

Low Temperature Heat Capacities and Thermodynamic Properties of the Ni_{1-x}Se -Phase

FREDRIK GRØNVOLD and TORKILD THURMANN-MOE

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Norway

and

EDGAR F. WESTRUM, JR. and NORMAN E. LEVITIN

Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.

Heat capacities of three nickel selenides with compositions $\text{Ni}_{0.95}\text{Se}$, $\text{Ni}_{0.875}\text{Se}$ and $\text{Ni}_{0.80}\text{Se}$, representing the Ni_{1-x}Se -phase with NiAs-like structure and cation vacancies, were measured in the range 5 to 350°K. No transitions or other heat-capacity anomalies were observed, except for slight upward trends in the heat-capacity values for $\text{Ni}_{0.875}\text{Se}$ and $\text{Ni}_{0.80}\text{Se}$ compared to those for $\text{Ni}_{0.95}\text{Se}$ above 250°K, which might possibly indicate the beginning of transitions. Values for the enthalpy function and entropy were calculated and tabulated for several temperatures. At 298.15°K the entropies are 8.754 eu for $\text{Ni}_{0.4872}\text{Se}_{0.5128}$ (*i. e.* $\text{Ni}_{0.95}\text{Se}$), 8.608 eu for $\text{Ni}_{0.4687}\text{Se}_{0.5313}$ (*i. e.* $\text{Ni}_{0.875}\text{Se}$ or Ni_7Se_8) and 8.506 eu for $\text{Ni}_{0.4444}\text{Se}_{0.5556}$ (*i. e.* $\text{Ni}_{0.80}\text{Se}$ or Ni_4Se_5).

The Ni_{1-x}Se -phase offers interesting possibilities for studying an order-disorder process as a function of composition and of temperature from a combined structural and thermodynamic point of view. It was shown by Alsén¹ that NiSe has a hexagonal structure of the NiAs-type in which each nickel atom is surrounded by six selenium atoms at the corners of a slightly irregular octahedron, or trigonal antiprism. These antiprisms are stacked on top of each other in the *c*-direction so that the nickel atoms form endless chains in this direction.

More recent work has shown² that the Ni_{1-x}Se -phase has a composition varying between $\text{Ni}_{0.98}\text{Se}$ and $\text{Ni}_{0.77}\text{Se}$ and that the stoichiometric 1:1 ratio is not included, at least not in the case of samples heat-treated at 550 and 400°C when examined by X-ray diffraction at room temperature. The structure is hexagonal only in the nickel-rich range, and additional, weak reflections are observed when $1-x$ is less than 0.91, indicating the presence of superstructure. For a sample with composition $\text{Ni}_{0.87}\text{Se}$ the superstructure was found to be orthorhombic with $A = a\sqrt{3}$, $B = 3a$ and $C = 3c$, where a and c are the dimen-

sions of the hexagonal unit. With further increase in the number of vacant Ni-positions below $\text{Ni}_{0.83}\text{Se}$, the basic structure changes from hexagonal to monoclinic, and at the composition $\text{Ni}_{0.80}\text{Se}$ the size of the unit cell is $A' = a\sqrt{3}$, $B' = a$, $C' = 2c$ and $\beta = 90.52^\circ$.

A determination of the atomic arrangement in $\text{Ni}_{0.80}\text{Se}$ has ascertained³ that there is a considerable degree of order among the vacancies after the 20 % missing nickel atoms. These vacancies are distributed in an ordered way in every other layer of metal atoms normal to the *c*-axis, while apparently almost no vacancies exist in the rest of the layers. Slight movements of nickel and selenium atoms in the vicinity of the vacancies are observed, but in general, the structure is little affected. The contraction in volume by the 5.32 % decrease in mass per unit cell is 5.26 %.

The Ni_{1-x}Se -phase shows metallic behavior, with a weak, almost temperature-independent paramagnetism. Thus its heat capacity behavior is expected to resemble that of the δ -phase in the nickel-tellurium system⁴ which shows no magnetic transitions and rather small variations in heat capacity as a function of composition.

The nickel selenides are rather different from the iron selenides⁵ in that no clear-cut separation into two-phase regions occurs within the Ni_{1-x}Se -phase. Therefore, it was thought of interest to carry out heat-capacity measurements on the nickel selenides in order to ascertain if the apparent absence of exsolution into phases of slightly different compositions is caused by failure of the nickel selenides to reach equilibrium (in contrast to what seems to be the case for the iron selenides), or by too small an entropy increment between ordered and slightly disordered states to cause such separation.

This requires studying a thermodynamic cycle involving free energy measurements as well as enthalpy and entropy measurements. The enthalpy of formation of the Ni_{1-x}Se -phase has been determined⁶ at 775°C, and high-temperature heat-capacity measurements are presently in progress to study entropy changes accompanying the order-disorder process.

In this paper are reported the results of low-temperature heat-capacity measurements carried out on three single-phase samples within the homogeneity range of the Ni_{1-x}Se -phase, having compositions $\text{Ni}_{0.95}\text{Se}$, $\text{Ni}_{0.875}\text{Se}$ and $\text{Ni}_{0.80}\text{Se}$.

EXPERIMENTAL

A. Preparation of the samples. The nickel selenides were prepared by fusion of high-purity nickel and selenium. "Nickel oxide, low in cobalt and iron" from the British Drug Houses Ltd. was reduced with dry, purified hydrogen gas at 500°C for 5 h. The resulting, malleable nickel was broken into pieces and reduced again, this time at 1 000°C for 4 h. Spectrographic analysis showed the presence of the following impurities (in ppm): Al(100), Ba(1), Ca(10), Co(10), Cr(1), Cu(1), Fe(10), Mg(50), Mn(1), Si(50).

The high-purity selenium was a gift from Bolidens Gruvaktiebolag. According to their analysis it contained these impurities (in ppm): Cl(2), Fe(0.8), K(0.3), Na(0.4), non-volatile matter (12). The following elements were not detected (the numbers indicate the sensitivity limit in ppm): Ag(0.03), Al(0.3), As(1), Bi(0.1), Ca(1), Cr(0.3), Cu(0.1), Hg(0.5), Mg(0.3), Mn(0.1), Ni(0.3), Pb(0.3), S(5), Si(1), Sn(0.3), Te(1), Zn(1).

Accurately-weighed quantities of nickel and selenium corresponding to the compositions $\text{Ni}_{0.95}\text{Se}$, $\text{Ni}_{0.875}\text{Se}$ and $\text{Ni}_{0.80}\text{Se}$ were heated in evacuated and sealed vitreous silica tubes. The samples were fused for 2 h at 1 050, 1 000 and 950°C, respectively. They were

then cooled, fragmented and annealed at 550°C for seven days and cooled over a period of two more days. X-Ray powder photographs of the samples were identical to those obtained earlier³.

B. *Cryostat and calorimeter.* The Mark I cryostat and technique employed in low-temperature adiabatic calorimetry will be described elsewhere⁷. Two different calorimeters were used, W-7 with a capacity of 40 cm³ was used for the Ni_{0.95}Se and Ni_{0.875}Se samples, while calorimeter W-17 with a capacity of 60 cm³ was used for the Ni_{0.80}Se sample. Both calorimeters are gold-plated and have four and two vanes, respectively. Separate series of measurements were carried out to determine the heat capacities of the empty calorimeters, using the same thermometer and heater and exactly the same amount of indium-tin solder for sealing the calorimeter and Apiezon-T grease for thermal contact with the thermometer and heater. The heat capacity of the empty calorimeter W-7 represented from 17 to 25 % of the total heat capacity, and that of calorimeter W-17 from 16 to 21 %.

Temperatures were measured with a capsule-type platinum resistance thermometer (laboratory designation A-3) within an axial well in the calorimeter. The thermometer was calibrated by the National Bureau of Standards, and the temperatures were judged to correspond with the thermodynamic temperature scale within 0.1°K from 5 to 10°K, 0.03°K from 10 to 90°K and 0.04°K from 90 to 350°K. Precision is considerably better, and the temperature increments are probably accurate to 0.001°K after corrections for quasi-adiabatic drift.

The thermometer resistance and power input were measured with a calibrated White double-potentiometer, calibrated resistances and a calibrated standard cell. An electric timer, operated by a calibrated tuning fork and amplifier, was automatically started at the beginning of the heating period and stopped at the end.

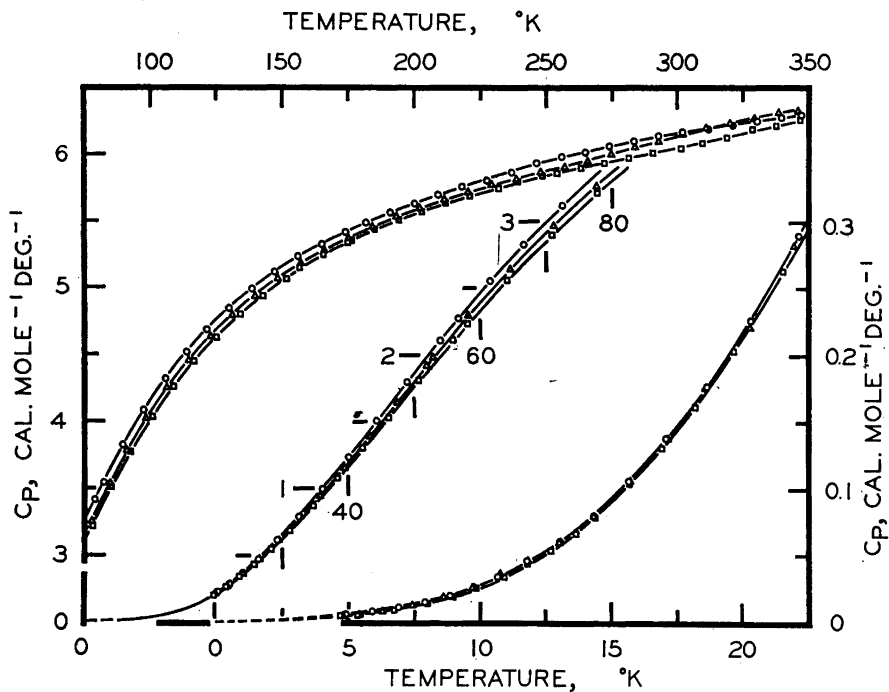


Fig. 1. Heat capacities of nickel selenides on a gram formula weight basis: O represents Ni_{0.4872}Se_{0.5128}, Δ represents Ni_{0.4667}Se_{0.5333} and □ represents Ni_{0.4444}Se_{0.5556}.

Table 1. Heat capacities of nickel selenides, cal °K⁻¹ "mole"⁻¹.

<i>T</i> , °K	<i>C_p</i>	<i>T</i> , °K	<i>C_p</i>	<i>T</i> , °K	<i>C_p</i>
Ni _{0.950} Se					
(formula weight Ni _{0.4872} Se _{0.5128} = 69.09 g)					
Series I		20.27	0.2266	156.18	5.234
		22.09	0.2900	165.03	5.326
56.71	2.270	24.11	0.3680	174.05	5.418
61.59	2.551	26.48	0.4719	183.04	5.498
66.77	2.821	29.29	0.6095	182.04	5.491
72.47	3.114	32.58	0.7884	191.02	5.565
78.89	3.409	36.14	0.9964	200.06	5.628
		40.01	1.233	209.17	5.696
Series II		44.32	1.503	218.35	5.756
		48.96	1.796	227.56	5.803
4.91	0.006	53.97	2.108	237.01	5.865
5.88	0.008			246.47	5.933
6.88	0.011	Series III		255.78	5.978
7.89	0.015			264.93	6.013
8.84	0.020	82.09	3.541	274.18	6.059
9.76	0.027	89.30	3.824	283.52	6.097
10.66	0.034	97.37	4.083	292.84	6.139
11.78	0.046	105.89	4.318	302.13	6.164
13.03	0.0610	113.91	4.517	311.55	6.190
14.32	0.0809	121.59	4.686	321.06	6.218
15.65	0.1050	129.88	4.846	330.48	6.247
17.08	0.1378	138.58	4.993	339.86	6.278
18.62	0.1767	147.33	5.119	347.33	6.296
Ni _{0.875} Se					
(formula weight Ni _{0.4667} Se _{0.5333} = 69.51 g)					
4.82	0.005	39.40	1.155	175.18	5.371
5.39	0.007	43.27	1.394	184.20	5.452
6.28	0.008	47.41	1.645	193.28	5.530
7.42	0.013	51.88	1.917	202.40	5.598
8.60	0.019	52.95	1.981	211.59	5.659
9.70	0.026	58.25	2.295	220.65	5.716
10.76	0.036	64.59	2.642	229.79	5.767
11.84	0.047	71.20	2.966	239.01	5.813
12.98	0.0604	77.54	3.255	248.11	5.863
14.27	0.0797	84.02	3.535	257.09	5.903
15.66	0.1056	90.82	3.787	265.97	5.949
17.11	0.1379	98.27	4.023	274.98	6.002
18.57	0.1757	106.39	4.252	283.88	6.052
20.13	0.2210	114.65	4.457	292.94	6.098
21.94	0.2820	123.00	4.635	302.05	6.155
24.12	0.3644	131.36	4.795	311.05	6.200
26.66	0.4734	139.77	4.934	320.15	6.237
29.47	0.6082	148.46	5.068	329.40	6.272
32.51	0.7665	157.25	5.185	338.66	6.317
35.80	0.9489	166.19	5.283	345.99	6.327

Table 1 (continued).

		Ni _{0.80} Se			
		(formula weight Ni _{0.4444} Se _{0.5556} = 69.96 g)			
Series I		337.72	6.214	25.77	0.4312
		346.76	6.256	28.30	0.5446
156.88	5.150			31.10	0.6830
165.84	5.250			34.58	0.8702
174.93	5.339			38.33	1.080
176.40	5.351	5.36	0.006	42.13	1.302
185.38	5.434	4.68	0.005	46.18	1.530
194.29	5.507	5.48	0.006	50.76	1.812
203.10	5.569	6.73	0.009	55.95	2.112
212.01	5.629	8.03	0.014	58.08	2.226
221.09	5.688	8.97	0.020	64.04	2.553
230.22	5.741	9.87	0.026	70.82	2.892
239.42	5.791	10.87	0.034	77.82	3.212
248.70	5.831	11.80	0.0439	84.76	3.510
254.12	5.855	12.67	0.0538	92.43	3.778
263.27	5.899	13.60	0.0669	100.64	4.035
272.43	5.937	14.38	0.0790	108.85	4.261
281.60	5.974	15.68	0.1042	116.87	4.455
290.82	6.010	16.89	0.1303	125.13	4.631
300.14	6.044	18.15	0.1615	134.31	4.803
309.57	6.083	19.63	0.2030	142.84	4.940
319.10	6.127	21.49	0.2630	151.64	5.066
328.61	6.169	23.56	0.3399		

The calorimeter was loaded with sample and evacuated, and helium added at 5 cm Hg pressure at about 25°C to provide thermal contact between calorimeter and sample. It was then placed in the cryostat and cooled. The mass of sample used was 162.675 g Ni_{0.95}Se, 171.863 g Ni_{0.875}Se and 172.998 g Ni_{0.80}Se.

RESULTS

The heat-capacity determinations are listed in Table 1 in chronological order, and expressed in terms of the thermochemical calorie, defined as 4.1840 abs joules. The ice point is taken to be 273.15°K and the atomic weights of nickel and selenium as 58.71 and 78.96, respectively. The data are expressed in terms of one mole of mixture, "mole", equivalent to the gram formula weight of Ni_γSe_{1-γ}, *i.e.*, 69.09 g Ni_{0.95}Se, 69.51 g Ni_{0.875}Se and 69.96 g Ni_{0.80}Se. An analytically-determined curvature correction for the finite temperature increments was applied to the observed values of $\Delta H/\Delta T$. The approximate temperature increments can usually be inferred from the adjacent mean temperature values in Table 1.

The heat capacity *versus* temperature curves are shown in Fig. 1. For Ni_{0.95}Se it has the usual sigmoidal shape, with no anomalies or other irregular behavior up to 350°K. For Ni_{0.875}Se and Ni_{0.80}Se a slight relative increase in the values compared to those of Ni_{0.95}Se is observed above 250°K. This might possibly indicate the beginning of transitions.

Table 2. Thermodynamic properties of nickel selenides, cal °K⁻¹ "mole"⁻¹.

T, °K	Ni _{0.950} Se (formula weight Ni _{0.4872} Se _{0.5128} = 69.09 g)			Ni _{0.875} Se (formula weight Ni _{0.4667} Se _{0.5333} = 69.51 g)			Ni _{0.80} Se (formula weight Ni _{0.4444} Se _{0.5556} = 69.96 g)		
	C _p ^o	S ^o -S ₀ ^o	$\frac{H^o-H_0^o}{T}$	C _p ^o	S ^o -S ₀ ^o	$\frac{H^o-H_0^o}{T}$	C _p ^o	S ^o -S ₀ ^o	$\frac{H^o-H_0^o}{T}$
10	0.028	0.0110	0.0080	0.029	0.0110	0.0080	0.027	0.0100	0.0073
15	0.093	0.0330	0.0241	0.093	0.0331	0.0242	0.090	0.0311	0.0229
20	0.218	0.0754	0.0556	0.217	0.0754	0.0556	0.215	0.0726	0.0540
25	0.406	0.1431	0.1059	0.401	0.1425	0.1054	0.398	0.1392	0.1036
30	0.647	0.2376	0.1753	0.634	0.2355	0.1734	0.628	0.2314	0.1712
35	0.928	0.3581	0.2624	0.903	0.3531	0.2581	0.892	0.3476	0.2550
40	1.233	0.5018	0.3645	1.195	0.4926	0.3568	1.177	0.4852	0.3523
45	1.548	0.6652	0.4785	1.499	0.6509	0.4668	1.471	0.6408	0.4603
50	1.862	0.8446	0.6012	1.803	0.8246	0.5852	1.765	0.8111	0.5761
60	2.459	1.238	0.8618	2.388	1.206	0.8376	2.327	1.183	0.8216
70	2.994	1.658	1.1290	2.914	1.614	1.0976	2.840	1.581	1.0739
80	3.455	2.088	1.3917	3.368	2.034	1.3538	3.297	1.991	1.3239
90	3.842	2.518	1.6432	3.752	2.453	1.5996	3.692	2.403	1.5657
100	4.161	2.940	1.8795	4.074	2.866	1.8314	4.022	2.809	1.7953
110	4.427	3.350	2.0994	4.345	3.267	2.0480	4.295	3.206	2.0106
120	4.652	3.745	2.3030	4.575	3.656	2.2492	4.523	3.590	2.2107
130	4.846	4.125	2.4913	4.772	4.030	2.4359	4.720	3.960	2.3963
140	5.013	4.491	2.6657	4.941	4.390	2.6089	4.895	4.316	2.5687
150	5.156	4.841	2.8270	5.087	4.736	2.7693	5.050	4.659	2.7291
160	5.277	5.178	2.9765	5.213	5.068	2.9182	5.182	4.989	2.8784
170	5.380	5.501	2.1149	5.322	5.387	3.0565	5.293	5.307	3.0173
180	5.472	5.811	3.2433	5.418	5.694	3.1850	5.387	5.612	3.1464
190	5.554	6.109	3.3628	5.503	5.990	3.3048	5.469	5.906	3.2665
200	5.630	6.396	3.4743	5.579	6.274	3.4167	5.546	6.188	3.3786
210	5.699	6.673	3.5786	5.649	6.548	3.5213	5.618	6.460	3.4835
220	5.764	6.939	3.6765	5.712	6.812	3.6195	5.683	6.723	3.5820
230	5.825	7.197	3.7686	5.770	7.067	3.7117	5.741	6.977	3.6747
240	5.886	7.446	3.8556	5.823	7.314	3.7986	5.791	7.223	3.7618
250	5.944	7.688	3.9379	5.872	7.553	3.8806	5.837	7.460	3.8439
260	5.997	7.922	4.0161	5.921	7.784	3.9581	5.883	7.690	3.9215
270	6.043	8.149	4.0904	5.971	8.008	4.0317	5.928	7.913	3.9950
280	6.085	8.369	4.1609	6.026	8.226	4.1020	5.969	8.129	4.0648
290	6.124	8.584	4.2279	6.085	8.439	4.1693	6.004	8.339	4.1310
300	6.160	8.792	4.2917	6.143	8.646	4.2342	6.044	8.543	4.1941
350	6.300	9.724	4.5689	6.288	9.610	4.5225	6.270	9.464	4.4742
273.15	6.057	8.219	4.1130	5.988	8.078	4.0542	5.942	7.982	4.0173
298.15	6.154	8.754	4.2801	6.133	8.608	4.2224	6.037	8.506	4.1826

Values of C_p , S_0° and $(H^\circ - H_0^\circ)/T$ for the three samples at selected temperatures are listed in Table 2. No values for the free energy function are given because of the uncertainty about complete ordering of the atoms and holes, just as for the iron-selenides. The enthalpy and entropy increments were computed by integration of the heat-capacity equation, obtained by successive approximations on an IBM 650 calculator. The heat-capacity values are considered to have a probable error of 1 % at 10°K and 0.1 % above 25°K. The estimated probable error in the entropy and enthalpy functions is 0.1 % above 100°K. Some of the data are given to an additional digit because of its significance when the entropies or enthalpies at different temperatures or compositions are compared. The effects of nuclear spin and isotopic mixing are not included in the entropy function.

The non-applicability of the Kopp-Neumann law is immediately evident, since the "molar" heat capacity, and also the entropy, decreases with increasing selenium content, although the heat capacity and entropy of selenium is higher than for nickel. Within the homogeneity range of the Ni_{1-x}Se -phase reasonable interpolations could have been made, but even over this narrow range of compositions deviations from additivity are observed. These deviations suggest that interpolations should be made with great caution, and might aid in the resolution of the factors contributing to the heat capacities of phases with NiAs-like structure and cation vacancies.

Acknowledgment. The partial support of the *Division of Research, U. S. Atomic Energy Commission*, and of *Norges Almenvitenskapelige Forskningsråd* are gratefully acknowledged.

The authors thank Bolidens Gruvaktiebolag for a generous supply of high-purity selenium and Bruce Justice and Elfreda Chang for assistance in the calorimetric measurements and reduction of the data.

REFERENCES

1. Alsén, N. *Geol. Fören. i Stockholm Förh.* **47** (1925) 19.
2. Grønvold, F. and Jacobsen, E. *Acta Chem. Scand.* **10** (1956) 1440.
3. Grønvold, F. *Paper presented at the 2. Nordiske Strukturmete*, Oslo 1955.
4. Westrum, E. F. Jr., Chou, C., Machol, R. E. and Grønvold, F. *J. Chem. Phys.* **28** (1958) 497.
5. Grønvold, F. and Westrum, E. F. Jr. *Acta Chem. Scand.* **13** (1959) 241.
6. Grønvold, F. *Paper presented at the XVI International Congress of IUPAC*, Paris 1957.
7. Westrum, E. F. Jr. and Beale, A. F. Jr. *To be published.*

Received November 14, 1959.