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Heat Capacity and Other Thermodynamic Properties of $CoTe_2$ from 5 to 1030 K and of $CoTe_{2.315}$ from 300 to 1040 K**

Jose A. R. Cheda[a, ***], **Edgar F. Westrum, Jr.**[a], and **Fredrik Grønvold***[, b]

[a] Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, U.S.A.

[b] Department of Chemistry, University of Oslo, Blindern, 0315 Oslo 3, Norway

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The heat capacity of orthorhombic (marcasite-type structure) cobalt ditelluride has been measured from 5 to 1030 K by adiabatic-shield calorimetry with alternate energy inputs and equilibrations. Above 900 K a marked increase in heat capacity occurs which probably signals a change in the composition of the $CoTe_2$-phase towards higher tellurium content. Values at 298.15 and 1000 K in $J\,K^{-1}\,mol^{-1}$ of the heat capacity ($C_{p,m}$), entropy $[S^\circ_m(T) - S^\circ_m(0)]$, and *Gibbs* energy function $-[G^\circ_m(T) - H^\circ_m(0)]\,T^{-1}$ are 75.23, 114.5, 49.93, and 132.4, 216.2, 139.17, respectively. Consistent with the metallic behavior of $CoTe_2$, deviation of the heat capacity from the *Debye* T^3-law was found at low temperatures. Comparison with the heat capacity of $FeTe_2$ shows a *Schottky*-like deviation with a maximum of $7.3\,J\,K^{-1}\,mol^{-1}$ at 80 K and evidences the influence of the additional 3 d-electron in cobalt compared to iron. Heat capacity measurements were made on $CoTe_{2.33}$ to ascertain the existence range of the $CoTe_{2+x}$-phase and the entropy of the associated structural disorder.

(Keywords: Cobalt telluride; Cobalt ditelluride; Heat capacity; 3d Electrons; Schottky contributions; Thermophysics)

Wärmekapazität und andere thermodynamische Parameter für $CoTe_2$ *von 5 bis 1030 K und für* $CoTe_{2.315}$ *von 300 bis 1040 K*

Es wurde die Wärmekapazität des orthorhombischen Kobaltditellurids (Markasit-Typ) zwischen 5 und 1030 K mittels adiabatisch abgeschirmter Kalo-

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*** Present address: Departamento de Quimica Fisica, Facultad de Quimicas, Universidad Complutense, Madrid 3, Spain.

rimetrie mit alternierender Energiezufuhr und Gleichgewichtseinstellung gemessen. Über 900 K tritt ein deutlicher Anstieg der Wärmekapazität ein, der möglicherweise einen Wechsel in der Zusammensetzung der $CoTe_2$-Phase zu einem höheren Tellur-Gehalt anzeigt. Entsprechende Werte bei 298.15 bzw. 1000 K in $J\,K^{-1}\,mol^{-1}$ für die Wärmekapazität ($C_{p,m}$), die Entropie $[S^\circ_m(T) - S^\circ_m(0)]$ und die *Gibbs* Energiefunktion $-[G^\circ_m(T) - H^\circ_m(0)]\,T^{-1}$ sind 75.23, 114.5, 49.93 bzw. 132.4, 216.2, 139.17. In Übereinstimmung mit dem metallischen Verhalten von $CoTe_2$ wurde bei niedrigen Temperaturen eine Abweichung der Wärmekapazität vom *Debye*'schen T^3-Gesetz gefunden. Ein Vergleich mit der Wärmekapazität von $FeTe_2$ zeigt eine *Schottky*-gemäße Abweichung mit einem Maximum von $7.3\,J\,K^{-1}\,mol^{-1}$ bei 80 K; dies zeigt den Einfluß der zusätzlichen 3d-Elektronen im Kobalt, verglichen mit Eisen. Es wurden Wärmekapazitätsmessungen an $CoTe_{2.33}$ durchgeführt, um den Existenzbereich der $CoTe_{2+x}$-Phase und die Entropie der damit zusammenhängenden strukturellen Unordnung zu ermitteln.

Introduction

In the cobalt-tellurium system two intermediate solid phases have been observed at ordinary pressure: the $Co_{1-x}Te$-phase with hexagonal NiAs-like structure and the $CoTe_{2+x}$-phase* with orthorhombic FeS_2-marcasite-type structure. The $CoTe_{2+x}$-phase has a noticeable range of homogeneity on the tellurium-rich side of the stoichiometric MeX_2 composition and this is related to vacancy formation in the cobalt lattice [1]. The limit is at about 69.6 atomic per cent Te near 770 K [2–4]. The composition of the $CoTe_{2+x}$-phase is estimated [4] to be $CoTe_{2.13}$ at the temperature at which decomposition into the $Co_{1-x}Te$-phase and a tellurium-rich liquid occurs. A study [5] of the variation in lattice constants with temperature also indicated a composition of $CoTe_{2.13}$ or $Co_{0.94}Te_2$ for the $CoTe_{2+x}$-phase in the vicinity of the decomposition temperature, (1040 ± 4)K, as determined by X-ray diffraction, differential thermal analysis, and quenching techniques.

Comparison of the heat-capacity behavior of $CoTe_2(m)$ with that of isostructural $FeTe_2$ should permit an analysis of the influence of the additional 3d-electron on heat capacity and thermodynamic properties and on the inherent properties of the $3d^6$ and $3d^7$ configurations. Furthermore, it is of interest to ascertain whether the unusually large increase in the heat capacity which is observed for $FeTe_2$ [6, 7] above 500 K occurs also in $CoTe_2(m)$.

In view of the existence of a high-pressure (pyrite-structure) polymorph, $CoTe_2(p)$ [8], the possibility of its occurrence in some temperature range under ordinary pressures needed exploration. Furthermore, if the contention by *Brostigen* and *Kjekshus* [2] that the symmetry of the $CoTe_2(m)$ structure is lower than usually assumed is correct, a solid-state

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* The phase is designated $CoTe_{2+x}$ or $CoTe_2(m)$ depending upon the context.

transition due to the change in symmetry from Pnn2 to Pnnm may take place. In a later paper [9], however, the lower symmetry space group (Pnn2) was no longer considered appropriate for marcasite itself, and it was suggested that similar considerations may apply to the structure of $CoTe_2(m)$.

From magnetic susceptibility measurements, *Vandenbempt* et al. [10] concluded that the *Curie-Weiss* law holds over the region 90 to 550 K with a moment of 1.94 BM ($\theta = 372$ K), whereas *Haraldsen* et al. [1] found 2.81 BM ($\theta = 540$ K). The subsequent suggestion by *Vandenbempt* et al. [10] that antiferromagnetic ordering occurs below 90 K was not confirmed by a *Mössbauer* study [11] at 4.2 K. $CoTe_2(m)$ is reported to be a metallic conductor [12] or possibly a semi-conductor [13], and energy-band successions have been suggested [10, 14]. The prospect of getting a rough measure of the thermal effect of the presence of conduction electrons and also of the excited electronic level- or band-populations is favorable for $CoTe_2(m)$, because of the very close structural correspondence with $FeTe_2$ for which heat-capacity results are also available in the low-temperature region [15].

The enthalpy of formation ($\Delta_f H_m^\circ$) of cobalt ditelluride has been determined by solution calorimetry by *Ariya* et al. [16] and more recently by *Komarek* et al. [17]. A discrepancy of a factor of about two remained unexplained. Direct determination of the enthalpy of reaction of cobalt (or cobalt monotelluride) and tellurium by *Morozova* et al. [18] yielded a value of $\Delta_f H_m^\circ$ for $CoTe_2(m)$ more in accord with that by *Komarek* et al. [17].

From electrochemical cell measurements [18–21] *Matlasevich* et al. [21] derived $\Delta_f H_m^\circ$ (700 K) by *Gibbs-Duhem* integration. The data were adjusted to 298.15 K by *Komarek* et al. [17], using the differential scanning calorimetry results by *Mills* [22, 23] for some cobalt tellurium alloys in the temperature range 200 to 750 K together with literature data for the elements. *Komarek* et al. [17] then found fairly satisfactory agreement between the results by *Matlasevich* et al. [21] and their own. More accurate analysis of the data requires knowledge of the thermodynamic properties of $CoTe_2$ provided in the present study.

In order to obtain a more complete picture of the existence range of the $CoTe_{2+x}$-phase and the associated structural disorder, some heat-capacity measurements on $CoTe_{2.33}$ have also been made.

Experimental

Samples

The $CoTe_2(m)$ and $CoTe_{2.33}(m)$ samples were synthesized from the elements. The 5 mm diameter "spectroscopically standardized" cobalt rods from Johnson

Matthey Metals Ltd., U.K., were reported to contain only the following impurities (ppm by mass):

$$Ag < 1,\ Al < 1,\ Ca < 1,\ Cu < 1,\ Fe < 3,\ Mg < 2,\ Si < 3.$$

In the spectrographic examination, 51 other elements were specifically sought but not detected. The tellurium used was a "special high purity semi-conductor grade Te", 99.999 mass per cent pure, from the American Smelting and Refining Co., New York. Stoichiometric amounts of the elements were heated in an evacuated and sealed silica glass tube directly to 770 K, the temperature was increased in 100 K increments each 30 min to 1 270 K, and the samples were held at this temperature for 2 h. They were crushed, transferred to the silica high-temperature calorimetric ampoule, tempered at 770 K for 7 days, and cooled in the furnace. The $CoTe_2(m)$ sample was reannealed at 770 K for 7 days before the cryogenic measurements were made.

X-ray powder photographs of the sample were taken in a *Guinier*-type camera with copper $K\alpha_1$-radiation. KCl was used as a calibration standard [$a(298\,K) = 629.19$ pm] [24]. The lattice constants for $CoTe_2$ are: $a = 532.5(4)$, $b = 631.7(5)$, $c = 390.3(4)$ pm; and for $CoTe_{2.33}$: $a = 531.5(4)$, $b = 631.0(5)$, $c = 387.2(4)$ pm, in good agreement with earlier results [1, 2].

Calorimetric Technique

1. 5 to 350 K, University of Michigan. The Mark II cryostat and adiabatic method employed have been described [25]. A gold-plated copper calorimeter (W-52, which incorporates a gold-gasketed screw closure and copper vanes) with a volume of 59 cm^3 and a mass of 33.2 g was used. Helium gas was added to the sample space (5.5 kPa at 300 K) to enhance thermal equilibration. The calorimeter was surrounded by a shield system provided with automatic temperature control. Temperatures were measured with a capsule-type, strain-free, platinum resistance thermometer (laboratory designation A-5), located in a central re-entrant well in the calorimeter.

2. 300 to 1 040 K, University of Oslo. The calorimetric apparatus and measuring technique have been described elsewhere [26]. The calorimeter was intermittently heated and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed vitreous silica tube of about 50 cm^3 volume tightly fitted into the silver calorimeter. A central well in the tube served for the heater and platinum resistance thermometer.

3. Calibrations and adjustments. 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, zinc, and antimony points. Temperatures are judged to correspond to IPTS-68 within 0.02 K from 4 to 350 K, within 0.05 K from 350 to 900 K, and within 0.1 K at 1 030 K. All determinations of mass, electrical potential, resistance, etc., 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 a separate series of experiments. They represented less than 26 per cent of the total in the case of the low-temperature calorimeter, and about 55 per cent in the case of the high-temperature calorimeter.

Small adjustments 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 masses of the gold gasket, helium gas, and Apiezon-T grease for the low-temperature calorimeter and for differences in mass of the vitreous silica containers for the high-temperature calorimeter. The mass of sample used was 190.1 g in the low-temperature calorimeter and 209.3 g in the high-temperature calorimeter. Buoyancy correction was made on the basis of a crystallographic density of 7.92 g cm^{-3} [1].

Results

The experimental molar heat capacities, corrected for curvature, are given in Table 1 and shown in Fig. 1 in the chronological sequence in which the data were taken. Thus, the temperature increments used usually can be inferred from the adjacent mean temperatures. The molar mass of $CoTe_2$ was taken as 314.13 g mol^{-1} on the IUPAC-1983 scale of atomic masses and that of $CoTe_{2.33}$ as 356.24 g mol^{-1}.

The standard deviations in the low-temperature calorimetric values of $CoTe_2$ above 25 K are 0.08 per cent. Below this temperature they gradually increase to about 10 per cent at 5 K. In the high-temperature calorimeter the estimated standard deviation is 0.2 per cent over the region 350 to 950 K. Above this temperature the standard deviation is about 0.4 per cent. Table 2 lists the smoothed values of the molar heat capacity for $CoTe_2(m)$ at selected temperatures. These values were obtained from polynomials computer-fitted through both sets of experimental points (5 through 950 K), as well as through the (integrated) thermodynamic functions. Points above 950 K were fitted separately and smoothly joined to the lower temperature values.

The low-temperature points for $CoTe_2(m)$ were fitted to the equation $C_{p,m}/T = \alpha T^2 + \gamma$ by least-squares and yielded constants $\alpha/(\mathrm{J\,K^{-4}\,mol^{-1}}) = 4.18 \cdot 10^{-4}$ and $\gamma/(\mathrm{J\,K^{-2}\,mol^{-1}}) = 1.37 \cdot 10^{-2}$. These coefficients were used in deriving the thermodynamic function values at 5 K.

The heat capacity of $CoTe_{2.33}$ was measured only above ambient temperature. The gradual rise in the heat capacity was enhanced in the 720 K region by the fusion of a small and varying amount of tellurium. On the basis of the enthalpy of fusion value for tellurium (17 370 J mol^{-1}) [27], the mole fraction is 0.015 ± 0.003 in series III, IV, and VI, while tellurium melting effect seems practically absent in Series VII. Obviously, the sample composition chosen was just at the Te-rich retrograde composition limit of the $CoTe_{2+x}$-phase. Therefore, we decided to adjust the experimental heat-capacity results for $CoTe_{2.33}$ in Table 1 to the composition $CoTe_{2.315}$ by subtracting the tellurium contribution. The smoothed heat-capacity values for $CoTe_{2.315}$ are given in Table 2. They presumably refer to single-phase material in the range 300 to at least 750 K. Above this temperature the $CoTe_{2+x}$-phase present becomes

Table 1. *Heat capacities of* $CoTe_2$ *and* $CoTe_{2.33}$

T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}	T/K	$C_{p,m}$/J K^{-1} mol^{-1}

$M(CoTe_2) = 314.13\ g\ mol^{-1}$

Low-Temperature Data (Ann Arbor)

Series I		241.62	73.76	Series III		22.01	4.648
86.22	48.66	251.25	74.22	4.43	(0.061)	24.42	6.130
94.66	52.01	260.84	74.73	5.18	0.130	27.08	7.929
104.35	55.27	279.84	75.44	6.08	0.159	30.02	10.11
114.49	58.24			6.90	0.243	33.28	12.67
124.16	60.67	Series II		7.91	0.310	36.75	15.54
133.46	62.68	275.92	75.19	8.93	0.410	40.24	18.41
143.08	64.43	285.51	75.73	9.91	0.536	43.38	21.38
153.04	66.02	295.06	76.07	10.94	0.682	47.78	24.54
162.78	68.53	304.55	76.27	12.01	0.841	51.61	27.56
182.20	69.54	314.20	76.48	13.09	1.067	56.08	30.96
192.36	70.46	324.17	76.73	14.26	1.364	61.69	34.97
202.39	71.30	334.32	76.78	15.51	1.728	67.27	38.58
212.32	72.09	342.58	77.24	16.82	2.151	73.18	41.97
222.36	72.72	347.91	77.28	18.31	2.770	80.42	45.86
231.92	73.30			19.98	3.561	89.48	50.04

High-Temperature Data (Oslo)

Series I		460.37	79.89	635.89	83.28	859.84	90.57
302.20	75.51	471.68	79.92	647.98	83.49	872.64	90.72
313.58	76.17	483.02	80.37	660.10	83.76	885.47	91.62
324.92	76.68	494.47	80.58	677.28	84.15	898.35	91.92
336.24	76.71	506.01	81.15	684.49	84.39	911.24	93.21
347.55	77.13	517.59	81.18	702.89	84.90	924.63	93.36
358.84	77.55	529.22	81.48	721.42	85.29	937.49	99.03
370.13	77.67	540.88	81.78	733.88	85.89	950.18	102.78
381.41	78.21	552.58	81.81	746.18	86.28	962.45	108.27
392.68	78.51	564.32	81.90	758.63	86.91	974.51	122.43

403.96	78.84	576.16	82.26	777.44	87.66	986.11	130.89	
415.24	78.99	588.00	82.26	796.21	87.93	997.48	132.09	
426.50	78.96	599.88	82.56	815.38	88.50	1 008.89	133.26	
437.77	79.23	611.85	82.62	834.39	89.37	1 020.33	136.56	
449.07	79.50	623.85	82.86	847.12	89.76	1 031.69	140.46	

$M(CoTe_{2.33}) = 356.24\,g\,mol^{-1}$

High-Temperature Data (Oslo)

Series I								
301.55	83.62	552.54	90.28	719.66	150.28[b]	792.99	101.53	
312.14	84.22	563.79	90.58	725.00	96.47	806.86	103.36	
321.59	84.85	575.07	91.01			820.65	106.53	
332.50	84.88	592.00	91.21	Series V		834.35	109.22	
343.41	85.05	609.07	91.77	478.96	88.84	847.89	110.9	
354.32	85.11	620.48	92.17	490.00	88.98	861.18	113.6[d]	
365.23	85.41	Series III		501.08	89.21	874.48	112.6[d]	
376.14	85.78	632.23	92.44	512.18	89.44	887.87	116.9	
387.06	86.15	643.71	92.57	523.31	89.58	901.37	118.2	
397.97	86.65	655.25	92.84			915.07	115.6[d]	
408.88	86.91	666.82	93.91	Series VI		928.75	119.5	
419.81	87.35	678.39	94.11	711.57	95.97	942.31	123.2	ΔT/K
430.74	87.71	689.98	94.57	719.51	118.75[c]	955.82	125.2	13.515
441.69	87.85	701.61	94.91	729.03	95.84	968.67	158.8	12.194
452.65	88.01	713.27	95.44			979.99	215.8	10.433
463.63	88.21	724.32	126.07[a]	Series VII		990.54	208.8	10.678
474.63	88.38	735.41	95.97	682.40	95.27[d]	1 001.40	198.1	11.038
		747.15	96.40	695.95	95.84[d]	1 012.66	185.5	11.481
485.66	88.48	758.92	97.17	709.60	96.54[d]	1 020.44	839	4.070
		770.71	97.64	723.38	95.94	1 024.90	676	4.864
Series II				737.26	96.24	1 029.40	979	4.127
530.09	89.34	Series IV		751.19	96.84	1 033.93	666	4.944
541.30	89.78	714.34	95.80	765.12	97.90	1 039.10	599	5.387
				779.06	98.33			

[a, b, c] These experimental determinations represent melting of excess tellurium admixed with the telluride phase and correspond to mole fractions of excess tellurium 0.018, 0.015, and 0.012, respectively. The corresponding ΔT's are 10.44 K, 4.185 K, and 9.043 K, respectively.

[d] Not included in computer fitting of curve.

Table 2. *Thermodynamic properties of* $CoTe_2$ *and* $CoTe_{2.315}$

T / K	$C_{p,m}$ / J K^{-1} mol^{-1}	$S^\circ_m(T) - S^\circ_m(0)$ / J K^{-1} mol^{-1}	$H^\circ_m(T) - H^\circ_m(0)$ / J mol^{-1}	$-[G^\circ_m(T) - H^\circ_m(0)]/T$ / J K^{-1} mol^{-1}
		$M(CoTe_2) = 314.13\,g\,mol^{-1}$		
5	0.117	0.088	0.243	0.038
10	0.552	0.276	1.728	0.105
15	1.565	0.665	6.668	0.218
20	3.561	1.366	19.047	0.414
25	6.503	2.462	43.868	0.707
30	10.096	3.958	85.16	1.119
40	18.21	7.959	226.22	2.304
50	26.31	12.899	449.09	3.917
60	33.77	18.37	750.2	5.865
70	40.25	24.07	1 121.2	8.057
80	45.68	29.81	1 551.7	10.419
90	50.17	35.46	2 031.6	12.889
100	53.88	40.95	2 552.4	15.42
120	59.67	51.31	3 690.9	20.55
140	64.03	60.85	4 930.0	25.64
160	67.31	69.63	6 245	30.59
180	69.62	77.70	7 616	35.39
200	71.23	85.12	9 025	39.99
220	72.49	91.97	10 463	44.41
240	73.63	98.33	11 924	48.64
260	74.66	104.26	13 407	52.69
280	75.47	109.82	14 909	56.58
298.15	76.04	114.58	16 284	59.97
300	76.09	115.05	16 425	60.30
320	76.59	119.98	17.952	63.88
350	77.26	126.87	20 259	68.99

400	78.44	137.27	24 151	76.89
450	79.69	146.58	28 105	84.12
500	80.85	155.03	32 119	90.80
550	81.77	162.79	36 185	96.99
600	82.53	169.93	40 293	102.78
650	83.43	176.57	44 441	108.20
700	84.77	182.80	48 643	113.31
750	86.53	188.71	52 920	118.14
800	88.31	194.35	57 300	122.73
850	89.79	199.75	61 750	127.10
900	92.41	204.94	66 290	131.28
950	102.77	210.15	71 110	135.30
1 000	132.42	216.07	77 110	139.19
1 030	144.39	221.70	82 591	142.17

T / K	$C_{p,m}$ / J K^{-1} mol^{-1}	$S^\circ_m(T) - S^\circ_m(298)$ / J K^{-1} mol^{-1}	$H^\circ_m(T) - H^\circ_m(298)$ / J mol^{-1}	$-[G^\circ_m(T) - H^\circ_m(0)]/T$ / J K^{-1} mol^{-1}
		$M(CoTe_{2.315}) = 354.33$ g mol^{-1}		
298.15	83.45	0	0	69.79
300	83.49	0.51	154	70.16
350	84.86	13.49	4 362	79.71
400	86.26	24.91	8 641	88.39
450	87.51	35.14	12 985	96.34
500	88.66	44.42	17 390	103.67
600	91.11	60.80	26 374	116.84
700	94.40	75.08	35 642	128.42
800	101.8	88.00	45 326	138.80
900	116.3	100.9	56 320	148.26
1 000	(200)	116.3	71 050	157.2
1 020	(800)	121.7	76 500	159.0
1 040	(600)	136.2	91 400	160.9

increasingly richer in cobalt, as does the coexisting liquid tellurium phase. Phase equilibrium is only partially attained above 950 K. The heat-capacity results in the region 968.80 to 1 039.01 K are thus only of an exploratory nature. The estimated standard deviation in heat capacity is

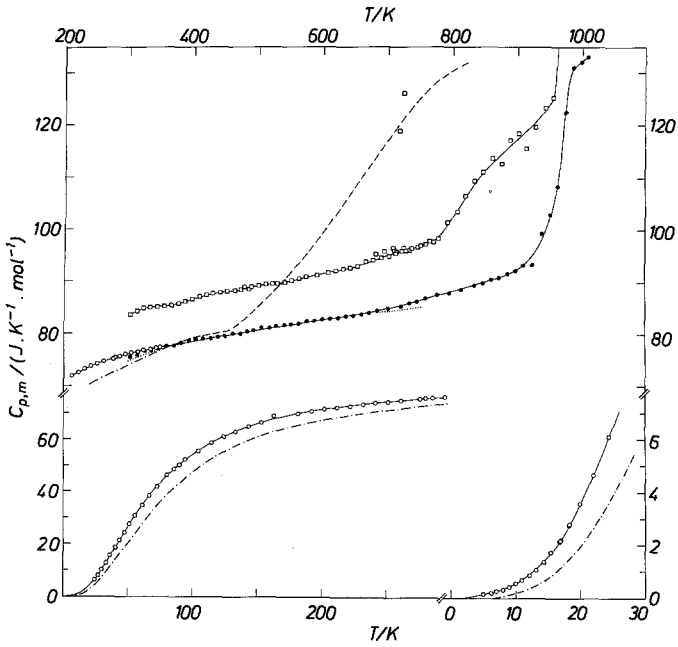

Fig. 1. The heat capacity of $CoTe_2$ and $CoTe_{2.33}$. The low-temperature data for $CoTe_2$ are represented by ○, the high-temperature data by ●, and the data for $CoTe_{2.33}$ are represented by □. Averaged dsc data on $CoTe_2$ by *Mills* [22, 23] are shown by ····, and data on $FeTe_2$ by *Mikler* et al. [6] and by *Westrum* et al. [15] are shown by — — and — · —, respectively

0.8 per cent over the region 300 to 850 K and might amount to 10 per cent at 960 K.

The heat capacity of $CoTe_{2.315}$ is about 0.5 per cent smaller on a mole-of-atom basis than that of $CoTe_2$ over the range 300 to 500 K. On the assumption that this decrease in heat capacity also persists in the lower temperature region we estimate that S°_m ($CoTe_{2.315}$, 298.15 K)—$S^\circ_m(CoTe_{2.315}, 0\,K) \approx 126\,J\,K^{-1}\,mol^{-1}$ and $H^\circ_m(CoTe_{2.315}, 298.15\,K)$—$H^\circ_m(CoTe_{2.315}, 0\,K) \approx 17\,900\,J\,mol^{-1}$. The non-stoichiometry of $CoTe_{2.315}$ arises from cobalt deficiency on the order of one vacancy to seven cobalt atoms. No superstructure formation has been reported earlier, or

observed here, which indicates that cation order is absent. Thus, the structural disorder entropy might amount to

$$\Delta S_m^\circ(CoTe_{2.315}, 0\,K) = (-R/0.864)(0.864 \ln 0.864 + 0.136 \ln 0.136)$$
$$= 3.83\,J\,K^{-1}\,mol^{-1}.$$

This value is tentatively used for deriving the standard *Gibbs* energy values for $CoTe_{2.315}$ in Table 2.

Discussion

The paramagnetism of $CoTe_2(m)$ indicates the presence of unpaired 3d electrons. The effective magnetic moment (2.2 BM at 720 K) [1] is much smaller than the moment (3.87 BM) expected for Co^{2+} in the high-spin state and somewhat higher than the value of 1.73 BM for the low-spin state in the spin-only approximation.

According to *Goodenough* [14] $CoTe_2(m)$ contains one itinerant 3d electron in a σ^*-band sufficiently wide to preclude cooperative magnetic ordering. The *Vandenbempt* et al. [10] alternative view presupposes antiferromagnetic ordering in $CoTe_2(m)$, in analogy with the assumption made for $CoSe_2(p)$ by *Adachi* et al. [28]. However, neither the present heat-capacity measurements nor the *Mössbauer* experiments by *Kjekshus* and *Nicholson* [11] show evidence of cooperative ordering related to localization of 3d-electrons into sub-bands and magnetic exchange interactions between them.

No lattice-dynamical analysis has been carried out for $CoTe_2(m)$, but the rare occasion of an isostructural, non-magnetic, semi-conducting analog with nearly the same molar mass, inter-atomic distances, and angles is present in the earlier-studied $FeTe_2$. The molar volume, which has been shown to be a more relevant predictor for lattice heat-capacity contributions in isostructural series of substances [29] than is the cationic mass, is 3.0 per cent larger for $CoTe_2$ than for $FeTe_2$. Moreover, the extra 3d-electron in cobalt compared to those in iron enhances the low-temperature heat capacity of $CoTe_2(m)$ relative to $FeTe_2(m)$.

A comparison of the derived θ_D-curves for $CoTe_2$ and for $FeTe_2$ (cf. Fig. 2)—in which C_p was converted to C_V by the *Nernst-Lindemann* relation—shows clearly the presence of excess low-temperature contributions for $CoTe_2(m)$, evidenced by the rather low θ_D values. The usual minimum in the low-temperature region is absent. The excess heat capacity in Fig. 3 rises to a rather pronounced maximum of $7.3\,J\,K^{-1}\,mol^{-1}$ at 80 K and then falls gradually with increasing temperature. It may imply a large increase in density of states just above the *Fermi* level, occasioned by the presence of bands with high-density regions. These

bands presumably derive from the broader bands assumed by *Goodenough* [14] and by *Vandenbempt* et al. [10]. In the absence of further details about the band structure of $CoTe_2(m)$ it remains to be investigated whether the lowest excited level or band is primarily an antibonding σ^* metal state, an overlapping anion p-band state, or of some other origin.

The resemblance of the excess heat capacity to a *Schottky*-type transition is illustrated in Fig. 3 which assumes two excited levels at 65 and 175 cm^{-1} above the ground level with degeneracies $g_0 : g_1 : g_2 = 1 : 1 : 3$ and

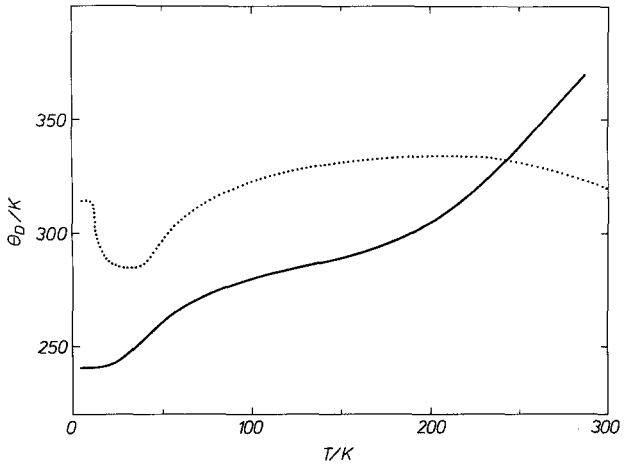

Fig. 2. *Debye*-theta values for $CoTe_2$ ——— and $FeTe_2$ ·····

1 : 1 : 2. The latter degeneracy values might derive from localization of electrons within the quarter-filled σ^* band proposed by *Goodenough* [14]. Neither alternative, however, accounts totally for the observed experimental difference. The relatively good fit in the region up to 100 K cannot be taken as proof of the uniqueness of the 1 : 1 : 3 proposal, but even so, the model might approximate the variation in the density of states. A 50 K lower *Debye*-θ value for $CoTe_2(m)$ than for $FeTe_2(m)$ also approximates the heat-capacity difference rather well in the same temperature region, cf. Fig. 3, but the excess is more probably related to electronic excitations than to differences in the lattice contributions.

The estimated value for the entropy of $CoTe_2(m)$ calculated through the cationic and anionic entropy contributions [30] for solid transition-metal chalcogenides is 100 $J\,K^{-1}\,mol^{-1}$ at 298.15 K, or about 14.5 $J\,K^{-1}\,mol^{-1}$ lower than that observed. The entropy contribution from the assumed 1 : 1 : 2 *Schottky* anomaly in Fig. 3 aggregates to $\sim 12\,J\,K^{-1}$

mol^{-1} at 298.15 K. Comparably high entropies which probably reflect contributions from population of low-lying electronic states or bands, which we have been unable to evaluate properly, occur for some other chalcogenides, e.g., NiS_2 and $NiSe_2$. In this connection the possible presence of orbital magnetic contributions should be considered. They are commonly observed in Co(II) complexes. Hence, the effect of orbital dis-

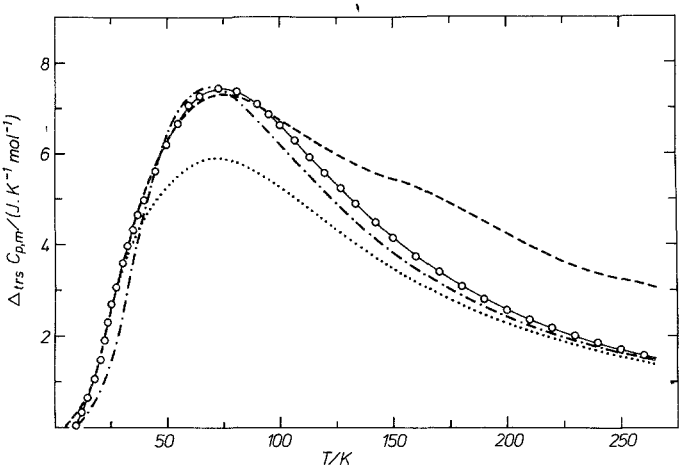

Fig. 3. Deviation of the experimental heat capacities of $CoTe_2$ from $FeTe_2$ — —; calculated *Schottky*-like curve for $E_1/hc = 65\,cm^{-1}$, $E_2/hc = 180\,cm^{-1}$ and $g_0 : g_1 : g_2 = 1 : 1 : 3$ ○ — ○; the same levels with $g_0 : g_1 : g_2 = 1 : 1 : 2$ ·····; *Debye* lattice heat capacity difference curve for $\theta_D = 330$ and 280 K · — ·

ordering might be observable in the heat capacity of $CoTe_2(m)$, just as it has been predicted [31] for the related ferromagnetic case and observed [32] for $CoS_2(p)$.

The heat-capacity increases for $CoTe_2$ and $CoTe_{2.315}$ above 300 K follow a different pattern from that observed for $FeTe_2$ [6, 7]. An unusual increase is observed already as low as 400 K in the latter, possibly occasioned by defect formation as in $FeSe_2$ [33]. For $CoTe_2(m)$ only a gradual increase in heat capacity, primarily from the dilational term, is observed up to 900 K. Above this temperature a sigmate increase is noted from about 96 $J\,K^{-1}\,mol^{-1}$ at 930 K to about 138 $J\,K^{-1}\,mol^{-1}$ at 1 030 K. The increase is presumably related to the precipitation of the $Co_{1-x}Te$-phase from originally stoichiometric $CoTe_2$ as the peritectic decomposition temperature for the $CoTe_2(m)$-phase is approached. Lack of equilibration during the ~ 60 minute periods between energy inputs is

noticeable in the negative drift rates on the order of $\sim 0.005\,\mathrm{K\ min^{-1}}$ above 950 K.

For $CoTe_{2.33}$ the departure from normal heat-capacity increase starts at 780 K. The increase is moderate up to 960 K, with slightly negative drift rates. Above 960 K the drift rate at first becomes considerably more negative ($\sim -0.02\,\mathrm{K\,min^{-1}}$). Then it shifts to large positive values with a maximum at 1 029 K—and finally it becomes more normal at the highest temperature.

The excess enthalpy increment for $CoTe_{2.315}$ due to its decomposition was of the order $20\,\mathrm{kJ\,mol^{-1}}$ relative to that of $CoTe_2(m)$ when the measurements had to be interrupted at 1 041.7 K due to instrumental problems. Thus, it is not certain that the decomposition reaction had gone to completion. The large positive drift rate presumably stems from exothermal recombination of the Te-depleted $CoTe_{2+x}$-phase and the Co-containing Te(l)-phase of non-equilibrium composition due to excessive temperature rise during the energy input. Apparently, the compositional change with temperature of the $CoTe_{2+x}$-phase is much more pronounced on the Te-rich than on the Co-rich side when the decomposition temperature is approached. In the absence of a reliable $\Delta_{\mathrm{decomp.}}H$-value, the actual compositional change with temperature remains uncertain. The excess enthalpy on the Co-rich side is only about $2.5\,\mathrm{kJ\,mol^{-1}}$ up to 1 037.4 K, where the measurements had to be discontinued. The low value is possibly due to a slower decomposition rate of the Co-rich $CoTe_{2+x}$-phase in this temperature region, since the composition of the decomposing peritectic is reported to be $CoTe_{2.13}$ [4, 5].

Evaluation of the formation properties of $CoTe_2(m)$ presents some difficulties due to the large spread in the thermodynamic values reported. Thus, *Ariya* et al. [16] found $\Delta_f H^\circ_m(CoTe_2, 298.15\,\mathrm{K}) = -135\,\mathrm{kJ\,mol^{-1}}$ by solution calorimetry, while *Komarek* et al. [17] found $-73.0\,\mathrm{kJ\,mol^{-1}}$. *Morozova* et al. [18] obtained $\Delta_f H^\circ_m(CoTe_2, 298.15\,\mathrm{K}) = (-80.3 \pm 1.2)\,\mathrm{kJ\,mol^{-1}}$ by reaction calorimetry.

Further $\Delta_f H^\circ_m(298.15\,\mathrm{K})$-values can be derived from the high-temperature Te-pressure measurements on cobalt tellurides by *Geffken* et al. [3] and the electrochemical-cell measurements by *Matlasevich* et al. [20, 21] in combination with the enthalpy and entropy values obtained here for $CoTe_2(m)$ and corresponding values for cobalt [34] and tellurium [27]. *Geffken* et al. [3] obtained $\Delta_f G^\circ_m(CoTe_2, 873\,\mathrm{K}) = -53.7\,\mathrm{kJ\,mol^{-1}}$ by *Gibbs-Duhem* integration, which results in $\Delta_f H^\circ_m(CoTe_2, 298.15\,\mathrm{K}) = -73.8\,\mathrm{kJ\,mol^{-1}}$. The *Gibbs-Duhem* integration by *Matlasevich* et al. [21] gave $\Delta_f G^\circ_m(CoTe_2, 700\,\mathrm{K}) = (-73.6 \pm 0.6)\,\mathrm{kJ\,mol^{-1}}$, which leads to $\Delta_f H^\circ_m(CoTe_2, 298.15\,\mathrm{K}) = (-83.4 \pm 1)\,\mathrm{kJ\,mol^{-1}}$. *Matlasevich* et al. [21] also derived $\Delta_f H^\circ_m(CoTe_2, 700\,\mathrm{K}) = (-82.6 \pm 3.1)\,\mathrm{kJ\,mol^{-1}}$ and

$\Delta_f S^\circ_m(CoTe_2, 700\,K) = (-13.2 \pm 5.5)\,kJ\,mol^{-1}$. The latter value is close to what we find: $\Delta_f S^\circ_m(CoTe_2, 700\,K) = (-14.9 \pm 2)\,J\,K^{-1}\,mol^{-1}$. The uncertainty is large at 700 K, which is in the range of the α- to β-transformation in cobalt. Excluding the $\Delta_f H^\circ_m(CoTe_2, 298.15\,K)$ stemming from—and practically equal to—the corresponding value at 700 K by *Matlasevich* et al. [21] and the largely diverging result by *Ariya* et al. [16], we obtain

$$\Delta_f H^\circ_m(CoTe_2, 298.15\,K) = (-78 \pm 7)\,kJ\,mol^{-1}$$

as the mean value of the remaining four sets of results. The associated entropy and *Gibbs* energy values are:

$$\Delta_f S^\circ_m(CoTe_2, 298.15\,K) = (-13.9 \pm 1.2)\,J\,K^{-1}\,mol^{-1}$$
$$\Delta_f G^\circ_m(CoTe_2, 298.15\,K) = -(74 \pm 8)\,kJ\,mol^{-1}.$$

The $\Delta_f H^\circ_m$- and $\Delta_f G^\circ_m$-values are rather uncertain, but we have at present no firm basis for depreciating one of the two discordant sets of values.

Formation data for samples in the range of $CoTe_{2.315}$ have been obtained by *Geffken* et al. [3] and by *Komarek* et al. [17]. The $\Delta_f G^\circ_m(873\,K)$-value of the former can be compared with the $\Delta_f H^\circ_m(298.15)$-value of the latter through the present results. Our assumption about $S^\circ_m(CoTe_{2.315}, 298.15\,K) = 129.8\,J\,K^{-1}\,mol^{-1}$, which includes $3.8\,J\,K^{-1}\,mol^{-1}$ of structural zero-point entropy, leads to $\Delta_f H^\circ_m(CoTe_{2.315}, 298.15\,K) = -77.2\,kJ\,mol^{-1}$. This is $9\,kJ\,mol^{-1}$ more positive than the extrapolated value for $CoTe_{2.30}$ ($-86.3\,kJ\,mol^{-1}$) in the solution calorimetric experiments by *Komarek* et al. [17]. The assumption of practical structural order in $CoTe_{2.315}$ would improve the agreement, but in order to make it complete, our estimated standard entropy would have to be lowered by $6\,J\,K^{-1}\,mol^{-1}$ more. We consider the required $S^\circ_m(CoTe_{2.315}, 298.15\,K) = 120\,J\,K^{-1}\,mol^{-1}$ to be unexpectedly low and find that more accurate formation determinations will be needed for obtaining a satisfactory thermodynamic characterization of the $CoTe_{2+x}$-phase.

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