

X-Ray and Magnetic Study of Nickel Selenides in the Range NiSe to NiSe₂

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Two nickel selenide phases are identified in the range NiSe to NiSe₂ by means of X-rays.

1. *The NiSe phase* has a broad range of homogeneity extending from NiSe_{1.00} to NiSe_{1.30}. Its structure is of a NiAs-like type up to the composition NiSe_{1.30}. At higher selenium content the structure becomes monoclinic (pseudo-hexagonal) with doubled *c*-axis. The lattice constants vary between these limits:

$$\begin{aligned} \text{NiSe}_{1.00} : a &= 3.6613 \text{ \AA}, & c &= 5.3562 \text{ \AA}. \\ \text{NiSe}_{1.30} : a &= 6.196 \text{ \AA}, & c &= 2 \times 5.232 \text{ \AA}, \\ & b &= 3.634 \text{ \AA}, & \beta &= 90.78^\circ. \end{aligned}$$

Weak reflections observed on single crystal photographs of NiSe_{1.15} are due to an orthorhombic superstructure with

$$a' = b\sqrt{3} = 6.2932 \text{ \AA}, \quad b' = 3b = 10.901 \text{ \AA}, \quad c' = 3c = 15.957 \text{ \AA}.$$

Density determinations show that the solid solution of selenium in the NiSe phase takes place by subtraction of nickel atoms with increasing selenium content. The observed density decreases from 7.269 g cm⁻³ for NiSe_{1.00} to 6.918 g cm⁻³ for NiSe_{1.30}.

2. *The NiSe₂ phase* has a structure of the pyrite (C2) type and a narrow range of homogeneity on the nickel-rich side of NiSe₂, with lattice constant decreasing from *a* = 5.9626 Å for NiSe_{1.975} to *a* = 5.9604 Å for NiSe_{2.00}. The shortest selenium-selenium distance is determined as 2.40 Å.

Magnetic measurements were carried out by the Gouy method. All samples are weakly paramagnetic and for those richer in selenium than NiSe_{1.07}, the susceptibility increases slightly with increasing temperature. The effective magnetic moment at 450° C is 1.08 Bohr magnetons for NiSe_{1.00} and 1.34 Bohr magnetons for NiSe_{2.00}.

A nickel selenide was described for the first time by Little¹ in 1859. He obtained a silver white, crystalline, non-magnetic product with composition close to NiSe (found 43.23 % Ni, calc. 42.64 % Ni) by heating a mixture of the elements. Fabre² made NiSe in the same way and used the product to determine the enthalpy of formation of NiSe by solution calorimetry in bromine water. His result has been re-evaluated by Rossini *et al.*³ who give $\Delta H_f^\circ = -10$ kcal/mole at 25° C.

In 1900, Fonzes-Diacon ⁴ prepared gray, crystalline NiSe by leading selenium vapor diluted with nitrogen over red hot nickel. In another experiment, a gray black mass of NiSe₂ was prepared by the action of hydrogen selenide on nickel(II) chloride at about 300° C. If the chloride was kept at red heat, the compounds Ni₂Se₃ or Ni₃Se₄ were formed instead. By heating any of these compounds in hydrogen at bright red heat, Fonzes-Diacon obtained a gold-colored compound which he assumed had the composition Ni₂Se.

The existence of a fifth nickel selenide was claimed by Meyer and Bratke ⁵ who heated mixtures of nickel powder and selenium with potassium carbonate at 1 250° C. Analysis of the crystalline reaction products gave the result: 37.8 % Ni, 61.6 % Se and on this basis they deduced the formula Ni₅Se₈ or 3NiSe · Ni₂Se₃, which corresponds to 38.25 % Ni and 61.75 % Se.

Nickel selenides have also been prepared by precipitation. Reeb ⁶ obtained a black precipitate by the action of hydrogen selenide or potassium selenide on a nickel salt solution containing acetic acid and sodium acetate. His experiments were repeated by Moser and Atynski ⁷, who found that the products contained 1.4 to 2.8 % more selenium than NiSe. They succeeded, however, in preparing almost stoichiometric NiSe by precipitating it from alcoholic solutions (found Ni:Se = 1:1.035).

Alsén ⁸ studied NiSe by means of X-rays and found that it had a hexagonal structure of the NiAs (*B8*) type. This was later confirmed by Levi and Baroni ⁹. As a result of electron diffraction studies these authors claimed the existence of two more NiSe phases, α -NiSe, which was amorphous, and γ -NiSe, which was found to be isomorphous with millerite (NiS).

The structure of NiSe₂ was established by de Jong and Willems ¹⁰ by X-ray diffraction studies on a sample prepared by heating a mixture of NiSe and selenium (in slight excess of NiSe₂) at 230° C for 48 hours. Although the product contained some elemental selenium, a phase with structure of the pyrite (*C2*) type was recognized. Its lattice constant and atomic parameter were determined. The lattice constant of NiSe₂ was later redetermined by Tengnér ¹¹.

The only known nickel selenide mineral is penroseite from Colquechaca, Bolivia. It was first studied by Gordon ¹² who proposed the formula 2PbSe₂ · 3CuSe · 5(Ni, Co)Se₂ or PbSe · Cu₂Se · 3(Ni, Co)Se₃. Ten years later, Herzenberg and Ahlfeld ¹³ also described a nickel selenide mineral from the same locality. They concluded that it had the formula (Ni, Cu)Se₂ and gave the name blockite to it. The structural identity of penroseite, blockite and artificial NiSe₂ was established by Bannister and Hey ¹⁴ by X-ray diffraction and chemical analysis.

In view of the many nickel selenides that have been described and as a continuation of the work going on in this institute on the chalcogenides of the transition elements, a systematic study of the nickel selenium system seemed highly desirable. An X-ray study of this system was therefore started in 1950 by Olaf Holwech ¹⁵ on the suggestion of professor Haakon Haraldsen.

The work has been continued by Osvald Knop, now at Nova Scotia Technical College, and by the present authors. While Mr. Knop has mainly been concerned with the nickel-rich region of the system, we have especially studied the selenium-rich region, and an account of our work in the NiSe-NiSe₂ region will be given here.

EXPERIMENTAL

The *nickel* used for preparing the alloys was made from "Nickel oxide, low in cobalt and iron" from the British Drug Houses Ltd. by reduction with hydrogen at 600° C until constant weight was obtained. A spectrographic analysis showed only the presence of traces of copper and magnesium as impurities in the metal.

Highly purified *selenium* was placed at our disposal by Bolidens Gruvaktiebolag, Sweden. It contained the following impurities: copper 0.0002%, iron 0.0007%, tellurium 0.003%, sulfur 0.01%, non volatile matter 0.003%.

The nickel selenides rich in nickel were synthesized by heating appropriate amounts of the elements in evacuated and sealed silica tubes. Samples in the composition range $\text{NiSe}_{0.80}$ to $\text{NiSe}_{1.333}$ (50.00 to 57.14 atomic % Se) were kept at 800° C for one day and furnace-cooled. The grayish, sintered products were then ground, homogenized by heating at 550° C for five days in pyrex tubes and afterwards air-cooled. One part of each sample was annealed at 300° C for six weeks and cooled down to room temperature during two weeks. X-ray photographs of these samples were not different from those of the 550° C annealing. The 300° C samples were therefore subjected to another annealing, this time at 400° C. After six weeks, they were slowly cooled. Changes were now noticed in some of the samples.

Samples with composition $\text{NiSe}_{1.95}$, $\text{NiSe}_{1.975}$, $\text{NiSe}_{2.00}$, $\text{NiSe}_{2.025}$ and $\text{NiSe}_{2.05}$ were prepared by mixing NiSe and selenium. They were heated for four weeks at 300° C but X-ray photographs proved this to be insufficient for complete reaction. After being transferred to new tubes they were heated at 400° C for another week and slowly cooled. Prepared in this way, the samples $\text{NiSe}_{1.95}$, $\text{NiSe}_{1.975}$ and $\text{NiSe}_{2.00}$ looked homogeneous, while small amounts of elemental selenium were observed in the samples $\text{NiSe}_{2.025}$ and $\text{NiSe}_{2.05}$.

X-Ray powder photographs of the samples were taken at $20 \pm 2^\circ \text{C}$ in 11.48 cm diameter cameras with asymmetric film mounting. In most cases filtered copper radiation was used, while iron radiation was used to obtain greater dispersion in the range from $\text{NiSe}_{1.80}$ to $\text{NiSe}_{1.40}$. The lattice constants are expressed in Å units, taking $\lambda\text{CuK}\alpha_1 = 1.54051 \text{ \AA}$ and $\lambda\text{FeK}\alpha_1 = 1.93597 \text{ \AA}$. The probable error in the lattice constants is estimated as 0.01% for the cubic structure, 0.02% for the hexagonal structure and 0.03% for the monoclinic structure. Lattice constants from earlier investigations have been transformed from kX to Å units by multiplication by the factor 1.00202.

Density determinations were carried out at 25° C by the vacuum pycnometric method. Approximately 2 g of substance were used in each experiment, and the displacement liquid was redistilled kerosene (200°–240° C fraction). The standard error in the density measurements is of the order 0.3% but the values found for powdered samples of this type are usually about 1% lower than those calculated on the basis of the unit cell dimensions.

Magnetic measurements were carried out by the Gouy method at different field strengths and temperatures. The samples were filled in thin-walled quartz tubes of about 1 mm internal diameter and to a height of about 80 mm. The field was calibrated at 20° C by means of $\text{Mn}_2\text{P}_2\text{O}_7$, which has a susceptibility of 102×10^{-6} per g at 20° C according to Foëx and Brunet¹⁶ and by means of an aqueous NiCl_2 solution, for which Nettleton and Sugden¹⁷ have given a formula for the susceptibility in terms of concentration and temperature.

To reduce the corrections for the empty tubes, a piece of quartz tubing was fused on to the bottom end of the specimen tube. In this way a correction for the empty tubes was avoided at room temperature and above, but a slight correction had to be taken into account below room temperature, with a maximum value of 0.043 mg.

RESULTS

A. X-Ray study and density measurements

In the range NiSe to NiSe_2 two phases were found, one with a broad range of homogeneity in the region $\text{NiSe}_{1.02}$ to $\text{NiSe}_{1.30}$, the other with a narrow range

of homogeneity close to $\text{NiSe}_{2.00}$. They will here be designated as the NiSe phase and the NiSe_2 phase, and the NiSe phase will be considered first.

The NiSe phase. Irrespective of whether samples with the composition $\text{NiSe}_{1.00}$ were heat-treated at 550°, 400° or 300° C they consisted of more than one phase. The major phase present was found to have a structure of the NiAs ($B8$) type. In addition, weak lines from phases richer in nickel were observed*.

The results of the lattice constant determinations of the NiSe phase for samples in the range $\text{NiSe}_{0.90}$ to $\text{NiSe}_{1.40}$ are listed in Table 1. Only the values found for samples heated at 550° C are given in the table, since the differences in cell dimensions due to the heat treatment are very small.

Table 1. Lattice constants of the NiSe phase.

Sample	$a, (b\sqrt{3})$ in Å	b in Å	c in Å	β
$\text{NiSe}_{0.90}$	(6.3410)	3.6610	5.3566	(90°)
$\text{NiSe}_{1.00}$	(6.3416)	3.6613	5.3562	(90°)
$\text{NiSe}_{1.04}$	(6.3330)	3.6564	5.3484	(90°)
$\text{NiSe}_{1.07}$	(6.3208)	3.6493	5.3407	(90°)
$\text{NiSe}_{1.10}$	(6.3092)	3.6426	5.3331	(90°)
$\text{NiSe}_{1.15}$	6.2932	3×3.6336	3×5.3190	(90°)
$\text{NiSe}_{1.175}$	(6.2824)	3.6279	5.3038	(90°)
$\text{NiSe}_{1.20}$	(6.2771)	3.6241	5.2951	(90°)
$\text{NiSe}_{1.225}$	6.235	3.631	2×5.277	90.2°
$\text{NiSe}_{1.25}$	6.224	3.635	2×5.260	90.52°
$\text{NiSe}_{1.275}$	6.206	3.635	2×5.250	90.63°
$\text{NiSe}_{1.30}$	6.196	3.634	2×5.232	90.78°
$\text{NiSe}_{1.40}$	6.199	3.635	2×5.230	90.77°

Within their limited accuracy the lattice constants found by Alsén⁸ for NiSe ($a = 3.67$ Å, $c = 5.34$ Å) agree reasonably well with ours. Alsén studied only a sample with composition ratio 1 : 1 and noted, in agreement with our findings, that NiSe was not a pure product.

At the composition $\text{NiSe}_{1.04}$ the interferences belonging to the NiAs type structure are shifted slightly compared to $\text{NiSe}_{1.00}$ and the extraneous lines have disappeared. The X-ray photographs show the simple $B8$ -pattern in the range from $\text{NiSe}_{1.04}$ to $\text{NiSe}_{1.20}$. Only the photographs of $\text{NiSe}_{1.04}$ and $\text{NiSe}_{1.07}$ are, however, free from weak additional lines. From the composition $\text{NiSe}_{1.10}$ on, many weak lines are observed in the low angle region, indicating that the true unit cell is larger than the $B8$ -cell. In Table 2 are listed the more characteristic lines occurring in the low angle region on a powder photograph of $\text{NiSe}_{1.15}$.

After several attempts, some single crystals were obtained of $\text{NiSe}_{1.15}$ and by means of Weissenberg photographs the superstructure was found to be orthorhombic with

$$a' = b\sqrt{3} = 6.2932 \text{ Å}, \quad b' = 3b = 10.901 \text{ Å}, \quad c' = 3c = 15.957 \text{ Å}.$$

* The phase relationships in the Ni-rich region are rather complicated. The three intermediate phases that have been identified in this concentration range will be considered in another communication.

Table 2. Superstructure lines observed in the low angle region on a powder photograph of $NiSe_{1.11}$ taken with Cu radiation.

I_{obs}	$\sin^2\Theta \times 10^4$		hkl	I_{obs}	$\sin^2\Theta \times 10^4$		hkl
	obs	calc			obs	calc	
w	76	73	011	m	606	600	200
m	144	143	012	vw	665	659	033
		150	100			673	211
m	212	210	003	vw	714	723	124
		223	021, 111			769	783
w	267	260	013	vst	812	810	133, 203
w	347	329	120			822	034
		360	103	823	041, 221		
w	476	472	031	m	848	839	006
w	498		?				

At the composition $NiSe_{1.20}$ the hexagonal structure still exists, but at $NiSe_{1.225}$ many of the reflections are split into several components, indicating a change to lower symmetry. This deformation is even more pronounced at the compositions $NiSe_{1.25}$, $NiSe_{1.275}$ and $NiSe_{1.30}$.

Small crystals were obtained of $NiSe_{1.25}$ in a preparation that had been heated in a sealed quartz tube at $750^\circ C$ for six weeks and then slowly cooled. By means of Weissenberg photographs the structure * was found to be pseudo-hexagonal, monoclinic, with identity periods: $a = 6.22 \text{ \AA}$, $b = 3.63 \text{ \AA}$, $c = 10.53 \text{ \AA}$.

By means of powder photographs the unit cell dimensions were determined more accurately (see Table 1). The assignment of indices to the powder photograph of $NiSe_{1.25}$ is seen from Table 3. The lattice dimensions of the remaining monoclinic samples, $NiSe_{1.225}$, $NiSe_{1.275}$ and $NiSe_{1.30}$, were then easily found and the results are listed in Table 1.

The unit cell dimensions of the NiSe phase are plotted against composition in Fig. 1. The orthohexagonal cell description is used and the corresponding lattice sub-periods are given in the figure to facilitate the comparison. It is seen that the lattice constants decrease almost linearly with increasing selenium content in the hexagonal range $NiSe_{1.02}$ to $NiSe_{1.20}$. Further addition of selenium causes a slight increase in the length of the b -axes. This is compensated by an abrupt contraction of the a -axis as soon as the monoclinic deformation starts.

From Fig. 1 the selenium-rich limit for the homogeneity range of the NiSe phase appears to be $NiSe_{1.30}$. This is in accordance with the fact that faint lines from the $NiSe_2$ phase are visible on the powder photographs of $NiSe_{1.333}$.

Density determinations were carried out on the NiSe phase in order to ascertain that the solid solution of selenium in NiSe takes place by subtraction of nickel atoms from the NiSe structure. The densities calculated under that assumption are listed in Table 4 together with the observed densities. The

* The atomic arrangement in $NiSe_{1.25}$ and $NiSe_{1.15}$ will be discussed in a forthcoming paper.

Table 3. Powder photograph data of $NiSe_{1.25}$ taken with Fe radiation, α_2 and β lines omitted.

I_{obs}	$\sin^2\Theta \times 10^4$		hkl	I_{obs}	$\sin^2\Theta \times 10^4$		hkl
	obs	calc			obs	calc	
vw	325	{324 329}	$\bar{1}01$ 101	m st	5 262 5 423	5 264 5 418	404 008
w	340	339	002	vw	5 774	5 785	217
w	795	794	011	vw	5 887	{5 861 5 884}	217 026
vw	950	951	110	vw	5 887	{5 861 5 884}	226 406
vw	965	966	200	w	6 832	{6 818 6 849}	226 226
vw	996	996	$\bar{1}03$	w	6 894	{6 882 6 956}	226 132
vw	1 010	1 012	103	w	6 894	{6 882 6 956}	226 132
vst	1 284	1 285	$\bar{1}12$	m	6 973	{6 967 6 979}	132 406
st	1 302	{1 294 1 295}	$\bar{2}02$ 112	w	7 034	{6 979 7 019}	422 422
m	1 324	1 316	202	w+	7 074	{7 061 7 063}	512 422
w	1 355	1 355	004	w+	7 074	{7 061 7 063}	512 422
w+	1 474	1 471	013	w	7 126	7 115	512
w-	1 770	1 765	211	vw	7 216	7 226	$\bar{1}27$
vst	2 295	{2 295 2 299}	$\bar{1}14$ $\bar{2}04$	w+	7 974	7 967	$\bar{1}34$
st	2 321	2 317	114	w+	7 999	7 989	134
m	2 350	2 343	204	m	8 023	8 014	424
w+	2 425	2 421	$\bar{2}13$	w	8 099	8 100	424
st	2 840	2 836	020	vw	8 164	8 158	514
vst	2 892	2 883	310	st	8 241	{8 236 8 254}	318 028
vw	3 172	{3 159 3 165 3 175}	121 022	m	8 370	8 366	318
m	3 974	{3 982 3 983}	$\bar{2}06$ $\bar{1}16$	st	8 557	8 555	330
m	4 021	4 015	116	w	8 649	8 647	417
w	4 137	4 130	$\bar{2}22$	m	8 698	8 698	600
m	4 158	4 152	222	w	9 386	{9 378 9 391}	$\bar{2}0.10$ $\bar{1}1.10$
w	4 197	{4 191 4 206}	024 314	w	9 439	9 445	1.1.10
vw	4 284	4 270	314	w	9 486	9 486	2.0.10
vw	4 382	4 371	107	w	9 655	9 655	136
m	5 131	5 135	$\bar{2}24$	st	9 689	{9 685 9 687}	426 136
st	5 174	{5 178 5 179}	404 224	st	9 728	9 716	516
				w	9 823	9 815	426
				w	9 883	9 878	516

good agreement between the two sets of values confirms the correctness of the above assumption. As to the question why the observed densities are consistently lower than the calculated ones, this seems primarily to be related to the large surface area of the powdered samples, and only to a smaller extent to missing metalloïd atoms.

In the case of $NiSe_{1.00}$ there is a significant difference in density due to the heat treatment. This may be understood by comparison with the X-ray results, as the $NiSe_{1.00}$ sample heat-treated at 300°C contained much stronger lines from phases richer in nickel than the sample heated at 550°C. Furthermore, the density of $NiSe_{0.95}$ heated at 300°C was only 7.142 g cm⁻³.

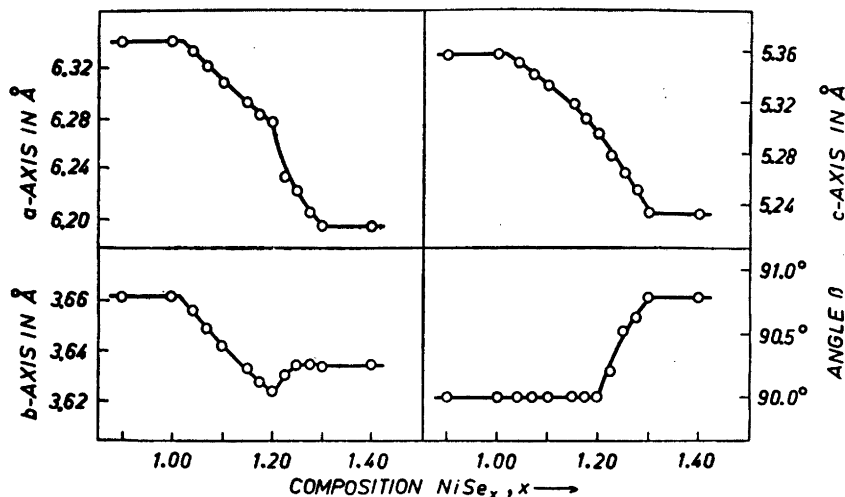


Fig. 1. Lattice constants of the NiSe phase as functions of composition.

In the NiSe structure each nickel atom is surrounded by six selenium atoms at the corners of a deformed octahedron (trigonal antiprism). The distances are 2.50 Å for NiSe_{1.00}, and 2.48 Å for NiSe_{1.20}. Each nickel atom is further surrounded by two nickel atoms at the distance $c/2 = 2.68$ Å (NiSe_{1.00}) and 2.65 Å (NiSe_{1.20}). The selenium atoms are arranged in a hexagonal close packing which is compressed in the c -direction so that the shortest distance between selenium atoms in adjacent planes is 3.41 Å against 3.66 Å for nearest neighbors in the hexagonal plane for NiSe_{1.00} and 3.38 Å against 3.62 Å for NiSe_{1.20}.

The NiSe₂ phase. X-Ray photographs of samples in the NiSe₂ region showed the existence of a phase with pyrite ($C2$) structure. While several lines from the NiSe phase were present in NiSe_{1.95}, only one line was present in NiSe_{1.975}

Table 4. Observed and calculated densities in $g\ cm^{-3}$ for the NiSe phase. The atomic weight unit is taken as 1.660×10^{-23} g.

Sample		D_{obs}	D_{calc}	Sample		D_{obs}	D_{calc}
NiSe _{1.00}	550° C	7.269	—	NiSe _{1.20}	550° C	6.974	7.051
NiSe _{1.00}	300° C	7.217	—	NiSe _{1.20}	300° C	6.980	7.051
NiSe _{1.04}	300° C	7.219	7.260	NiSe _{1.225}	550° C	6.915	7.052
NiSe _{1.07}	550° C	7.169	7.214	NiSe _{1.25}	550° C	6.890	7.027
NiSe _{1.10}	550° C	7.132	7.170	NiSe _{1.25}	300° C	6.927	7.027
NiSe _{1.10}	300° C	7.127	7.170	NiSe _{1.275}	550° C	6.894	7.009
NiSe _{1.15}	300° C	7.052	7.098	NiSe _{1.30}	300° C	6.918	6.997
NiSe _{1.175}	550° C	6.993	7.080	NiSe _{1.333}	300° C	6.914	—

that could possibly be attributed to the NiSe phase. No foreign lines were found in NiSe_{2.00}, NiSe_{2.025} or NiSe_{2.05}.

The lattice constant was determined for these five samples and the results are listed in Table 5. A slight contraction of the unit cell takes place from NiSe_{1.975} to NiSe_{2.00}, which denotes that the NiSe₂ phase has a narrow range of homogeneity on the nickel-rich side of NiSe₂. The lattice constant value found by Tengnér¹¹ for NiSe₂, $a = 5.960 \text{ \AA}$, is in perfect agreement with the present results, while the value $a = 6.034 \pm 0.003 \text{ \AA}$ found by de Jong and Willems¹⁶ is considerably higher.

Table 5. Lattice constants and densities of samples in the NiSe₂ region.

Composition	a in \AA	D_{obs} in g cm^{-3}
NiSe _{1.95}	5.9628	6.730
NiSe _{1.975}	5.9626	6.724
NiSe _{2.00}	5.9604	6.720
NiSe _{2.025}	5.9605	6.703
NiSe _{2.05}	5.9603	6.693

Results of the density determinations carried out in the NiSe₂ region are also listed in Table 5. The observed density of NiSe_{2.00} (6.720 g cm^{-3}) is as usual a little lower than the X-ray density (6.792 g cm^{-3}). The density calculated for NiSe_{1.975} assuming different types of solid solution is given in Table 6. Since a decrease in density from NiSe_{2.00} to NiSe_{1.975} is not compatible with the observations, it is concluded that nickel atoms are taken up interstitially in this range.

Table 6. Calculated densities for NiSe_{1.975}. The atomic weight unit is taken as $1.660 \times 10^{-23} \text{ g}$.

Type of solid solution	Formula	D_{calc} in g cm^{-3}
Interstitial	Ni _{1.015} Se ₂	6.808
Substitutional	Ni _{1.008} Se _{1.992}	6.780
Subtractive	NiSe _{1.975}	6.723

In structures of the pyrite (C2) type, each metal atom is surrounded octahedrally by six metalloid atoms, and each metalloid atom is surrounded tetrahedrally by one metalloid atom and three metal atoms. The metalloid metalloid distance is equal to $a(1-2x)\sqrt{3}$, where x is a parameter to be determined. De Jong and Willems found $x = 0.375$ for NiSe₂, which led to a selenium selenium distance of 2.61 \AA . This value is rather large, and a redetermination of the parameter was therefore undertaken.

The relative intensities of the NiSe_2 reflections were determined photographically from powder photographs taken with Cu radiation. The best agreement between observed and calculated intensities was obtained with $x = 0.384$. The results are listed in Table 7. In the left column are found the $\sin^2\theta$ values for the α_1 reflections.

Table 7. Observed and calculated intensities for NiSe_2 with $x = 0.384$, Cu radiation.

$\sin^2\theta \times 10^4$	<i>hkl</i>	I_{obs}	I_{calc}	$\sin^2\theta \times 10^4$	<i>hkl</i>	I_{obs}	I_{calc}
499	111	0.2	1.4	6 019	{600}	4.6	{0.0}
674	200	14	31		{442}		{3.4}
837	210	100	100	6 184	610	5.4	4.3
1 007	211	85	83	6 350	{611}	18	{4.8}
1 339	220	12	11		{532}		{13}
1 502	221	1.5	1.0	6 691	620	1.7	{1.3}
1 843	311	50	55		{621}		{1.2}
2 008	222	6.1	3.9	6 854	{540}	3.8	{0.1}
2 177	320	25	32		{443}		{0.7}
2 343	321	31	44	7 018	541	0.8	0.5
2 679	400	8.3	7.3	7 184	533	9.0	7.3
				7 355	622	2.7	1.8
2 835	{410}	2.0	{0.7}		{630}		{7.1}
	{322}		{0.5}	7 520	{542}	13	{5.1}
3 001	411	1.3	0.7				
3 159	331	0.7	0.2	7 684	631	13	11
3 351	420	2.7	1.9	8 020	444	3.8	3.6
3 508	421	20	17	8 187	632	2.1	2.2
3 680	332	11	8.4	8 353	543	0.9	0.8
4 015	422	4.5	2.9		{711}		{0.0}
4 174	430	1.2	0.6	8 520	{551}	2.7	{2.9}
4 337	431	2.3	0.8		640	9.5	11
				8 686			
4 512	{511}		{18}		{720}		{14}
	{333}	23	{2.1}	8 853	{641}	21	{13}
4 834	{520}		{3.0}		{721}		{20}
	{432}	22	{16}	9 019	{633}	23	{7.2}
5 000	521	15	12		{552}		{7.1}
5 349	440	18	18	9 354	642	5.4	8.3
5 511	{522}	0.8	{0.1}	9 523	{722}	1.4	{0.6}
	{441}		{0.4}		{544}		{0.6}
5 681	433	0.5	0.2				
5 851	531	0.8	0.4	9 853	{731}	27	{33}
					{553}		{47}

According to the present results, the selenium selenium distance is 2.40 Å. The nickel selenium distance is, however, only slightly altered by the new constants, 2.49 Å now against 2.50 Å from the data by de Jong and Willems*.

B. Magnetic properties

All samples studied were found to be weakly paramagnetic and to have susceptibilities that were only slightly dependent on the temperature. In the range NiSe to $\text{NiSe}_{1.07}$, the susceptibility decreases with increasing tempera-

* The distance nickel selenium given by de Jong and Willems¹⁰ as 2.47 Å is not consistent with their data. The correct value should be $a \sqrt{3x^2 - 2x + \frac{1}{3}} = 2.50$ Å.

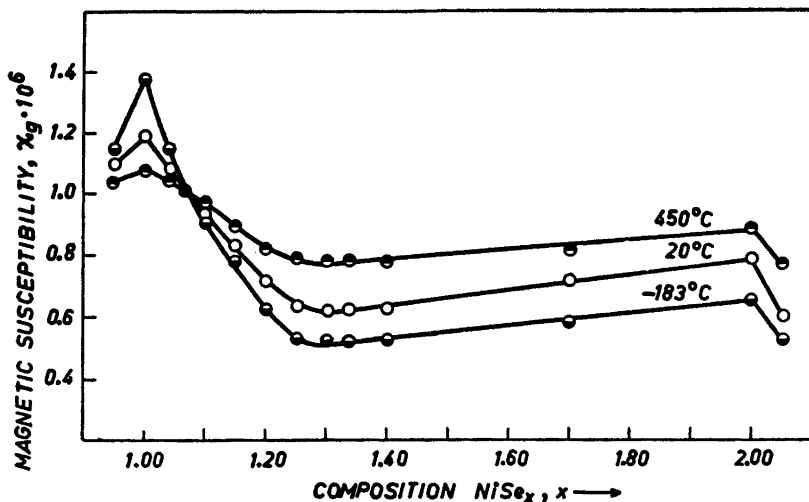


Fig. 2. Magnetic susceptibilities of the nickel selenides at -183° , 20° and 450° C.

ture while the opposite is true for all samples with higher selenium content than $\text{NiSe}_{1.07}$ in the temperature range studied. The results of the measurements are listed in Table 8. No specimen was found to have field strength dependent susceptibility and only the mean values of the results at $H_{\text{max}} = 4\ 015$, $4\ 700$ and $5\ 110$ Ørstedes are recorded in the table.

Table 8. Magnetic susceptibility of the nickel selenides, $\chi_g \times 10^6$.

Sample	Temperature $^\circ\text{C}$					
	-183	-78	20	150	300	450
$\text{NiSe}_{0.95}$	1.15	1.12	1.10	1.07	1.05	1.04
$\text{NiSe}_{1.00}$	1.38	1.24	1.19	1.13	1.08	1.08
$\text{NiSe}_{1.04}$	1.15	1.10	1.08	1.07	1.06	1.05
$\text{NiSe}_{1.07}$	1.01	1.00	1.00	0.99	1.00	1.00
$\text{NiSe}_{1.10}$.92	.92	.94	.95	.97	.98
$\text{NiSe}_{1.15}$.79	.82	.84	.85	.87	.90
$\text{NiSe}_{1.20}$.63	.68	.72	.75	.79	.83
$\text{NiSe}_{1.25}$.53	.57	.64	.66	.75	.80
$\text{NiSe}_{1.30}$.53	.57	.62	.67	.74	.79
$\text{NiSe}_{1.33}$.52	.57	.63	.67	.74	.79
$\text{NiSe}_{1.40}$.53	.58	.63	.68	.73	.78
$\text{NiSe}_{1.70}$.58	.65	.72	.75	.80	.82
$\text{NiSe}_{2.00}$.66	.73	.79	.82	.85	.90
$\text{NiSe}_{2.05}$.53	.56	.60	.75	.76	.77

The susceptibility isotherms at -183° , 20° and 450°C are drawn in Fig. 2 and they show the phase relationships very clearly. A pronounced maximum close to $\text{NiSe}_{1.00}$ defines the nickel-rich limit of the homogeneity range of the NiSe phase. With increasing selenium content especially the -183°C isotherm has a non-linear character which is indicative of a single phase domain. At about the composition $\text{NiSe}_{1.30}$ minima occur in the isotherms and they define the selenium-rich limit of the NiSe phase. From the composition $\text{NiSe}_{1.30}$ on, the susceptibilities increase linearly and reach another maximum at $\text{NiSe}_{2.00}$. The decrease which is observed from $\text{NiSe}_{2.00}$ to $\text{NiSe}_{2.05}$ is probably due to the selenium phase.

In cases where the magnetic susceptibility of a substance is inversely proportional to the absolute temperature (*i. e.* the Curie law is fulfilled) a definite electronic state might be ascribed to the magnetic atom. This condition is far from fulfilled for the nickel selenides, and one can therefore only hope to obtain information about the magnetic state of the nickel atom at high temperatures, where the disturbing interactions are smaller. Since the magnetic susceptibility of the nickel selenides does not even obey the Curie-Weiss law, this information is best obtained by calculating the effective magnetic moment of the nickel atom.

This has been done * for NiSe and NiSe_2 and the results are shown in Fig. 3. The effective magnetic moment rises to 1.08 B. M. (Bohr magnetons) at 450°C

* The susceptibilities are corrected for induced diamagnetism with the value -17.7×10^{-6} mole $^{-1}$ for Ni^{+2} according to Asmussen¹⁸ and the value -47.58×10^{-6} mole $^{-1}$ for Se^{-2} according to Angus¹⁹.

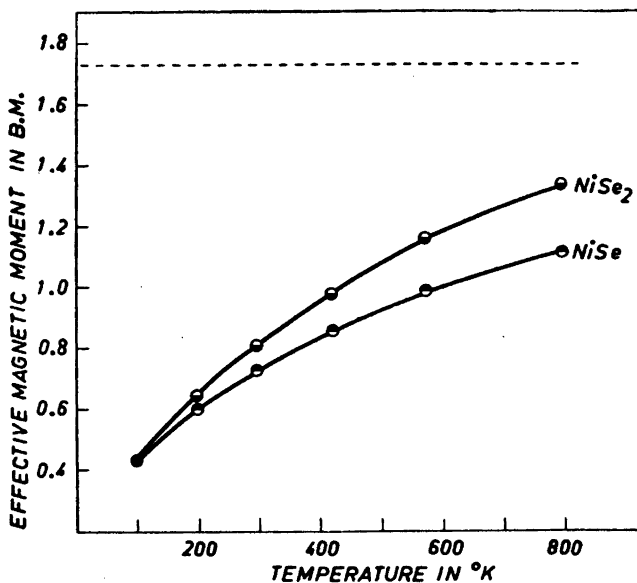


Fig. 3. Effective magnetic moments of NiSe and NiSe_2 as functions of temperature.

for NiSe and to 1.34 B. M. for NiSe₂. The slope of the curves is rather flat and the effective magnetic moments are of a much smaller magnitude than expected for Ni⁺² ions.

According to Van Vleck²⁰, the magnetic moment of the free, gaseous Ni⁺² ion is 5.56 B. M. at room temperature when the effect of the multiplet width is taken into account. When the crystalline field is so strong as to destroy the coupling of the spin angular momentum *S* and the orbital angular momentum *L* to a quantized resultant *J*, a "spin only" value of 2.83 B. M. is expected for Ni⁺². Also in case of nickel(II) forming covalent d²sp³ bonds the same value might be expected. The magnetism of the nickel selenides is, however, so weak that it cannot be explained satisfactorily in any of these ways.

The departure of the magnetism from Curie's law shows that strong interactions are present between the paramagnetic ion and its neighbors. It is not yet known to what extent this is due to interactions between paramagnetic ions, leading to antiferromagnetism, and to interactions with neighboring diamagnetic ions.

DISCUSSION

Of all the nickel selenides described by earlier investigators in the composition range NiSe to NiSe₂ only the NiSe phase and the NiSe₂ phase exist. The variable composition of the NiSe phase might, however, account for the conclusions by some of the earlier investigators about the existence of other intermediate phases. Thus, the compound 3NiSe · Ni₂Se₃ postulated by Meyer and Bratke⁵, falls well within the homogeneity range of the NiSe phase.

The nickel selenide with approximate composition Ni₃Se₄, consisted according to Fonzes-Diacon⁴ of a mixture of cubic crystals and a product containing slightly less selenium. It seems probable that the latter product, which he was not able to avoid, was the NiSe phase and that the cubic crystals were of the NiSe₂ phase. The polymorphism of NiSe which was found by Levi and Baroni⁹ has not been observed in the present study. Their γ-NiSe is presumably identical with one of the phases we have observed on the nickel-rich side of NiSe. The same is probably also the case with the cubic NiSe crystals found by Little¹ and Fonzes-Diacon⁴.

The atomic configuration in the NiSe and NiSe₂ phases is rather alike in that each nickel atom is surrounded octahedrally by six selenium atoms at practically the same distances, 2.50 Å in NiSe and 2.49 Å in NiSe₂. The values for the NiSe phase agree very well with the sum of the metallic radii given by Pauling²¹. In NiSe_{1.00} the coordination number of the nickel atom is 8 and that of the selenium atom is 6 and the radius sum is 1.19 Å + 1.31 Å = 2.50 Å. For NiSe_{1.20} the coordination numbers are 7.3 and 5 and the radius sum is 1.19 Å + 1.29 Å = 2.48 Å, in perfect agreement with the observed value (2.48 Å). In NiSe₂, nickel has coordination number 6 and selenium 4 which makes the radius sum 1.15 Å + 1.26 Å = 2.41 Å.

In structures of the pyrite (*C2*) type, the conditions are favorable for deriving characteristic radii since the metalloid atoms are bonded to each other. For NiSe₂ the empirical radius of the selenium atom is 1.20 Å (see

p. 1448) and the radius of the nickel atom is thus $2.49 \text{ \AA} - 1.20 \text{ \AA} = 1.29 \text{ \AA}$. The nickel radius found here is considerably smaller than the octahedral covalent d^2sp^3 radius 1.39 \AA for Ni(II) given by Pauling and Huggins²². This is not very surprising, however, as Lewis and Elliott²³ found that NiSe₂ is a conductor of electricity. The nickel atom might perhaps more aptly be designated as Ni(III), with electrons transferred to the conduction band. The transition of Ni(II) to Ni(III) causes a decrease in radius of 0.09 \AA according to Pauling and Huggins.

A compilation of the interatomic distances in the diselenides of manganese, iron, cobalt and nickel is found in Table 9. FeSe₂ has a structure of the marcasite (C18) type and it is interesting to note that it has the largest selenium selenium distance among the four compounds. This case is analogous to the sulfide case where Buerger²⁶ showed that the sulfur sulfur bond distance for marcasite was appreciably larger than for pyrite and for MnS₂, CoS₂ and NiS₂ as well — see Haraldsen²⁷. It thus seems that the conditions for the metalloid atoms to form sp^3 bonds are not so favorable in the marcasite structure as in the pyrite structure, which is in keeping with the larger deformation of the tetrahedral configuration. The sp^3 orbitals might therefore to some extent be taken up by unshared pairs, thus increasing the distance between the metalloid atoms and leaving fewer electrons for the conduction band.

Table 9. Shortest interatomic distances in Å for some diselenides.

Substance	Me-Se	Se-Se	Me-Me	Authors
MnSe ₂	2.70	2.38	4.55	Elliott ²⁴
FeSe ₂	2.37	2.50	3.58	Tengnér ¹¹
CoSe ₂	2.42	2.43	4.14	Böhm <i>et al.</i> ²⁵
NiSe ₂	2.49	2.40	4.22	Present

The selenium selenium distances in MnSe₂, CoSe₂ and NiSe₂ are almost equal with 1.20 \AA as mean value for the radius of the selenium atom. A rather abrupt decrease in the distance metal selenium and therefore also in the metal radius is observed as one goes from manganese ($r = 1.50 \text{ \AA}$) to iron ($r = 1.17 \text{ \AA}$). From then on the radius rises again to cobalt ($r = 1.22 \text{ \AA}$) and nickel ($r = 1.29 \text{ \AA}$). The anomalously large manganese radius was explained by Pauling²¹ as a result of $4s4p^3$ resonating bonds for manganese compared to $3d^24s4p^3$ bonds for iron. The magnetic measurements of Haraldsen and Klemm²⁸ on natural MnS₂ (hauerite-)indicated the presence of five unpaired 3d electrons in manganese at high temperatures, which leaves no 3d orbitals available for bond formation. FeS₂ shows, as recently confirmed by Serres²⁹, almost zero magnetism so that in this compound all 3d electrons are paired. The six 3d electrons of Fe⁺² presumably make use of three 3d orbitals, and the remaining two 3d orbitals are utilized in the d^2sp^3 bond formation.

Huggins³⁰ has suggested that d orbitals with principal quantum number one higher than normal might be used for bond formation in compounds of the

pyrite (C2) type and that intermediate bond types comprising both kinds of orbitals were possible. These outer orbitals are not so useless for bond formation as the separation of the energy levels of the free ion indicates, since they have their maximum probability density further out in space and can thus overlap appreciably with orbitals of the surrounding atoms. Actual overlap calculations carried out by Craig *et al.*³¹ have confirmed Huggins' predictions and provided support for the view that 4d orbitals may be used for σ -bond formation in "ionic" complexes involving the first transition group metals.

The magnetic behavior of NiSe₂ seems to support this view. At low temperatures the octahedral bonds might be of a 3d4s4p³4d type with zero magnetism, and as the temperature is raised, the 4d character of the bonds increases. Simultaneously, unpaired electrons populate the available 3d orbitals and the effective magnetic moment of NiSe₂ increases. Evidently, the bonds do not relinquish much of their 3d character, since the effective magnetic moment does not even reach the "spin only" value for one unpaired electron per nickel atom at 450° C, *i.e.* 1.73 B.M.

The magnitude and temperature dependence of the effective magnetic moment for the NiSe and NiSe₂ phases are rather similar to what was found for the corresponding cobalt selenides by Bøhm, Grønvold, Haraldsen and Prydz²⁵ and the cobalt tellurides by Haraldsen, Grønvold and Hurlen³². Discussion of these relationships will be postponed to a later paper.

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