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Thermodynamic properties of the nickel silicide NiSi between 8 and 400 K

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Abstract

The molar heat capacities of NiSi have been determined by low-temperature adiabatic calorimetry at temperatures between 8 and 400 K. From the heat capacity data the derived thermodynamic functions $\Delta_0^T H^0$ and S^0 were calculated.

At $T = 298.15$ K a molar standard heat capacity of 45.55 ± 0.05 J K^{-1} mol^{-1} and a molar standard entropy of 47.58 ± 0.04 J K^{-1} mol^{-1} have been found. The entropy of formation for NiSi was calculated to be -1.11 ± 0.08 J K^{-1} mol^{-1}.

Keywords: Nickel silicide; NiSi; Adiabatic calorimeter; Heat capacity; Entropy of formation

1. Introduction

Because of its technological importance the system nickel–silicon is widely investigated and well understood [1]. One of the existing intermetallic compounds in the nickel–silicon system, the NiSi phase, is a promising material for applications in Si microelectronics [2]. Numerous papers deal with experimental or calculated thermodynamic data, like enthalpies of formation or heat capacities [3–8]. But, less information is available about the entropies of formation of the silicides. For NiSi only the value $\Delta_f S_{NiSi}(298.15\ K) = -4.2 \pm 1.0$ J K^{-1} mol^{-1} [9], based on experimental data, was published. Furthermore, a thermodynamic calculation of the Ni–Si phase diagram gives the value of $\Delta_f S_{NiSi}(298.15\ K) = 8.6$ J K^{-1} mol^{-1} [6], which seems to be unexpectedly large.

In this work, the heat capacity of single-crystal NiSi measured by low-temperature adiabatic calorimetry is reported. From the derived molar standard entropy the entropy of formation of NiSi is calculated.

2. Experimental

The synthesis and pulling of NiSi was done in one run by the Czochralski technique, in the same manner like the preparation of iron silicides single-crystals [10]. Before melting the charge material, the apparatus was evacuated to approximately 10^{-5} mbar, backfilled with pure argon (mass fraction 0.99999), and evacuated again. Growth runs were carried out in a dynamic vacuum of 10^{-5} mbar. Nickel (mass fraction

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>0.99998, Alfa) and silicon (mass fraction 0.999999, Atomergic Chemicals) reacted inside an Al_2O_3 crucible. An extra 5% silicon above the stoichiometric amount was added to compensate for volatilization of silicon during the growth process. After 1 h, needed for reaction and homogenization, the seed crystal was partly immersed in the melt and the growth process was started.

The single crystal were characterized by means of raster electron microscopy (REM), electron microprobe analysis and X-ray powder diffraction (Siemens D5000). The material does not exhibit any microscopic inhomogeneities. The powder diffraction pattern indicates pure NiSi. The lattice constants of the orthorhombic unit cell were determined as $a = 5.18305 \pm 0.00047$ Å, $b = 3.33531 \pm 0.0004$ Å, $c = 5.61518 \pm 0.00057$ Å. The composition was determined by electron microprobe analysis and lead to the empirical formula $NiSi_{0.991}$.

The single crystal were broken into pieces of 1–3 mm. For calorimetric measurements 4.0480 g NiSi (molar mass 86.7789 g mol^{-1}) were used.

The heat capacitiy measurements were performed in a low-temperature adiabatic calorimeter (laboratory designation CAL VII). This calorimeter, its measuring system, and the measurement procedure were described in detail previously [11]. The calorimeter vessel is made of gold-plated copper, with a re-entrant well for the thermometer and heater assembly. The sample was loaded into the calorimeter vessel and the vessel was purged by carefully evacuating and adding helium, in order to remove any moisture from the sample. Finally, to facilitate thermal contact between sample and calorimeter, the vessel was closed under a helium pressure of 1000 Pa at 300 K. The thermometer used was calibrated to the IPTS-68 scale (Oxford Instruments) and corrected to the IST 90 scale according to [12].

The estimated uncertainty in the determination of the heat capacities is about 2% between 10 and 30 K and about 0.2% from 30 to 100 K. Above 100 K the uncertainty is less than 0.1% [10].

3. Results

The experimental result is shown in Fig. 1, the data are given in Table 1. Neither phase transitions nor anomalies are present. The experimental data were fitted with a polynomial function in order to determine the thermodynamic functions $\Delta_0^T H^0$ and S^0. The results are shown in Table 2. The obtained standard molar heat capacity and standard molar heat entropy show significant differences compared with data in literature (Table 3).

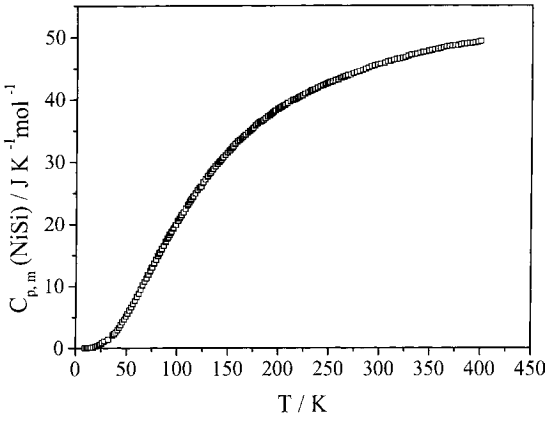

Fig. 1. Experimental molar heat capacity of NiSi.

With Eq. (1) the molar heat capacity at constant volume can be split up in an electronic contribution γ and a lattice contribution β at low temperatures:

$$C_v = \gamma \cdot T + \beta \cdot T^3. \quad (1)$$

Using the reliable assumption that below 25 K, C_v is sufficiently approximated by C_p both contributions were obtained by a least square fit: $\beta = 0.0299$ mJ K^{-4} mol^{-1}, $\gamma = 2.57$ mJ K^{-2} mol^{-1}. These values are in good agreement with the results of Meyer et al.: $\beta = 0.0317$ mJ K^{-4} mol^{-1}, $\gamma = 1.73$ mJ K^{-2} mol^{-1} [13]. The low value of the electronic heat capacity $\gamma \cdot T$ agrees with the low electron density at the Fermi level [14]. The Debye temperature Θ_D was computed after Eq. (2) from the value of the lattice contribution β:

$$\Theta_D^3 = 12\pi^4 nRT^3/5C_v, \quad (2)$$

where n is the number of atoms per formula unit, and C_v the molar heat capacity at constant volume. A Debye temperature $\Theta_D = 506$ K ($\Theta_D = 497$ K after [13]) was calculated, the high value is due to the strong interactions in the silicide and the large hardness of this material.

Table 1
Experimental molar heat capacity of NiSi

Series 1		Series 2		Series 3		Series 4		Series 5		Series 6		Series 7	
T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
81.48	15.16	8.97	0.0495	12.17	0.0770	31.97	1.435	65.75	10.18	199.65	38.53	304.26	45.89
83.87	15.83	10.67	0.0707	14.06	0.1358	32.16	1.403	67.59	10.71	201.91	38.74	307.19	46.09
86.24	16.54	12.18	0.0967	15.73	0.1307	36.34	2.094	69.44	11.31	204.89	39.06	310.12	46.17
88.60	17.25	14.00	0.1354	17.55	0.1952	37.89	2.283	71.30	11.83	207.87	39.36	313.04	46.35
90.96	17.91	15.63	0.1453	19.57	0.2948	39.47	2.549	73.16	12.46	210.84	39.72	315.97	46.45
93.34	18.56	17.47	0.1775	21.65	0.4151	41.07	2.916	75.03	13.03	213.81	39.96	318.88	46.55
95.72	19.25	19.46	0.2829	23.79	0.6047	42.70	3.288	76.91	13.66	216.79	40.07	321.79	46.66
98.11	19.88	21.51	0.3817	26.03	0.8416	44.34	3.746	78.79	14.24	219.76	40.39	324.69	46.80
100.50	20.59	23.65	0.5683	28.35	1.1463	46.01	4.204	80.68	14.87	222.74	40.63	327.59	46.96
102.90	21.21	25.87	0.7807			47.69	4.659	82.58	15.42	225.71	40.89	330.49	47.15
105.30	21.81	28.17	1.0966			49.40	5.129	84.48	16.03	228.69	41.16	333.38	47.24
107.71	22.47					51.12	5.599	86.38	16.55	231.67	41.43	336.28	47.35
110.12	23.16					52.86	6.101	88.29	17.16	234.65	41.64	339.17	47.48
112.54	23.78					54.62	6.597	90.21	17.69	237.63	41.85	342.06	47.59
114.96	24.34					56.39	7.126	92.12	18.28	240.61	42.08	344.95	47.66
117.39	24.95					58.18	7.629	94.05	18.79	243.59	42.31	347.83	47.77
119.82	25.53					59.98	8.260	95.97	19.37	246.57	42.50	350.70	47.88
122.25	26.06					61.78	8.766	97.90	19.89	249.55	42.70	353.58	48.01
124.68	26.63					63.60	9.459	99.84	20.50	252.54	42.83	356.45	48.11
127.11	27.17					65.43	10.07	101.77	20.95	255.52	43.04	359.32	48.22
129.55	27.71					67.27	10.68	103.71	21.47	258.51	43.21	362.18	48.33
131.99	28.24					69.12	11.25	105.65	21.94	261.49	43.41	365.03	48.48
134.43	28.77					70.98	11.83	107.60	22.46	264.48	43.60	367.89	48.55
136.88	29.26					72.85	12.40	109.54	22.99	267.46	43.77	370.75	48.57
139.32	29.70					74.73	13.01	111.49	23.50	270.45	43.97	373.60	48.66
141.77	30.11					76.62	13.62	113.44	23.99	273.44	44.20	376.45	48.63
144.23	30.60					78.51	14.22	115.40	24.45	276.42	44.37	379.29	48.75
146.68	31.06					80.40	14.84	117.35	24.96	279.41	44.50	382.13	48.87
149.14	31.49					82.31	15.40	119.31	25.41	282.40	44.70	384.97	48.92
151.59	31.91					84.22	16.01	121.27	25.86	285.38	44.89	387.81	48.95
154.05	32.35					86.13	16.53	123.23	26.06	288.36	45.09	390.64	49.03
156.51	32.88					88.05	17.14	125.19	26.75	291.33	45.30	393.48	49.13
158.97	33.27					89.97	17.67	127.16	27.19	294.30	45.45	396.32	49.20
161.43	33.52					91.90	18.25	129.12	27.63	297.26	45.59	399.15	49.34
163.89	33.94					93.84	18.77	131.09	28.05	300.22	45.76		
166.36	34.28					95.77	19.36	133.06	28.47				
168.82	34.66					97.71	19.87	135.03	28.88				
171.29	34.96					99.66	20.47	137.00	29.31				

Table 1 (*Contnued*)

Series 1		Series 2		Series 3		Series 4		Series 5		Series 6		Series 7	
T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
173.75	35.36							138.97	29.67				
176.22	35.80							140.94	29.98				
178.69	36.21							142.92	30.36				
181.16	36.46							144.89	30.74				
183.63	36.61							146.87	31.09				
186.10	36.98							148.84	31.45				
188.58	37.31							150.82	31.78				
191.05	37.50							152.80	32.13				
193.52	37.87							154.78	32.52				
195.99	38.20							156.76	32.95				
198.46	38.43							158.74	33.26				
200.94	38.68							160.72	33.48				
203.41	38.89							162.70	33.74				
205.89	39.14							164.68	34.06				
208.36	39.43							166.67	34.34				
210.84	39.72							168.65	34.65				
213.31	39.90							170.63	34.92				
215.79	39.98							172.62	35.16				
218.26	40.21							174.60	35.51				
220.75	40.45							176.59	35.89				
223.22	40.68							178.57	36.16				
225.70	40.90							180.56	36.46				
228.18	41.13							182.54	36.54				
230.66	41.33							184.52	36.74				
233.14	41.50							186.50	37.04				
235.62	41.68							188.49	37.32				
238.10	41.88							190.47	37.48				
240.57	42.08							192.45	37.69				
243.06	42.26							194.43	38.01				
245.54	42.45							196.42	38.23				
248.02	42.60							198.40	38.43				
250.50	42.77												
252.98	42.94												
255.46	43.08												
257.94	43.24												
260.42	43.40												
262.91	43.58												
265.39	43.75												
267.88	43.91												

Table 2
Thermodynamic functions of NiSi at selected temperatures

T (K)	C_p (J K^{-1} mol^{-1})	S^0(J K^{-1} mol^{-1})	$\Delta_0^T H^0$(J mol^{-1})
10	0.0153	0.0087	0.0309
20	0.2199	0.0856	0.9153
30	0.9471	0.3305	6.183
40	2.436	0.8420	22.42
50	4.691	1.679	57.47
60	7.533	2.848	118.2
70	10.71	4.315	209.2
80	13.98	6.023	332.7
90	17.19	7.912	488.6
100	20.22	9.926	675.8
110	23.02	12.02	892.2
120	25.56	14.15	1135
130	27.86	16.31	1403
140	29.93	18.45	1692
150	31.78	20.58	2001
160	33.44	22.69	2327
170	34.93	24.76	2669
180	36.27	26.78	3025
190	37.48	28.77	3394
200	38.58	30.72	3774
210	39.58	32.62	4165
220	40.48	34.47	4566
230	41.31	36.29	4975
240	42.08	38.06	5392
250	42.78	39.79	5816
260	43.44	41.48	6247
270	44.04	43.13	6685
280	44.61	44.75	7128
290	45.14	46.32	7577
300	45.64	47.86	8031
310	46.11	49.37	8489
320	46.56	50.84	8953
330	46.98	52.28	9420
340	47.38	53.70	9892
350	47.77	55.08	10368
360	48.14	56.43	10848
370	48.49	57.75	11331
380	48.83	59.05	11817
390	49.16	60.32	12307
400	49.48	61.57	12801
273.15	44.23	43.64	6824
298.15	45.55	47.58	7946

Based on the molar standard entropies of silicon of $S^0_{Si}(298.15\ K) = (18.82\pm0.08)$ J K^{-1} mol^{-1} [15] and nickel $S^0_{Ni}(298.15\ K) = (29.87\pm0.08)$ J K^{-1} mol^{-1} [15] the molar entropy of formation of NiSi was calculated: $\Delta_f S^0_{NiSi}(298.15\ K) = (-1.11\pm0.08)$ J K^{-1} mol^{-1}.

Table 3
Molar standard heat capacity and molar standard entropy of NiSi at 298.15 K

	C_p (298.15 K) (J K^{-1} mol^{-1})	S^0 (298.15 K) (J K^{-1} mol^{-1})
Kalishevich [9]	44.6	44.5
Extrapolated after Schimpf [16]	45.41	–
Calculated after an Mey [6]	43.26	40.16
This work	45.55 ± 0.05	47.58 ± 0.04

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