Heat capacity and thermodynamic properties of FeSb₂ from 5 to 1021.2 K
Enthalpy of decomposition[a]

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The heat capacity of FeSb₂ has been measured by adiabatic-shield calorimetry from 5 to 1021.2 K. At the latter temperature the phase decomposes into the FeSb phase and an antimony-rich melt. The heat capacity increases regularly over the entire temperature range, except for a high value at 898 K which is related to the fusion of a small amount of antimony. The enthalpy of peritectic decomposition of FeSb₂ at 1021.2 K is (12910 ± 30) cal$_{th}$ mol^{-1}. 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 and 1000 K are 19.08, 25.98, 12.881, and 24.80, 51.01, and 32.25 cal$_{th}$ K^{-1} mol^{-1}, respectively. The present results together with the Gibbs free energy of formation values from the literature give the formation values:

	298.15 K	850 K
ΔG_f° /kcal$_{th}$ mol^{-1}	-6.40 ± 0.30	-5.08 ± 0.27
ΔS_f° /cal$_{th}$ K^{-1} mol^{-1}	-2.30 ± 0.09	-2.43 ± 0.27
ΔH_f° /kcal$_{th}$ mol^{-1}	-7.08 ± 0.40	-7.14 ± 0.38

1. Introduction

Current interest in the compounds crystallizing in the FeS₂-marcasite structure has led to considerable research into their properties. Studies on one such structurally well-characterized compound, FeSb₂,[1–7] revealed an apparently anomalous temperature dependence[2, 8, 9] and field-strength dependence[2] in the magnetic susceptibility. With the hope of gaining some insight into this behavior, Holseth et al.[5] performed neutron-diffraction studies from 4.2 to 298 K on FeSb₂ and found no evidence for cooperative magnetism. On this basis they proposed that the anomalous temperature dependence in the magnetic susceptibility may be due to discrete or dissolved impurities. Electrical and magnetic measurements were performed on well-characterized samples of FeSb₂ by Fan et al.,[6] and they concluded

that $FeSb_2$ is a semiconductor or a semimetal with an extremely narrow band gap. This work has been further supported by the study of the Mössbauer effect from 6.4 to 560 K by Steger and Kostiner.[10] They were able to fit their results to a function which indicated that the temperature dependence of the quadrupole splitting is the result of an electrical process which involves the thermal population of an empty conduction band. In the light of this proposal, a study of the heat capacity of $FeSb_2$ would offer conclusive evidence for the absence of cooperative phenomena in the compound, and also show the effect of band population.

The thermodynamic properties of iron + antimony alloys were first studied by Körber and Oelsen[11] and by Oelsen[12] by mixing the metals in a calorimeter. For $FeSb_2$ the enthalpy of formation at 298.15 K was reported to be $-(3.6 \pm 0.4)$ $kcal_{th}\ mol^{-1}$.* Geiderikh et al.[13] derived partial and integral thermodynamic functions from e.m.f. studies in the temperature range 670 to 970 K. More recently Dynan and Miller[14] measured antimony activities by the Knudsen-cell technique and derived partial molar thermodynamic quantities for both components over the entire composition range at 893 K. Reasonably good agreement with the integral Gibbs free energies by Geiderikh et al.[13] was obtained, but with a significantly more negative entropy of formation for $FeSb_2$. More reliable values for the entropy and enthalpy of formation of $FeSb_2$ should result from the present study.

In addition to the work on the solid alloys, Vecher et al.[15] measured activities for liquid (iron + antimony) alloys in the range from pure antimony to $Fe_{0.25}Sb_{0.75}$ at 1125 K. As indicated by the presence of solid intermetallic compounds, the system shows negative deviations from ideal behavior. Vecher et al.[15] found that $FeSb_2$ is formed by a peritectic reaction of the FeSb and Sb phases at 1021 K, while Kurnakov and Konstantinov[16] reported the peritectic temperature as (1001 ± 2) K and Holseth[17] gave (1004.6 ± 0.5) K.

2. Experimental

SAMPLE PREPARATION

Iron diantimonide was synthesized from high-purity iron and antimony. The iron was Specpure rods from Johnson Matthey Chemicals Limited, U.K., in which the following impurities had been detected (mass fraction $\times 10^6$): Ca, 1; Cr, <1; Cu, 3; Mg, 3; Mn, <1; Si, 3. The high-purity antimony from Bradley Mining Co., San Francisco, Cal., U.S.A. was reported to contain the following impurities (mass fraction $\times 10^6$): As, 10; Fe, 3; Pb, 2.

The mixture of the elements was heated slowly to 1070 K and kept at this temperature for 1 d. It was then crushed, tempered at 970 K for 7 d, crushed again and tempered at 870 K for 21 d, and furnace-cooled to 300 K.

X-ray photographs of the sample were taken in a Guinier-type camera of 80 mm diameter. $Cu(K\alpha_1)$ radiation was used with KCl as a calibration substance for which $a(293\ K) = 629.19$ pm.[18] The structure was orthorhombic with lattice constants:

$$a = 583.0(1)\ \text{pm}, \qquad b = 653.4(1)\ \text{pm}, \qquad c = 319.5(1)\ \text{pm} \dagger$$

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* Throughout this paper $cal_{th} = 4.184$ J; Torr = $(101.325/760)$ kPa.
† (x) indicates standard deviation in last digit.

in good agreement with earlier findings by Hägg[1] [$a = 583.1$ pm, $b = 653.3$ pm, $c = 319.5$ pm], Holseth and Kjekshus[3] [$a = 583.28(5)$ pm, $b = 653.76(5)$ pm, $c = 319.73(3)$ pm], and Fan et al.[6] and Yamaguchi et al.[7] [$a = 582.9(1)$ pm, $b = 653.5(1)$ pm, $c = 319.6(1)$ pm].

CALORIMETRIC TECHNIQUE

5 to 350 K, University of Michigan. Heat-capacity measurements were made in the Mark II adiabatic cryostat which has been described previously.[19] The sample was contained in a gold-plated copper calorimeter (laboratory designation W-52) which incorporated a gold-gasketed seal and gold-plated copper vanes to enhance conductivity. The calorimeter has a mass of 33 g and an internal volume of 59 cm³. To facilitate rapid thermal equilibration, a small amount of helium gas was introduced. The temperature of the calorimeter was measured with a platinum capsule-type 25 Ω (nominal) resistance thermometer (laboratory designation A-5) inserted into a re-entrant well in the calorimeter.

The sample was loaded into the calorimeter under an atmosphere of nitrogen in a dry-box. The stainless-steel vessel containing the calorimeter was connected to a high-vacuum line and was evacuated, and a small amount of helium gas was admitted (134 Torr at 300 K). The calorimeter was then sealed, placed in the cryostat, and cooled.

300 to 1030 K, University of Oslo. The calorimetric apparatus and measuring technique have been described.[20] 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 0.03 K from 5 to 300 K and within 0.05 K between this temperature and 900 K. The uncertainty rises to 0.2 K at 1030 K. Resistance, energy, and mass 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 experiments. The heat capacity of the sample was about 75 per cent of the total in the low-temperature calorimeter above 15 K and about 60 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 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 FeSb₂ sample used in the calorimeters was about 190 g.

3. Results

TABLE 1. Experimental heat capacity of iron diantimonide $M(FeSb_2) = 299.35$ g mol^{-1}
($cal_{th} = 4.184$ J)

$\dfrac{T}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{cal_{th}\,K^{-1}\,mol^{-1}}$
Low-temperature results—University of Michigan						
Series I		226.65	18.42	84.77	10.26	19.53	0.467
101.28	12.11	236.61	18.57	94.73	11.42	21.37	0.631
107.63	12.74	246.49	18.67	104.23	12.40	23.38	0.835
116.33	13.52	256.33	18.77	113.67	13.28	25.62	1.101
125.38	14.27	266.12	18.85			27.97	1.402
134.81	14.96	275.87	18.95	Series IV		30.28	1.531 ^{a}
144.17	15.57	285.88	19.00	4.90	0.007		
153.65	16.11	296.14	19.07	6.14	0.010	Series V	
163.06	16.57	306.37	19.14	7.01	0.015	30.12	1.713
173.38	17.01	316.58	19.19	8.06	0.021	32.73	2.105
184.50	17.41	326.75	19.21	8.93	0.032	35.81	2.603
195.41	17.74	336.90	19.29	9.88	0.043	40.14	3.324
206.16	18.01	346.03	19.30	10.80	0.060	44.67	4.097
				11.74	0.076	48.36	4.726
Series II		Series III		12.82	0.103	52.47	5.429
188.87	17.56	64.65	7.328 ^{a}	14.09	0.146	57.70	6.317
198.15	17.83	64.29	7.447	15.44	0.203	63.74	7.294
207.62	18.05	68.43	7.976	16.84	0.278	69.29	8.122
216.99	18.26	75.18	9.004	18.10	0.358		
	High-temperature results—University of Oslo						
Series I		488.65	19.98	707.72	21.21	799.44	22.01
303.64	19.07	497.98	20.01	717.51	21.30	815.94	22.21
312.84	19.12	507.33	20.00	727.30	21.42	832.22	22.39
322.15	19.21	516.70	20.03	737.13	21.56	848.36	22.54
331.42	19.27	526.07	20.05	746.97	21.68	864.46	22.69
340.68	19.29	535.44	20.16	756.82	21.75	880.93	22.87
349.92	19.30	544.69	20.17	766.69	21.88		
359.15	19.43	554.10	20.18	776.57	21.99	Series V	
368.36	19.44	563.49	20.21	786.48	22.02	892.44	23.27
377.54	19.45	572.84	20.31	796.41	22.16	897.84	33.26 ^{c}
386.70	19.54	582.24	20.34	806.35	22.26	903.28	23.19
395.81	19.52	591.69	20.41			909.16	23.17
404.92	19.57	610.15	20.46	Series III		915.06	23.33
414.00	19.62	610.68	20.51	816.30	22.32	926.90	23.45
423.07	19.64	620.28	20.56	826.29	22.38	944.66	23.65
		629.91	20.61	836.29	23.45 ^{b}	961.00	23.88
Series II		639.56	20.72	846.30	22.59	975.93	24.28
423.56	19.63	649.25	20.74	856.38	22.65	990.86	24.73
432.83	19.68	658.95	20.85			1005.81	25.00
442.10	19.73	668.68	20.89	Series IV		1017.09	35.56
451.40	19.78	678.42	21.02	749.13	21.74	1021.08	33420
460.72	19.78	688.17	21.09	766.00	21.78	1023.25	80.06
470.02	19.86	697.94	21.14	782.79	2.198	1031.58	33.59
479.33	19.90						

^{a} Not curvature corrected and not used in final curve-fitting routine.
^{b} Shield control unreliable.
^{c} $\Delta T = 4.9952$ K.

TABLE 2. Enthalpy of decomposition (ΔH_d) of iron diantimonide C_p(n-t) denotes the estimated non-transitional heat capacity; M(FeSb$_2$) = 299.35 g mol^{-1}

(cal$_{th}$ = 4.184 J)

$\langle T \rangle$	ΔT	C_p	C_p(n-t)	ΔH_{excess}	T_{final}
K	K	cal$_{th}$ K^{-1} mol^{-1}	cal$_{th}$ K^{-1} mol^{-1}	cal$_{th}$ mol^{-1}	K
1017.088	7.6023	35.56	25.3	78	1020.889
1021.079	0.3787	33420	25.4	12647	1021.268
1023.253	3.9719	80.06	33.59	185	1025.240

$$\Delta H_d/\text{cal}_{th}\ \text{mol}^{-1} = 12910 \pm 30$$
$$\Delta S_d/\text{cal}_{th}\ \text{K}^{-1}\ \text{mol}^{-1} = 12.64 \pm 0.03$$

The experimental heat capacities for the low- and high-temperature ranges are given in table 1 and the enthalpy determination is summarized in table 2. 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 high-temperature results are shown in figure 1 and some of the low-temperature results in figure 2.
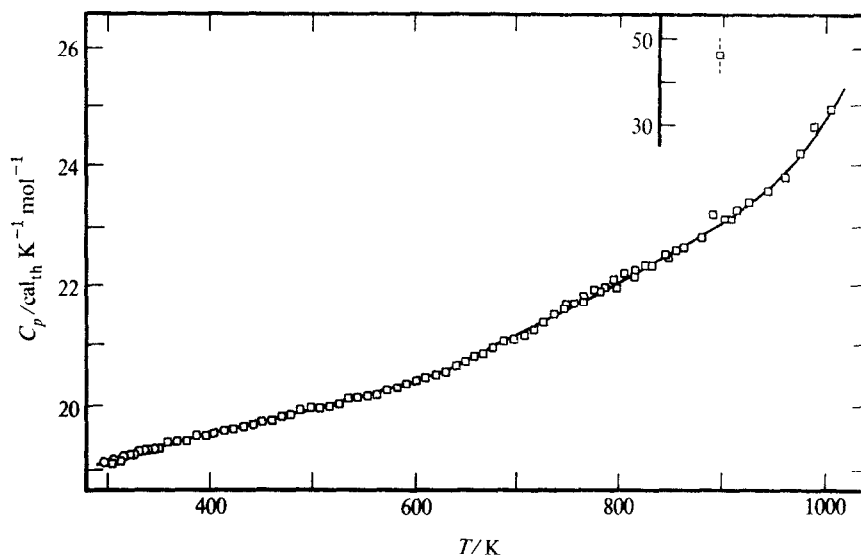

FIGURE 1. Molar heat capacity of FeSb$_2$ from 300 to 1030 K. ○, results from low-temperature calorimetry; □, results from high-temperature calorimetry.

The estimated standard deviation of a single measurement in the low-temperature determinations is about 5 per cent at 10 K and 0.08 per cent over the region 30 to 350 K. The corresponding value for the high-temperature determinations is 0.22 per cent, excluding two high values (one at 892.44 K and the other at 897.84 K). The experimental heat capacities for the low- and high-temperature regions were fitted to
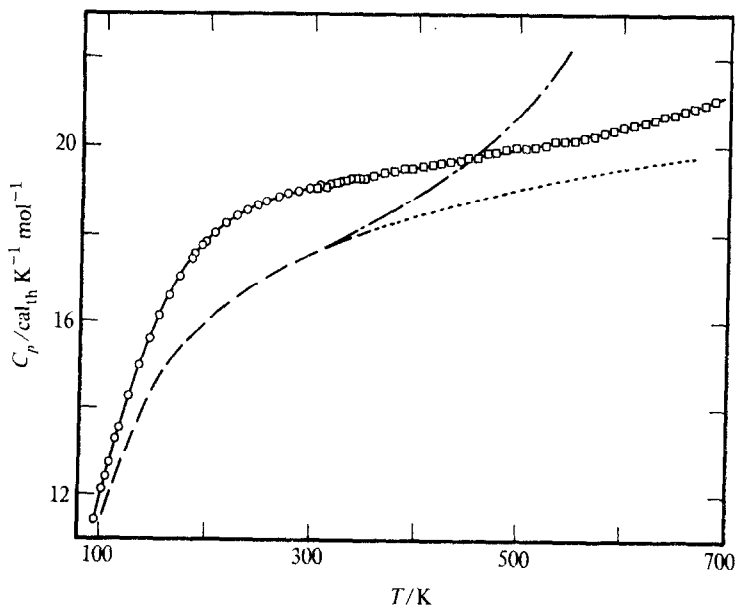
FIGURE 2. Molar heat capacity of $FeSb_2$ from 100 to 700 K compared with that for $FeTe_2$. O, Results for $FeSb_2$ from low-temperature calorimetry; □, results for $FeSb_2$ from high-temperature calorimetry; ————, results for $FeTe_2$ by Westrum et al.;[26] —·—·—, results for $FeTe_2$ by Mikler et al.;[21] ———, extrapolated lattice heat capacity for $FeTe_2$.

polynomials in temperature by the method of least squares. The fitting and especially the joins between fitted 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 extrapolated by this linear relation. From this plot the electronic heat-capacity coefficient was found to be zero within the experimental error limits.

The high heat-capacity point at 897.84 K and to a slight extent also the one at 892.44 K are attributed to fusion of the antimony phase present. The observed excess enthalpy, 52.3 $cal_{th}\,mol^{-1}$, corresponds to the presence of 1.1 mole per cent of Sb under ideal conditions [$\Delta H_m(Sb) = 4750\ cal_{th}\,mol^{-1}$]. The effect of this antimony is not included in the values of thermodynamic functions as we have no evidence that $FeSb_2$ is non-stoichiometric at the melting temperature of antimony, and no thermal effect of the separation of antimony from the $FeSb_2$ phase was detected in the heat-capacity results.

The sample does decompose peritectically at 1021.2 K, see table 2, and the enthalpy of decomposition is $\Delta H_d = (12910\pm30)\ cal_{th}\,mol^{-1}$. The larger than usual uncertainty arises from the unknown heat-capacity behavior in the two-phase region above the peritectic decomposition temperature. The rather high heat capacity at 1031.58 K is presumably related to the rapidly increasing solubility of FeSb(s) in the antimony melt, but its temperature dependence is not known at present and a rather pronounced positive drift remained after the energy input. Thus, complete equilibration was not achieved, and the derived heat capacity might be too high.

TABLE 3. Thermodynamic functions of iron diantimonide ($FeSb_2$)
($cal_{th} = 4.184$ J)

$\dfrac{T}{K}$	$\dfrac{C_p}{cal_{th}\ K^{-1}\ mol^{-1}}$	$\dfrac{S^\circ(T) - S^\circ(0)}{cal_{th}\ K^{-1}\ mol^{-1}}$	$\dfrac{H^\circ(T) - H^\circ(0)}{cal_{th}\ mol^{-1}}$	$\dfrac{-\{G^\circ(T) - H^\circ(0)\}/T}{cal_{th}\ K^{-1}\ mol^{-1}}$
5	(0.007)	(0.003)	(0.010)	(0.001)
10	0.045	0.016	0.114	0.004
15	0.183	0.055	0.623	0.014
20	0.506	0.147	2.258	0.034
25	1.024	0.312	6.008	0.072
30	1.692	0.556	12.744	0.131
35	2.470	0.874	23.114	0.214
40	3.302	1.258	37.532	0.320
45	4.155	1.696	56.16	0.448
50	5.017	2.178	79.09	0.596
60	6.690	3.242	137.71	0.947
70	8.236	4.392	212.46	1.356
80	9.631	5.584	301.93	1.810
90	10.875	6.792	404.58	2.297
100	11.981	7.996	519.0	2.806
110	12.963	9.185	643.8	3.332
120	13.836	10.351	777.9	3.869
130	14.612	11.490	920.2	4.411
140	15.30	12.598	1069.8	4.957
150	15.90	13.675	1225.9	5.502
160	16.43	14.718	1387.5	6.046
170	16.88	15.73	1554.1	6.586
180	17.27	16.70	1724.9	7.121
190	17.60	17.65	1899.3	7.650
200	17.87	18.56	2076.7	8.173
210	18.11	19.43	2256.6	8.688
220	18.30	20.28	2438.7	9.196
230	18.46	21.10	2622.5	9.696
240	18.60	21.89	2807.8	10.188
250	18.71	22.65	2994.4	10.671
260	18.81	23.38	3182.0	11.146
270	18.89	24.10	3370.5	11.612
280	18.97	24.78	3559.8	12.071
290	19.03	25.45	3749.9	12.521
300	19.09	26.10	3940.5	12.962
273.15	18.92	24.32	3430.1	11.758
298.15	19.08	25.98	3905.2	12.881
400	19.58	31.66	5874	16.97
500	19.96	36.07	7851	20.36
600	20.45	39.74	9869	23.30
700	21.21	42.95	11949	25.88
800	22.12	45.84	14115	28.20
900	23.11	48.50	16375	30.31
1000	24.80	51.01	18760	32.25
1021.2	25.41	51.54	19290	32.65
		Peritectic decomposition		
1021.2 [a]	(33.59)	64.18	32200	32.65
1030	(33.59)	64.47	32490	32.92

[a] FeSb(c) + liquid.

Values of the heat capacity, C_p, entropy $\{S°(T) - S°(0)\}$, enthalpy $\{H°(T) - H°(0)\}$, and the function $-[\{G(T) - H°(0)\}/T]$ are given for selected temperatures in table 3. Up to 350 K the heat capacity is judged precise to ± 0.2 per cent and the other thermodynamic functions to ± 0.15 per cent, which corresponds to twice the standard deviation in the results. In the higher temperature region the corresponding precision indices are 0.4 and 0.3 per cent, respectively.

4. Discussion

THERMOPHYSICAL PROPERTIES

The heat capacity of $FeSb_2$ increases quite regularly over the entire temperature region. There is no definite sign of pre-peritectic decomposition and thus no support for the X-ray diffraction results by Fan et al.[6] that $FeSb_2$ decomposes into FeSb and Sb under vacuum at 573 K. The temperature of decomposition found here, (1021.2 ± 0.2) K, is in complete agreement with that found by Geiderikh et al.[13] (1021 K), while the results by Kurnakov and Konstantinov,[16] (1001 ± 2) K, and by Holseth,[17] (1004.6 ± 0.5) K, are considerably in error.

No evidence of an antiferromagnetic transition between 800 K and 1000 K suggested by Rosenqvist[2] and by Holseth and Kjekshus[8] was observed. This is consistent with the observation by the latter authors that no purely magnetic reflections were obtained in their neutron-diffraction study of $FeSb_2$ around 300 K. Hence, iron is in a non-magnetic ground state which presumably arises from the $3d^4$ configuration.

The heat capacity of $FeSb_2$ does not show the pronounced increase at higher temperatures which is characteristic of $FeTe_2$,[21, 22] see figure 2. Similar behavior in $FeSe_2$ has been attributed to defect formation[23] while neither isostructural FeS_2,[24] nor isoelectronic $NiSb_2$,[25] show comparable excess heat capacities in the higher temperature region. A comparison between the heat capacities of $FeSb_2$
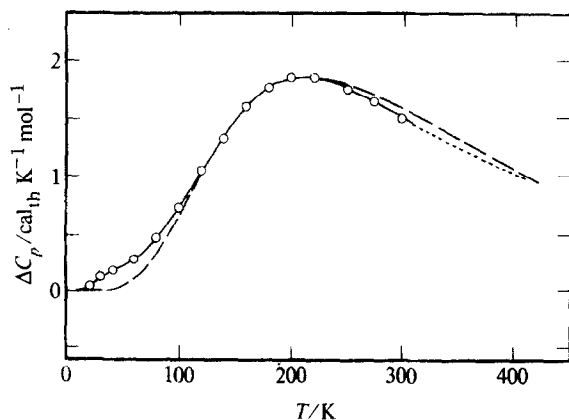

FIGURE 3. Excess molar heat capacity for $FeSb_2$ relative to that of $FeTe_2$, $\bigcirc$. Calculated Schottky heat capacity for $E_1/hc = 300$ cm^{-1}, $E_2/hc = 500$ cm^{-1}, and g_0, g_1, $g_2 = 1, 1, 2$, — — —.

and FeTe₂[26] in the lower-temperature region shows the former to be considerably higher in the region 100 to 350 K with a maximum excess of 1.9 cal_{th} K^{-1} mol^{-1} around 200 K; see figure 3.

In the Goodenough[27] and the Fan *et al.*[6] composite picture the 3d electron b-band is filled with 4 electrons while the next doubly degenerate $a_{\parallel}$-band is empty. Steger and Kostiner[10] concluded from the unusual temperature dependence of the Mössbauer quadrupole splitting that electrons were promoted across a wavenumber gap of only 265 cm^{-1}. This is approximately the same as the value derived by Fan *et al.*[6] from electric conductivity measurements (about 210 cm^{-1}). If the band is assumed to be narrow and its population approximated by a Boltzmann distribution we find that excitation from a 4-fold degenerate b-band does not produce the observed increase in heat capacity. Thus, either the b-band might be split, or further levels or bands in addition to $a_{\parallel}$ and σ^* are also being populated. We are not at this time able to decide between the various alternatives, but remark that surprisingly good agreement is obtained, see figure 3, if a split 2(b)-band is succeeded by (2)$a_{\parallel}$ and (4)σ^* (in Goodenough's picture) with $E_1/hc = 300$ cm^{-1} and $E_2/hc = 500$ cm^{-1}.

THERMODYNAMICS OF FORMATION

The Gibbs free energy of formation (ΔG_f°) results by Geiderikh *et al.*[13] and Dynan and Miller[14] at 830 and 893 K, respectively, agree reasonably well. Adjusting for the small temperature dependence of ΔG_f° in this region we take the average value at 850 K, $\Delta G_f^\circ = -(5.08 \pm 0.27)$ $kcal_{th}$ mol^{-1}, as representative. From the present results and literature data[28] the entropy of formation of FeSb₂ is $\Delta S_f^\circ = -(2.43 \pm 0.27)$ cal_{th} K^{-1} mol^{-1} at the same temperature. This value is intermediate between that reported by Geiderikh *et al.*,[13] -1.8 cal_{th} K^{-1} mol^{-1}, and that by Dynan and Miller,[14] -4.2 cal_{th} K^{-1} mol^{-1}, and is presumably more accurate. The enthalpy of formation is accordingly $\Delta H_f^\circ = -(7.14 \pm 0.38)$ $kcal_{th}$ mol^{-1} at 850 K and practically the same at 298 K. This value is considerably more negative than the direct calorimetric value determined by Körber and Oelsen[11] and Oelsen,[12] $\Delta H_f^\circ = -(3.6 \pm 0.4)$ $kcal_{th}$ mol^{-1}, but is in rather good agreement with the result by Geiderikh *et al.*[13] The following formation values are recommended:

	298.15 K	850 K
$\Delta G_f^\circ / kcal_{th}$ mol^{-1}	-6.40 ± 0.30	-5.08 ± 0.27
$\Delta S_f^\circ / cal_{th}$ K^{-1} mol^{-1}	-2.30 ± 0.09	-2.43 ± 0.27
$\Delta H_f^\circ / kcal_{th}$ mol^{-1}	-7.08 ± 0.40	-7.14 ± 0.38

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