The Crystal Structure of $Fe_{.28}Ni_{.28}Te_{.44}$

GUNVOR ÅKESSON and ERLING RØST

Kjemisk institutt, Universitetet i Oslo, Oslo 3, Norway

The crystal structure of $Fe_{.28}Ni_{.28}Te_{.44}$, quenched from 650°C, has been determined by X-ray single crystal methods. The structure is rhombohedral with lattice constants $a = 7.157$ Å and $\alpha = 32.22°$ (in hexagonal setting $a = 3.972$ Å and $c = 20.34$ Å). The space group is $R3m$, and all atoms are situated on three-fold axis in position $3a$ (hexagonal setting). The z parameters are 0 and 0.483 for tellurium, and 0.236, 0.870, and 0.609 for metal atoms. Reduced occupancy is assumed for the metal atoms.

The structure is a layer structure. Hexagonal tellurium layers are stacked in the sequence ABCABC. Every second space between the tellurium layers is open, whereas metal atoms occupy both the octahedral and the tetrahedral positions in the other spaces.

A phase with approximate composition $Ni_{1.5}Fe_{1.5}Te_2$ and rhombohedral crystal structure has been reported by Stevels.[1] The lattice constants are given as $a = 7.213$ Å, $\alpha = 30°50'$ or, in hexagonal setting, $a = 3.981$ Å, $c = 20.510$ Å. The metal/tellurium ratio in this phase can vary within certain limits. A crystal structure was suggested for this phase, based on the space group $R\bar{3}m$. Referring to hexagonal indexing of the structure, the tellurium atoms are situated in position $6(c)$ with $z = 0.254$ and the metal atoms distributed over the position $3(a)$, and $6(c)$ with $z = 0.129$. The structure determination was based on powder diffraction data, and the agreement between observed and calculated intensities is reported to be "not very satisfactory for a number of weak reflections". Stevels [1] also found that a certain change in the structure takes place at 140°C. For the high temperature phase he suggested the positions: Me_I in $3(a)$, Me_{II} in $18(h)$ with $x = 0.064$, $z = 0.131$ and with Te in position $6(c)$ with $z = 0.249$. Also this structure was referred to space group $R\bar{3}m$.

The existence of the phase with rhombohedral structure has been confirmed by Røst and Åkesson.[2] At 600°C the phase extends within the following composition ranges: $17-32$ at. % Fe, $24-41$ at. % Ni, and $41-45$ at. % Te. The lattice constants of the phase increase with decreasing tellurium content, possibly due to varying population of partly occupied metal sites in the structure.

EXPERIMENTAL

The procedure for preparing the samples and the methods for X-ray examination and density measurement of powdered samples are described elsewhere.[2] Single crystals were obtained at about 650°C by heating powdered samples of $Fe_{.28}Ni_{.28}Te_{.44}$ in evacuated and sealed silica tubes in an oven with a certain temperature gradient. Small amounts of iodine were added as transport agent. The crystals were quenched into water. Single crystal photographs were obtained in an integrating Weissenberg camera of 53.3 mm diameter using MoKα-radiation, and multiple film technique was used with Sn-foils between the films. The intensities were estimated photometrically, the weak ones also visually. The crystal used for single crystal photographs was 0.05 mm long by 0.02 mm. Corrections for X-ray absorption were made assuming the crystal to be cylindrical.

The structure determination was carried out by three-dimensional Patterson and Fourier syntheses and by a full-matrix least squares programme.[3] In the calculations no attempt was made to distinguish between Fe and Ni, and the mean values of the atomic form factors were used for the metal positions. Unobserved reflections were omitted in the final calculations.

CRYSTAL DATA
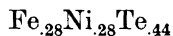
$Fe_{.28}Ni_{.28}Te_{.44}$
Hexagonal setting: $a = 3.972 \pm 0.001$ Å, $c = 20.34 \pm 0.01$ Å, unit cell volume $= 277.9$ Å^3.
Rhombohedral setting: $a = 7.157$ Å, $\alpha = 32.22°$.
Observed density: 7.13 g cm^{-3}.
Unit cell content: 13.52 atoms (hexagonal cell), i.e. 5.94 (6) Te atoms and 7.58 metal atoms (Fe + Ni).
Reflections present: $-h + k + l = 3n$
Possible space groups: $R3$, $R\bar{3}$, $R32$, $R3m$, $R\bar{3}m$.

RESULTS AND DISCUSSION

The stoichiometric composition of the crystal used for the X-ray investigation is not necessarily equal to that of the main sample. The variation of the tellurium/metal ratio of the phase is, however, rather limited, and a small variation of the Fe/Ni ratio would not seriously affect the X-ray results.

Table 1. Positional parameters (z), temperature factors assuming isotropy (B) and anisotropy (b_{ij}), and reliability factors (R). Estimated deviations are given in parenthesis. For the metal positions 84.2 % occupancy is assumed.

		Te1	Te2	Me3	Me4	Me5	R %
	z	0	0.4830 (3)	0.236 (3)	0.870 (1)	0.609 (2)	
Isotropic							8.9
	B	0.56 (6)	2.0 (2)	5.6 (8)	1.8 (4)	1.7 (3)	
	z	0	0.4825 (2)	0.231 (1)	0.868 (1)	0.607 (1)	
Anisotropic	$b_{11}=b_{22}=b_{12}$	0.012 (2)	0.030 (3)	0.12 (1)	0.037 (8)	0.041 (7)	6.5
	b_{33}	0.0004 (1)	0.0021 (3)	0.0013 (6)	0.0009 (6)	0.0003 (3)	

Table 2. Observed and calculated structure factors assuming isotropic temperature factors. The columns contain k, l, $|F_o|$, and $|F_c|$, respectively.

h = 0

k	l	$|F_o|$	$|F_c|$
0	6	162	167
0	9	106	104
0	12	98	99
0	15	162	162
0	18	94	101
0	21	96	100
0	27	47	49
1	2	210	215
1	5	198	178
1	8	353	324
1	14	66	77
1	17	99	106
1	23	117	113
2	4	146	141
2	7	101	107
2	10	138	141
2	13	129	126
2	16	127	119
2	19	47	43
2	25	63	68
2	31	58	58
3	0	219	216
3	3	28	30
3	6	113	111
3	9	53	52
3	12	65	62
3	15	97	103
3	18	75	65
3	21	69	67
4	2	99	104
4	5	52	53
4	8	116	117
4	11	20	25
4	14	48	48
4	17	59	55
4	23	53	63
5	4	61	57
5	10	64	62
5	13	55	48
5	16	55	47
5	22	56	27
6	0	56	65
6	6	40	48

h = 1

k	l	$|F_o|$	$|F_c|$
0	4	221	182
0	7	129	130
0	10	169	166
0	13	158	158
0	16	148	148
0	19	50	48
0	25	64	76
0	31	65	64
1	0	426	349
1	3	66	70
5	8	66	65

h = 2

k	l	$|F_o|$	$|F_c|$
0	2	170	177
0	5	121	123
0	8	240	247
0	14	85	68
0	17	98	89
0	23	119	98
1	4	90	114
1	7	124	91
1	10	97	122
1	13	99	103
1	16	49	99
1	19	66	41
1	25	56	61
1	31	183	52
2	0	100	179
2	6	47	99
2	9	57	45
2	12	91	56
2	15	57	90
2	18	66	58
2	21	27	60
2	24	29	28
2	27	101	34
3	5	49	93
3	8	106	102
3	14	45	45
3	17	57	50
4	4	60	58
4	7	58	53
4	10	29	40
4	13	60	57
4	16	49	44
5	0	55	43
5	6	61	59
6	0	46	45

h = 3

k	l	$|F_o|$	$|F_c|$
1	2	121	117
1	5	55	62
1	8	134	136
1	11	26	24
1	14	51	52
1	17	59	61
1	23	67	70
2	4	67	69
2	7	60	55
2	10	83	76
2	13	54	59
2	16	59	57
2	19	37	33
2	25	42	43
3	4	92	89
3	7	63	61
3	10	34	39
3	15	54	53
4	2	48	53
4	5	22	26
4	8	56	54

h = 4

k	l	$|F_o|$	$|F_c|$
0	4	69	76
0	7	67	61
0	10	95	84
0	13	56	66
0	16	56	64
0	19	45	35
0	25	54	47
2	2	75	69
2	8	72	72
2	14	29	37
2	17	30	39
3	4	37	43
3	7	30	32
3	10	49	44

h = 5

k	l	$|F_o|$	$|F_c|$
0	2	81	76
0	8	70	80
0	14	36	39
1	4	45	49
1	7	44	37
1	10	61	52

Refinements of the structure assuming the space group $R\bar{3}m$ were tried, but no acceptable accordance was obtained between observed and calculated intensities. Acceptable results were, however, obtained assuming the space group $R3m$ which represents a lower symmetry. Successive structure refinements led to the atomic positions referred to in Table 1. All the atoms are placed on three-fold axis in the three-fold positions $3(a)$: $0,0,z, + (0,0,0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3};$ $\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$. This means that reduced occupancy must be assumed for the metal positions. Refinements assuming isotropic temperature factors and equal occupancy (84.2 %) of all three metal positions led to a reliability factor * of 0.089. Least squares refinements assuming anisotropic temperature factors gave a reliability factor of 0.065. The differences in atomic position compared to those referring to isotropic temperature factors are, however, insignificant. Observed and calculated structure factors given in Table 2 refer to the calculations assuming isotropic temperature factors. The atomic positions are denoted Te1, 2, and Me3, 4, 5. The temperature factor of the metal atom Me3 is rather great compared with those of the other atoms. This may indicate that the position Me3 is less populated than the other metal positions. Refinements were therefore carried out under this assumption, but a significantly better solution of the structure was not obtained.
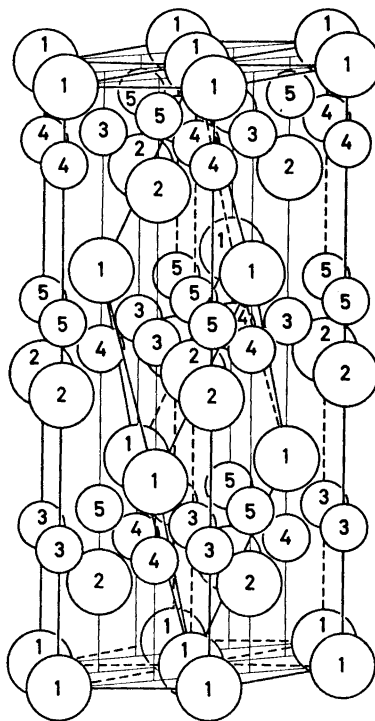

Fig. 1. The crystal structure of $Fe_{.28}Ni_{.28}Te_{.44}$. Large circles represent tellurium atoms and small ones are metal atoms. All atoms are situated on the 3-fold axes which are indicated by lines parallel to the c-axis. Both the hexagonal and the rhombohedral cells are indicated.

* Reliability factor $R = \sum ||F_o| - |F_c||/\sum|F_o|$

A perspective view of the structure is given in Fig. 1. The greater circles represent tellurium, and the smaller ones represent metal atoms. All the atoms are placed on three-fold axis which are indicated in the figure by lines parallel to the c-axis. The rhombohedral unit cell is also indicated. This structure is a marked layer structure with the tellurium atoms arranged in hexagonal layers perpendicular to the trigonal axis. The tellurium atoms are stacked in the sequence ABCABC, which is the same sequence as in a close-packed cubic arrangement. The interplanar distances are, however, alternating between 3.05 and 3.72 Å. The metal atoms occupy both the octahedral and tetrahedral positions in every second intermediate space between the tellurium layers, whereas every second interval is quite empty. According to the stoichiometric composition of the sample the average occupancy of the metal positions is 82.4 %.

Table 3. Interatomic distances for Fe$_{.28}$Ni$_{.28}$Te$_{.44}$. Number of equal distances are given in parentheses.

Te1 – Te1	3.97	(6)		Me3 – Te1	3.10	(3)
– Te2	3.80	(3)		– Te2	3.82	(3)
– Me3	3.10	(3)		– Me4	2.37	(3)
– Me4	2.69	(1)		– Me5	2.45	(3)
– Me5	2.60	(3)				
				Me4 – Te1	2.69	(1)
Te2 – Te1	3.80	(3)		– Te2	2.53	(3)
– Te2	3.97	(6)		– Me3	2.37	(3)
– Me3	2.83	(3)		– Me5	2.72	(3)
– Me4	2.53	(3)				
– Me5	2.53	(1)		Me5 – Te1	2.60	(3)
				– Te2	2.53	(1)
				– Me3	2.45	(3)
				– Me4	2.72	(3)

Interatomic distances in the structure are given in Table 3. In the plane perpendicular to the trigonal axis each Te atom is coordinated to six other Te atoms at a distance of 3.97 Å (the a-axis). At one side of this plane the Te atoms are coordinated to three Te atoms at 3.80 Å, and at the other side to four metal atoms at distances shorter than 2.70 Å.

The metal atoms are rather closely packed. The position Me3 is octahedrally coordinated by Te atoms whereas a tetrahedral coordination was found for Me4 and Me5. In addition, the metal atoms are surrounded by six metal atoms with bond distances varying from 2.37 Å to 2.72 Å. The distance 2.37 Å which was found between Me3 and Me4 is surprisingly short. This may indicate that position Me3 has a lower degree of occupancy than the other metal positions. The relatively high temperature factor found for Me3 (see Table 2) supports this assumption. However, calculations assuming varying degree of occupancy for the metal positions have been carried out, but a definite solution of this problem was not found.

The present structure is a layer structure with bonds of van der Waals type between the layers. The length of these Te – Te distances are 3.80 Å. Such a structure with weak interplane bonds is in good accordance with the behav-

iour of the sample which is graphite-like when crushed in a mortar. Layer structure formation occurs frequently among ditellurides of transition elements, especially those with $Cd(OH)_2$-type structure and related structures. The Te − Te distances between the layers vary from about 3.4 to 4.0 Å. Also more metal-rich tellurides with layer structures have been described. In CuTe (orthorhombic) the Te − Te distances between layers are 3.98 Å,[4] and in $FeTe_{0.9}$(tetragonal) the corresponding distances are 3.82 Å.[5] Both these phases are reported to form plate-like crystals. In the phase $FeTe_{0.9}$ nickel can be partly substituted for iron.[1,2] This leads to an increase of the metal to tellurium ratio, and the cleavage tendency| of the phase disappears successively. When about half of the iron is replaced with nickel, however, the structure changes to the rhombohedral layer structure described in the present investigation.

REFERENCES

1. Stevels, A. L. N. *Thesis*, Groningen 1969; *Philips Res. Reports Suppl. No. 9* (1969).
2. Røst, E. and Åkesson, G. *Acta Chem. Scand.* **26** (1972) 3662.
3. Dahl, T., Gram, F., Groth, P., Klewe, B. and Rømming, C. *Acta Chem. Scand.* **24** (1970) 2232.
4. Anderko, K. and Shubert, K. *Z. Metallk.* **45** (1954) 371.
5. Grønvold, F., Haraldsen, H. and Vihovde, J. *Acta Chem. Scand.* **8** (1954) 1929.