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On the System Fe – Ni – Se

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The phase relations of the ternary system Fe–Ni–Se at 580°C are examined, and the section of the phase diagram at this temperature is presented.

The lattice constants of a body centred tetragonal phase having the formula $(Fe_xNi_{1-x})_{11}Se_8$, which exists for values of x lying in the range $0.04<x<0.23$, are approximately $a=7.2$ and $c=11.4$ Å.

A second ternary phase having the $B10-C38$ ($PbO-Fe_2As$) structure exists for amounts of components extending over the following ranges: 17–41 at.-% Fe, 11–41 at.-% Ni, 42–48.5 at.-% Se.

Complete interchangeability of iron and nickel is possible in the $B8-C6$ ($NiAs-Cd(OH)_2$)-like phase, whereas only limited substitution of iron for nickel is possible in Ni_6Se_5 and $NiSe_2$ (pyrite type), and of nickel for iron in $FeSe_2$ (marcasite type).

About half of the nickel can be replaced by iron in the *fcc* high temperature phase $Ni_{3\pm x}Se_2$ at 700°C. The magnetic susceptibility of this phase increases appreciably with increasing iron content.

According to Hägg and Kindström [1] there exists a phase FeSe with the $B10$ (PbO) type structure in the iron-selenium system. The composition of this phase, which is stable below 457.6°C, has, however, been shown to be $FeSe_{0.96}$ by Haraldsen and Grønvold.[2,3] At 600°C, the $B8-C6$ ($NiAs-Cd(OH)_2$) type structure has a range of homogeneity extending from about 50 to 57.5 at.-% selenium.[1] A change from hexagonal to monoclinic symmetry occurs at 53.7 at.-% Se. At lower temperatures there exist several superstructures of this phase. $FeSe_2$ crystallizes with the marcasite type structure ($C18$) below 585°C.[4]

The phase relations of the nickel-selenium system at 580°C have been summarized in a previous publication.[5] The phases stable at this temperature are: Ni_3Se_2 with rhombohedral structure, Ni_6Se_5 which is orthorhombic, $NiSe_{1.02}-NiSe_{1.30}$ with $B8-C6$ type structure, and the pyrite type $NiSe_2$. A *fcc* high temperature phase $Ni_{3\pm x}Se_2$ exists above 600°C.[6]

Metallic iron crystallizes in the α-phase with *bcc* structure below 911°C, whereas γ-phase nickel has a *fcc* structure. Appreciable amounts of iron are soluble in the γ-phase nickel, while the solubility of nickel in the α-phase iron

is more limited. The phase relations at various temperatures are summarized by Owen and Liu.[7] The α-phase metal is ferromagnetic below 780°C whereas the Curie temperature of the γ-phase is appreciably lower.

EXPERIMENTAL

The *iron* used in the present investigation was "Ferrum reductum pro analysi" supplied by E. Merck A.G., Darmstadt, and the *nickel* was prepared from "NiO low in Co and Fe" from the British Drug Houses Ltd., London. Both samples were treated with dry oxygen-free hydrogen gas at 600°C, and after complete reduction the temperature was raised to about 1000°C. The selenium used was an extremely pure sample received as a gift from Boliden Gruvaktiebolag, Sweden.

The alloys were synthesized by heating appropriate proportions of the elements in evacuated and sealed silica tubes. The majority of samples were heated to fusion temperature and annealed at 580°C. Samples containing more than 53 at.—% Se were made by adding the required amount of selenium to finely ground metal-rich samples. Equilibrium conditions were achieved in such samples after annealing for a few days at 580°C. The samples were quenched in water after annealing.

The alloy samples were examined by X-ray powder methods using a Guinier type focusing camera with Cu$K\alpha_1$ radiation and KCl ($a=6.2919$ Å) as calibrating agent. A 19 cm Unicam camera was used for high temperature X-ray investigations.

Further examinations were carried out by metallographic methods, differential thermal analysis, and by means of high temperature magnetic measurements using the Faraday method. Densities were measured at 25°C using a pycnometric method with kerosene as displacement liquid.

PHASE RELATIONSHIPS AT 580°C

In the phases of the ternary system Fe—Ni—Se, extensive mutual interchange of iron and nickel is possible, resulting in several broad areas of solid solubility. The compositions of the alloys prepared and the phases present in the various samples at 580°C are given in Table 1, where the homogeneity regions are denoted by capital letters as follows:

A: Fe_xNi_{1-x} ($0.96<x\leq 1$); *bcc* structure.
B: Fe_xNi_{1-x} ($0\leq x<0.81$); *fcc* structure.
C: Ni_3Se_2, rhombohedral structure.
D: $(Fe_xNi_{1-x})_6Se_5$ ($0\leq x<0.045$); orthorhombic structure.
E: $(Fe_xNi_{1-x})_{11}Se_8$ ($0.042<x<0.23$); tetragonal structure.
F: *B*10—*C*38 (PbO—Fe_2As) structure type.
(17—41 at.-% Fe, 11—41 at.-% Ni, 42—48.5 at.-% Se).
G: *B*8—*C*6 (NiAs—$Cd(OH)_2$) type structure (50.5—59.5 at.-% Se).
I: $(Fe_xNi_{1-x})Se_2$ ($0.82<x\leq 1$); marcasite (*C*18) type structure.
H: $(Fe_xNi_{1-x})Se_2$ ($0\leq x<0.55$); pyrite (*C*2) type structure.

The compositions of the samples and the number of phases present in each are also shown in the at.-% plots in Figs. 1 (a) and (b). The phase boundaries and tie-lines separating the two- and three-phase regions are shown as broken lines in the diagrams. A few tie-line directions through two-phase samples are shown as dotted lines.

Table 1. Sample compositions in at.-%, and phases present at 580°C.

No.	Fe	Ni	Se	Phases	No.	Fe	Ni	Se	Phases	No.	Fe	Ni	Se	Phases
1	70.0	5.0	25.0	A+B+G	32	11.5	46.0	42.5	E+G	62	18.7	30.5	50.7	F+G
2	60.0	10.0	30.0	B+G	33	4.8	52.4	42.8	D+E	63	39.4	9.9	50.8	F+G
3	56.0	14.0	30.0	B+F+G	34	6.0	50.9	43.2	D+E+G	64	24.5	24.5	51.0	F+G
4	55.0	15.0	30.0	B+F+G	35	1.5	54.2	44.3	D+E	65	48.8	0.0	51.2	G
5	54.0	16.0	30.0	B+F	36	0.5	55.2	44.3	C+D	66	43.0	5.0	52.0	G
6	50.0	20.0	30.0	B+F	37	27.8	27.8	44.5	B+F	67	30.0	18.0	52.0	G
7	22.0	48.0	30.0	B+F	38	20.0	35.0	45.0	F+G	68	23.8	23.8	52.4	G
8	19.0	51.0	30.0	B+E+F	39	3.0	52.0	45.0	D+E+G	69	23.6	23.6	52.8	G
9	17.5	52.5	30.0	B+E	40[a]	0.0	54.6	45.5	C+D+G	70	23.3	23.3	53.5	G
10	5.2	64.8	30.0	B+E	41	16.0	38.0	46.0	F+G	71	22.8	22.8	54.5	G
11	3.0	67.0	30.0	B+C+E	42	14.0	40.0	46.0	E+F+G	72	22.2	22.2	55.6	G
12	0.0	61.0	39.0	B+C	43	5.0	49.0	46.0	D+E+G	73	0.0	43.5	56.5	G
13	50.0	10.0	40.0	B+F+G	44	6.4	47.4	46.2	E+G	74	21.7	21.7	56.7	G
14	16.8	43.2	40.0	B+E+F	45	43.0	10.0	47.0	B+F+G	75	21.3	21.3	57.4	G
15	13.0	47.0	40.0	B+E	46	35.3	17.7	47.0	B+F	76	42.5	0.0	57.5	G
16	2.5	57.5	40.0	B+C+E	47	44.1	8.8	47.1	B+F+G	77	37.7	6.9	58.3	G
17	0.5	59.5	40.0	B+C+E	48	28.0	25.0	47.1	F+G	78	20.8	20.8	58.3	G+I
18	0.0	60.0	40.0	C	49	35.2	17.5	47.4	F	79	34.0	6.8	59.2	G
19	2.2	56.6	41.2	B+C+E	50	1.8	50.5	47.7	D+G	80	36.2	3.8	60.0	G+H
20	0.0	58.5	41.5	C+D	51	41.2	10.0	48.8	B+F+G	81	33.3	6.7	60.0	G+H+I
21	11.6	46.5	41.9	B+E	52	34.7	16.5	48.8	F+G	82	32.0	8.0	60.0	G+I
22	28.5	28.5	42.1	B+F	53	49.0	2.0	49.0	B+G	83	18.9	18.9	62.2	G+I
23	17.3	40.6	42.1	F	54	50.0	0.0	50.0	A+G	84	17.0	17.0	66.0	G+I
24	15.9	42.0	42.1	E+F	55	45.0	5.0	50.0	B+G	85	33.3	0.0	66.7	H
25	14.6	43.3	42.1	E+F	56	40.0	10.0	50.0	F+G	86	26.8	6.5	66.7	H+I
26	13.5	44.3	42.1	E+F	57	25.0	25.0	50.0	F+G	87	20.8	12.5	66.7	H+I
27	11.6	46.3	42.1	E	58	15.0	35.0	50.0	F+G	88	16.6	16.6	66.7	I
28	5.8	52.1	42.1	E	59	5.0	45.0	50.0	E+G	89	10.0	23.3	66.7	I
29	3.0	54.9	42.1	E	60	9.9	39.6	50.5	G	90	0.0	33.3	66.7	I
30	2.0	55.9	42.1	C+D+E	61	0.0	49.5	50.5	G	91	16.5	16.5	67.0	I+Se
31	23.1	34.7	42.2	B+F										

[a] Equilibrium not obtained in sample 40.

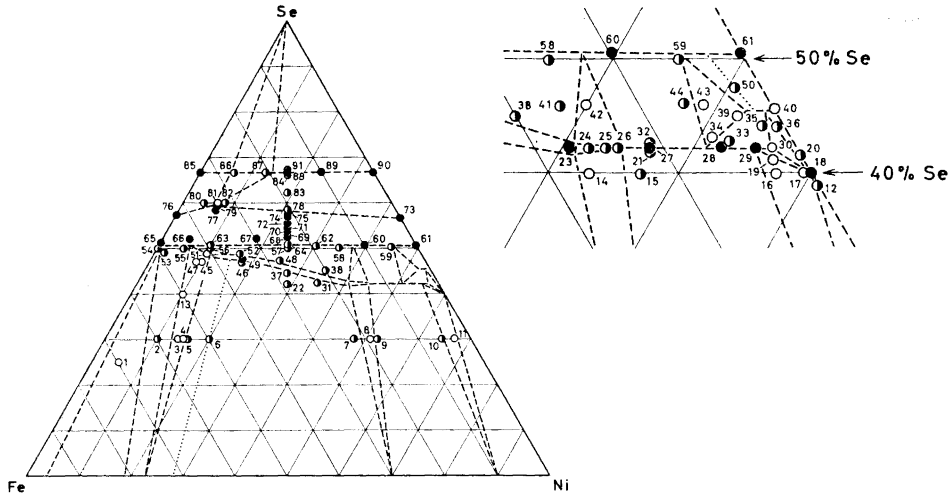

Fig. 1 a, b. Ternary plots of alloy composition in at.-%. Filled, half filled, and open circles represent samples containing one, two and three phases, respectively. Phase boundaries and tie-lines limiting two, and three phase fields are shown as broken lines. The dotted lines represent tie-line directions through two phase samples.

Fe—Ni alloys. On referring to the results of Owen and Liu,[7] one finds that about 4 at.-% Ni can be dissolved in the *bcc* α-phase, and 80.8 at.-% Fe in the *fcc* Ni.

Lattice constants of the metallic γ-phase in some two- and three-phase samples were determined, and the compositions of the metal phases determined by comparing the values with those reported for Fe—Ni alloys by Owen and Sully.[8] The results of these determinations are to be found in Table 2. Some of the tie-line directions were found in this way. The *B*8 type FeSe phase existing in equilibrium with the two metal phases contains <2 at.-% Ni. This was shown by the presence of α-type metal in sample 54 (FeSe) and of

Table 2. Lattice constants and compositions of the metallic Fe/Ni-phase in two- and three-phase samples.[a]

Sample No.	Mean composition	Lattice constants (Å)	Composition of metal phase
11	$Fe_{.030}Ni_{.670}Se_{.300}$	3.536	90 at.-% Ni
9	$Fe_{.175}Ni_{.525}Se_{.300}$	3.558	72 » »
8	$Fe_{.190}Ni_{.510}Se_{.300}$	3.560	70 » »
6	$Fe_{.500}Ni_{.200}Se_{.300}$	3.582	28 » »

[a] Determination of composition based on comparisons of lattice constants with those reported for Fe-Ni alloys by Owen and Sully.[8]

Table 3. Lattice constants and compositions of the *B*8 type phase in two- and three-phase samples.

Sample No.	Mean composition	Lattice constants a (Å)	c (Å)	At.-% Fe in *B*8 type phase
42	$Fe_{.14}Ni_{.40}Se_{.46}$	3.662	5.471	12.40
43	$Fe_{.05}Ni_{.49}Se_{.46}$	3.662	5.399	4.65
50	$Fe_{.018}Ni_{.505}Se_{.477}$	3.662	5.377	2.18

the γ-type metal in sample 53 ($Fe_{.49}Ni_{.02}Se_{.49}$) as found in the high temperature magnetic investigations.

Ni_3Se_2. No substitution of iron for nickel could be observed in this phase. Thus, sample 17 ($Fe_{.005}Ni_{.595}Se_{.400}$) containing only 0.5 at.-% iron, contains metal and the ternary phase $Me_{11}Se_8$ in addition to Ni_3Se_2. Cobalt has also been shown to be insoluble in Ni_3Se_2.[5]

$(Fe,Ni)_6Se_5$. The difficulty of preparing pure samples of Ni_6Se_5 has been discussed in a previous publication.[5] On the basis of X-ray and metallographic examinations of a series of samples, and of the tie-line determinations, a solubility of approximately 2.5 at.-% iron appears to be possible at 580°C. The tie-line determinations were based on the lattice constants of the NiAs type phase in two- and three-phase samples (Table 3). The composition of this phase was estimated by comparison with the lattice constants given in Table 6.

The ternary phase $(Fe,Ni)_{11}Se_8$. The crystal structure of this phase is tetragonal, and systematically absent reflections are those with $h+k+l=2n+1$, indicating a body centred structure. The lattice constants of a number of samples are given in Table 4.

The a-axis increases slightly with increasing Fe/Ni ratio, whereas the c-axis is practically constant. The density of sample 27 was found to be 7.135 g cm^{-3}, which, within experimental errors, corresponds to 22 metal and 16 selenium atoms per unit cell. This structure is clearly isomorphous with that of $(C_xoNi_{1-x})_{11}Se_8$ ($0.03<x<0.37$) found by Haraldsen *et al.*[5]

A crystal structure determination of $(Fe,Ni)_{11}Se_8$ is at present being performed using single crystal X-ray diffraction data.

Table 4. Lattice constants *versus* composition of $(Fe_xNi_{1-x})_{11}Se_8$.

Sample No.	x	Lattice constants a (Å)	c (Å)	Unit cell volume (Å^3)
30	0.035	7.164	11.403	585.2
29	0.052	7.168	11.403	585.9
28	0.100	7.178	11.401	587.5
27	0.200	7.208	11.393	591.9
26	0.234	7.217	11.410	594.4

The B10—C38 type phase. Below 457.6°C this phase region includes the binary $NiSe_{0.96}$ compound, but at elevated temperatures it is stable only in the ternary region. Nickel-rich samples of this phase decompose on quenching, but metallographic investigations nevertheless gave information on the phase relationships at the annealing temperature. Further investigations were performed by means of high temperature X-ray diffraction and differential thermal analysis. The transformation temperature of sample 51 ($Fe_{.412}Ni_{.100}Se_{.488}$) was determined to be approximately 560°C, and on increasing further the nickel content, the phase is stable to temperatures in the region of 650°C. At this temperature, the phase extends almost to the composition of sample 21 ($Fe_{.116}Ni_{.465}Se_{.419}$). At lower temperatures, the solubility of nickel decreases, and at room temperature (slowly cooled samples) the hickel-rich limit contains less nickel than sample 37 ($Fe_{.278}Ni_{.276}Se_{.445}$). With this composition, the phase is stable above 400°C. For sample 23 ($Fe_{.173}Ni_{.406}Se_{.421}$), the transition temperature is 580°C.

The crystal structure of the present phase is tetragonal and of the $B10—C38$ (rickardite) type. Lattice constants of some of the samples are presented in Table 5. The density of sample 49 was found to be 5.96 g cm^{-3}, corresponding to a unit cell content of 1.98 (*i.e.* 2) selenium and 2.20 metal atoms.

On taking the thermal expansion into account, one finds a slight but definite increase in the *a*-axis with increasing Fe/Ni fraction, whereas the *c*-axis decreases. In crystal structures of the $B10—C38$ type, metal atoms are in close contact in layers in the (001) plane, and the *a*-axis increase is accordingly a result of the greater effective dimension of iron atoms as compared with those of nickel. The decrease in the *c*-axis on the other hand, is clearly due to a decreasing number of interstitial metal atoms with increasing Fe/Ni fraction.

The B8—C6 type phase. At 580°C, complete interchange of iron and nickel is possible in this phase. Along the metal-rich boundary of the phase, X-ray powder patterns of the nickel-rich samples are very sharp, whereas those rich in iron are rather diffuse. The latter effect is probably due to a progressive change in composition towards greater selenium fraction as the temperature is lowered. High temperature X-ray powder patterns of iron-rich samples taken at 580°C show, however, very sharp reflections from the hexagonal phase, and it seems probable that the phase boundary at this temperature

Table 5. Lattice constants and temperature of observation for the phase with $B10—C38$ type structure.

Sample No.	Composition Fe	Ni	Se	Lattice constants *a* (Å)	*c* (Å)	Temperature of observation
a	.510	.000	.490	3.770	5.518	room temp.
49	.352	.175	.474	3.741	5.571	» »
37	.278	.278	.445	3.75	5.71	590°C
31	.231	.347	.422	3.74	5.74	560°C
23	.173	.406	.421	3.73	5.76	600°C

a Results according to Grønvold.[3]

Table 6. Lattice constants *versus* composition of quenched samples from the $B8-C6$ type region.

Sample No.	Composition			Lattice constants				Structure
	Fe	Ni	Se	$a(a\sqrt{3})$ (Å)	b (Å)	c (Å)	$\beta°$	
61	.000	.495	.505	(6.343)	3.662	5.357		Hexagonal
59	.050	.450	.500	(6.343)	3.662	5.402		»
60	.099	.396	.505	(6.343)	3.662	5.448		»
62	.187	.305	.507	(6.342)	3.661	5.538		»
64	.245	.245	.510	(6.330)	3.655	5.620		»
[a]	.500	.000	.500	(6.253)	3.610	5.928		»
68	.238	.238	.524	(6.293)	3.633	5.550		»
69	.236	.236	.528	(6.286)	3.630	5.543		»
70	.233	.233	.535	6.249	3.634	11.045	90.81	Monoclinic
71	.228	.228	.545	6.237	3.616	10.978	90.82	»
72	.222	.222	.556	6.225	3.589	10.908	91.15	»
74	.217	.217	.567	6.178	3.579	10.852	91.58	»
75	.213	.213	.574	6.160	3.576	10.810	91.63	»
78	.208	.208	.583	6.149	3.570	10.779	91.43	»
73	.000	.435	.565	6.200	3.636	10.477	90.78	»
77	.377	.069	.583	6.137	3.530	10.978	91.45	»
79	.340	.068	.592	6.117	3.521	10.929	91.20	»
76	.425	.000	.575	6.177	3.524	11.223	91.85	»

[a] High temperature measurement of FeSe at 500°C according to Hirone and Chiba.[9]

contains nearly 50 at.-% selenium, as is also suggested for the binary iron selenides by Hirone and Chiba.[9]

Lattice constants for several samples belonging to the $B8-C6$ type homogeneity region were determined, and are presented in Table 6.

Along the metal-rich boundary of the phase, the a-axis decreases slightly with increase in the Fe/Ni ratio, whereas the c-axis increases considerably. For samples containing equal amounts of iron and nickel, a decrease in the lattice dimensions occurs with increasing selenium fraction, and according to the investigations carried out on quenched samples, the structure changes from hexagonal to monoclinic symmetry at 53.3 at.-% selenium. The increase in the c-axis with increasing iron fraction, is due to the close metal-metal contact along this axis in the NiAs type structure. An increase in the selenium content leads to a subtraction of metal atoms from the lattice, and accordingly to a decrease in the lattice dimensions.

$(Fe,Ni)Se_2$, marcasite (C18) type. A limited proportion of the iron in the marcasite type $FeSe_2$ can be replaced by nickel. At 580°C the phase limit is close to sample 86 ($Fe_{.268}Ni_{.065}Se_{.667}$), since this is a two-phase sample, containing traces only of the pyrite type phase. The crystal structure is orthorhombic, and the lattice constants of sample 86 are,

$$a = 5.822,\ b = 4.838,\ \text{and}\ c = 3.609\ \text{Å}.$$

The lattice constants determined for sample 85 ($FeSe_2$) are,

$$a = 5.782,\ b = 4.799,\ \text{and}\ c = 3.583\ \text{Å}.$$

$(Fe,Ni)Se_2$, pyrite (C2) type structure. In the pyrite type $NiSe_2$, more than half of the nickel can be replaced by iron at 580°C. The lattice constants of a number of samples, which are given in Table 7, show that Vegard's law is obeyed.

Table 7. Lattice constants of the pyrite type $(Fe_xNi_{1-x})Se_2$.

Sample No.	x	a (Å)
90	0.000	5.965
89	0.300	5.917
88	0.500	5.885
87 [a]	0.625	5.874
86 [a]	0.800	5.874

[a] Two-phase samples.

The lattice dimensions of the two diselenide structures, having no close metal-metal contact, decreases with increasing Fe/Ni ratio. This is in contrast with the results found for the phases richer in metal, in which short intermetallic bonds exist.

The phase relationships at about 580°C for the system Fe—Ni—Se are shown in the ternary plot in Fig. 2. The regions of homogeneity are shown as heavy lines or as shaded areas. In two-phase fields, tie-line directions are indicated, and the open triangles show the threephase fields.

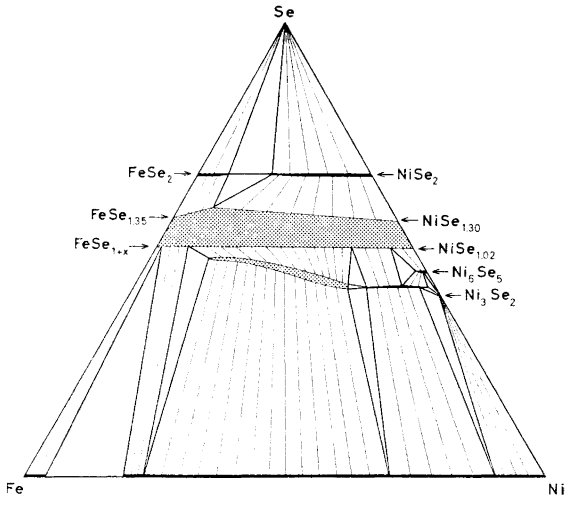

Fig. 2. Isothermal section of the Fe—Ni—Se phase diagram at 580°C. Single phase fields are shown as heavy lines or shaded areas, two phase fields are indicated by tie-lines, and three phase fields by open triangles.

THE HIGH TEMPERATURE PHASE $(Fe,Ni)_{3\pm x}Se_2$

The phase $Ni_{3\pm x}Se_2$, with *fcc* structure, is stable between approximately 600 and 780°C. A degree of variation in composition is possible, resulting in an increase in the lattice dimensions with increasing metal fraction. The unit cell probably contains four selenium atoms in a close packed arrangement with metal atoms distributed over tetrahedral and octahedral holes. The precise crystal structure has yet to be determined, however.

High temperature investigations have shown that at least 50 % of the nickel atoms can be replaced by iron, and that with increasing Fe/Ni ratio, the metal fraction of the phase decreases somewhat. Thus, around 700°C, the samples 15 ($Fe_{.13}Ni_{.47}Se_{.40}$) and 22 ($Fe_{.285}Ni_{.286}Se_{.421}$) both contain metal in addition to the high temperature phase. Sample 38 ($Fe_{.20}Ni_{.35}Se_{.45}$), on the other hand, contains small amounts of the NiAs type phase. Extension of the phase in the direction of metal-selenium appears accordingly to be rather limited.

The samples listed in Table 8 were all found to be of a single phase, and the lattice constants given were determined by means of high temperature X-ray diffraction. The expected increase in lattice dimensions with increasing Fe/Ni fraction is neutralized by a progressive decrease in the total metal content of the phase.

High temperature magnetic measurements were carried out for a number of samples of this phase, the temperature being gradually lowered from approximately 800°C. The commencement of decomposition of the *fcc* phase was indicated by a discontinuity in the susceptibility *versus* temperature curves. Values of susceptibility below the transition temperature were not exactly reproducible, probably owing to imperfect equilibrium. The susceptibility was relatively independent of temperature in the region of the *fcc* phase, and average values are given in Table 9, where the assumed transforma-

Table 8. Lattice constants *versus* composition of the *fcc* high temperature phase.

Sample No.	Composition			a (Å)	t (°C)
	Fe	Ni	Se		
[a]	0	.608	.392	5.427	630
[a]	0	.574	.426	5.343	640
21	.116	.465	.419	5.421	750
23	.173	.406	.421	5.438	710
37	.278	.278	.445	5.430	760

[a] Results from Grønvold *et al.*[4]

Table 9. Average magnetic susceptibilities χ_g (per g) and χ_{at} (per mole of metal) below 800°C, and transition temperature of the *fcc* high temperature phase.

Sample No.	Composition			Susceptibility		Transition temperature (°C)
	Fe	Ni	Se	$\chi_g \times 10^6$	$\chi_{at} \times 10^6$	
12	0	.610	.390	1.68	225	600
18	0	.60	.400	1.44	204	620
20	0	.585	.415	1.37	203	600
29	.030	.549	.421	2.17	299	610
32	.115	.406	.425	4.34	551	620
23	.173	.460	.421	5.64	698	680
37	.278	.278	.445	8.05	1020	720

tion temperatures of the *fcc* phase, are also given. χ_{at} refers to the paramagnetic contribution of the metal atoms to the susceptibility, and corrections are made for induced diamagnetism, *viz.*: Fe^{2+}, -13×10^{-6}; Ni^{2+}, -12×10^{-6}; and Se^{2-}, -48×10^{-6} per mole.[10]

The paramagnetism increases rapidly with increasing Fe/Ni ratio, and the susceptibility may be expressed in the form,

$$\chi_{at} = x\chi_{Fe} + (1-x)\chi_{Ni}$$

where x is the mole fraction of iron compared with the total metal content.

$$\chi_{Fe} = 1850\times10^{-6},\ \chi_{Ni} = 210\times10^{-6}$$

The susceptibility contribution from nickel corresponds well with that found for NiSe of the $B8$ type structure (215×10^{-6} at 450°C) [11] whereas the susceptibility per mole of iron is somewhat less than has been observed for the $B8$ type $FeSe_{1.13}$ (2400×10^{-6} at 700°C).[12]

According to the results of magnetic measurements, the transformation between the rhombohedral low temperature Ni_3Se_2 phase and the *fcc* $Ni_{3\pm x}Se_2$, takes place at 620°C, whereas for binary samples on either side of Ni_3Se_2 the transformation temperatures are definitely lower. This indicates the existence of two eutectoid compositions of the high temperature phase corresponding to what was found earlier for the nickel-sulfur system.[13]

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