On the System Co-Ni-Se

H A A K O N   H A R A L D S E N,   R O L F   M Ø L L E R U D   and   E R L I N G   R Ø S T

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

The isothermal section at 580°C of the phase diagram of the ternary system Co—Ni—Se has been determined mainly on the basis of quenched samples.

A phase with composition $(Co_xNi_{1-x})_{11}Se_8$ was found with x varying from 0.03 to 0.37. The crystal structure is body centered tetragonal with lattice constants: $a = 7.157$ and $c = 11.342$ Å for $(Co_{0.36}Ni_{0.64})_{11}Se_8$.

In the phase $(Co_xNi_{1-x})_6Se_5$ with orthorhombic structure cobalt can substitute nickel in the region $0.00 \leq x < 0.13$.

A continuous interchange of nickel and cobalt is possible both in the $B8$ (NiAs)-type and in the $C2$ (pyrite)-type structures. Lattice constant data for several alloys are presented.

In the binary system nickel-selenium a phase Ni_3Se_2 with rhombohedral structure has been described by several authors.[1-3] This structure transforms at about 600°C into a face centered cubic structure according to Grønvold et al.,[4] while a hexagonal structure was suggested for a corresponding phase by Kuznecov et al.[5]

Another phase, Ni_6Se_5, with orthorhombic crystal structure exists above 400°C according to Grønvold et al.[4] Also for this phase a hexagonal structure was suggested by Kuznecov et al.[5]

Furthermore the phase with $B8$ (NiAs)- $C6$ (Cd(OH)$_2$)-structure type exists between the limits $NiSe_{1.02}$ and $NiSe_{1.30}$ at 550°C.[6] The structure changes from hexagonal to monoclinic symmetry near $NiSe_{1.20}$. By X-ray investigation of samples annealed at 400°C the pyrite-type diselenide was found to exist in the range $NiSe_{1.975}$ to $NiSe_{2.00}$.[6]

In the system cobalt-selenium a phase Co_9Se_8 with pentlandite-type structure exists in samples quenched from 400°C.[7] This phase was not observed in samples quenched from 600°C. At 600°C the $B8$-$C6$-type structure was found to exist in the range from $CoSe_{1.02}$ to $CoSe_{1.37}$. The structure is monoclinic for samples containing more selenium than $CoSe_{1.15}$. The pyrite-type diselenide has a narrow range of homogeneity close to $CoSe_{2.0}$.

At high temperature nickel and cobalt form a continuous solid solution with face centered cubic structure. Below 477°C cobalt and also cobalt-rich alloys crystallize with close-packed hexagonal structure.[8]

The present investigation of the ternary system Co—Ni—Se is a continuation of the investigations of binary iron group chalcogenides carried out in this institute. The investigation is based mainly on samples annealed at 580°C, at which temperature the formation of the nonquenchable high temperature phase $Ni_{3\pm x}Se_2$ is avoided. Further, this temperature is above the stability ranges of the Co_9Se_8-phase and of the hexagonal structure type of metallic cobalt.

EXPERIMENTAL

The *cobalt* and *nickel* metals were prepared from "NiO, low in Co and Fe" and "Cobalt Oxide, specially pure" from The British Drug Houses Ltd. The oxides were reduced with dry, oxygen-free hydrogen gas. After completion of the reduction, the metals were heated in hydrogen atmosphere at about 1100 and 1000°C, respectively.

The *selenium* used was a gift from Bolidens Gruvaktiebolag, Sweden. It carried the analysis (in ppm): Na (0.1), As (1), S (< 0.5) and Cl (<0.5).

Most of the alloys were prepared by melting together calculated amounts of the elements in evacuated and sealed silica tubes. The samples were then annealed for one day at 580°C and quenched in water. Samples containing more than 56.5 at.-% selenium were made by reacting finely ground samples of $(Co,Ni)Se_x$ ($1 < x < 1.3$) with additional amounts of selenium. Two days annealing at 580°C was sufficient to obtain equilibrium even for $(Co,Ni)Se_2$.

The alloys were examined by metallographic methods, by X-ray diffraction and density measurements. X-Ray powder patterns were taken in an 11.48 cm Debye-Scherrer-type camera and in a Guinier-type focusing camera using $CuK\alpha_1$ radiation and with KCl ($a = 6.2919$ Å) as a calibrating standard.[9] The densities were measured at 25°C by the vacuum pycnometric method with kerosene as displacement liquid.

PHASE RELATIONSHIPS AT 580°C

In addition to the phases found in the binary system, one phase existing in the ternary region was also found. The composition of this phase can be described by the formula $(Co_xNi_{1-x})_{11}Se_8$ (see below). Extended interchangeability of cobalt and nickel was observed for all phases present, except the phase Ni_3Se_2.

Table 1 contains a list of the samples made in this investigation and references to the phase regions to which they belong. The different phases are denoted as: Me (cobalt-nickel alloys), Ni_3Se_2, $Me_{11}Se_8$, Me_6Se_5, $B8$—$C6$ (NiAs—Cd(OH)$_2$-type region), $MeSe_2$ and Se (liquid phase). Two and three phase regions are designated by Roman numerals as follows:

I: Me + $B8$—$C6$,
II: Me + $Me_{11}Se_8$ + $B8$—$C6$,
III: Me + $Me_{11}Se_8$,
IV: Me + Ni_3Se_2 + $Me_{11}Se_8$,
V: Me + Ni_3Se_2,
VI: Ni_3Se_2 + $Me_{11}Se_8$,
VII: Ni_3Se_2 + $Me_{11}Se_8$ + Me_6Se_5,

VIII: Ni_3Se_2 + Me_6Se_5,
IX: $Me_{11}Se_8$ + Me_6Se_5,
X: Me_6Se_5 + $B8$—$C6$,
XI: $Me_{11}Se_8$ + Me_6Se_5 + $B8$—$C6$,
XII: $Me_{11}Se_8$ + $B8$—$C6$,
XIII: $B8$—$C6$ + $MeSe_2$,
XIV: $MeSe_2$ + Se.

Within each phase region the samples are numbered in order of increasing selenium content. The compositions of the samples prepared can also be

Table 1. Compositions in atomic-% of the samples prepared.

Sample No.	Composition Co	Ni	Se	Phase region	Sample No.	Composition Co	Ni	Se	Phase region
1	51.0	19.0	30.0		40	2.0	55.0	43.0	
2	52.2	5.8	42.0		41	6.0	49.8	44.2	IX
3	46.4	11.6	42.0		42	4.0	51.8	44.2	
4	40.6	17.4	42.0	I	43	2.0	53.8	44.2	
5	50.0	0.0	50.0		44	0.0	55.0	45.0	*
6	37.5	12.5	50.0		45	0.0	54.0	46.0	
7	33.3	16.7	50.0						
8	53.60	23.40	23.00		46	7.00	47.55	45.45	
9	33.33	33.33	33.33		47	6.00	48.55	45.45	**
10	31.25	31.25	37.50		48	5.00	49.55	45.45	
11	29.50	29.50	41.00		49	5.25	47.25	47.50	
12	37.70	20.30	42.00	II	50	1.00	51.50	47.50	
13	35.00	23.00	42.00		51	10.00	40.00	50.00	X
14	22.00	35.88	42.12		52	8.00	42.00	50.00	
15	27.75	27.75	44.50		53	0.00	50.00	50.00	
16	26.50	26.50	47.00						
17	38.5	38.5	23.0		54	8.2	48.8	43.0	XI
18	10.5	59.5	30.0		55	8.0	47.8	44.2	
19	14.7	44.3	41.0		56	14.25	42.75	43.00	
20	11.8	47.2	41.0		57	11.00	44.80	44.20	
21	8.5	50.5	41.0		58	18.50	37.00	44.50	
22	19.5	39.2	41.3	III	59	13.50	40.50	46.00	XII
23	17.1	40.9	42.0		60	25.00	25.00	50.00	
24	14.5	43.5	42.0		61	16.70	33.30	50.00	
25	9.7	48.3	42.0		62	12.50	37.50	50.00	
26	4.5	53.5	42.0						
27	7.00	63.00	30.00		63	00.00	48.00	52.00	
28	1.00	59.00	40.00	IV	64	23.81	23.81	52.38	
29	2.22	56.23	41.55		65	23.25	23.25	53.50	
					66	22.75	22.75	54.50	B8−C6
30	4.6	65.4	30.0	V	67	00.00	45.50	54.50	
31	2.0	68.0	30.0		68	7.22	36.26	56.52	
					69	21.74	21.74	56.52	
32	0.0	60.0	40.0	Ni_3Se_2	70	21.27	21.27	57.45	XIII
33	1.55	56.90	41.55	VI	71	20.00	20.00	60.00	
34	21.00	36.88	42.12		72	33.33	0.00	66.67	
35	10.52	47.36	42.12	$Me_{11}Se_8$	73	27.80	5.53	66.67	
					74	16.67	16.67	66.67	$MeSe_2$
36	0.80	58.20	41.00	VII	75	8.33	25.00	66.67	
37	1.30	56.58	42.12		76	0.00	33.33	66.67	
38	0.0	58.0	42.0	VIII	77	14.45	14.45	71.10	XIV
39	1.0	54.8	44.2						

* $Me_3Se_2 + Me_6Se_5 + B8−C6$ ⎱
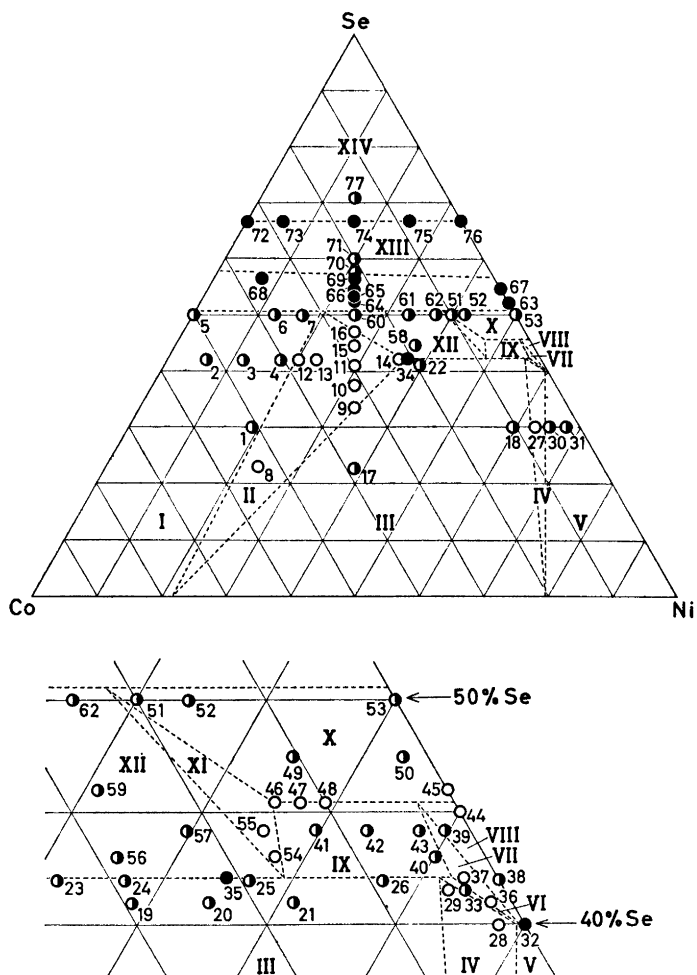** $Me_{11}Se_8 + Me_6Se_5 + B8−C6$ ⎰   Equilibrium not obtained in these samples.

Fig. 1a, b. Ternary plot of the cobalt-nickel-selenium alloy composition in atomic-%. Filled, half filled, and open circles represent samples containing one, two, and three phases, respectively. The phase boundaries and the tie lines limiting the different phase fields are dotted. The composition of the nickel-rich samples with 40 to 50 at.-% selenium are shown in Fig. 1b.

found in Figs. 1 a, b. Samples containing one phase are shown as filled circles, while those containing two and three phases are shown as half filled and open circles, respectively.

The homogeneity range of the ternary phase is estimated on the basis of the following observations: X-ray reflections from the ternary phase only were observed on photographs of samples 23, 25, and 26, containing 42.0 at.-% selenium, but a slight ferromagnetism indicates the presence of small

amounts of metal. In samples 34 and 35 with 42.12 at.-% selenium no ferro-magnetism was noted. On the other hand samples with 43.0 at.-% selenium (40, 54, and 56) contain considerable amounts of the Me_6Se_5-phase or the $B8$-type phase in addition to the $Me_{11}Se_8$-phase. Accordingly, the selenium content of this phase must be practically constant. In agreement with X-ray and density data a mutual interchange of cobalt and nickel is possible in this phase from a composition near sample 37 to near that of sample 34. Its com-position can be represented by the formula $(Co_xNi_{1-x})_{11}Se_8$, with $0.03 < x < 0.27$.

In the phase Ni_3Se_2 no observable solubility of cobalt was found, since sample 28 which contains only 1.0 at.-% cobalt was found to be a three phase sample with $Me_{11}Se_8$ and metal in addition to the major phase Ni_3Se_2.

Equilibrium conditions were not reached in binary samples with composi-tions near Ni_6Se_5. Thus, in samples 44 and 45 the $B8$-type phase, Ni_3Se_2 and Ni_6Se_5 were all present. The reason must be that relatively large crystals of the $B8$-type NiSe phase segregate from the liquid phase on cooling. When the temperature is kept below 650°C where the phase Ni_6Se_5 is stable, the reaction rate is apparently very low. Even after repeated crushing and anneal-ing equilibrium was not established in the temperature range 580—650°C. The same difficulty in reaching equilibrium conditions was also experienced for the ternary samples 46, 47, and 48, all containing 45.45 at.-% selenium corresponding to the formula $(Co,Ni)_6Se_5$. In samples 39, 41, and 42 with 44.2 at.-% selenium, however, the $B8$-type phase was not present. These are all two phase samples in which the $(Co_xNi_{1-x})_6Se_5$-phase apparently is in equilibrium with Ni_3Se_2 (sample 39) or $Me_{11}Se_8$ (samples 41 and 42). In sample 55 which also contains 44.2 at.-% selenium, the $B8$-type structure is found in addition to $Me_{11}Se_8$ and Me_6Se_5. As a conclusion of these observations a substitution of cobalt for nickel in this phase can be described by the formula $(Co_xNi_{1-x})_6Se_5$ with $0 \leq x < 0.13$.

For stoichiometric CoSe and NiSe two phases were observed in agreement with earlier results.[7,6] Also the ternary samples with 50 at.-% selenium prepared in this investigation were found to contain two phases. Probably, the metal-rich phase boundary of the $B8$-type phase extending from $CoSe_{1.02}$ to $NiSe_{1.02}$ contains approximately the same amount of selenium throughout the ternary region. The selenium-rich boundary of this phase from $CoSe_{1.37}$ to $NiSe_{1.30}$ passes between sample 69, $(Co_{0.5}Ni_{0.5})Se_{1.30}$ and 70, $(Co_{0.5}Ni_{0.5})Se_{1.35}$. Thus, the selenium-rich boundary of the phase follows an almost straight line.

A continuous solid solubility is also found between $CoSe_2$ and $NiSe_2$ at 580°C.

The results of this phase analysis are given in Fig. 2, which shows an isothermal section of the ternary equilibrium diagram at 580°C. The single-phase regions are shown as heavy lines or a hatched area. Two phase regions are indicated by the presence of tie lines, while three phase areas are shown as open triangles.
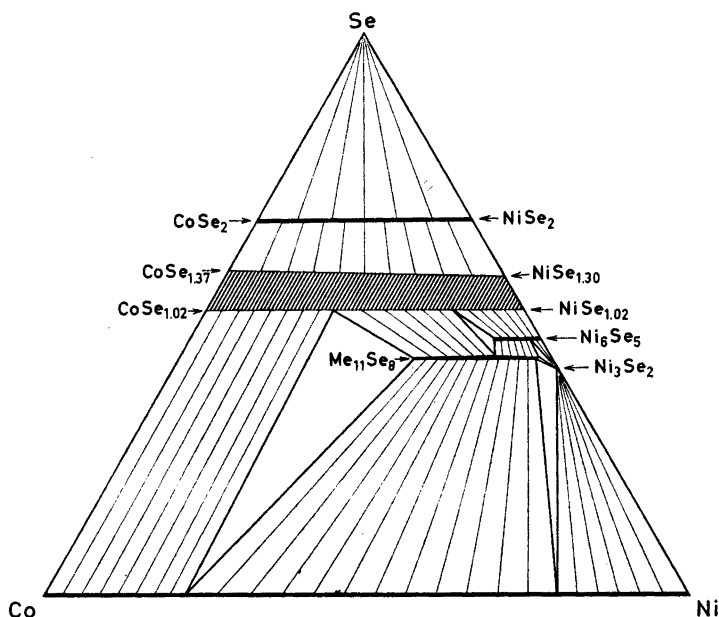
Fig. 2. Isothermal section of the Co—Ni—Se phase diagram at 580°C. Single phase fields are shown as heavy lines and a hatched area, two phase fields are denoted by tie lines and the three phase fields are open triangles.

STRUCTURAL DATA

The phase $(Co_xNi_{1-x})_{11}Se_8$. After some days annealing of sample 35 at about 650°C a few crystals were obtained. Weissenberg photographs showed that the crystal structure symmetry is tetragonal. The unit cell is body centered since all reflections with $h + k + l = 2n + 1$ are missing. Intensities of the reflections hkl and $\bar{h}kl$ were judged to be equal, leading to $I4/mmm$, $I\bar{4}2m$, $I4mm$ or $I422$ as probable space groups.

The indexed powder data from sample 34 are listed in Table 2. The lattice constants of this sample, which has a composition near the cobalt-rich boundary of the phase, are $a = 7.157$ and $c = 11.342$ Å. The lattice constants of sample 26, near the nickel-rich limit, were determined to be $a = 7.157$ and $c = 11.388$ Å. Thus, the c-axis increases slightly when nickel substitutes cobalt in $(Co_xNi_{1-x})_{11}Se_8$. The densities of samples 34 and 26 were both determined to be 7.28 gcm^{-3}, corresponding to 37.9 (38) atoms per unit cell in sample 34 and 38.1 (38) in sample 26, *i.e.* two formula units $(Co_xNi_{1-x})_{11}Se_8$. (The fact that sample 26 is a two phase sample with very small amounts of metal was not taken into account in the calculation of the latter value).

A phase with composition and structure similar to that described above has also been observed in the system Fe—Ni—Se.[10]

Table 2. X-Ray powder data of $(Co_{0.36}Ni_{0.64})_{11}Se_8$ (Sample 34), $CuK\alpha_1$-radiation.

| I_{obs} | $\sin^2 \theta \times 10^5$ | | hkl |
	obs	calc	
w +	1 617	1 619	101
vw	1 844	1 845	002
w +	2 314	2 317	110
m	5 310	5 309	103
w	6 252	6 253	211
vst	6 476	6 478	202
w	7 382	7 379	004
m	9 269	9 268	220
w	9 698	9 696	114
w	9 937	9 943	213
vw	10 891	10 886	301
st	11 110	11 113	222
w	11 580	11 583	310
m −	12 686	12 689	105
w +	13 423	13 428	312
w +	14 583	14 576	303
m −	15 516	15 520	321
w	16 605	16 603	006
st	16 647	16 647	224
m −	17 316	17 322	215
st	18 534	18 534	400

The phase Ni_3Se_2. A redetermination of the rhombohedral lattice constants of this phase gave $a = 4.2365$ Å and $\alpha = 90.70°$, which is in good accordance with those of Agarwala and Sinha [2] ($a = 4.24$ Å, $\alpha = 90.64°$) and Hiller and Wegener [3] ($a = 4.2375$ Å, $\alpha = 90.70°$).

The phase $(Co_xNi_{1-x})_6Se_5$. According to Grønvold *et al.*[4] the phase Ni_6Se_5 has an orthorhombic crystal structure with lattice constants $a = 3.437$, $b = 11.856$, and $c = 17.064$ Å. The lattice constants measured on the three phase sample 55 are $a = 3.429$, $b = 11.849$, and $c = 17.01$ Å. This decrease in the lattice constants with increasing cobalt content is an additional indication of the solubility of cobalt in this phase.

Table 3. Lattice constants at the metal-rich phase boundary of the $B8$-type structure measured on samples $(Co_xNi_{1-x})Se$ quenched from 580°C.

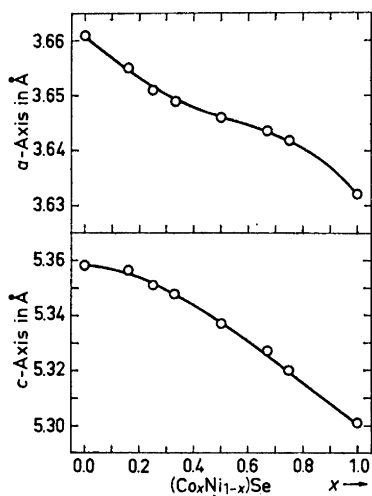| Sample	x	a in Å	c in Å
5	1.00	3 6315	5 3011
6	0.75	3.6423	5.3203
7	0.67	3.6436	5.3268
60	0.50	3.6460	5.3370
61	0.33	3.6493	5.3484
62	0.25	3.6505	5.3510
52	0.16	3.6546	5.3571
53	0.00	3.6615	5.3578

Fig. 3. Lattice constants of the metal-rich phase boundary of the *B*8-type phase as measured on two phase samples with gross composition $(Co_xNi_{1-x})Se$.

The difficulty in preparing a pure sample of the Ni_6Se_5 phase is discussed above. However, by substituting small amounts of tellurium for selenium, single phase samples have been obtained and the unit cell content determined to be four formula units.[11]

The B8—C6-type phase. The lattice constants of the *B*8 (NiAs)-type phase have been determined for a series of samples $(Co_xNi_{1-x})Se$, with 50 at.-% selenium. The results are listed in Table 3 and plotted in Fig. 3. The *c*-axis decreases smoothly with increasing cobalt content whereas the *a*-axis decreases somewhat irregularly.

The lattice constants of the *B*8-type phase in sample 12, $Co_{0.377}Ni_{0.203}Se_{0.420}$, containing three phases were determined to be $a = 3.645$ and $c = 5.333$ Å. On comparing these results with the lattice constants of the *B*8-type structure as plotted in Fig. 3, a composition $(Co_{0.59}Ni_{0.41})Se_{1.02}$ was deduced in good accordance with the derived positions of the tie lines limiting the three phase area II.

Table 4. Lattice constants of the $B8—C6$-type structure of samples $(Co_{0.5}Ni_{0.5})Se_x$.

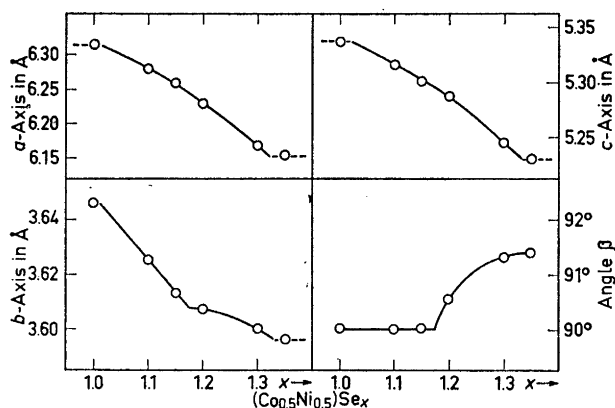| Sample	x	$a, (a\sqrt{3})$ in Å	b in Å	c in Å	$\beta°$
60 *	1.00	(6.315)	3.646	5.337	90
64	1.10	(6.279)	3.625	5.317	90
65	1.15	(6.258)	3.613	5.302	90
66	1.20	6.228	3.607	2 × 5.288	90.55
69	1.30	6.168	3.600	2 × 5.245	91.32
70 *	1.35	6.153	3.596	2 × 5.231	91.40

* Two phase samples.

Fig. 4. Lattice constants of the $B8-C6$-type phase containing equal amounts of nickel and cobalt, as functions of the selenium content.

Another series of lattice constants was measured on samples with Co:Ni ratio one to one. The results are listed in Table 4 and plotted in Fig. 4. From the variation in lattice constants it was concluded that the phase extends from $MeSe_{1.02}$ to $MeSe_{1.33}$. The lattice constants decrease with increasing selenium content in a similar way as for the binary cobalt and nickel selenides. Near $MeSe_{1.17}$ the structure changes from hexagonal to monoclinic symmetry,

Table 5. Lattice constants of $(Co_xNi_{1-x})Se_2$ with cubic $C2$-type structure.

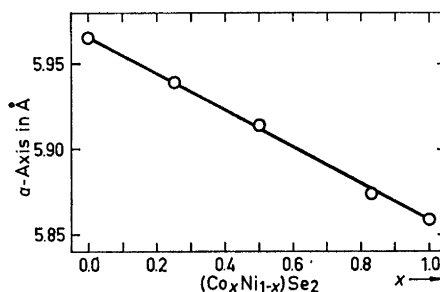| Sample	x	a in Å
72	1.00	5.859
73	0.83	5.874
74	0.50	5.914
75	0.25	5.939
76	0.00	5.965

Fig. 5. Lattice constants *versus* composition for the cubic $C2$-type phase.

and at the same composition a break is observed in the b-axis. The c-axis is doubled in the monoclinic region, just as observed for the nickel selenides.

The C2 (pyrite)-type phase $(Co_xNi_{1-x})Se_2$. The lattice constants of this cubic structure are listed in Table 5 and plotted in Fig. 5. They obey Vegard's law within the limits of experimental error. Also for the corresponding ternary disulfides $(Co_xNi_{1-x})S_2$, solid solubility has been observed in the temperature range from $500-700°C$.[12] In the latter system an exsolution process has taken place at $400°C$. In the present investigation the same decomposition tendency into two $C2$-type phases was observed in slowly cooled samples of $(Co,Ni)Se_2$. The phase relationships at lower temperatures have not yet been determined.

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