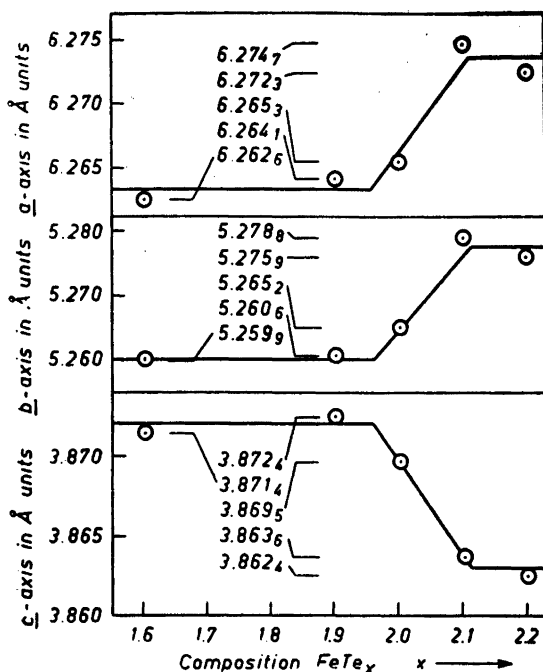
Fig. 1. Lattice constants of the orthorhombic ε-phase in the range $FeTe_{1.60}$ to $FeTe_{2.20}$.

$FeTe_{0.8}$ where the β-phase exists in equilibrium with the α-phase, iron, these lattice constants were computed:

$$a = 3.823_0 \text{ Å}, \quad c = 6.276_7 \text{ Å}.$$

In equilibrium with the phase richer in tellurium the following lattice constants were found for the β-phase:

$$a = 3.819_8 \text{ Å}, \quad c = 6.280_5 \text{ Å}.$$

The slight variation in the lattice constants leads us to assume that the β-phase has only a narrow range of homogeneity, and as the ferromagnetism * of $FeTe_{0.88}$, which is probably due to iron, has disappeared almost completely at $FeTe_{0.90}$, the range of homogeneity of the α-phase should be close to the composition $FeTe_{0.90}$.

At the stoichiometric composition FeTe many additional interferences from a phase richer in tellurium are observed. There exists thus, at lower temperatures, no iron telluride phase with the composition FeTe. At the composition $FeTe_{1.50}$ all interferences belonging to the tetragonal β-phase have disappeared and interferences from a new intermediate phase — *the ε-phase* —

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* The magnetic properties of the iron tellurides will be discussed in another communication.

Table 1. Lattice constant determinations of orthorhombic $FeTe_2$ in Å units. Axes in standard setting (Pnnm) of the International Tables [10]. Transformation to the old (Pmnn) marcasite orientation in terms of the present: $00\bar{1}/010/100$ and to the orientation after Buerger [11] (Pnnm) → present: $010/100/00\bar{1}$.

a	b	c	Authors
6.273	5.352	3.857	Tengnér [5]
6.27	5.29	3.86	Thompson [6]
6.265_3	5.265_2	3.869_5	Present

which is identical with the $FeTe_2$-phase with marcasite structure found by Tengnér [5], exist alone on all photographs of preparations up to the composition $FeTe_{2.5}$. In this preparation the strongest tellurium interferences are observed.

In order to establish the composition limits of the ε-phase at "room temperature" a series of preparations was made, annealed for 14 days at 425° C and slowly cooled to room temperature. X-ray photographs show that $FeTe_{1.60}$ and $FeTe_{1.90}$ have practically the same cell dimensions. The two phase region between the β- and ε-phase thus extends at least to the composition $FeTe_{1.90}$. With further increase in the tellurium content the lattice dimensions start to change at about $FeTe_{1.95}$. As shown in Fig. 1 the a- and especially the b-axis increase with increasing tellurium content until the composition $FeTe_{2.10}$ is reached, while the c-axis shows a slight decrease in the same concentration range. The ε-phase is accordingly assumed to be homogeneous in the range $FeTe_{1.95}$ to $FeTe_{2.10}$ (66.1 to 67.7 atomic % Te). This is the first marcasite-like phase which has been shown to have a metalloid content exceeding the formula AB_2.

In Table 1 are listed the results of our lattice constant determination of $FeTe_2$, together with the results of Tengnér [5] and Thompson [6]. The agreement between Tengnér's results and ours is very good for the a- and c-axis, but there is a remarkable disagreement regarding the length of the b-axis. The lattice constants of the mineral Frohbergite as determined by Thompson [6] agree well with our values for synthetic $FeTe_2$.

No indications of the existence of iron tellurides higher than $FeTe_2$ have been found. In Table 2 are listed the lattice constants determined for tellurium

Table 2. Lattice constants of tellurium in Ångström units.

Sample	a-axis	c-axis	T °C
$FeTe_2$ + Te	4.454_9	5.922_9	20 ± 2
Tellurium	4.456_0	5.925_1	20 ± 2
Te, Straumanis[9]	4.45591 ±0.00012	5.92687 ±0.00002	20

in a two-phase preparation consisting of the ε-phase and tellurium. In Table 2 is also found our lattice constant determination of pure tellurium, together with the precision determination made by Straumanis [9]. The results indicate that the solubility of iron in tellurium is small.

b. Phase relations in preparations quenched from 600° C

When we consider the phase relations in preparations quenched from 600° C, we find that the β- and ε-phases still appear on the photographs. In addition to these, another intermediate phase — *the δ-phase* — is found in the composition range $FeTe_{1.40}$ to $FeTe_{1.50}$. A closer study revealed that the quenched δ-phase has a pseudo-hexagonal structure at the composition $FeTe_{1.40}$ (58.33 atomic % Te) which is close to the iron rich limit of the phase. The structure was tentatively indexed as monoclinic, and the corresponding lattice constants are listed in Table 3. The monoclinic deformation disappears with increasing tellurium content and the phase becomes hexagonal at the composition $FeTe_{1.50}$. No two phase region has been observed and, consequently, the monoclinic and the hexagonal structures probably belong to the same phase.

Table 3. Lattice constants of the δ-phase in Ångström units.

Sample	a	b, $(a\sqrt{3})$	c	β
$FeTe_{1.40}$	3.846	6.661	5.641	90.2°
$FeTe_{1.50}$	3.816_2	(6.610_1)	5.654_8	(90°)
Fe_xTe_y, Oftedal [3]	3.808	(6.596)	5.662	(90°)
	±0.003		±0.005	

The lattice constants of $FeTe_{1.50}$ are also listed in Table 3, together with the values found by Oftedal [3]. The agreement between the cell dimensions and intensities of our δ-phase and the Fe_xTe_y-phase with $B8$-like structure found by Oftedal shows that they are no doubt identical.

It is known from the investigation of chromium sulfides, selenides and tellurides by Haraldsen *et al.*[12] that a $B8$ (NiAs)-like phase exists in the composition range $CrX_{1.40-1.50}$ (X = S, Se or Te). The same deviating composition has now been found for the hexagonal iron telluride. The analogy between the iron tellurium δ-phase and the chromium chalcogen phases goes even further, as a continuous change from monoclinic to hexagonal structure is observed for these phases in the same composition range. The δ-phase is, however, only obtained in quenched preparations, while the corresponding chromium chalcogenides are also obtained in slowly cooled preparations.

A series of FeTe samples was annealed and quenched from successively lower temperatures starting with 600° C. When the annealing temperature was 500° C, interferences from the δ-phase could still be observed, while at 480° C the δ-phase had disproportionated into the β- and ε-phases. This is in

good agreement with a thermal analysis made on $FeTe_{1.50}$ by which the decomposition temperature was determined to be $488° \pm 2°$ C.

Some experiments were carried out at 600° C to see how quickly the hexagonal δ-phase was formed from the β- and ε-phases. Even after an annealing time of 15 minutes the δ-phase appeared with as sharp and well defined interferences as it did after 24 hours annealing time. On the other hand, experiments with five minutes annealing time proved insufficient to obtain sharp interferences.

c. Phase relations in preparations quenched from 750° C

The β-, as well as the δ- and ε-phases, are found at their respective places in preparations quenched from 750° C. In addition to this, the existence of still another phase was noted. The phase was observed on powder photographs of the preparations FeTe, $FeTe_{1.05}$, $FeTe_{1.10}$ and $FeTe_{1.15}$, when quenched from $750 \pm 30°$ C. The composition of this phase — *the γ-phase* — is judged to be around $FeTe_{1.10}$. The composition is, however, somewhat uncertain since the photographs have blurred interferences and high background blackening.

During annealing experiments made in order to obtain single crystals of the γ-phase condensates were sometimes observed in the top of the silica tube *. X-ray photographs of the condensates showed a mixture of the γ- and δ-phases.

It is difficult to decide if the γ-phase is appreciably volatile under the present conditions. Another possibility is that the β-phase volatilizes and condenses in the cooler part of the tube, where it reacts with tellurium vapor from dissociated iron telluride. In this way also a mixture of the γ- and the δ-phases could be obtained.

To summarize the results of the phase analysis of the system iron tellurium we may describe the four intermediate phases which were found as follows:

1) The tetragonal β-phase with composition close to $FeTe_{0.90}$ exists in the quenched and slowly cooled preparations.
2) The γ-phase with unknown structure exists close to the composition $FeTe_{1.10}$ and is only stable around 750° C.
3) The monoclinic-hexagonal δ-phase with a composition range $FeTe_{1.40}$ to $FeTe_{1.50}$ is only stable above 488° C.
4) The orthorhombic ε-phase with composition $FeTe_{1.95}$ to $FeTe_{2.10}$ is found both in quenched and slowly cooled preparations.

CRYSTAL STRUCTURES OF THE IRON TELLURIDE PHASES

a. The β-phase, $FeTe_{0.90}$

The crystals obtained of the β-phase consisted of layers, partly forming rectangular pyramides, often double, with a slight angular distortion of the

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* An attempt to obtain larger quantities of this distillate by one months annealing of $FeTe_{1.3}$ at 750° C was unsuccessful as the silica tube was strongly attacked, and the condensate in the upper part of the tube had been subject to various reactions.

layers, and partly forming tiny needles growing in the layer plane. Some of the needles had small excrescences normal to the needle axis.

Rotation photographs have been taken of many of these crystals and also of a tabular crystal with metallic luster. One photograph was taken with the rotation axis normal to the plate and two others with the rotation axis at right angles to the first. The last two photographs were identical and different from the first one. Accordingly, the crystal should have tetragonal structure with the c-axis normal to the plate. Photographs of the needle-shaped crystals showed that the a-axis was the needle axis of these crystals. The following identity periods were found: $a = b = 3.8$ Å, $c = 6.3$ Å.

The photographs were examined closely with regard to superstructure interferences, but no indications of a larger unit cell were found on photographs of crystals grown at 800° C.

In order to establish the cell content of the β-phase, a density determination was carried out on $FeTe_{0.90}$ in vacuum with kerosene as pycnometer liquid. The density was found to be 6.77_7 g/cm³ at 20° C. Using $1.660 \cdot 10^{-24}$ as the atomic weight unity in gram, a cell content of 2.19 Fe atoms and 1.98 Te atoms is found. This result shows that the structure of $FeTe_{0.90}$ can be considered as an AB-interstitial structure with the formula $Fe_{1.11}Te$ or Fe_9Te_8.

Table 4. Observed and calculated intensities of interferences from tetragonal $FeTe_{0.90}$.
$z_1 = 0.285$, $z_2 = 0.70$.

$\sin^2\Theta \cdot 10^4$	hkl	I_{obs}	I_{calc}	$\sin^2\Theta \cdot 10^4$	hkl	I_{obs}	I_{calc}
238	001	1	0.2	—	005	—	0.2
—	100	—	0	6012	301	3	3.2
880	101	8	7.4	6084	222	1	0.9
952	002	1	0.3	6368	204	6	4.7
1282	110	1	1.1	6397	310	1	1.4
1521	111	2	2.9	6580	105	1	0.9
1593	102	1	1.0	6659	311	2	3.7
2136*	003	2	1.6	—	302	—	0.7
2235	112	10	10	7010	214	4	4.9
2563	200	4	4.8	7223	115	8	9.6
—	201	—	0.2	7262	223	4	6.0
2780	103	3	2.4	7363	312	18	20
—	210	—	0	7908	303	5	3.7
—	113	—	0.2	—	320	—	0
3441	211	7	6.5	8505	205	2	2.1
3511	202	1	0.9	—	313	—	0.8
3802	004	2	1.0	8572	321	15	15
4151	212	1	1.1	—	006	—	0.1
4445	104	2	1.8	8929	224	15	14
4701	203	3	4.0	9146	215	6	5.6
—	114	—	0.2	9192	106	18	13
5129	220	2	3.6	9287	322	3	4.2
5344	213	5	4.0	9575	304	11	10
—	221	—	0.1	9836	116	18	15

* At this and higher angles the α doublet is resolved and the $\sin^2\Theta$ value refers to the α_1 component.
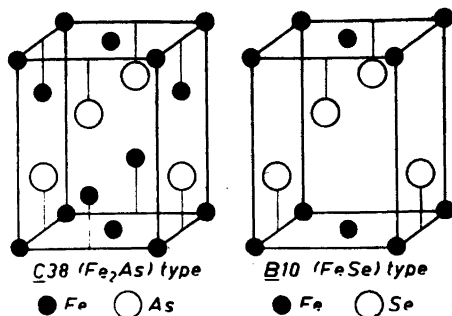
Fig. 2. Atomic arrangement for the B10 and C38 structure types.

The only systematic missing reflections on our Weissenberg photographs are those of the type $hk0$ with $h + k = 2n + 1$. They characterize the space groups $P4/n$ (C_{4h}^3) and $P4/nmm$ (D_{4h}^7). Apparently, the structure of the β-phase is closely related to the structure of tetragonal FeSe, found by Hägg and Kindström[13]. This structure is of the tetragonal PbO type ($B10$) with iron atoms in the oxygen positions: $(a) 0,0,0; 1/2,1/2,0$, and selenium in the lead positions: $(c) 0,1/2, z; 1/2,0, \bar{z}$. The intensities on the single crystal photographs showed accordingly that two iron atoms occupy positions (a) while the two tellurium atoms are in (c) with $z = 0.285$.

Intensities, determined photometrically for all interferences occurring on a powder photograph of $FeTe_{0.90}$ taken with $FeK\alpha$ radiation, are listed in Table 4 together with the calculated intensities and the $\sin^2\Theta$ values. To facilitate comparison, the observed and calculated values of 112 have been set equal. The agreement between observed and calculated intensities is seen to be very satisfactory.

The tetragonal β-phase has a typical layer structure. This caused a pronounced, pre-ferred orientation in the powder samples used originally, and too high intensities for the reflections from the basal planes and all other planes forming small angles with them, relative to the reflections from the prism planes.

The formation of crystal flakes was best prevented by letting the iron and tellurium react at 500° C and allowing only a short time for homogenization. Prepared in this way, the sample did not consist of flakes and the irregular intensity relationship was avoided.

The tetragonal $FeTe_{0.90}$ contains 0.2 interstitial iron atoms per unit cell. There are two reasonable positions for these atoms in the space group D_{4h}^4: $(b) 0,0,1/2; 1/2,1/2,1/2$, or $(c) 0,1/2, z; 1/2,0, \bar{z}$, with $z \approx 0.70$. If we assume that the excessive iron atoms are distributed on the (c) positions — the intensities in Table 4 have been calculated for that assumption — the structure can be regarded as a transition link between the $B10$ structure type and the $C38$ type, found by Elander, Hägg and Westgren[14] for Fe_2As and Cu_2Sb. The difference between these two structure types is seen from Fig. 2, in that two additional metal atoms located are in $(c) 0,1/2, z; 1/2,0, \bar{z}$, with $z \approx 0.70$ in the $C38$ structure.

A transition between the $B10$ and $C38$ structure type similar to that for tetragonal $FeTe_{0.90}$ was found by Forman and Peacock [15] for Rickardite, $Cu_{4-x}Te_2$ (x = 1.2). The structure is described as being of the $C38$ type, but grossly defective, with an almost invariant proportion of vacant Cu-positions in (c). Therefore, Rickardite $Cu_{1.40}Te$ may also be counted as a link between the $B10$ and $C38$ types. It can furthermore be mentioned that Haraldsen and Grønvold [16] found that tetragonal FeSe has a composition which deviates slightly from the stoichiometric ratio, and that Forman and Peacock [15] also observed a defective composition for Cu_2Sb. A study of the nickel tellurium system, which has been carried out in this institute by Jan Barstad has likewise revealed a phase with similar tetragonal structure close to the composition Ni_3Te_2.

In the $B10$ structure the Te atoms are arranged in a distorted cubic close packing (ideal for $c/a = 1.414$ and $z = 0.25$) with eight of the twelve Te atoms at a distance of 3.82 Å and the rest at 4.49 Å. This gives a Te radius of 1.91 Å, which is definitely shorter than the ionic radius of Te^{-2} (2.11 Å according to Goldschmidt [17] or 2.21 Å according to Pauling [18]). Each Te atom is further surrounded by 4 Fe atoms at a distance of 2.60 Å or far shorter than the sum of the ionic radii for Fe^{+2} and Te^{-2} (which is 0.83 Å + 2.11 Å = 2.94 Å according to Goldschmidt [17]), but close to the sum of the elemental radii (1.24 Å + 1.43 Å = 2.67 Å).

The deviation from the composition FeTe of the iron telluride led us to investigate whether or not the tetragonal PbO also had a non-stoichiometric composition. LeBlanc and Eberius [19] ascribed a range of homogeneity to PbO between PbO and $PbO_{1.10}$. However, Byström [20] found no signs of a range of homogeneity for the tetragonal PbO-phase in his thorough X-ray work on lead oxides. In addition to X-ray studies, which confirmed Byströms results at this point, we have also carried out chemical analyses of PbO samples carefully prepared in different ways. By reduction with dry, purified hydrogen gas, the lead was determined as metal and the oxygen as water, absorbed in phosphorus pentoxide. The results of these analyses are listed in Table 5. They indicate that the composition of tetragonal PbO does not deviate appreciably from the stoichiometric ratio.

Table 5. Analyses of four lead monoxides.

Oxide sample	Oxide weight in gram	Found (gram)		PbO_x
		Pb	O	x
PbO, red, tetragonal from NaOH solution	1.3915₈	1.2907₀	—	1.012
PbO, tetragonal	1.2534₂	1.1632₂	—	0.998
PbO, tetragonal, from $PbCO_3$	1.1999₂	1.1133₆	0.0857₃	0.997
PbO, orthorhombic, from PbO tetr. heated 24 hours at 700° C	1.2947₈	1.2003₄	0.0917₂	0.990

b. The γ-phase, FeTe$_{1.1}$

The structure of the γ-phase has not yet been established, and the phase can therefore only be characterized by means of the position and relative intensities of the interferences. In Table 6 are listed the results from the best X-ray photograph obtained in a 5.75 cm diameter camera.

Table 6. Interferences observed on a photograph of the γ-phase, FeTe$_{1.10}$, heated for 7 days at 750° C and quenched. FeKα,β radiation.

I_{obs}	Θ	$\sin^2\Theta \cdot 10^4$	I_{obs}	Θ	$\sin^2\Theta \cdot 10^4$
m	17.3	884	w +	40.6	4235
st +	19.2	1082	vw	41.5	4391
v w	19.8	1147	vw	42.3$_5$	4538
w	20.6	1238	w —	43.1	4669
v w	22.4	1452	w	44.5	4913
v w	23.5	1590	w —	46.7	5297
w	24.0	1654	vw	48.2$_5$	5566
v st	26.7	2019	w —	48.7	5661
v w	27.5	2132	w —	49.4$_5$	5773
st	28.1$_5$	2226	vw	50.0$_5$	5876
st +	28.8	2321	w —	52.6	6311
w	30.3	2545	w —	53.4	6445
w —	31.6$_5$	2753	w	54.5	6628
v w	32.6	2903	w	55.6	6808
w +	35.1$_5$	3314	w —	56.5	6954
m	35.8$_5$	3430	w —	56.8	7002
v st	36.5	3538	w +	57.9	7176
w	37.9	3773	m	58.2$_5$	7231

c. The δ-phase, FeTe$_{1.5}$

The density determination of a preparation FeTe$_{1.50}$ with kerosene as pycnometer liquid gave the value 7.63$_3$ g/cm³ at 20° C. This density corresponds to 1.99 Te atoms and 1.33 Fe atoms per unit cell, and confirms the idea that the $B8$-like structure can be considered as an AB subtractive structure. The X-ray density of FeTe$_{0.667}$ is 7.674 g/cm³.

Compared to the ordinary $B8$ (NiAs)-structure, 0.67 Fe atoms are missing per unit cell Fe$_2$Te$_2$. These atoms can either be missing at random from the positions (a) 0,0,0, and (b) 0,0,1/2, or position (a) can be fully occupied while position (b) is only filled to one third with iron atoms. The latter distribution constitutes a transition stage between the $B8$ and the $C6$ structure types. In Table 7 are listed the observed intensities of a FeTe$_{1.50}$ preparation together with those calculated using the assumption of random missing (I_1) and preferential missing of iron atoms (I_2). In both cases the atomic parameters are assumed to remain unchanged compared to those of the $B8$ type. The first alternative seems to give the best agreement between the observed and calculated intensities, i.e. the iron atoms are probably distributed at random over the twofold (a) positions of the space group $C\ 6/mmc$. This is in contrast

Table 7. Observed and calculated intensities of $FeTe_{1.50}$. Assumption I_1: 0.67 Fe atoms in 000; 0.67 Fe atoms in $00\frac{1}{2}$. Assumption I_2: 1 Fe atom in 000; 0.33 Fe atoms in $00\frac{1}{2}$.

$\sin^2\Theta \cdot 10^4$	$hkil$	I_{obs}	I_1	I_2	$\sin^2\Theta \cdot 10^4$	$hkil$	I_{obs}	I_1	I_2
—	0001	—	0	0.2	—	$11\bar{2}3$	—	0	0.2
856	$10\bar{1}0$	2	0.5	0.5	5549	$10\bar{1}4$	2	0.4	0.4
1154	$10\bar{1}1$	12	14	9.4	6005	$21\bar{3}0$	2	0.4	0.4
1173	0002	2	1.5	1.5	6071	$20\bar{2}3$	8	6.9	4.8
2034	$10\bar{1}2$	10	13	13	6294	$21\bar{3}1$	20	14	10
2574	$11\bar{2}0$	*10*	*10*	*10*	7171	$21\bar{3}2$	13	12	12
—	0003	—	0	0.0	7262	$11\bar{2}4$	20	20	20
—	$11\bar{2}1$	—	0	0.3	—	0005	—	0	0.0
3438	$20\bar{2}0$	1	0.3	0.3	7713	$30\bar{3}0$	13	11	11
3497 *	$10\bar{1}3$	10	7.3	9.7	—	$30\bar{3}1$	—	0	0.3
3723	$20\bar{2}1$	6	7.0	9.6	—	$20\bar{2}4$	—	0.7	0.7
3740	$11\bar{2}2$	6	4.6	4.6	8179	$10\bar{1}5$	13	13	8.5
4601	$20\bar{2}2$	6	5.5	5.5	8631	$21\bar{3}3$	35	31	42
4695	0004	3	2.4	2.4	8881	$30\bar{3}2$	17	12	12
					—	$11\bar{2}5$	—	0	2.0

* At this and higher angles the α-doublet is resolved and the listed $\sin^2\Theta$ value refers to the α_1-component.

to the view of Tengnér [5] on the $CoTe$-$CoTe_2$ transition and of Hoschek and Klemm [21] on the VSe—VSe_2 transition according to which the subtraction of metal atoms from the MeX ($B8$) structure, needed to give the MeX_2 ($C6$) structure, is supposed to cause vacant positions in every other metal layer in the hexagonal plane, except for compositions close to MeX. The Fe_2Te_3 phase is, however, only stable at high temperatures where random distribution is more probable.

In the δ-phase, each Te atom is surrounded on the average by 4 Fe atoms at the corners of a right trigonal prism at a distance of 2.62 Å. Each Fe atom is surrounded by 6 Te atoms at the same distance. The iron atoms have furthermore 2 Fe atoms as neighbors at $c/2 = 2.83$ Å. The tellurium atoms form an approximately hexagonal close-packing, the shortest distance between atoms in adjacent layers (3.60 Å) being smaller than between atoms within the layer (3.82 Å). Although the Te—Te distance is smaller than it is in the tetragonal structure, and the ionic radius of Fe^{+3} is smaller than it is for Fe^{+2}, the Fe—Te distance remains practically unchanged, indicating the presence of metallic (covalent) bonds.

d. The ε-p h a s e, $FeTe_2$

In accordance with Tengnér's [5] results, the X-ray powder photographs of the ε-phase could be indexed assuming an orthorhombic unit cell. The extinctions are of the type $h0l$ absent when $h + l = 2n + 1$ and $0kl$ absent when $k + l = 2n + 1$ and they characterize the space groups $Pnnm$ (D_{2h}^{12})

Table 8. Observed and calculated intensities of the ε-phase ($FeTe_{1.90}$), assuming marcasite structure with parameters $x = 0.365$ and $y = 0.225$.

$\sin^2\Theta \cdot 10^4$	hkl	I_{obs}	I_{calc}	$\sin^2\Theta \cdot 10^4$	hkl	I_{obs}	I_{calc}
—	110	—	0.7	6277	141	2	1.8
866	101	3	4.1	—	510	—	0.7
964	{200, 011}	3	{0.1, 3.0}	6326	402	5	4.9
1204	111	13	19	—	240	—	0.1
1295	210	13	17	6510	232	18	14
1359	020	5	4.3	6598	501	3	4.2
1591	120	2	0.8	6667	412	2	1.1
1918	211	2	1.1	—	430	—	0.5
2218 *	121	13	18	—	213	—	0.8
2311	220	3	1.4	6940	511	18	15
2499	{310, 002}	7	{1.4, 8.4}	7005	241	8	6.7
2774	301	16	12	7222	123	18	15
2935	221	3	2.5	—	520	—	0.8
—	112	—	0.2	7496	431	9	9.0
3113	311	6	5.9	—	340	—	1.3
3285	130	3	2.7	7675	422	35	32
—	202	—	0.1	—	332	—	0.6
—	320	—	0.3	7777	303	15	14
3675	031	2	0.5	7917	{042, 223}	15	{15, 2.5}
3782	212	15	16	—	521	—	0.1
—	400	—	2.4	8115	313	6	9.0
3853	022	6	4.0	8152	142	6	5.6
3911	131	8	7.5	8193	341	35	23
4002	230	7	6.5	8597	600	5	3.0
4095	122	2	0.8	8671	033	2	1.0
4129	321	7	5.0	8700	150	2	1.1
—	410	—	0.5	8806	512	3	2.5
4622	231	2	1.2	—	242	—	0.6
—	411	—	0.1	8906	133	24	21
4808	222	2	1.8	8939	610	20	20
4988	312	2	1.9	—	530	—	0.0
5183	420	15	10	9088	051	15	24
—	330	—	0.2	9126	323	30	18
5423	040	6	4.1	9239	440	13	9
5666	140	2	1.6	9332	151	13	16
5782	132	4	4.4	9370	432	7	2.9
—	421	—	0.1	9423	250	16	17
5817	331	3	4.1	9561	611	3	4.8
5860	103	2	1.9	9622	233	8	6.2
5954	013	2	1.3	9642	531	46	53
—	322	—	0.5	—	413	—	0.5
6207	113	10	10	9822	522	7	9

* At this and higher angles the α-doublet is resolved and the $\sin^2\Theta$ value refers to the α_1-component.
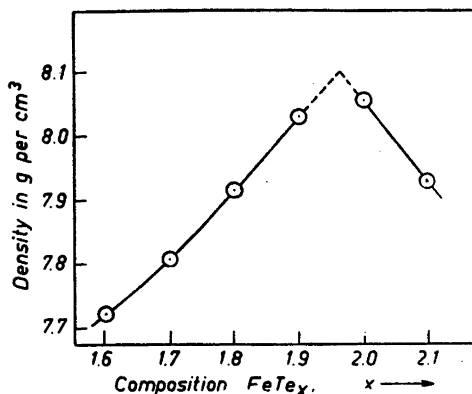
Fig. 3. Observed densities in the composition range $FeTe_{1.60}$ to $FeTe_{2.10}$.

and Pnn (C_{2v}^{10}). In the space group $Pnnm$ the marcasite grouping is realized with the atoms in the following positions:

2 Fe atoms in (a) 0,0,0; 1/2, 1/2, 1/2,

4 Te atoms in (g) $x, y, 0$; $\bar{x}, \bar{y}, 0$; 1/2—x, 1/2 + y, 1/2; 1/2 + x, 1/2—y, 1/2.

By a systematic variation of the x and y parameters the best agreement with observed intensities was obtained with $x = 0.365$ and $y = 0.225$. These values are very close to the values $x = 0.36$ and $y = 0.22$ found by Tengnér. In Table 8 are listed the results of the calculations, together with the observed relative intensities of the interferences and the $\sin^2\Theta$ values.

In $FeTe_2$ each Fe atom is surrounded by 6 Te atoms at the corners of a deformed octahedron at the distances Fe—2Te = 2.58 Å and Fe—4Te = 2.56 Å, while each Te atom is surrounded by one and two iron atoms at the same distances. The tellurium radius is found from the shortest Te—Te distance to be 1.45 Å. This is appreciably larger than the tetrahedral Te radius [18], 1.32 Å.

The homogeneity range of the ε-phase $FeTe_2$ is not only noted from changes in the position of the X-ray interferences but also from changes in their intensity. As the changes are especially noticeable on high angle interferences with low l values they are probable due to alterations in the parameter values, and the observed intensities of the $FeTe_{2.10}$ interferences are in fact reproduced better with the parameter values $x = 0.36$ and $y = 0.22$ than with the values used for $FeTe_2$.

Marcasite-like phases with metalloid deficit have been known since Buerger[22] in 1932 found by chemical analysis that loellingite had the composition $FeAs_{1.78}$*. Two years later Buerger [24] concluded from available analytical data that marcasite itself had a sulfur deficient composition which corresponded to the

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* Chemical analysis of a loellingite from Kuortane, Finland, and a comparison with seven other analyses reported in the literature led Pehrman [23], in contrast to Buerger, to the conclusion that the composition of loellingite is usually close to MeX_2.

Table 9. Calculated densities for $FeTe_{1.95}$ and $FeTe_{2.10}$.

Sample	Type of solid solution	Formula	Calc. density in g/cm³
$FeTe_{1.95}$	Interstitial Substitutional Subtractive	$Fe_{1.026}Te_2$ $Fe_{1.017}Te_{1.983}$ $FeTe_{1.950}$	8.131 8.063 7.928
$FeTe_{2.10}$	Interstitial Substitutional Subtractive	$FeTe_{2.100}$ $Fe_{0.968}Te_{2.032}$ $Fe_{0.952}Te_2$	8.402 8.130 8.002

formula $FeS_{1.985}$. By means of magnetic measurements and density determinations Haraldsen, Rosenqvist and Grønvold [25] found that chromium diantimonide is homogeneous at the composition $CrSb_{1.85}$. In all these phases the metal excess was combined with a substitution of metal for metalloid atoms, giving the formulae: $Fe_{1.06}As_{1.92}$, $Fe_{1.01}S_{1.99}$, $Cr_{1.05}Sb_{1.95}$.

A metal excess was also observed in the iron ditelluride and density determinations were carried out to find the composition limits and cell content of the ε-phase. The densities were determined as usual by means of kerosene displacement in vacuum at 20° C. The results are shown in Fig. 3. Extrapolation of the two parts of the curve gives a maximum density close to the composition $FeTe_{1.95}$. This agrees very well with the X-ray results and supports the conclusion that the ε-phase is homogeneous at this composition.

In many cases it is possible to decide between the different types of solid solution in non-stoichiometric compounds by means of density determinations. The three types of solid solution to be taken into account are interstitial, substitutional and subtractive. The densities calculated for these three possibilities and the corresponding formulae for $FeTe_{1.95}$ are listed in Table 9.

The density of $FeTe_{1.95}$ has not been determined experimentally but from the densities of the adjacent samples a density of 8.09 g/cm³ is interpolated. It is therefore evident that the solid solution does not take place by subtraction of tellurium atoms. As a rule, densities found by the liquid displacement method used here, are about 0.5 % too low. Accordingly, the interstitial solid solution type is considered as the most probable.

At the stoichiometric composition $FeTe_2$ the calculated density 8.092 g/cm³ is in good agreement with the observed value 8.05_1 g/cm³. The observed density for $FeTe_{2.10}$ is 7.92_7 g/cm³ and a comparison with the calculated values in Table 9 shows that the assumption of a subtractive solid solution is needed to account for the low density observed. Thus, within the whole range of homogeneity of the ε-phase from $FeTe_{1.95}$ to $FeTe_{2.10}$, a removal of iron atoms from the lattice takes place with increasing tellurium concentration.

SUMMARY

Iron tellurium alloys with compositions ranging from Fe_2Te to $FeTe_3$ have been studied by means of X-ray diffraction. The existence of four intermediate phases was revealed.

1. The β-phase, $FeTe_{0.9}$ or Fe_9Te_8, with a narrow homogeneity range, is found to have tetragonal structure with the lattice constants:

$a = 3.823_0$ Å, $c = 6.276_7$ Å at the iron rich limit,

and

$a = 3.819_8$ Å, $c = 6.280_5$ Å at the tellurium rich limit.

Space group: $P4/nmm$, with 2 Fe in (a) and 2 Te in (c) with $z_1 = 0.285$. Excessive 0.2 Fe atoms are probably located in (c) with $z_2 \approx 0.70$. The observed density of $FeTe_{0.90}$ is 6.77_7 g/cm^3.

2. The γ-phase, $FeTe_{1.1}$, is stable in the temperature range around 750° C. Its structure is not yet known.

3. The δ-phase, $FeTe_{1.4}$—$FeTe_{1.5}$, has a structure of $B8$ (NiAs)-like type and is stable above 488° C. The lattice constants of the hexagonal $FeTe_{1.50}$ are:

$a = 3.816_2$ Å, $c = 5.654_8$ Å.

The observed density 7.63_3 g/cm^3 shows that the phase is of the AB subtractive type with missing iron atoms.

A monoclinic deformation is observed at the iron rich side of the homogeneity range.

4. The ε-phase, $FeTe_2$, with orthorhombic structure of the $C18$ (marcasite) type, has a range of homogeneity between $FeTe_{1.95}$ and $FeTe_{2.10}$. The lattice constants are:

$a = 6.264_1$ Å, $b = 5.260_6$ Å, $c = 3.872_4$ Å for $FeTe_{1.90}$,
$a = 6.274_7$ Å, $b = 5.278_8$ Å, $c = 3.863_6$ Å for $FeTe_{2.10}$.

For $FeTe_2$, the best agreement between the observed and calculated X-ray intensities was obtained using the parameters x = 0.365 and y = 0.225.

The density determinations indicate that some iron atoms are in interstitial positions in $FeTe_{1.95}$ and are missing in $FeTe_{2.10}$.

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