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The Crystal Structure of $(Fe_xNi_{1-x})_{22}Se_{16}$

ERLING RØST and KJELL HAUGSTEN

Kjemisk Institutt A, Universitetet i Oslo, Oslo 3, Norway

The crystal structure of the compound $(Fe_xNi_{1-x})_{22}Se_{16}$, ($x=0.2$) has been determined using X-ray methods. The crystal system is body centred tetragonal, with the lattice constants $a=7.208$ and $c=11.393$ Å. The most probable space group is $I\bar{4}m2$, and the selenium and metal atoms are distributed as follows:

8 Me at (*g*):	0.275,	0.275,	0
8 Me at (*i*):	0.278,	0 ,	0.326
4 Me at (*f*):	0 ,	0.5 ,	0.024
2 Me at (*c*):	0 ,	0.5 ,	0.25
8 Se at (*i*):	0.242,	0 ,	0,115
8 Se at (*i*):	0 ,	0.221,	0.349

It was not possible to determine the mutual distribution of iron and nickel atoms.

The existence of the two isomorphous phases $(Co_xNi_{1-x})_{22}Se_{16}$ and $(Fe_xNi_{1-x})_{22}Se_{16}$ was reported by Haraldsen *et al.*[1] In a later paper by Røst and Haugsten,[2] the value of x of the latter phase was given as $0.04<x<0.23$ at 580°C. The crystal system of this phase was found to be body centred tetragonal, with the lattice dimensions $a=7.164$ and $c=11.403$ Å at the nickel-rich phase limit, whereas the corresponding values for the iron-rich sample are $a=7.217$ and $c=11.410$ Å. On further increase in the Fe/Ni ratio, another phase region with tetragonal structure appears. The lattice constants of this phase are $a=3.73$ and $c=5.76$ Å at 600°C. The structure is assumed to be of the rickardite ($Cu_{2.8}Te_2$) type, which is an intermediate between the $C38(Ni_2In)$ and the $B10(PbO)$ type structures.

The existence of the two ternary phases $(Fe,Ni)_{22}Se_{16}$ and $(Co,Ni)_{22}Se_{16}$ has been confirmed by Stevels *et al.*[3] Under special conditions, they also obtained a similar metastable phase in the binary system Ni—Se.

EXPERIMENTAL

Single crystals of $(Fe_xNi_{1-x})_{22}Se_{16}$ were obtained by the transport reaction method, using iodine as transporting agent. Samples used in an earlier investigation,[2] with the composition corresponding to $x=0.2$, $(Fe_{.116}Ni_{.463}Se_{.421})$ and traces of iodine were enclosed in evacuated silica tubes and annealed at ~600°C in a furnace in which there was a small temperature gradient. A number of small crystals were obtained after six weeks treatment, the one employed in the X-ray investigation being ~0.05 mm long by 0.02 mm.

Single crystal photographs were obtained using Mo*K*α-radiation in an integrating Weissenberg camera of 57.3 mm diameter. The multiple film technique was applied, using Sn foils between the films, and intensity data were obtained during rotation of the crystal about the *b*-axis (the needle axis of the crystal). The determination of structure was based on reflections from the layers *h*0*l* to *h*6*l*, and of a total number of 370 reflections, only 191 were observable. The unobserved reflections were omitted from the final least squares refinements.

The atomic form factors employed were those given by Hanson *et al.*[4] Those for the metal atoms, were interpolated assuming 20 % Fe and 80 % Ni in each metal position. No corrections were made for absorption or secondary extinction.

CRYSTAL DATA *

$Fe_{.116}Ni_{.463}Se_{.421}$.
Tetragonal
$a=7.208\pm0.002$ Å, $c=11.393\pm0.003$ Å.
Unit cell volume 585.9 Å^3.
Observed density 7.135 g cm^{-3}.
Unit cell content 38.01 (38) atoms, *i.e.* 16 Se and 22 Me atoms (average 4.4 Fe and 17.6 Ni atoms).
Systematically absent reflections:
hkl when $h+k+l=2n+1$.
Intensities of *hkl* and $\bar{h}kl$ were estimated to be equal.
Possible space groups:
$I422$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$, and $I4mmm$.

RESULTS AND DISCUSSION

The iron-rich samples of $(Fe_xNi_{1-x})_{22}Se_{16}$, and the nickel-rich rickardite-type phase of the Fe—Ni—Se system differ only slightly in gross composition.[2] The lattice constants of the former phase are approximately double those of the latter, and furthermore, the X-ray powder patterns of the two phases show similarities, even though the larger unit cell of $(Fe_xNi_{1-x})_{22}Se_{16}$ gives rise to a number of additional reflections. The choice of space group for $(Fe_xNi_{1-x})_{22}Se_{16}$ was therefore based on an assumed structural resemblance to the rickardite-type phase. In this structure type, the atomic arrangement is assumed to be as follows:

2 Me	at $0\ 0\ 0$,	$\frac{1}{2}\ \frac{1}{2}\ 0$,
2 Se	at $0\ \frac{1}{2}\ z_1$,	$\frac{1}{2}\ 0\ z_1$,
x Me	at $0\ \frac{1}{2}\ z_2$,	$\frac{1}{2}\ 0\ z_2$.

The z_1- and z_2-parameters are of the order of 0.25—0.30 and 0.7, respectively, in this structure.

* Taken in part from an earlier investigation.[2]

Of the possible space groups for $(Fe,Ni)_{22}Se_{16}$, $I\bar{4}m2$ appears to be the most fitting for the description of a structure which is comparable with that of the rickardite type, and the present determination is therefore based on this space group. The refinement of parameters was carried out by successive three dimensional Fourier syntheses, and by least squares refinements using programs written by Dahl *et al.*[5] The full matrix least squares program was carried out using the weighting scheme No. 1:

for $F_o \leqq FB$, $w = A1(F_o)^{B1}$
for $F_o > FB$, $w = A2(F_o)^{B2}$
by taking $A1 = 1.0$, $A2 = 14.5$, $B1 = 0$, $B2 = -0.5$ and $FB = 211$.

Only minor displacements in the Se positions occurred during the course of the work, whereas some of the metal positions were radically changed from

Table 1. Positional parameters (x,y,z), temperature factors (B), and estimated standard deviations (σ) for $(Fe_xNi_{1-x})_{22}Se_{16}$.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Me_I in 8(g)	0.2751	0.0008	0.2751	0.0008	0	—	0.62	0.11
Me_{II} in 8(i)	0.2784	0.0012	0	—	0.3256	0.0007	0.92	0.13
Me_{III} in 4(f)	0	—	0.5	—	0.0240	0.0011	0.90	0.18
Me_{IV} in 2(c)	0	—	0.5	—	0.25	—	0.43	0.22
Se_I in 8 (i)	0.2418	0.0008	0	—	0.1154	0.0005	0.55	0.08
Se_{II} in 8 (i)	0	—	0.2211	0.0009	0.3494	0.0004	0.43	0.08

Table 2. Observed and calculated structure factors of $(Fe_xNi_{1-x})_{22}Se_{16}$. The columns contain h, l, $|F_o|$, and $|F_c|$, respectively.

k = 0			
h	1		
0	2	120	83
0	4	160	148
0	6	381	394
0	8	283	276
0	12	130	116
0	18	95	81
1	1	85	70
1	3	116	121
1	5	202	209
1	7	104	108
1	9	198	209
1	13	121	129
1	15	103	106
2	2	342	322
2	4	100	96
2	6	327	329
2	8	75	64
2	10	220	229
2	12	108	93
2	14	110	97
2	18	79	96
3	1	89	88
3	3	189	193
3	5	80	77
3	7	111	121
3	9	237	241
3	11	116	120
3	15	127	136
4	0	709	705
4	2	76	47
4	4	120	126
4	6	239	255
4	8	207	214
4	12	89	75
5	1	129	134
5	5	207	222
5	7	147	158
5	9	125	125
5	13	160	177
5	15	89	72
6	0	93	87
6	2	179	193
6	6	165	188
6	10	142	150
7	1	103	105
7	3	135	143
7	7	126	130
7	9	149	180
7	11	114	120
7	15	138	126
8	0	273	293
8	4	91	90
8	6	80	78
8	8	111	114
9	1	79	87
9	5	138	146
9	7	103	119
9	9	91	71
9	13	141	144
10	0	123	130
10	2	87	95
10	6	108	108
k = 1			
h	1		
1	4	126	141
2	1	114	107
2	3	95	97
2	5	182	194
2	7	80	78
2	9	137	136
2	11	137	130
2	13	129	130
2	15	116	105
3	0	157	154
3	2	133	141
3	4	111	114
3	8	106	105
4	3	77	68
4	5	139	153
4	7	79	74
4	9	141	149
4	13	95	99
4	15	76	77
5	2	87	92
5	4	140	139
5	8	59	60
6	1	45	59
6	5	99	100
6	9	75	77
6	11	93	82
7	0	121	117
7	2	123	137
7	4	89	81
7	8	95	109
8	5	104	85
k = 2			
h	1		
2	0	320	289
2	2	336	315
2	4	614	611
2	6	78	62
2	8	70	58
2	10	128	117
2	12	81	71
3	1	191	178
3	3	166	166
3	5	60	52
3	9	190	197
3	11	90	84
3	13	148	134
4	2	226	227
4	4	61	52
4	6	251	256
4	10	172	169
4	12	77	67
4	14	85	78
5	1	97	89
5	5	211	225
5	7	122	116
5	9	42	50
5	11	161	173
5	13	84	96
5	15	108	111
6	0	162	172
6	2	126	132
6	4	305	335
7	1	131	141
7	3	141	138
7	9	159	174
8	2	127	129
8	6	140	144
9	5	143	145
10	4	115	130
k = 3			
h	1		
3	0	157	128
3	8	108	98
3	10	100	88
4	1	86	73
4	3	114	109
4	5	76	62
4	7	121	108
4	9	170	171
4	11	111	98
4	15	91	104
5	0	112	105
5	2	182	185
5	4	162	161
5	6	68	66
5	8	105	104
6	1	115	118
6	3	70	55
6	9	121	113
6	13	103	86
7	0	100	90
7	10	97	90
8	7	85	78
9	2	130	131
9	4	122	114
k = 4			
h	1		
4	0	491	509
4	4	116	109
4	6	177	167
4	8	180	173
5	1	97	88
5	5	169	173
5	7	120	108
5	9	119	94
5	13	149	140
6	0	60	54
6	2	166	155
6	6	149	151
6	10	139	115
7	1	96	87
7	3	104	89
7	7	127	115
7	9	147	131
7	11	90	101
8	0	213	228
8	4	80	71
8	8	117	98
9	5	126	120
k = 5			
h	1		
5	4	98	100
5	8	105	90
5	14	112	105
6	5	138	127
6	7	79	77
6	11	119	116
7	0	114	104
7	2	159	171
7	4	138	121
7	8	129	112
8	5	92	102
k = 6			
h	1		
6	0	124	104
6	4	207	206
7	1	109	105
7	9	114	106
8	2	106	88
8	6	105	86

Table 3. Interatomic distances in $(Fe_xNi_{1-x})_{22}Se_{16}$. The estimated standard deviations are in the range 0.006 to 0.013 Å.

From Me I	(0.275	0.275	0)	
- Se I	(0.242	0	0.115)	2.39 Å
"	(0	0.242	-0.115)	" "
- Se II	(0.279	0.5	0.151)	2.36 "
"	(0.5	0.279	-0.151)	" "
- Me II	(0.5	0.222	0.174)	2.59 "
"	(0.222	0.5	-0.174)	" "
- Me III	(0	0.5	0.024)	2.58 "
"	(0.5	0	-0.024)	" "
From Me II	(0.278	0	0.326)	
- Se I	(0.242	0	0.115)	2.41 Å
"	(0.5	0.258	0.385)	2.54 "
"	(0.5	-0.258	0.385)	" "
- Se II	(0	0.221	0.349)	2.58 "
"	(0	-0.221	0.349)	" "
- Me I	(0.225	0.225	0.5)	2.59 "
"	(0.225	-0.225	0.5)	" "
- Me II	(0.5	0.222	0.174)	2.84 "
"	(0.5	-0.222	0.174)	" "
- Me III	(0.5	0	0.524)	2.77 "
From Me III	(0	0.5	0.024)	
- Se I	(0	0.242	-0.115)	2.45 Å
"	(0	0.758	-0.115)	" "
- Se II	(0.279	0.5	0.151)	2.47 "
"	(-0.279	0.5	0.151)	" "
- Me I	(0.275	0.275	0)	2.58 "
"	(0.275	0.725	0)	" "
"	(-0.275	0.275	0)	" "
"	(-0.275	0.725	0)	" "
- Me II	(0.222	0.5	-0.174)	2.77 "
"	(-0.222	0.5	-0.174)	" "
- Me IV	(0	0.5	0.25)	2.58 "
From Me IV	(0	0.5	0.25)	
- Se II	(0	0.221	0.349)	2.31 Å
"	(0	0.779	0.349)	" "
"	(0.279	0.5	0.151)	" "
"	(-0.279	0.5	0.151)	" "
- Me III	(0	0.5	0.024)	2.58 "
"	(0	0.5	0.476)	" "

From Se I	(0.242	0	0.115)	
- Se I	(-0.242	0	0.115)	3.49 Å
"	(0	0.242	-0.115)	3.60 "
"	(0	-0.242	-0.115)	" "
"	(0.758	0	0.115)	3.72 "
"	(0.5	0.258	0.385)	4.04 "
"	(0.5	-0.258	0.385)	" "
- Se II	(0	0.221	0.349)	3.56 "
"	(0	-0.221	0.349)	" "
"	(0.279	-0.5	0.151)	3.64 "
"	(0.279	0.5	0.151)	" "
"	(0.5	0.279	-0.151)	4.09 "
"	(0.5	-0.279	-0.151)	" "
- Me I	(0.275	0.275	0)	2.39 "
"	(0.275	-0.275	0)	" "
- Me II	(0.278	0	0.326)	2.41 "
"	(0.5	0.222	0.174)	2.54 "
"	(0.5	-0.222	0.174)	" "
- Me III	(0.5	0	-0.024)	2.45 "
From Se II	(0	0.221	0.349)	
- Se II	(0	-0.221	0.349)	3.19 Å
"	(0.279	0.5	0.151)	3.63 "
"	(-0.279	0.5	0.151)	" "
"	(0	0.779	0.349)	4.02 "
"	(-0.221	0	0.651)	4.11 "
"	(0.221	0	0.651)	" "
- Se I	(0.242	0	0.115)	3.56 "
"	(-0.242	0	0.115)	" "
"	(0.5	0.258	0.385)	3.64 "
"	(-0.5	0.258	0.385)	" "
"	(0.258	0.5	0.615)	4.09 "
"	(-0.258	0.5	0.615)	" "
- Me I	(0.225	0.225	0.5)	2.36 "
"	(-0.225	0.225	0.5)	" "
- Me II	(0.278	0	0.326)	2.58 "
"	(-0.278	0	0.326)	" "
- Me III	(0	0.5	0.476)	2.47 "
- Me IV	(0	0.5	0.25)	2.31 "

those of the rickardite-type structure. Refinements were performed assuming anisotropic temperature factors, and attempts were made to distinguish between iron and nickel atoms. The quality of the intensity material appears to be insufficient for such determinations, however. The final refinements were therefore executed assuming isotropic temperature factors, the atomic form factors for the metal atoms being taken as the weighted mean for Fe and Ni. Refinements proceeded until no parameter shifts occurred, resulting in a reliability factor ($\sum||F_o|-|F_c||/\sum|F_o|$) of 0.069. The positional parameters and temperature factors of the atoms, together with estimated standard deviations, are to be found in Table 1, while the values of the observed and calculated structure factors are given in Table 2.

A perspective view of an eighth part of the unit cell ($a/2$, $b/2$, $c/2$) is shown in Fig. 1. The unit cell of the rickardite-type structure is shown in the same figure, for comparison.

Interatomic distances in $(Fe,Ni)_{22}Se_{16}$ are presented in Table 3, where the shortest Me—Me distances are seen to have the substantially equal values of 2.58 and 2.59 Å. The shortest Me—Se distances are 2.31 Å, and the shortest

Se—Se distances are 3.19 Å. The metal atoms Me_I, Me_{III}, and Me_{IV} are coordinated with four Se atoms in a distorted tetrahedral arrangement, and Me_{II} by five Se atoms in a distorted quadrangular prism. In addition to the Se atoms, the metal atoms are surrounded by a varying number of metal atoms, and the Me—Se distances are clearly dependent on the coordination

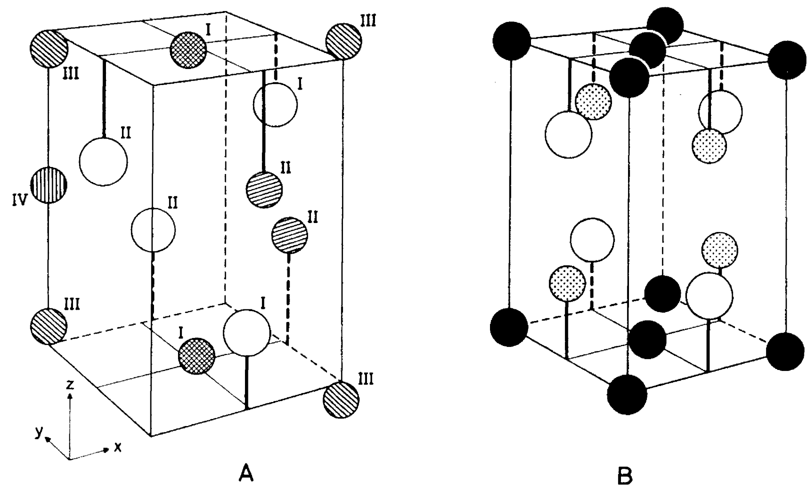

Fig. 1. A: An eighth part of the unit cell of $(Fe_xNi_{1-x})_{22}Se_{16}$: $a/2$, $b/2$, $c/2$ Open circles represent the selenium positions, the others being those of the metal atoms. B: A unit cell of the rickardite type structure. The dotted circles represent partly occupied metal positions.

number. Thus the shortest Me—Se distances (2.31 Å) are those from the Me_{IV} atoms which have only two metal atoms in addition to the four Se atoms as nearest neighbours. The corresponding distances from Me_I, which is coordinated with four metal and four selenium, are 2.36 (2) and 2.39 Å (2). The Me—Se distances are even greater when measured from the positions Me_{II} and Me_{III}, in accordance with the larger coordination number.

The environments of the metal atoms in the present structure are similar to those found in the metal-rich binary phases $Fe_{1+x}Se$ and Ni_3Se_2. In the former, having the B10—C38 type structure, the Fe atoms are tetrahedrally coordinated with four Se atoms at 2.37 Å, and four Fe atoms at 2.66 Å[6,7]. In the rhombohedral phase Ni_3Se_2, the Ni atoms are tetrahedrally surrounded by four Se atoms at 2.36 Å, and by four Ni atoms at a distance of 2.57 Å.[8] The similarity in the Me—Se distances of the latter two structures indicates that one cannot expect to distinguish between Fe and Ni atoms on the basis of interatomic distances and coordination numbers in $(Fe,Ni)_{22}Se_{16}$. The fact that Stevels *et al.*[3] have obtained this phase in the binary system Ni—Se (as a metastable compound), may indicate that the Fe atoms are not necessarily associated with fixed positions, but possibly distributed over all of the metal positions.

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