Enthalpy Increment Measurements from 4.5 K to 350 K and the Thermodynamic Properties of the Titanium Silicide TiSi(cr)[†]

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Enthalpy increments for TiSi(cr) were measured from 4.5 K to 350 K with an adiabatic calorimeter. A small anomaly, of unknown origin, was detected between 5 K and 15 K. From the present measurements and other measurements in the literature, the enthalpy relative to 0 K, the entropy, and the heat capacity of TiSi(cr) to 1500 K were calculated. The coefficient for the heat capacity of the conduction electrons, γ_{el}, was estimated from the measurements. Thermodynamic properties for formation from the elements at 298.15 K were also given.

Introduction

This contribution is part of a program of determination of the thermodynamic properties of metal−silicide materials, in general, and the titanium silicides, in particular. The present work provides new thermodynamic measurements and thermodynamic functions for TiSi(cr) that complement previous measurements for $TiSi_2$ (Archer et al., 1995) and Ti_5Si_3 (Archer et al., 1996). The measurements are enthalpy increments measured for small differences in temperature, on the order of 1.5 K to 5 K, with an adiabatic calorimeter. These measurements were combined with higher temperature enthalpy-increment measurements and represented with a least-squares generated equation. The entropy, enthalpy relative to 0 K, and the heat capacity of TiSi to 1500 K were calculated from the equation.

Experimental Section

Cooling of liquid TiSi alloys from the melt resulted in the production of a significant amount of secondary phases, as suggested by the phase diagram and previous study of this system. Production of high-purity TiSi samples was thus more problematic than in the case of $TiSi_2$ or Ti_5Si_3, requiring repeated high-temperature anneals interspersed with powdering of the sample. Ingots of TiSi were produced by means of arc melting in a titanium gettered, argon atmosphere (Feder et al., 1993; Grosman and Cotts, 1993). The titanium and the silicon used in sample preparation were of high-purity, <0.01 and <0.005 mol % metallic impurities. Pieces of each TiSi ingot were finely powdered in an acetone medium. Glass slides were coated with a thin layer of Vaseline petroleum jelly, and the powder was sprinkled onto the slide. X-ray diffraction analysis was performed in a standard $\theta-2\theta$ geometry using Cu Kα radiation. This analysis indicated that the sample was not single phase. The TiSi sample was powdered and then placed in a tantalum crucible and annealed in a vacuum furnace (1 mPa) at a temperature of 1423 K for 18 h. After cooling, the annealed ingot was again powdered and analyzed by X-ray diffraction, which revealed a primarily single-phase material. The annealing process was repeated; after cooling, X-ray diffraction analysis revealed a pattern corresponding to a single phase. The observed lattice parameters were a = 0.6522 nm, b = 0.3640 nm, and c = 0.5022 nm. Selected, relatively large, pieces of powder were polished for optical microscope and scanning electron microscope analysis. Optical micrographs revealed grain sizes between 0.1 mm and 0.5 mm, primarily of single phase. The level of contamination by secondary phases was estimated to be approximately 1.0%, by mass. Scanning electron microscopy analysis was consistent with optical microscopy results, with identification of secondary phases indicating primarily $TiSi_2$. While estimates of secondary-phase concentrations were not exact, the indication is that the sample may be Si rich on the order of 0.3%. The previously determined thermodynamic properties for $TiSi_2$ (Archer et al., 1995) were used to correct the present measured enthalpy increments for the $TiSi_2$ impurity.

The calorimetric apparatus has been described previously (Archer, 1995). The TiSi that was loaded into the calorimeter was in the form of a powder. After loading, the calorimeter was evacuated and then approximately 8 kPa (300 K) of helium was sealed in the calorimeter. The mass of the sample used for the measurements was 10.3243 g of which 0.1032 g were assumed to be $TiSi_2$. The mass of the sample corresponded to approximately 37% of the internal volume of the calorimeter. The density of this titanium silicide was calculated from the X-ray data to be 4.23 g·cm^{-3}. The formula weight was taken to be 75.966 g·mol^{-1}. The measured enthalpy increments of the filled calorimeter were converted into enthalpy increments for TiSi by

[†] Certain commercial materials and suppliers are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommedation or endorsement by either the U.S. Government or the National Institute of Standards and Technology nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.
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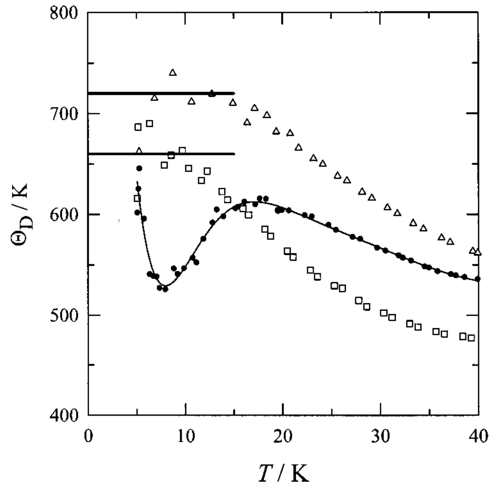

Figure 1. Values of the apparent Debye temperature against temperature calculated from measured enthalpy increments for TiSi, $TiSi_2$, and Ti_5Si_3. The symbols are as follows: ●, TiSi; △, $TiSi_2$; □, Ti_5Si_3. The two horizontal lines are the Debye temperatures obtained from the least-squares equations for $TiSi_2$ and Ti_5Si_3.

subtraction of enthalpy increments for the empty calorimeter and for the small differences in the amounts of helium and vacuum grease between the empty and filled calorimeters. The measured enthalpy increments were also corrected for the small amount of $TiSi_2$ contained in the sample by means of the previously reported values (Archer et al., 1995). The enthalpy increments were corrected for the small systematic biases in the calorimetric system using the equations

$$\epsilon\Delta H_m = -[\{(T_2 + T_1)/2\} - 100\ K](0.00001\ K^{-1})\Delta H_m \qquad (T_1 > 100\ K) \quad (1)$$

$$\epsilon\Delta H_m = -0.0025\Delta H_m \qquad (T_2 < 13.8) \quad (2)$$

where T_2 and T_1 are the larger and the smaller of the two temperatures for the enthalpy increment, respectively, and $\epsilon\Delta H_m$ is the correction added to the substance's enthalpy increment, ΔH_m. The origin of these corrections has been described previously (Archer, 1995).

Results and Discussion

The measured enthalpy increments for TiSi(cr) are given in Table 1. Above 50 K, the measurements for this TiSi(cr) sample are expected to be uncertain by no more than 0.05−0.1%, dependent upon the particular temperature. These uncertainty values were based on the following: the previous measurements of enthalpy increments for calorimetric reference materials (Archer, 1995, 1997), the present reproducibility, and the percentage of the total measured enthalpy increment that was due to the TiSi sample. Below 20 K, the results must be considered less accurate, partly due to limits in the accuracy of platinum resistance thermometer temperature scales below 20 K and partly due to an unfavorable percentage of the total measured enthalpy increment being due to the titanium silicide sample. The contribution of the enthalpy of the TiSi to the total measured enthalpy increment was a minimum of 7.2% near 20 K and increased in percentage with both increasing and decreasing temperatures from 20 K. The sample contributed 15% of the total enthalpy increment for the lowest temperature measurement. The increasing contribution of TiSi to the total enthalpy increment at temperatures less than 20 K is a result of TiSi possessing a much larger contribution to the enthalpy increment from the conduction electrons than does copper, which comprised the bulk of the calorimeter. By uncertainty, we mean a value that is the sum of imprecision and our expectation of what small potential calorimetric biases might remain following correction for the known calorimetric bias, described above. Because the latter quantity, namely, the small uncompensated calorimetric bias, is quantified only by a half-order of magnitude, i.e., we believe it to be in the vicinity of ±0.01% to ±0.03%, for $T > 50$ K for a sample whose enthalpy increments are comparable to those of the standard materials used previously (Archer, 1995, 1997), we have not tried to quantify it with any sort of confidence interval, particularly as the latter quantity refers to probability, which we have no means to gauge.

At temperatures below 20 K, an anomaly was present in the measured enthalpy increments. This anomaly can be easily visualized by extracting an apparent Debye temperature from the measurements and comparing it to values for other titanium silicides. For such a comparison, it was necessary to estimate the contribution to the internal energy of titanium silicide due to conducting electrons, γ_{el}. This value was estimated from

$$\Delta H_m(T_1 \rightarrow T_2)/(T_2^2 - T_1^2) = 2(3R\pi^4/5)\Theta_D^{-3}(T_2^4 - T_1^4)/(T_2^2 - T_1^2) + \gamma_{el}/2 \quad (3)$$

where R is the gas constant and Θ_D is the Debye temperature. Equation 3 is obtained from the low-temperature limit of the Debye theory for internal energy, neglect of the difference between internal energy and enthalpy for a condensed phase at low temperatures, and the addition of the conducting-electrons term. The value of γ_{el} estimated by us was 0.0014 $J \cdot mol^{-1} \cdot K^{-2}$. Values of the apparent Debye temperature, Θ_D, were estimated from the measured enthalpy increments by means of eq 3 and are shown in Figure 1. Also shown in Figure 1 are values calculated for $TiSi_2$ and Ti_5Si_3. The behavior for TiSi is not that expected from lattice vibration alone and is indicative of the anomaly. The measurements given in Table 1 are in chronological order. Several passes through the region of temperature corresponding to the anomaly were made, with one of the passes having been made after warming the calorimeter and its contents to 312 K. All of these measurements agreed within expected precisions.

After the measurements were completed, the sample of TiSi was removed from the calorimeter and examined for the presence of impurity elements that might have caused the anomaly. No other metal impurities were found. The measurements for TiSi reported here were performed prior to measurements on NaCl(cr), KBr(cr), and Cu(cr) (Archer, 1997). No indication of such an anomaly was found for any of these substances, so we do not believe it to have arisen from some change in the calorimeter. At the present time, the source of the anomaly is unknown. Its effect on the calculated properties of TiSi is small, less than ~0.05% of the entropy at 298.15 K and less than 0.01% of $H_m(T{=}298.15K) - H_m(T{=}0K)$.

Thermodynamic properties for TiSi were calculated from a least-squares representation using a cubic-spline method described previously (Archer, 1992; Archer et al., 1996). Briefly, a function $f(T)$ was used, where

$$f(T) = [T\{(C^\circ_{p,m} - \gamma_{el}T)/C^\circ_p\}^{-1/3} - bT]/T^\circ \quad (4)$$

and where T is temperature, T° is 1 K, $C^\circ_{p,m}$ is the molar

Table 1. Enthalpy Increment Measurements for TiSi(cr)

T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/ (J·mol^{-1})	σ^a	δ^b	T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/ (J·mol^{-1})	σ^a	δ^b
302.9941	307.9569	218.060	0.1	−0.02	4.3901	6.1492	0.0168	5.0	−5.27
307.9453	312.9604	221.481	0.1	−0.06	6.1589	7.8951	0.0323	5.0	0.68
312.9425	317.9545	222.566	0.1	−0.04	7.8373	9.7812	0.0560	4.0	−4.48
317.9308	322.9522	224.111	0.1	−0.04	9.7754	11.7267	0.0843	4.0	0.82
322.9223	327.9356	224.909	0.1	−0.01	11.7143	13.8590	0.1230	5.0	−0.78
327.8985	332.9225	226.408	0.1	−0.02	14.2578	16.0167	0.1442	3.0	0.87
332.8772	337.9118	228.012	0.1	0.02	16.0081	18.3506	0.2607	2.0	0.70
337.8584	343.8918	274.582	0.1	0.03	18.3386	20.6678	0.3704	2.0	2.06
343.8285	349.8475	275.443	0.1	0.08	4.5280	5.8158	0.0122	5.0	−2.05
305.1865	310.1398	218.121	0.1	−0.05	5.7826	7.5640	0.0300	5.0	2.49
310.1262	315.1314	221.601	0.1	−0.04	40.4019	43.4032	5.905	0.1	−0.01
315.1117	320.1266	223.242	0.1	−0.02	43.3864	46.2569	7.021	0.1	0.06
320.1009	325.1128	224.151	0.1	−0.05	46.2427	49.1530	8.627	0.1	−0.03
325.0802	330.0980	225.613	0.1	0.01	49.1398	52.1037	10.489	0.1	−0.07
330.0580	335.0861	227.020	0.1	−0.03	52.0908	55.0826	12.491	0.1	0.12
335.0367	340.0628	228.007	0.1	0.00	55.0709	58.0831	14.591	0.1	−0.03
340.0048	345.0407	229.507	0.1	0.03	58.0707	61.1109	16.895	0.1	−0.13
80.4505	83.4009	34.151	0.1	−0.02	61.0985	64.1738	19.424	0.1	−0.12
83.3995	86.8389	42.898	0.1	−0.07	64.1618	67.2625	22.054	0.1	−0.07
86.8362	90.2831	46.273	0.1	−0.21	67.2507	70.3644	24.703	0.1	−0.07
90.2790	93.7453	49.959	0.1	−0.06	70.3522	73.4828	27.502	0.1	0.03
93.7408	97.2099	53.329	0.1	−0.08	73.4714	76.6187	30.347	0.1	−0.03
97.2045	100.6912	56.944	0.1	−0.05	76.6069	79.7690	33.268	0.1	−0.02
100.6847	104.1737	60.275	0.1	−0.05	79.7570	82.9285	36.220	0.1	0.07
104.1674	107.6651	63.770	0.1	0.10	82.9164	86.0908	39.109	0.1	0.11
107.6564	111.1682	67.189	0.1	0.02	86.0772	89.2752	42.240	0.1	0.04
111.1593	114.6767	70.447	0.1	0.01	89.2619	92.4697	45.210	0.1	−0.05
114.6675	118.1936	73.659	0.1	−0.08	92.4557	95.6631	48.078	0.1	−0.02
118.1833	121.7099	76.717	0.1	−0.04	95.6487	98.8666	51.108	0.1	0.03
121.6993	125.2407	79.938	0.1	−0.13	98.8525	102.0832	54.151	0.1	0.04
125.2296	128.7719	83.039	0.1	0.09	102.0270	106.2964	75.778	0.1	0.01
128.7603	132.2975	85.643	0.1	−0.02	106.2881	110.5299	80.032	0.1	0.00
132.2848	135.8329	88.631	0.1	−0.04	110.5203	114.7833	85.177	0.1	0.11
135.8196	139.3684	91.359	0.1	0.00	114.7728	119.0460	89.808	0.1	−0.03
139.3553	142.9083	93.942	0.1	−0.13	119.0343	123.3081	94.266	0.1	0.00
142.8941	146.4473	96.567	0.1	−0.03	123.2958	127.5822	98.835	0.1	−0.01
146.4324	149.9935	99.233	0.1	−0.03	127.5694	131.8701	103.376	0.1	0.01
149.9783	153.5356	101.645	0.1	0.11	131.8572	136.1572	107.425	0.1	0.01
153.5196	157.0871	104.083	0.1	−0.04	136.1437	140.4373	111.163	0.1	0.01
157.0700	160.6342	106.382	0.1	0.11	140.4232	144.7324	115.352	0.1	0.00
160.6184	164.3864	114.714	0.1	0.02	144.7176	149.0290	119.094	0.1	0.03
164.3720	168.1418	117.139	0.1	0.05	149.0119	153.3287	122.799	0.1	0.05
168.1277	171.8983	119.255	0.1	−0.09	153.3128	157.6252	126.014	0.1	0.01
171.8828	175.6538	121.521	0.1	−0.02	157.6085	161.9229	129.350	0.1	0.03
175.6375	179.4153	123.895	0.1	0.02	161.9041	166.2223	132.637	0.1	0.06
179.3985	183.1674	125.672	0.1	0.05	166.2031	170.5254	135.773	0.1	0.06
183.1501	186.9256	127.862	0.1	0.05	170.5054	174.8361	138.686	0.1	−0.13
186.9081	190.6788	129.584	0.1	0.04	174.8140	178.0562	105.784	0.1	−0.01
190.6607	194.4397	131.732	0.1	0.05	178.0373	181.2944	107.836	0.1	0.02
194.4211	198.1982	133.360	0.1	−0.01	181.2770	184.5297	109.167	0.1	0.02
198.1785	201.9540	135.087	0.1	0.04	184.5118	187.7653	110.628	0.1	0.01
201.9342	205.7100	136.643	0.1	−0.04	187.7472	192.0777	149.255	0.1	−0.10
205.6879	209.4640	138.279	0.1	−0.02	192.0566	196.3748	151.399	0.1	0.03
209.4414	213.2142	139.694	0.1	−0.02	196.3544	200.6754	153.777	0.1	0.03
213.1911	216.9675	141.226	0.1	−0.09	200.6539	204.9676	155.618	0.1	−0.03
216.9433	220.7114	142.437	0.1	−0.03	204.9448	209.2697	158.169	0.1	−0.01
220.6853	224.4544	143.841	0.1	−0.05	209.2466	213.5649	159.795	0.1	−0.11
224.4275	228.2025	145.480	0.1	0.00	213.5393	217.8532	161.687	0.1	−0.04
228.1748	231.9559	147.020	0.1	0.00	217.8263	222.1544	164.169	0.1	0.00
231.9273	236.7819	190.611	0.1	0.00	222.1254	226.4489	165.716	0.1	−0.05
236.7482	241.5899	192.143	0.1	0.02	226.4191	230.7423	167.544	0.1	0.02
241.5540	246.3928	193.977	0.1	0.04	235.0039	239.3306	170.981	0.1	0.03
246.3588	251.1927	195.587	0.1	0.03	239.2954	243.6124	172.193	0.1	0.05
251.1555	255.9920	197.302	0.1	−0.04	243.5750	247.8935	173.533	0.1	−0.07
255.9515	260.7902	199.163	0.1	0.00	247.8541	252.1763	175.271	0.1	0.02
260.7477	265.5908	200.978	0.1	0.01	252.1355	256.4642	176.928	0.1	0.02
265.5459	270.4997	207.389	0.1	0.11	256.4225	260.7436	177.999	0.1	0.05
270.4532	275.3951	208.279	0.1	0.03	260.6995	265.0266	179.464	0.1	0.00
275.3467	280.2951	209.951	0.1	−0.02	264.9805	269.2976	180.458	0.1	0.09
280.2413	285.1958	211.630	0.1	−0.03	269.2448	273.5732	182.007	0.1	0.03
285.1380	290.0857	212.824	0.1	0.01	273.5176	277.8429	182.906	0.1	−0.04
290.0238	294.9804	214.502	0.1	−0.01	277.7844	282.1145	184.313	0.1	0.00
294.9150	299.8605	215.325	0.1	0.00	282.0525	286.3804	185.315	0.1	0.01
299.7907	304.7458	217.072	0.1	0.04	286.2447	290.6558	189.942	0.1	0.01

Table 1 (Continued)

T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/ ($J \cdot mol^{-1}$)	σ^a	δ^b	T_1/K	T_2/K	$\Delta H_m(T_1 \rightarrow T_2)$/ ($J \cdot mol^{-1}$)	σ^a	δ^b
290.5957	294.9172	187.088	0.1	0.00	53.5093	56.5322	13.571	0.1	0.02
294.8537	299.1842	188.655	0.1	0.10	56.5144	59.5625	15.821	0.1	0.01
299.1171	303.4448	189.357	0.1	0.03	59.5452	62.6212	18.256	0.1	0.05
303.3744	307.6973	190.093	0.1	0.04	62.6048	65.6993	20.762	0.1	−0.03
307.6242	311.9480	190.931	0.1	0.00	65.6830	68.8042	23.462	0.1	−0.06
311.8708	316.1911	191.648	0.1	0.00	68.7878	71.9282	26.193	0.1	−0.20
4.3820	5.7297	0.0127	5.0	1.30	71.9112	75.0606	29.016	0.1	0.00
5.6341	7.0256	0.0211	5.0	4.45	75.0439	78.2049	31.893	0.1	0.04
6.9724	8.9115	0.0479	4.0	1.43	30.5028	33.2062	2.062	0.5	−0.60
8.8721	10.8358	0.0722	4.0	−0.69	33.1869	35.8549	2.720	0.3	0.32
10.8214	12.8623	0.1033	4.0	−0.41	35.8345	38.5467	3.576	0.3	0.21
12.8522	14.9884	0.1470	4.0	1.07	38.5263	41.2868	4.587	0.3	−0.67
14.9822	17.1366	0.1999	2.5	−0.63	41.2666	44.0731	5.849	0.2	−0.17
17.1195	19.4433	0.2972	2.5	−1.78	44.0535	46.9068	7.285	0.2	−0.23
19.4305	21.7907	0.4336	2.5	0.49	46.8875	49.7869	8.949	0.1	−0.02
21.7739	24.2264	0.6230	0.6	−0.60	49.7677	52.6925	10.741	0.1	0.15
24.2062	26.6746	0.8803	0.6	0.70	52.6751	55.6375	12.730	0.1	0.04
26.6554	29.2223	1.2434	0.6	−0.37	55.6202	58.6071	14.862	0.1	0.10
29.2022	31.8237	1.726	0.5	−0.23	58.5901	61.6119	17.191	0.1	0.00
31.8031	34.4793	2.351	0.5	−0.33	61.5953	64.6303	19.572	0.1	0.06
34.4597	37.1882	3.171	0.3	0.53	64.6143	67.6849	22.211	0.1	0.02
37.1705	39.9719	4.169	0.3	−0.19	67.6691	70.7539	24.809	0.1	−0.06
39.9555	42.7913	5.351	0.2	0.02	70.7380	73.8304	27.503	0.1	0.12
5.0134	6.4658	0.0168	5.0	−2.02	73.8144	76.9198	30.253	0.1	0.08
6.4418	8.2237	0.0372	4.0	2.47	76.9039	80.0494	33.387	0.1	0.10
8.2291	10.1335	0.0610	4.0	−1.84	80.0332	83.1946	36.374	0.1	0.14
10.1103	12.1343	0.0962	4.0	4.83	83.1789	86.3410	39.130	0.1	−0.03
12.1455	14.3109	0.1288	4.0	−3.44	86.3243	89.5162	42.367	0.1	0.01
14.3047	16.5118	0.1882	2.5	0.60	89.4973	92.6860	45.194	0.1	0.06
16.4891	18.7810	0.2668	2.5	−1.58	92.6678	95.8799	48.361	0.1	0.02
18.7528	21.1037	0.3943	2.5	1.20	95.8613	99.0770	51.287	0.1	0.09
21.0756	23.4719	0.5543	0.6	0.07	99.0592	102.2750	54.057	0.1	0.01
23.4562	25.9194	0.7898	0.6	−0.03	302.8073	306.9730	182.923	0.1	−0.02
25.9022	28.4118	1.1112	0.6	0.40	306.9647	311.1429	184.372	0.1	0.00
28.3922	30.9772	1.552	0.5	0.11	311.1287	315.3200	185.674	0.1	−0.05
30.9575	33.6138	2.131	0.5	−0.23	315.2999	319.4900	186.570	0.1	0.03
33.5936	36.3053	2.878	0.3	0.05	319.4638	323.6544	187.217	0.1	−0.05
36.2850	39.0726	3.840	0.3	0.10	323.6204	327.8244	188.629	0.1	−0.02
41.8665	44.7173	6.226	0.3	−0.17	327.7830	331.9850	189.311	0.1	−0.01
44.6972	47.6187	7.822	0.2	−0.10	331.9363	336.1513	190.674	0.1	0.02
47.5865	50.5544	9.584	0.1	−0.02	336.0960	340.3125	191.444	0.1	0.02
50.5350	53.5277	11.484	0.1	0.06					

[a] σ is the percentage uncertainty assigned to the observation for the purposes of the least-squares calculation. [b] δ is the percentage difference of the calculated enthalpy increment from that observed.

Table 2. Least-Squares-Estimated Knot Positions and γ_{el}

T_i/K	d_i	T_i/K	d_i	T_i/K	d_i
0	44.5000	22	32.9332	180	12.9771
2	44.5000	30	28.8057	240	12.9250
5	38.2305	40	24.4054	300	13.4619
7	32.7967	55	20.3508	400	14.9028
10	33.1605	75	17.3790	1600	23.5448
14	34.9076	100	15.2899		
18	34.5736	130	13.9206		

$\gamma_{el}/C°_p = 0.0014\ K^{-1}$

heat capacity, $C°_p$ is 1.0 $J \cdot K^{-1} \cdot mol^{-1}$, γ_{el} is the coefficient for the contribution to the heat capacity of the conduction electrons, and b is arbitrarily chosen to be 0.24 for the present case. The function $f(T)$ of eq 4 was fitted with a cubic spline using polynomials of the form

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i \quad (5)$$

where the subscript i refers to the polynomial that contains the specified value of T and spans the temperature range T_i to T_{i+1}. A particular (T_i, d_i) pair is referred to as a "knot". A "natural spline" end condition (i.e., second derivative equal to 0) was imposed at the highest temperature end knot. The two lowest temperature knots were fixed to have values that corresponded to a Debye temperature of 700 K, a value intermediate between values determined previously for $TiSi_2$ and Ti_5Si_3. There is no physical basis for this assignment other than the observation that the apparent Debye temperatures for TiSi were intermediate to those of $TiSi_2$ and Ti_5Si_3 at temperatures above those for the anomaly. The temperatures at which the anomaly occurred are such that we cannot extract the low-temperature limit of the Debye temperature from the measurements. The calculated heat capacity was thus

$$C°_{p,m}/C°_p = \left(\frac{T}{T°f(T) + bT}\right)^3 + \gamma_{el}T/C°_p \quad (6)$$

Equation 6 was integrated numerically to obtain the enthalpy. The model was determined by fitting to the selected values with a nonlinear least-squares program. The vector of residuals was calculated using the numerical integration of eq 6 to obtain the enthalpy increments. The estimated square root of the variance for the least-squares procedure was calculated from twice the irreproducibility for a full calorimeter determination and the percentage of the observed enthalpy due to the TiSi sample. These values, given in Table 1, actually corresponded approximately to a 95% confidence interval rather than the square root of the variance. In the current work, the first two knot

Table 3. Thermodynamic Properties of TiSr(cr) Calculated from Equations 4−6

T/K	$C_{p,m}$/ ($J \cdot K^{-1} \cdot mol^{-1}$)	$H_m(T) - H_m(0K)$/ ($kJ \cdot mol^{-1}$)	S_m/ ($J \cdot K^{-1} \cdot mol^{-1}$)
5	0.0090	0.000	0.008
10	0.0380	0.000	0.022
15	0.0794	0.000	0.044
20	0.1667	0.001	0.077
25	0.3331	0.002	0.131
30	0.6204	0.005	0.215
35	1.0640	0.009	0.341
40	1.6837	0.015	0.522
45	2.4732	0.026	0.764
50	3.413	0.040	1.072
55	4.482	0.060	1.447
60	5.663	0.085	1.887
65	6.930	0.117	2.389
70	8.260	0.155	2.951
75	9.632	0.200	3.568
80	11.033	0.251	4.234
85	12.447	0.310	4.945
90	13.858	0.376	5.697
95	15.254	0.448	6.484
100	16.628	0.528	7.301
110	19.281	0.708	9.011
120	21.778	0.913	10.797
130	24.099	1.143	12.633
140	26.245	1.395	14.499
150	28.215	1.667	16.378
160	30.014	1.958	18.257
170	31.653	2.267	20.127
180	33.148	2.591	21.979
190	34.512	2.929	23.808
200	35.757	3.281	25.611
210	36.894	3.644	27.383
220	37.930	4.018	29.124
230	38.878	4.403	30.831
240	39.745	4.796	32.504
250	40.542	5.197	34.143
260	41.275	5.606	35.748
270	41.949	6.022	37.318
280	42.571	6.445	38.855
290	43.144	6.874	40.359
298.15	43.581	7.227	41.561
300	43.677	7.308	41.831
325	44.85	8.415	45.37
350	45.84	9.549	48.73
400	47.5	11.883	54.96
500	50.0	16.766	65.85
600	52.1	21.88	75.2
700	53.8	27.17	83.3
800	55.2	32.62	90.6
900	56.5	38.21	97.2
1000	57.6	43.92	103.2
1100	58.7	49.73	108.7
1200	59.6	55.65	113.9
1300	60.5	61.66	118.7
1400	61.3	67.75	123.2
1500	62.0	73.91	127.5

positions were set to have identical values which corresponded to $\Theta_D = 700$ K.

Also included in the representation were the enthalpy increment measurements from Golutvin (1959). The higher temperatures for these enthalpy increments ranged from 377.65 K to 1352.15 K and the lower temperature was 298.15 K. These values were assigned a square root of variance of ± 1 $kJ \cdot mol^{-1}$, independent of temperature. Meschel and Kleppa (1998) reported one enthalpy increment for the change in temperature of 298.15 K to (1473 $\pm$ 2) K. Their enthalpy increment value was an average of six determinations that had a standard deviation of 2.2 $kJ \cdot mol^{-1}$. This average value was assigned a square root of variance of 1 $kJ \cdot mol^{-1}$, approximately the standard deviation of the mean. The representation of the experimental results, over the full range of temperature, required

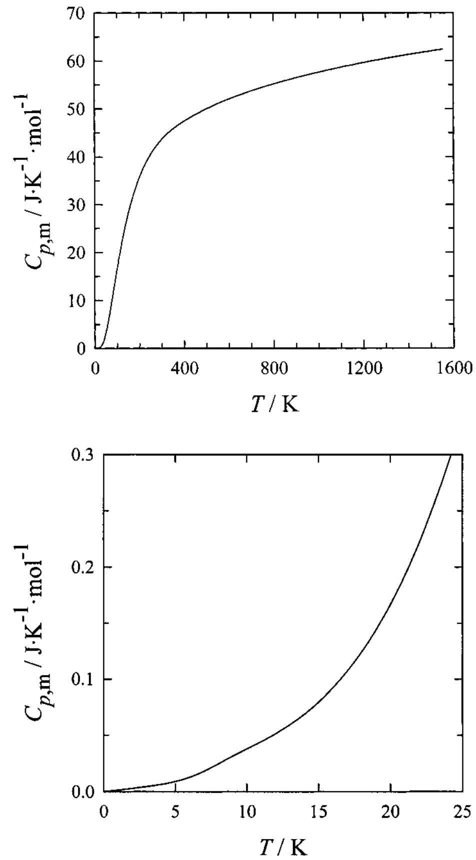

Figure 2. Heat capacity against temperature for TiSi calculated from the least-squares estimated equation.

17 variable values for the knot positions and utilized the estimated values of γ_{el} and Debye temperature described above. The optimized knot positions are given in Table 2. Values of thermodynamic properties of TiSi(cr), calculated from eqs 4−6, are given in Table 3. Figure 2 shows the heat capacity calculated from the fitted equation.

The differences of the present measured values from the least-squares estimated model are shown in Figure 3. The root-mean-square difference of the present measurements from the fitted model was approximately 0.06% for temperatures greater than 50 K. The enthalpy increment from Meschel and Kleppa (1998) was 1.6 $kJ \cdot mol^{-1}$ smaller than that calculated from the fitted equation. Thus, the model falls within one standard deviation of the random variable. The measurements from Golutvin (1959) showed a 1 $kJ \cdot mol^{-1}$ root-mean-square difference from the fitted equation. The measurements for temperatures below 800 K showed a negative bias, but measurements above this temperature showed an average deviation of +250 $J \cdot mol^{-1}$ and thus were in reasonable agreement with the Meschel and Kleppa measurements.

Combination of the present 298.15 K entropy with the reference values of the entropies of titanium and silicon (Chase et al., 1985) gave an entropy of formation of −8.0 $J \cdot K^{-1} \cdot mol^{-1}$ for 298.15 K. Schlesinger (1990) reviewed enthalpies of formation reported previously and recommended −157.2 $kJ \cdot mol^{-1}$ for the enthalpy of formation of TiSi(cr) at 298.15 K, obtained from the measurements described by Savin (1973). There are two more recent determinations of the enthalpy of formation of TiSi(cr) in the literature. Kematick and Myers (1996) obtained $\Delta_f H_m^\circ$ = (−143.0 $\pm$ 10) $kJ \cdot mol^{-1}$ from Knudsen effusion mass spectrometry. Meschel and Kleppa (1998) obtained $\Delta_f H_m^\circ$ = (−145.2 $\pm$ 3.8) $kJ \cdot mol^{-1}$ from direct synthesis calorim-

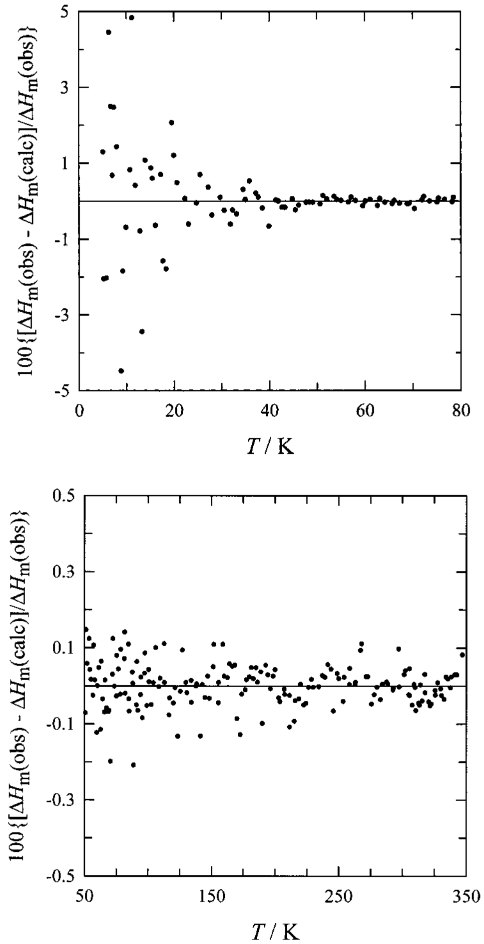

Figure 3. Differences of the present measurements from the fitted model, in percent.

etry. These most recent two values are in statistical agreement with each other but not with the earlier value given by Savin. Combination of the Meschel and Kleppa value with the entropy of formation gives $\Delta_f G_m° = (-142.8 \pm 3.8)$ kJ·mol^{-1}.

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Literature Cited

Archer, D. G. Thermodynamic Properties of the NaCl + H_2O System. I. Thermodynamic Properties of NaCl(cr). *J. Chem. Phys. Ref. Data* **1992**, *21*, 1−21.

Archer, D. G. Enthalpy Increment Measurements from 4.5 to 318 K for Bismuth(cr). Thermodynamic Properties from 0 K to the Melting Point. *J. Chem. Eng. Data* **1995**, *40*, 1015−1024.

Archer, D. G. Enthalpy Increment Measurements for NaCl(cr) and KBr(cr) from 4.5 K to 350 K. Thermodynamic Properties of the NaCl + H_2O System. 3. *J. Chem. Eng. Data* **1997**, *41*, 2281−292.

Archer, D. G.; Sabella, S. E.; Stillman, S. E.; Cotts, E. J. Enthalpy Increment Measurements from 4.5 to 350 K and the Thermodynamic Properties of Titanium Disilicide(cr) to 1700 K. *J. Chem. Eng. Data* **1995**, *40*, 1237−1241.

Archer, D. G.; Filor, D.; Oakley, E.; Cotts, E. J. Enthalpy Increment Measurements from 4.5 K to 350 K and the Thermodynamic Properties of Ti_5Si_3(cr). *J. Chem. Eng. Data* **1996**, *41*, 571−575.

Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd ed. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1.

Feder, K.; Gance, K.; Cotts, E. J. Calorimetric Study of Solid State Reactions. *Pure Appl. Chem*. **1993**, *65*, 895−900.

Golutvin, Yu. M. Heat Contents and Heat Capacities in the Titanium−Silicon System. *Russ. J. Phys. Chem*. **1959**, *33*, 164−168.

Grosman, D.; Cotts, E. J. Averaged Interdiffusion Coefficient During Solid-State Amorphization Reactions between Metal Layers. *Phys. Rev. B* **1993**, *48*, 5579−5584.

Kematick, R. J.; Myers, C. E. Thermodynamics of the Phase Formation of the Titanium Silicides. *Chem. Mater*. **1996**, *8*, 287−291.

Meschel, S. V.; Kleppa, O. J. Standard Enthalpies of Formation of Some 3d Transition Metal Silicides by High-Temperature Direct Synthesis Calorimetry. *J. Alloys Compd*. **1998**, *267*, 128−135.

Savin, V. D. Thermographic Determination of the Thermochemical Characteristics of Processes and Materials. *Russ. J. Phys. Chem*. (*Engl. Transl*.) **1973**, *47*, 1423.

Schlesinger, M. E. Thermodynamics of Solid Transition Metal Silicides. *Chem. Rev*. **1990**, *90*, 607−628.

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