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HEAT CAPACITY OF NIOBIUM CHLORIDES IN THE RANGE 6–320 K

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The heat capacities of $NbCl_5$ and Nb_3Cl_8 samples with less than $1 \cdot 10^{-3}$ mass-% of impurities were determined over the range 6–320 K by an adiabatic calorimeter. An anomaly was found in Nb_3Cl_8 within the 7–13 K range. Comparisons of C_p values of Nb_3Cl_8 are made with the theoretical works of Tarassov. The qualitative fit is quite good.

Our investigations on the heat capacities of niobium chlorides form part of our work to obtain reliable and co-ordinated information about the thermodynamics of the niobium-chlorine system. There are no publications on the thermal properties of niobium chlorides at low temperature.

The samples of $NbCl_5$ and Nb_3Cl_8 were prepared according to [1] and [2], respectively. The compositions of the samples were checked by gravimetry [2].

	Nb, wt.%		Cl, wt.%	
	found	calc.	found	calc.
$NbCl_5$	34.30±0.09	34.39	65.50±0.13	65.61
Nb_3Cl_8	49.40±0.10	49.53	50.45±0.10	50.47

X-ray phase analysis showed that the obtained substances comprised single phases, with X-ray diagrams corresponding completely with those in [2]. Spectral analysis revealed mass percentages of impurities (I, Cl, Al, Si, Sn, Fe, Zn, V, Cr, Ni and Ce) of less than 1.10^{-3}.

The heat capacity measurements were made with a vacuum adiabatic calorimeter with periodic input of heat. The calorimetric vessel containing the sample was made of nickel, a material with high resistance to corrosion. Temperature was measured with a platinum resistance thermometer.

The average deviation of the experimental heat capacity from the smoothed curve for the empty vessel was less than 0.05% in the range 30–320 K, increasing up to 0.3% below 30 K.

The control measurements made on pure benzoic acid were in agreement with standard data [3]. The heat capacity of benzoic acid with a mass of

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3.2240 g was measured at 48 points from 8 to 278 K. The average deviations $(C_p - C_{stand})/C_{stand}$ were less than 0.2% above 50 K, and about 1.0% from 8 to 30 K.

Because of the hygroscopic character of niobium chlorides, the vessel was filled with sample in a "dry" chamber.

The heat capacity of $NbCl_5$ (6.6436 g) was measured at 96 points from 7.52 to 322.96 K (Table 1) and that of Nb_3Cl_8 (5.5400 g) at 78 points in the range 7.47 to 337.85 K (Table 2). The average deviation of the experimental heat capacity from the smoothed C_p (T) dependence for each of the samples was about 0.1% in the range 30 to 300 K, and 1.0% below 30 K. To calculate the thermodynamic function, it was necessary to extrapolate C_p (T) from 7 to 0 K. Extrapolation to $T \rightarrow 0$ was carried out using Debye's T^3 limiting law, and yielded S^o (7 K) $= 0.37$ J·deg^{-1}·mol^{-1} or 0.2% from S^o (298.15 K) for $NbCl_5$, and S^o (7 K) $= 0.19$ J·deg^{-1}·mol^{-1} or 0.06% from S^o (298.15 K) for Nb_3Cl_8.

Table 1 Experimental heating capacity of $NbCl_5$ in J·deg^{-1}·mol^{-1}·M($NbCl_5$) = 270.175 g·mol^{-1}

T,K	C_p^o	T,K	C_p^o	T,K	C_p^o	T,K	C_p^o
Series 1		202.20	129.6	157.07	117.2	15.22	8.633
222.07	133.5	206.43	130.6	161.70	118.9	17.64	11.74
225.98	134.0	211.06	131.6	221.75	133.9	Series 6	
229.85	134.6	215.64	132.6	Series 4		47.68	49.26
233.50	135.4	219.97	133.5	14.00	7.013	50.80	52.77
237.11	136.2	224.25	134.1	15.28	8.663	53.72	55.74
240.90	136.7	Series 3		16.50	10.18	57.82	59.75
244.65	137.3	79.68	78.14	18.98	13.43	62.84	64.66
249.91	138.1	83.03	80.75	20.15	14.85	67.29	68.54
254.73	138.9	86.23	83.00	21.61	16.96	71.58	71.99
258.70	139.4	89.74	85.24	23.24	19.18	75.57	75.22
262.92	140.2	93.56	87.72	25.01	21.46	Series 7	
267.89	141.0	97.43	90.37	26.77	23.82	7.52	1.624
272.82	141.4	101.15	92.64	28.47	26.02	7.98	1.662
277.98	141.9	104.54	94.64	30.26	28.35	8.65	2.036
283.09	142.6	108.22	96.63	32.69	31.38	9.38	2.502
Series 2		112.18	98.41	34.60	33.96	10.14	3.073
162.62	118.9	116.02	100.3	36.86	36.74	10.94	3.761
166.36	120.4	119.75	102.0	39.25	39.71	11.80	4.557
170.29	121.5	123.40	104.0	41.71	42.60	Series 8	
174.65	122.7	127.88	105.6	Series 5		299.81	144.6
179.43	124.3	132.64	108.1	8.47	2.001	304.40	145.1
184.14	125.3	137.02	109.8	11.06	3.731	308.94	145.6
188.79	126.5	141.80	111.9	11.89	4.538	313.45	146.1
193.39	127.6	148.01	114.0	12.83	5.805	317.92	146.4
197.93	128.8	152.34	115.5	14.02	6.949	322.36	146.6

Table 2 Experimental heat capacity of Nb_3Cl_8, in $J \cdot deg^{-1} \cdot mol^{-1} \cdot M(Nb_3Cl_8) = 562.354\ g \cdot mol^{-1}$

T,K	C_p^o	T,K	C_p^o	T,K	C_p^o	T,K	C_p^o
Series 1		247.87	245.5	152.83	195.7	Series 6	
297.80	258.8	255.60	248.5	159.14	200.4	7.47	1.318
301.06	259.5	263.50	250.8	165.58	205.0	8.15	2.085
305.78	260.2	271.33	253.5	Series 4		9.71	2.452
311.60	262.1	278.84	254.8	22.86	11.79	10.56	2.605
317.40	263.6	286.54	256.6	24.91	14.31	11.35	2.990
323.20	262.3	Series 3		26.91	16.73	12.28	3.298
329.14	261.9	81.24	108.6	28.75	19.02	13.31	3.923
337.85	261.7	84.40	113.4	35.56	28.46	14.50	4.768
Series 2		88.11	119.4	44.93	45.24	15.91	5.730
172.95	209.9	92.56	126.2	51.11	55.48	17.71	7.066
179.22	214.9	96.99	133.0	57.99	67.80	19.67	8.678
186.00	218.5	101.20	139.4	65.45	80.46	21.26	10.21
193.25	222.1	105.62	145.3	72.75	92.18	Series 7	
200.37	226.4	110.44	151.1	Series 5		7.82	1.265
207.36	230.0	115.73	157.5	310.60	261.7	8.47	1.874
214.23	232.6	121.26	165.3	313.98	261.9	9.28	2.240
221.02	235.6	126.58	171.3	317.17	262.6	10.25	2.496
227.71	238.4	132.73	177.6	319.90	263.7	11.29	2.899
234.33	240.5	139.65	184.6	322.64	262.2	12.35	3.395
240.87	243.2	146.34	190.5				

At 298.15 K, the calculated data were as follows:

	$NbCl_5$	Nb_3Cl_8
C_p^o (298.15 K), $J \cdot deg^{-1} \cdot mol^{-1}$	144.3±0.2	258.9±0.3
ϕ^o (298.15 K), $J \cdot deg^{-1} \cdot mol^{-1}$	117.0±0.2	152.2±0.3
S^o (298.15 K), $J \cdot deg^{-1} \cdot mol^{-1}$	216.4±0.4	316.6±0.6
H^o (298.15 K) $- H^o$ (0 K), $J \cdot mol^{-1}$	29650±60	49020±100

The C_p (T) curve for $NbCl_5$ has no anomalies, while that for Nb_3Cl_8 has an anomaly within the range 7–13 K, the maximum deviation being almost 100 per cent of the regular part (Fig. 1). The surplus enthalpy of this transition $\Delta H_{tr} = 2.52\ J \cdot mol^{-1}$ and $\Delta S_{tr} = 0.266\ J \cdot deg^{-1} \cdot mol^{-1}$. The temperature of the maximum of the anomaly coincides with the critical superconducting temperature of niobium, but X-ray analysis of our sample and an estimation of the anomaly in niobium do not permit an explanation of the anomaly in Nb_3Cl_8 in terms of the presence of pure metal. In a fairly wide temperature range above the anomaly, from 12 to 45 K, the heat capacity of Nb_3Cl_8 is proportional, with good accuracy, to T^2. Such extraordinary behaviour of $C_p(T)$ may suggest a strong anisotropy of the crystal structure

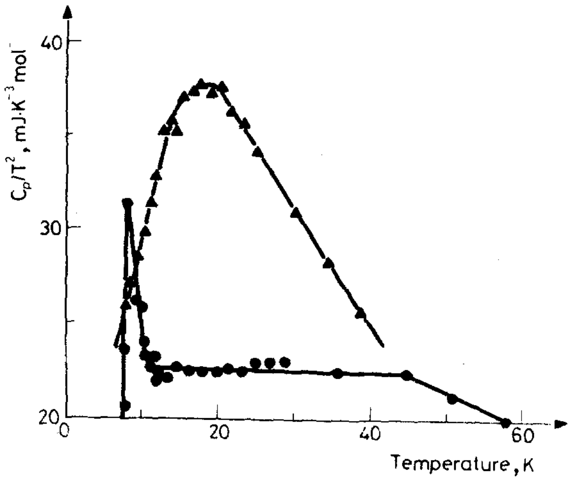

Fig. 1 C_p/T^2 as a function of temperature for two niobium chlorides. ▲ $NbCl_5$, ● Nb_3Cl_8

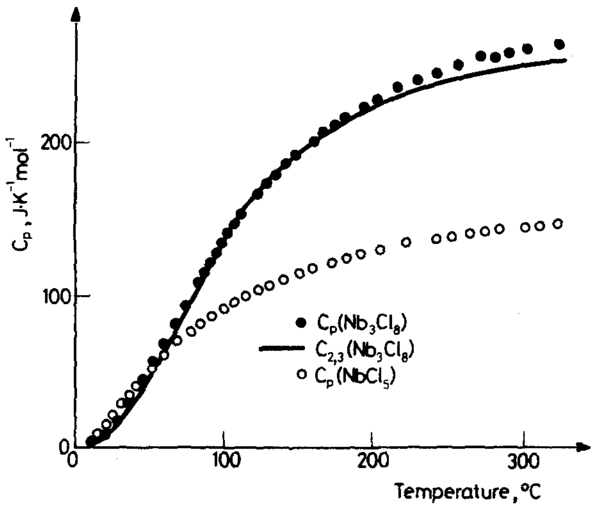

Fig. 2 The temperature dependences of heat capacities for two niobium chlorides and Tarassov $C_{2,3}$ function.

of Nb_3Cl_8. In fact, Nb_3Cl_8 has a CdI_2-type structure, which consists of layers [4].

Within the limits of the Tarassov theory [5], the characteristic temperatures θ_2 and θ_3 were calculated and the function $C_{2,3}$ was determined. In the range 80 to 190 K, function $C_{2,3}$ (θ_2 = 460 K, θ_3/θ_2 = 0.05) coincides with good accuracy (about 1.0%) with the experimental C_p values (Fig. 2). Below 80 K, the derivations increased to about 10% which can probably be explained by the difference between the actual phonon spectrum and that accepted in the model (for example, the presence of cluster groups of Nb_3 results in additional modes in the phonon spectrum). The difference between the $C_{2,3}$ function and C_p values above 190 K can be explained by the presence of an anharmonic contribution to the heat capacity. However, even approximate evaluations of θ_2 and θ_3 allow the conclusion of considerable anisotropy of the binding energy in Nb_3Cl_8. Since the structural studies of Nb_3Cl_8 corroborate its layered structure, it may be presumed that a weak energy is involved in the interaction between the layers. In this case, the quantity θ_3/θ_2 characterizes the relative energy of interaction between the layers, in comparison with the binding energy between the atoms in the layers.

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Zusammenfassung – Die Wärmekapazitäten von $NbCl_5$- und Nb_3Cl_8-Proben mit Verunreinigungsgehalten 10^{-3} Masse-% wurden mit einem adiabatischen Kalorimeter bei 6 bis 320 K bestimmt. Am Nb_3Cl_8 wurde eine Anomalie bei 7 bis 13 K nachgewiesen. Die C_p-Werte von Nb_3Cl_8 werden mit theorischen Ergebnissen von Tarassov verglichen, die qualitative Übereinstimmung ist gut.

РЕЗЮМЕ — С помощью адиабатического калориметра в области температур 6—320 К определены теплоемкости образцов $NbCl_5$ и Nb_3Cl_8 с содержанием примесей менее, чем $1\cdot10^{-3}$ весовых процента. Для Nb_3Cl_8 в области температур 7—13 К обнаружена аномалия. Сопоставление полученных значений C_p для Nb_3Cl_8 с теоретически установленными, показало их хорошее качественное совпадение.