

Heat capacity and thermodynamic properties of CrSb₂ from 5 to 1050 K. Magnetic transition and enthalpy of decomposition^a

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The heat capacity of CrSb₂ has been measured by adiabatic calorimetry from 5 to 991.3 K. At the latter temperature the CrSb₂-phase decomposes into the CrSb-phase and an antimony-rich melt. The heat capacity of the two-phase mixture was measured from 991.3 to 1050 K. The heat capacity of CrSb₂ shows a small sharp λ -type transition with a maximum at 274.1 K where the change from the antiferromagnetic to the paramagnetic state occurs. The low entropy of the clearly cooperative part of the transition, $\Delta S_t = 0.12 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$, shows that this contribution is only a small part of the total. From an estimate of the lattice heat capacity of CrSb₂ outside the λ -transition region we find an excess heat capacity amounting to about $1.7 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ at 300 K, $1.6 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ at 500 K, and $1.1 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ at 800 K, which we attribute to the population of excited electronic states in CrSb₂. The total transitional entropy amounts to about $2.6 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ at 900 K only slightly more than the $R \ln 3 (= 2.17 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1})$ expected from randomization of two unpaired spins per chromium atom. The enthalpy of the peritectic decomposition of CrSb₂ at 991.3 K is $(8325 \pm 20) \text{ cal}_{\text{th}} \text{ mol}^{-1}$.

The high heat capacity above 991 K is presumably related to the solution of CrSb(s) in the melt. Thermodynamic functions have been evaluated and the values of C_p , $\{S^\circ(T) - S^\circ(0)\}$, and $\{-\{G^\circ(T) - H^\circ(0)\}/T\}$ at 298.15 K are (19.66 ± 0.02) , (27.46 ± 0.03) , $(14.009 \pm 0.014) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. CrSb₂ loses antimony on approaching the peritectic temperature and the composition of the decomposing phase is in the range CrSb_{1.90} to CrSb_{1.95}. To explore further the homogeneity range of the CrSb₂-phase some heat-capacity measurements on CrSb_{1.85} have also been carried out. Combination of the present results with standard Gibbs energies of formation at 850 K from the literature gives for CrSb_{2.00}:

	298.15 K	850 K
$\Delta G_f^\circ/\text{kcal}_{\text{th}} \text{ mol}^{-1}$	-4.46 ± 0.13	-5.10 ± 0.03
$\Delta S_f^\circ/\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	0.05 ± 0.12	1.59 ± 0.13
$\Delta H_f^\circ/\text{kcal}_{\text{th}} \text{ mol}^{-1}$	-4.45 ± 0.12	-3.75 ± 0.12

1. Introduction

In chromium + antimony, two intermediate phases exist, the monoantimonide with the hexagonal NiAs-structure and the diantimonide with the orthorhombic FeS₂

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(marcasite)-structure.⁽¹⁾ The concomitant study of the magnetic properties showed a maximum in susceptibility of CrSb_2 near 600 K and indicated the presence of two unpaired spins per chromium atom at high temperatures, and thus formally quadrivalent chromium in CrSb_2 . Foëx and Graff⁽²⁾ had reported that CrSb_2 showed anti-ferromagnetic behaviour just as does CrSb , but no results were presented. In a later susceptibility study by Holseth and Kjekshus⁽³⁾ the unusual susceptibility behaviour was confirmed and it was suggested that CrSb_2 might be antiferromagnetic with a Néel temperature close to the decomposition temperature. Adachi *et al.*⁽⁴⁾ interpreted their susceptibilities over the range 77 to 900 K in terms of the excitation of electrons from a singlet to a triplet spin state with an energy separation of 7 kJ mol^{-1} . The same energy gap was derived from low-temperature resistivity measurements. Accordingly, a broad Schottky-type heat-capacity maximum of $2.03 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ at 288 K was expected. Adachi *et al.*⁽⁴⁾ carried out heat-capacity measurements only above 330 K and the results gave no confirmation of the correctness of their model.

In view of possible antiferromagnetic spin ordering Adachi *et al.*⁽⁴⁾ performed neutron-diffraction experiments near 300 K, but did not observe any magnetic reflections. Similar experiments by Holseth *et al.*⁽⁵⁾ showed antiferromagnetic ordering at 4.2 K with doubled cell dimensions in the b- and c-directions. The magnetic spin quantum number is 0.97 per chromium atom and the magnetic moments are coupled parallel in each 011 plane of the magnetic unit cell, but in opposite directions in adjacent planes and with orientation approximately normal to the 101 plane. Of all the compounds with marcasite-structure, CrSb_2 is the only one which shows clear evidence of cooperative magnetic ordering. In view of the observed cooperative ordering a study of the heat capacity of CrSb_2 in the critical region seemed especially interesting. In addition, the increase in magnetic susceptibility to a maximum value around 600 K should also be reflected in the heat capacity and not result in a linear temperature relation such as that reported by Adachi *et al.*⁽⁴⁾

A further point of interest is the extent of the homogeneity range of the CrSb_2 -phase. Haraldsen *et al.*⁽¹⁾ found that the chromium-rich composition limit was at about 65 moles per cent of Sb, *i.e.* about $\text{CrSb}_{1.86}$ from magnetic measurements near 700 K. Since no detectable changes occurred in the lattice constants of the CrSb_2 -phase with composition the phase was assumed to be non-stoichiometric. On the other hand, Holseth *et al.*⁽⁶⁾ asserted on the basis of X-ray-diffraction and density measurements on slowly cooled samples that the composition was stoichiometric: 1,2. In order to gain further information about the extension of the homogeneity range of the CrSb_2 -phase as a function of temperature a sample with composition $\text{CrSb}_{1.85}$ was also studied in the high-temperature calorimeter, as the presence of small amounts of the CrSb -phase can be determined quantitatively from the antiferromagnetic transformation near 685 K, and minute amounts of antimony (with dissolved chromium) from the melting process around 900 K.

Finally, it is of interest to correlate the present results with the thermochemical data for CrSb and CrSb_2 by Gerasimov *et al.*,⁽⁷⁾ by Goncharuk and Lukashenko,⁽⁸⁾ and by Vecher *et al.*,⁽⁹⁾ and with the heat capacities for CrSb ,^(10, 11) in order to obtain a consistent picture of the thermodynamic properties of the chromium antimonides.

2. Experimental

SAMPLE PREPARATION

Chromium diantimonide was synthesized from high-purity chromium and antimony *via* the monoantimonide. The electrolytic flake chromium was a gift from Dr Warren deSorbo and the Research Laboratory of The General Electric Company at Schenectady, New York. It was hydrogen-treated, 99.97 mass per cent pure, and contained the following impurities (mass fraction $\times 10^6$): Fe, <70; O, <60; other metals total, <100. The high-purity antimony from Bradley Mining Co., San Francisco, California, was reported to contain the following impurities (mass fraction $\times 10^6$): As, 10; Fe, 3; Pb, 2.

A mixture of equal amounts of the elements was heated at 1300 K for 24 h and then furnace cooled and finely crushed. No free chromium was observed. The stoichiometric amount of antimony to give CrSb₂ was added and the mixture heated to 900 K for 6 weeks, to 770 K for 4 weeks, and to 670 K for 2 weeks. After the first decomposition determination, the sample was crushed, reheated to 920 K for 18 d, and cooled in the furnace overnight.

X-Ray photographs of the sample were taken in Guinier-type cameras of 80 mm diameter. Cu ($K\alpha_1$) radiation was used, with KCl as a calibration substance for which $a(293\text{ K}) = 629.19\text{ pm}$.⁽¹²⁾ The structure was orthorhombic with lattice constants: $a = (602.5 \pm 0.2)\text{ pm}$, $b = (687.3 \pm 0.2)\text{ pm}$, $c = (326.6 \pm 0.2)\text{ pm}$, in good agreement with earlier findings.^(1, 5, 6)

The CrSb_{1.85} sample was prepared similarly from the same chromium and antimony samples. It was finally heat treated at 890 K for two weeks, cooled in the furnace, finely crushed again, and transferred to the calorimetric ampoule. On the X-ray photograph only one very weak line from the CrSb-phase was observed. The lattice constants of the CrSb₂-phase were $a = (602.6 \pm 0.2)\text{ pm}$, $b = (687.4 \pm 0.2)\text{ pm}$, $c = (326.9 \pm 0.2)\text{ pm}$. Thus, no significant difference from the values for stoichiometric CrSb₂ was observed.

CALORIMETRIC TECHNIQUE

From 5 to 350 K, University of Michigan. The heat capacity of CrSb₂ was measured in the Mark II adiabatic calorimetric cryostat described elsewhere.⁽¹³⁾ A gold-plated copper calorimeter (W-52) with an internal volume of 59 cm³ was used. Temperatures were measured with a capsule-type platinum resistance thermometer (A-5) located within a central well in the calorimeter. The calorimeter was loaded with sample, evacuated, and helium gas was added at 8.4 kPa pressure at 300 K to provide thermal contact between sample and calorimeter. It was then sealed, placed in the cryostat, and cooled.

From 300 to 1050 K, University of Oslo. The calorimetric apparatus and measuring technique have been described.⁽¹⁴⁾ The calorimeter was intermittently heated, and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed silica-glass tube of about 50 cm³ volume, tightly fitted into the silver calorimeter. A central well in the tube served for the heater and platinum resistance thermometer.

Calibrations. The platinum resistance thermometer for the low-temperature calorimeter

had been calibrated by the U.S. National Bureau of Standards, and that for the high-temperature calorimeter locally, at the ice, steam, tin, zinc, and antimony points. Temperatures are judged to correspond to IPTS-68 within 0.02 K from 4 to 300 K, and within 0.05 K between this temperature and 900 K. The uncertainty rises to 0.2 K at 1050 K. Masses, potentials, resistances, and times were measured with reference to instruments calibrated by the U.S. National Bureau of Standards.

The heat capacities of the empty calorimeters were determined in separate series of

TABLE 1. Heat capacity of CrSb₂
(cal_{th} = 4.184 J; M = 295.496 g mol⁻¹)

T K	C_p cal _{th} K ⁻¹ mol ⁻¹	T K	C_p cal _{th} K ⁻¹ mol ⁻¹	T K	C_p cal _{th} K ⁻¹ mol ⁻¹	T K	C_p cal _{th} K ⁻¹ mol ⁻¹
Low-temperature results							
Series I							
		342.84	19.96	77.80	9.924	43.62	4.860
		350.81	20.04	83.81	10.648	48.24	5.655
100.57	12.320			89.45	11.264	53.36	6.493
107.95	12.955	Series III		94.80	11.782	58.42	7.271
116.17	13.613			99.92	12.253		
124.04	14.188	188.36	17.44	Series X			
131.61	14.704	196.23	17.71	Series VII			
139.00	15.17	201.69	17.90			59.86	7.514
146.23	15.58	ΔH Det'n A		4.44	0.007	64.77	8.239
153.25	15.94	250.51	19.53	5.08	0.009	72.53	9.265
160.09	16.27	255.53	19.69	5.54	0.012	78.76	10.051
167.54	16.62	260.51	19.87	6.12	0.017		
175.60	16.94	265.45	20.09	7.05	0.026	Series XI	
183.52	17.25	268.89	20.26	7.81	0.031	ΔH Det'n D	
191.32	17.56	270.84	20.40	8.55	0.045	ΔH_t Det'n E	
199.01	17.81	272.75	20.60	9.32	0.062		
206.60	18.10	274.08	20.72	10.15	0.084	Series XII	
		244.66	20.12	11.13	0.115		
		275.25	19.87	12.20	0.157		
		276.25	19.71	13.25	0.217	269.95	20.34
177.02	17.00	277.04	19.64	14.32	0.287	271.07	20.42
186.15	17.36	279.93	19.58	15.44	0.378	272.18	20.55
195.11	17.69			16.74	0.494	273.28	20.82
203.93	17.98	Series IV		18.40	0.672	273.96	21.51
212.63	18.27			20.62	0.949	274.20	21.44
221.17	18.57	194.79	17.65	23.33	1.335	274.54	20.31
229.59	18.84	ΔH_t Det'n B		26.30	1.809	275.00	19.98
237.95	19.10	285.72	19.55	29.80	2.404	275.35	19.92
246.22	19.37					275.59	19.87
254.40	19.66	Series V		Series VIII		275.84	19.84
262.48	19.96					276.21	19.77
270.41	20.40	197.82	17.74	29.26	2.308	276.68	19.65
278.43	19.53	ΔH_t Det'n C		31.85	2.770	277.04	19.64
286.51	19.54	288.44	19.56	34.34	3.220		
294.64	19.65			36.86	3.671	Series XIII	
302.73	19.72	Series VI		40.17	4.262		
310.79	19.76					277.39	19.56
318.83	19.84	59.45	7.451	Series IX		277.62	19.54
326.84	19.89	65.97	8.410			277.96	19.54
334.84	19.93	71.27	9.102	40.46	4.312	278.54	19.53
						279.12	19.48

TABLE 1—Continued

$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{T}{K}$	$\frac{C_p}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
Higher-temperature results							
	Series I	568.90	20.85	867.03	22.17	851.30	21.94
		580.12	20.84	885.62	22.23	868.56	21.99
330.30	19.92	591.32	20.88	897.53	28.12		
340.98	20.00	602.55	20.86	909.54	22.25		
351.63	20.08	613.86	20.88			Series IV	
362.29	20.12	625.20	20.89				
372.79	20.26	636.60	20.92				
383.44	20.36	648.06	20.96	300.14	19.77	984.69	133.0
394.11	20.38	659.57	20.96	310.81	19.84	991.20	8281
404.80	20.46	671.11	21.03	321.43	19.91	994.91	831.4
415.49	20.53	682.66	21.11	332.04	19.96	1006.00	34.72
426.21	20.56	694.19	21.19	342.65	20.04	1020.73	36.42
436.95	20.60	705.79	21.28			1035.18	38.19
447.71	20.70	717.51	21.33			1049.32	40.37
458.50	20.71	729.29	21.42				
469.31	20.71	741.10	21.44	700.30	21.17		
480.16	20.76	752.86	21.47	716.72	21.18	913.00	22.83
491.03	20.77	776.18	21.55	733.22	21.37	928.17	22.97
501.94	20.80	788.26	21.60	749.81	21.49	945.49	23.38
512.89	20.82	800.37	21.67	766.49	21.57	963.04	23.59
524.47	20.81	812.43	21.78	783.26	21.65	975.98	28.38
535.50	20.77	824.46	21.85	800.14	21.73	982.76	61.47
546.59	20.82	836.52	21.90	817.09	21.81	986.77	157.7
557.72	20.87	848.68	22.04	834.14	21.88	988.70	390.6
						993.92	812.7
						1002.26	34.35

experiments. The heat capacity of the sample represented from 80 to 90 per cent of the total in the low-temperature calorimeter and from 55 to 61 per cent in the high-temperature calorimeter.

Small corrections were applied for temperature excursions of the shields from the calorimeter temperature and for "zero drift" of the calorimeter temperature. Further small corrections were applied for differences in amounts of (indium + tin) solder,⁽¹⁵⁾ helium gas, and Apiezon-T grease for the low-temperature calorimeter, and for differences in mass of the silica-glass containers for the high-temperature calorimeter. The mass of CrSb₂ sample used was 204.78 g in the low-temperature calorimeter and 205.07 g in the high-temperature calorimeter. The mass of CrSb_{1.85} used was 216.02 g.

3. Results

The experimental heat capacities for the low- and high-temperature ranges are given in table 1 and enthalpy determinations are summarized in tables 2 and 3. Since the heat capacities are listed in chronological sequence, the temperature increments employed in the determinations may usually be inferred from the temperature differences between adjacent determinations. The experimental low-temperature results are shown in figure 1. A small lambda-shaped maximum was observed at 274.08 K. The heat

TABLE 2. Enthalpy of magnetic transition of CrSb₂
 (cal_{th} = 4.184 J, M = 295.496 g mol⁻¹)

Designation	T_1 K	T_2 K	$\frac{H(T_2)-H(T_1)}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{H(290 \text{ K})-H(199 \text{ K})}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$
Detn B	199.10	281.56	1402.14	1550.85
Detn C	200.88	285.00	1434.12	1551.34
Detn E	213.92	289.24	1297.53	1551.34
				Mean: (1551.2 ± 0.4)
Non-transitional enthalpy:				$\frac{1521.7}{\Delta H_t: 29.5 \pm 0.4}$

 TABLE 3. Enthalpy of decomposition of the CrSb₂-phase
 (cal_{th} = 4.184 J)

T K	ΔT K	C_p cal _{th} K ⁻¹ mol ⁻¹	ΔH_{excess} cal _{th} mol ⁻¹	T_{fin} K
CrSb _{2.00} Series IV				
984.69	12.876	133.0	1417	991.13
991.20	0.1211	8281	1000	991.25
994.91	7.318	831.4	5839	998.59
1006.10	14.867	34.72	0	1013.43
From series V:				
Excess enthalpy below 978.25 K:			59	
Enthalpy of decomposition:			8317	
CrSb _{2.00} Series V				
913.00	16.990	22.83	8.2	921.50
928.17	17.189	22.97	9.3	936.76
945.49	17.438	23.38	14.6	954.21
963.04	17.672	23.59	16.7	971.88
975.98	8.195	28.38	46.4	980.08
982.76	5.356	61.47	207	985.44
986.77	2.664	157.7	359	988.10
988.70	1.203	390.6	443	989.30
993.92	9.245	812.7	7225	998.54
1002.26	7.44	34.35	0	1005.98
Enthalpy of decomposition:			8330	
(3/2.85)CrSb _{1.85}				
980.85	6.080	22.36	0	983.89
987.22	6.643	24.77	15	990.54
990.86	0.6214	558.1	333	991.16
991.27	0.2061	31040	6392	991.37
991.85	0.9681	719.7	665	992.33
995.12	5.583	35.41	13	997.92
1000.00	5.802	33.65	0	1002.90

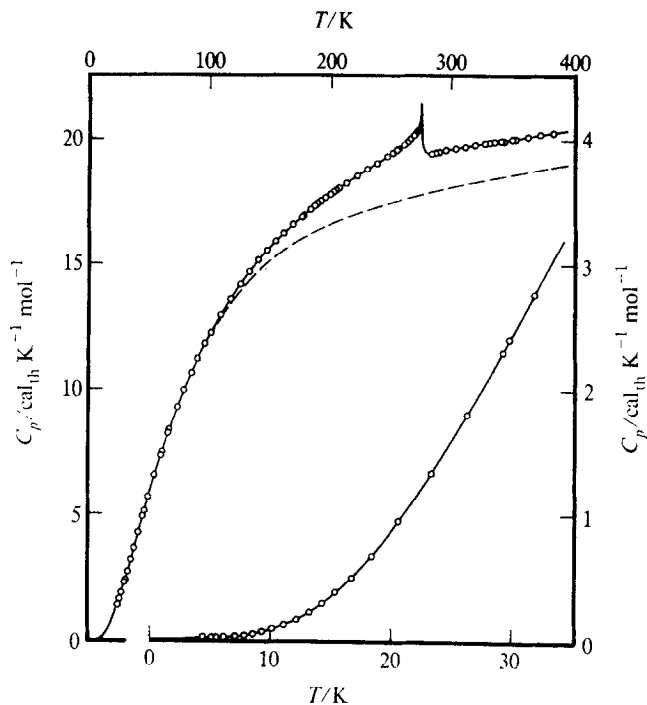


FIGURE 1. Low-temperature heat capacity of CrSb₂. Experimental points have been omitted in the transition region for clarity.

capacities in the region below the peak temperature and well above the transition were reproducible to within 0.1 per cent. The enthalpy increments across the transition were readily reproduced within 0.1 per cent regardless of the rate of cooling through the transition and whether or not the sample had been taken to 4 K (see table 2). On the high-temperature side of the transition, the precision is somewhat lower but only one value (at 910 K) deviates from the smoothed curve by more than 0.5 per cent.

The experimental heat capacities for the low- and high-temperature regions were computer fitted to polynomials in temperature by the method of least squares. The fitting and especially the joins between the fitting segments were checked by inspection of a plot of dC_p/dT against T . At the lowest temperatures the heat capacities were smoothed with the aid of a plot of C_p/T against T^2 and the thermodynamic functions were extrapolated with this linear relation. From this plot the electronic heat capacity coefficient γ was found to be zero within experimental error. Within the transition regions the heat capacities were read from large-scale plots and the thermodynamic functions were calculated by numerical integration. The high heat-capacity point at 897.53 K corresponds to an excess enthalpy of $66.5 \text{ cal}_{\text{th}} \text{ mol}^{-1}$ which is attributed to the antimony phase present.† We think that CrSb₂ is characteristically hypostoichiometric and have therefore included the excess in the integrated thermodynamic functions for the composition CrSb₂. The sample decomposes peritectically at 991.3 K, or

†Throughout this paper $\text{cal}_{\text{th}} = 4.184 \text{ J}$.

42 K higher than reported by Williams⁽¹⁶⁾ and more recently by Holseth.⁽¹⁷⁾ The enthalpy of decomposition is $\Delta H_d = (8325 \pm 20) \text{ cal}_{\text{th}} \text{ mol}^{-1}$, including the enthalpy from the pre-peritectic phase reaction, see table 3. The peritectic decomposition of the CrSb_2 -phase results in a mixture of the solid CrSb -phase and an antimony-rich liquid, and the rising heat capacity above 991.3 K is presumably related to the increasing solubility of the CrSb -phase in the melt.

Values of C_p , $\{S^\circ(T) - S^\circ(0)\}$, $\{H^\circ(T) - H^\circ(0)\}$, and $-\{G^\circ(T) - H^\circ(0)\}/T$ are given for selected temperatures in table 4. From 25 to 350 K the heat capacity is judged precise to ± 0.2 per cent and the other thermodynamic functions to ± 0.15 per cent. This uncertainty corresponds to twice the standard deviation. In the higher-temperature region the corresponding precision indices are 0.5 and 0.3 per cent, respectively-

TABLE 4. Thermodynamic functions of CrSb_2
($\text{cal}_{\text{th}} = 4.184 \text{ J}$, $M = 295.496 \text{ g mol}^{-1}$)

T K	C_p $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	$S^\circ(T) - S^\circ(0)$ $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$	$H^\circ(T) - H^\circ(0)$ $\text{cal}_{\text{th}} \text{ mol}^{-1}$	$-\{G^\circ(T) - H^\circ(0)\}/T$ $\text{cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$
5	0.011	0.003	0.013	0.001
10	0.080	0.027	0.199	0.007
15	0.339	0.099	1.134	0.023
20	0.868	0.263	4.047	0.061
25	1.596	0.532	10.147	0.126
30	2.439	0.896	20.198	0.223
35	3.338	1.340	34.630	0.350
40	4.227	1.844	53.55	0.505
45	5.101	2.392	76.88	0.684
50	5.950	2.974	104.52	0.883
60	7.529	4.201	172.06	1.333
70	8.945	5.470	254.57	1.833
80	10.203	6.748	350.44	2.368
90	11.304	8.015	458.10	2.925
100	12.268	9.257	576.1	3.496
110	13.13	10.47	703.1	4.075
120	13.90	11.64	838.3	4.657
130	14.60	12.78	980.9	5.239
140	15.22	13.89	1130.0	5.817
150	15.78	14.96	1285.1	6.391
160	16.27	15.99	1445.4	6.959
170	16.72	16.99	1610.4	7.520
180	17.12	17.96	1779.6	8.070
190	17.49	18.90	1952.6	8.618
200	17.85	19.80	2129.3	9.155
210	18.20	20.68	2309.5	9.683
220	18.53	21.54	2493.2	10.203
230	18.85	22.37	2680.0	10.713
240	19.17	23.17	2870.1	11.216
250	19.51	23.96	3063.5	11.710

TABLE 4—Continued

T K	C_p cal _{th} K ⁻¹ mol ⁻¹	$S^\circ(T) - S^\circ(0)$ cal _{th} K ⁻¹ mol ⁻¹	$H^\circ(T) - H^\circ(0)$ cal _{th} mol ⁻¹	$-\{G^\circ(T) - H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹
260	19.85	24.74	3260.3	12.196
270	20.36	25.49	3461.0	12.670
274.08 ^a	(21.35)	25.78	3545.2	12.850
280	19.51	26.19	3719.3	12.910
290	19.58	26.91	3849.7	13.639
300	19.68	27.58	4046	14.093
350	20.07	30.64	5040	16.24
400	20.42	33.35	6052	18.22
450	20.68	35.77	7080	20.03
500	20.80	37.95	8117	21.72
550	20.82	39.94	9158	23.29
600	20.86	41.75	10200	24.75
650	20.98	43.42	11245	26.12
700	21.20	44.99	12300	27.41
750	21.46	46.46	13367	28.64
800	21.72	47.85	14445	29.79
850	22.00	49.17	15538	30.89
900	22.26	50.44	16645	31.95
904.0	(22.28)	50.54	16734	32.03
904.0 ^b	(22.28)	50.61	16800	32.03
950	22.57	51.72	17833	32.95
991.3	22.81	52.68	18770	33.75
991.3 ^c	33.09	61.08	27093	33.75
1000 ^c	34.00	61.37	27384	33.99
1050 ^c	40.42	63.18	29237	35.33
273.15	20.78	25.73	3525.6	12.820
298.15	19.66	27.46	4009.6	14.009

^a Peak of magnetic transition.^b CrSb₂-phase+Sb(l). The exact fusion temperature of Sb+dissolved Cr has not been determined.^c CrSb+Sb(l).

4. Discussion

MAGNETIC CONTRIBUTION

From the magnetic-susceptibility and neutron-diffraction⁽⁵⁾ results each chromium atom has two unpaired electrons. The randomization of their spins (neglecting further contributions from orbital states) should result in a magnetic entropy: $S_m = R \ln 3 = 2.17 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. Obviously, only a fraction of this entropy ($0.12 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$) comes out in the clearly cooperative part of the transition. The heat capacity of CrSb₂ is, however, unusually high over a wide range in temperature above the transition at 274.1 K, see figure 2. This is evident by comparing it with the isostructural analogs FeTe₂,⁽¹⁸⁾ CoTe₂,⁽¹⁹⁾ and FeSb₂.⁽²⁰⁾ None of these is especially suitable as a "lattice heat capacity model", however, as they apparently differ substantially in vibrational properties, and the latter two are also influenced by conduction-electron contributions.

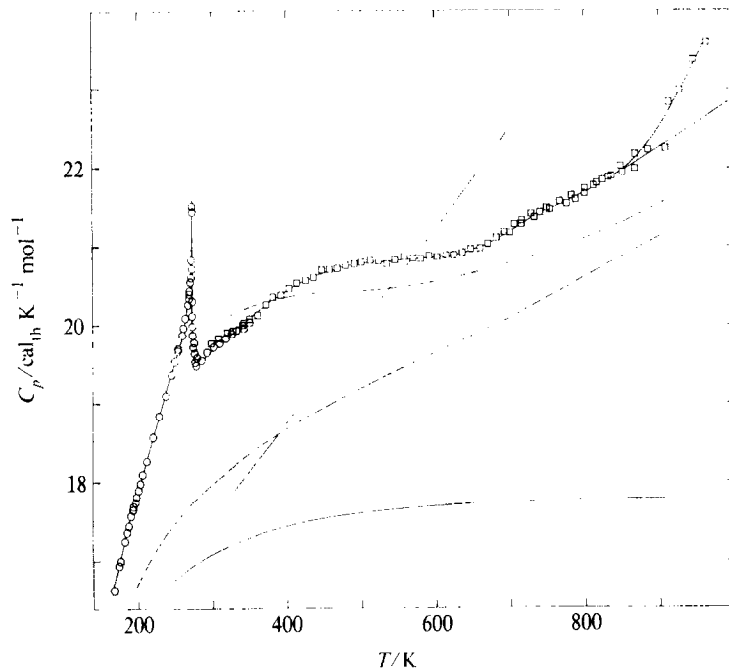


FIGURE 2. High-temperature heat capacity of CrSb_2 . \square , High-temperature calorimeter (Oslo); \circ , Low-temperature calorimeter (Michigan); ---, heat capacity reported by Adachi *et al.*;⁽⁴⁾ —, estimated vibrational contribution, C_V ; - · - ·, vibrational+dilational (Nernst-Lindemann) contribution, $C_V + C_d$; · · · ·, $C_V + C_d + C_{\text{Schottky}}$ C_{Schottky} being calculated from the energy levels and degeneracies given by Adachi *et al.*;⁽⁴⁾ The line below the experimental curve at 900 K is the estimated non-transitional heat capacity.

We therefore chose to derive the lattice heat capacity of CrSb_2 from an estimate of its effective Debye temperature and application of a dilational heat-capacity term according to the Nernst and Lindemann⁽²¹⁾ relation.

The constant Debye temperature used for calculating $C_V(\text{lattice})$ in the higher-temperature region was taken as the maximum of θ_D in the lower-temperature region. The resulting value, $\theta_D = 290$ K, obtains at 90 K. The dilational heat capacity is

$$C(d) = C_p - C_V = AC_p^2(T/T_m),$$

where the constant $A = 0.00713$ K mol cal_{th}⁻¹ according to Nernst and Lindemann and $T_m = 991.3$ K is approximated by the peritectic decomposition temperature found here. The resulting non-transitional heat capacity at constant pressure is indicated in figure 2. Accordingly, the excess magnetic heat capacity is 1.7, 1.6, and 1.1 cal_{th} K⁻¹ mol⁻¹ at 300, 500, and 800 K, respectively. Although an excess heat capacity was not observed by Adachi *et al.*⁽⁴⁾ they nevertheless associated the magnetic behavior with a transition from a singlet spin ground state to a triplet state with a splitting $E/hc = 570$ cm⁻¹. Accordingly, a Schottky heat-capacity contribution with a maximum 2.03 cal_{th} K⁻¹ mol⁻¹ at 288 K would be expected. As indicated in figure 2, the observed heat-capacity maximum is in excellent accord with this prediction; the peak

temperature (274.1 K) is somewhat lower than their estimate based on the assumed energy of the triplet state.

Even though this model appears to fit the magnetic susceptibilities (disregarding the rather arbitrary subtraction of a temperature-independent susceptibility term) it is not in agreement with the neutron-diffraction results which point to the existence of two unpaired electrons per chromium atom in the ground state rather than none. According to our estimate, the total magnetic entropy up to 900 K is about $2.6 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$, or well above $R \ln 3 (= 2.17 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1})$. In the search for further magnetic contributions the orbital components ought to be considered, and according to ligand field theory the ground term of the d^2 configuration in an octahedral field is ${}^3T_{1g}$ with a total degeneracy: $3 \times 3 = 9$. The exact splittings of the ground term are not known but we assume that the first excited state (connected with the disappearance of cooperative magnetism) is a doublet, and that this state is followed rather closely by some of the remaining states. As part of the non-cooperative electronic entropy is obviously evolved at high temperatures, the peritectic decomposition of the CrSb₂-phase obscures a significant portion of the Schottky contribution. It should also be remarked that the Nernst-Lindemann approximation often results in excessively high dilational heat capacities and the estimated magnetic entropy at 900 K, $2.6 \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$, might thus represent a lower limit.

COMPOSITION RANGE

The heat capacities show that the antimony-rich composition limit of the CrSb₂-phase is nearly stoichiometric in the melting region of the antimony phase around 900 K. The excess enthalpy in this range, $66.5 \text{ cal}_{\text{th}} \text{ mol}^{-1}$, corresponds to the presence of 1.4 mole per cent of Sb under ideal conditions: $\{\Delta H_m(\text{Sb}) = (4750 \pm 150) \text{ cal}_{\text{th}} \text{ mol}^{-1}\}$.⁽¹⁵⁾ The same amount of Sb would, however, be present if 0.7 mole per cent of the Cr in "CrSb₂" remained unreacted during the formation of an exactly stoichiometric diantimonide, but this alternative is considered as less likely in view of the repeated crushings and heat treatments of the sample. Furthermore, measurements in the decomposition range clearly show that the CrSb₂-phase changes composition before the peritectic temperature (991.3 K) is reached.

To get more definite information about the composition range of the CrSb₂-phase four series of heat-capacity measurements were carried out on CrSb_{1.85} in the temperature range of the antiferromagnetic to paramagnetic transition of CrSb. From the excess enthalpy, see table 5, the composition of the CrSb₂-phase in equilibrium with the CrSb-phase could be deduced by assuming that about half of the magnetic transformation enthalpy for CrSb is found inside a 150 K range around the peak at 685 K.

The large spread in the values is taken as an indication that the chromium-rich limit of the CrSb₂-phase changes with temperature. Thus, the high value from Series I was obtained from continuous runs after initial slow cooling to 300 K. The recombination of CrSb and CrSb₂ to increase the chromium content of the diantimonide phase might have been only partially complete. The low values of Series II and III were obtained after the sample had been subjected to high temperatures (770 and 900 K, respectively)

TABLE 5. Magnetic enthalpy of the CrSb-phase in CrSb_{1.85} and corresponding composition limit of the CrSb₂-phase (cal_{th} = 4.184 J)

	$\Delta H_m/\text{cal}_{\text{th}} \text{ mol}^{-1}$	n in CrSb _{n}
Series I	137	1.93
Series II	72	1.89
Series III	70	1.89
Series IV	104	1.91

and then tempered at about 550 K, which might allow for a more complete recombination of the CrSb and CrSb₂-phases, or uptake of chromium in the CrSb₂-phase. The intermediate value in Series IV was obtained after relatively fast cooling from 870 to 500 K without tempering before the heat-capacity measurements were begun. These results are taken as an indication that the CrSb₂-phase is richest in chromium around 700 K.

The non-stoichiometry of the decomposing CrSb₂-phase is reflected in the enthalpy of decomposition measurements. As seen from table 3, CrSb_{2.00} decomposes over a temperature interval several times wider than that for CrSb_{1.85}. This is especially clear from the thoroughly equilibrated determinations of Series V for CrSb₂. The more rapid determinations of Series IV possibly shows slightly less pre-peritectic reaction. Not enough data are available to give the exact composition of the peritectically decomposing CrSb₂-phase, but it appears to be in the range CrSb_{1.90} to CrSb_{1.95}.

The composition of the CrSb₂-phase was stated to be exactly stoichiometric by Holseth and Kjekshus.⁽⁶⁾ Their conclusion referred to samples which had been cooled from 890 K to room temperature over a period of 4 d. It does not preclude a changing composition of the CrSb₂-phase with temperature. The magnetic results by Haraldsen *et al.*⁽¹⁾ indicated the composition CrSb_{1.86} at 700 K, and the present results indicate the composition CrSb_{1.89} at the same temperature. Thus, non-stoichiometry of the CrSb₂-phase in the chromium-rich direction is apparently favored at intermediate temperatures, while upon a further decrease in temperature the phase composition is expected to approach the exact 1,2 stoichiometric value.

THERMODYNAMICS OF FORMATION

Standard Gibbs energies of formation at 850 K have been reported by Gerasimov *et al.*,⁽⁷⁾ by Goncharuk and Lukashenko,⁽⁸⁾ and by Vecher *et al.*⁽⁹⁾ from electrochemical-cell measurements. The results are closely concordant, and that by Goncharuk and Lukashenko with its tenfold higher reported accuracy has been adopted here. From the temperature dependence of the e.m.f.'s the standard entropy of formation for CrSb_{2.00}: $\Delta S_f^\circ = (4.93 \pm 0.63) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$ was derived by Goncharuk and Lukashenko, while Gerasimov *et al.* and Vecher *et al.* reported $\Delta S_f^\circ = (3.3 \pm 1.5) \text{ cal}_{\text{th}} \text{ K}^{-1} \text{ mol}^{-1}$. All these values are considered less reliable than the one derivable from the presently obtained entropy of CrSb₂ and the entropies of

the elements.⁽¹⁵⁾ We accordingly recommend the following formation values for CrSb₂ at 850 and 298.15 K:

	298.15 K	850 K
$\Delta G_f^\circ/\text{kcal}_{\text{th}} \text{mol}^{-1}$	-4.46 ± 0.13	-5.10 ± 0.03
$\Delta S_f^\circ/\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	0.05 ± 0.12	1.59 ± 0.13
$\Delta H_f^\circ/\text{kcal}_{\text{th}} \text{mol}^{-1}$	-4.45 ± 0.12	-3.75 ± 0.12

The standard Gibbs energies of formation for CrSb₂ are shown in figure 3 together

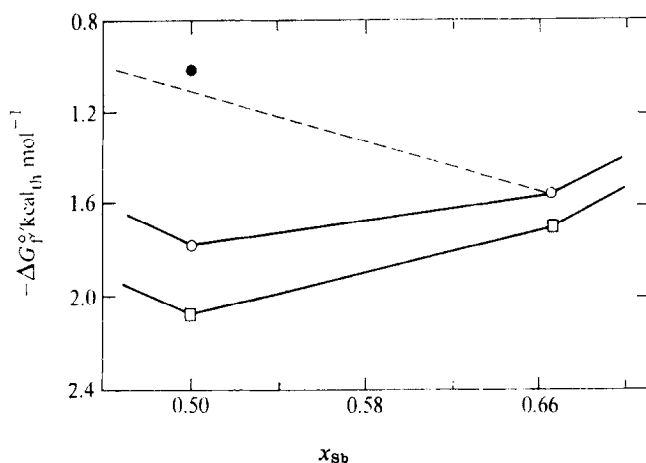


FIGURE 3. □, ΔG_f° for $\frac{1}{3}\text{CrSb}$ and $\frac{1}{3}\text{CrSb}_2$ at 850 K according to Goncharuk and Lukashenko;⁽⁸⁾ ○, values transposed to 298.15 K using heat-capacity data; ●, value obtained⁽¹⁰⁾ for $\frac{1}{3}\text{CrSb}$ after a slight adjustment of Goncharuk and Lukashenko's entropy of formation for CrSb at 850 K; ---, ΔG_f° for a mixture of Cr and CrSb₂.

with those for CrSb. The value for CrSb at 850 K is taken from the work by Goncharuk and Lukashenko.⁽⁸⁾ It was transposed to 298 K by Grønvold and Haraldsen⁽¹⁰⁾ after a slight reduction of the large entropy of formation found by Goncharuk and Lukashenko. Low-temperature heat capacities for CrSb⁽¹¹⁾ provide an even lower entropy and determine the thermodynamic stability of CrSb relative to a mixture of Cr and CrSb₂ at 298 K.

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