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Heat capacity of copper hydride

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Abstract

The heat capacity of copper hydride has been measured in the temperature range 2–60 and 60–250 K using two adiabatic calorimeters. Special procedure for the purification of CuH has been applied and a careful analysis of sample contamination has been performed. The experimental results have been extrapolated up to 300 K due to instability of the copper hydride at room temperature. From the temperature dependence of heat capacity the values of entropy $S^\circ(T)$, thermal part of enthalpy $H^\circ(T) - H^\circ(0)$ and Gibbs function $[-(G^\circ(T) - H^\circ(0))]$ have been calculated assuming $S^\circ(0) = 0$. The standard absolute entropy, standard entropy of formation from the elements and enthalpy of decomposition of copper hydride from the elements have been calculated and found to be $130.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (H_2), $-85.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (H_2), $-55.1\,\mathrm{kJ\,mol^{-1}}$ (H_2), respectively. These new results gave the possibility of discussion on thermodynamic properties of copper hydride. Debye temperature has been for the first time determined experimentally.

Keywords: Heat capacity; Copper hydride; Entropy

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1. Introduction

Copper hydride, one of the oldest known hydrides, has been the object of several investigations. Among the metal–hydrogen systems copper hydride occupies specific place from the point of view of nature of metal–hydrogen bonding. It does not belong to the group of metallic hydrides because of its dielectric properties, and to the group of ionic hydrides due to its large lattice volume expansion contrary with saline hydrides where lattice contraction is observed in respect to the pure metal. It seems to be similar to aluminium trihydride which according to NMR data [1] is non-metallic material having relatively strong Al–H bonds with significant covalence contribution. Also the volume change calculated per atom of hydrogen due to hydride formation is almost the same for both hydrides. Copper hydride can be easily synthesised by several methods involving Cu^{2+} reduction [2–4], but its properties such as enthalpy of decomposition or thermal stability determined so far show large discrepancies. Thermodynamic properties of copper hydride have not been sufficiently studied. The lack of results is due to the difficulties caused by the low thermal stability and presence of admixtures in the samples of CuH, which can significantly influence the results of investigations. The attempts to synthesise copper hydride from the elements, to avoid the above-mentioned problems, failed so far as a solubility of hydrogen in metallic copper is very low at normal pressure of hydrogen even at high temperature. The enthalpy of decomposition of CuH was the only property published in the open literature [5–7]. No attempts to determine

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entropy or evaluate any other thermodynamic characteristics of CuH have been reported.

The aim of this work is the measurement of temperature dependence of C_p of copper hydride in 2–250 K temperature range and computation of the values of entropy $S^\circ(T)$, thermal part of enthalpy $H^\circ(T) - H^\circ(0)$ and Gibbs function $[-(G^\circ(T) - H^\circ(0))]$ over 0–300 K range. The standard absolute value of entropy of copper hydride will be used to calculate the standard entropy of formation. The heat of decomposition of copper hydride at standard conditions will be calculated based on the thermal part of enthalpy of CuH.

2. Experimental

Samples of copper hydride were synthesised by reduction of aqueous copper sulphate with hypophosphorous acid according to the procedure described earlier [8]. The precipitate was cooled, filtered and rinsed with ice water and cold absolute alcohol to reduce water content. The powder dried in air was stored for further investigations in carbon dioxide at −50 °C.

Because impurities in the copper hydride could lead to confusing results we put particular attention on purity of the samples we used, and several analytical methods have been employed to characterise our object of investigations.

The hydrogen content was determined by volumetric analysis as being equal to around 0.9 in atomic ratio. X-ray analysis was used to determine the crystallographic structure and presence of solid impurities in the sample (Fig. 1). It showed pure wurtzite structure of CuH with lattice parameters $a = 2.90$ Å and $c = 4.61$ Å, that is in good agreement with that obtained by Goedkoop and Andresen [9]. No traces of metallic copper or cuprous oxide were observed.

To study the temperature dependence of heat capacity two adiabatic calorimeters covering different temperature ranges were employed. The design of calorimeters and the procedure of measurements have been described elsewhere [10,11]. Copper hydride was pressed into tablets under pressure about 3 kbar prior to measurements. The average weight of the samples was 300 mg. The measurements were carried out for 2–60 and 60–250 K temperature regions separately. During the process of achieving adiabatic condition the sample was pumped at room temperature for 2 h. This procedure allowed to get rid of the possible traces of volatile admixtures and caused partial decomposition of the hydride. We used the Karl–Fischer titration method to determine the

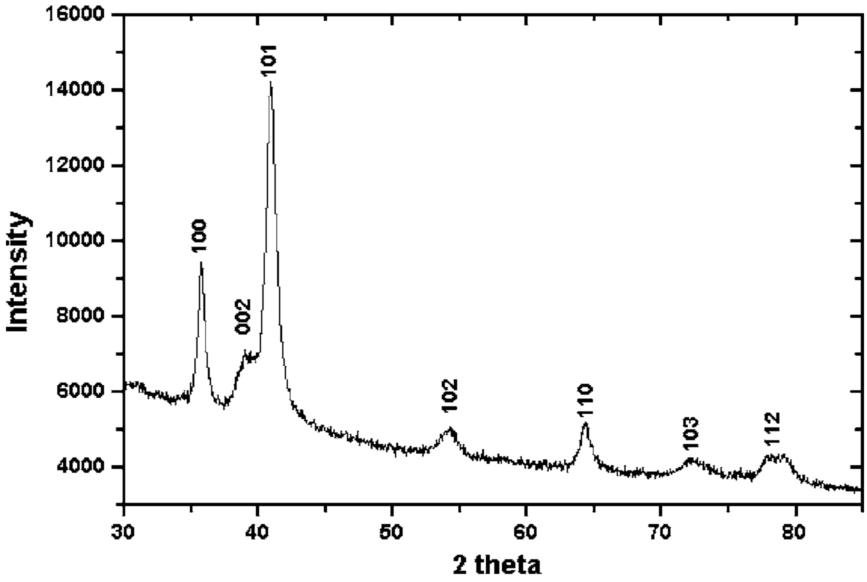

Fig. 1. X-ray diffraction pattern of CuH (Cu Kα).

Table 1
Composition of the samples and temperature ranges of measurements

Sample number	Hydrogen (mass%)	$CuH_{0.78}$ (mass%)	Cu (mass%)	H_2O (mass%)	Temperature range (K)
1	0.95	78	20	2	2–60
2	1.06	87	11	2	60–250
3	0.74	61	35	4	60–250
4	0.91	75	22	3	60–250

content of water in CuH. The final content of hydrogen in copper hydride was determined by volumetric method after measurements.

We have noticed that the sample after measurements contained some amounts of copper and cuprous oxide. The presence of Cu_2O can be explained by rapid oxidation of fine copper particles on air during transportation of the sample from the calorimeter to the Dewar vessel after heat capacity measurements. The quantity of copper oxide has been estimated by X-ray analysis and a correction has been made to calculate copper hydride composition. Knowing the quantities of water, cuprous oxide and hydrogen content, the atomic ratio of hydrogen over copper in copper hydride has been calculated to be 0.78. The compositions of CuH samples under investigations are presented in Table 1.

The content of water was determined only for sample 2. As the samples were similarly prepared, we assumed that the water contents were near the same. For samples 3 and 4 this value was fitted in order to minimize the deviation of the results. In temperature range 2–60 K experiments were carried out on two samples, but only one of them was analysed with respect to hydrogen concentration and other admixtures. The second sample during the attempt to divide it into smaller pieces rapidly exploded. This is the proof of the purity of sample used in the measurements, as a completely pure copper hydride is pyrophoric. The courses C_p versus T for both samples were identical which could be interpreted as possessing the same chemical composition.

3. Results

The results of heat capacity measurements for the four samples are presented in Tables 2–5. The heat capacity of ice [12,13] and copper [14] were extracted from the raw experimental data.

Table 2
The results of heat capacity measurements for sample 1

Temperature (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	Temperature (K)	C_p ($J\,K^{-1}\,mol^{-1}$)
2.96	0.0115	14.40	1.184
3.08	0.0122	15.03	1.358
3.20	0.0130	15.69	1.565
3.33	0.0138	16.37	1.754
3.47	0.0154	17.08	1.997
3.61	0.0175	17.84	2.303
3.79	0.0183	18.62	2.592
3.96	0.0206	19.42	2.864
4.12	0.0201	20.25	3.004
4.31	0.0231	21.08	3.394
4.49	0.0259	21.99	3.803
4.68	0.0301	22.96	4.285
4.88	0.0345	23.99	4.752
5.08	0.0360	25.60	5.281
5.30	0.0406	26.67	5.792
5.53	0.0469	27.83	6.350
5.77	0.0559	29.05	6.887
6.02	0.0603	31.19	7.597
6.28	0.0705	33.50	8.729
6.55	0.0821	35.03	9.123
6.83	0.0952	36.53	9.740
7.12	0.1017	38.12	10.38
7.42	0.1234	39.74	11.11
7.74	0.1418	41.43	11.52
8.07	0.1550	43.20	12.20
8.41	0.1827	45.04	12.34
8.77	0.2135	46.80	12.76
9.13	0.2351	48.84	13.35
9.80	0.3200	50.92	13.75
10.21	0.3637	53.10	14.56
10.67	0.4353	55.37	14.80
11.14	0.4926	57.74	15.45
11.62	0.5794	60.06	16.16
12.13	0.6637	62.46	16.59
12.66	0.7735	64.90	17.26
13.21	0.8752	67.37	17.05
13.80	1.037		

Table 3
The results of heat capacity measurements for sample 2

Temperature (K)	C_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Temperature (K)	C_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
66.73	18.28	153.70	24.86
68.27	18.29	155.43	24.88
68.35	18.51	157.15	24.96
69.04	18.94	158.88	25.06
69.83	19.09	160.62	25.11
70.61	18.97	162.35	25.20
71.39	19.12	164.08	25.30
72.17	19.27	165.82	25.34
72.94	19.37	167.56	25.47
73.71	19.32	169.30	25.55
75.01	19.65	171.03	25.55
76.76	19.70	172.77	25.65
78.51	20.08	174.51	25.75
80.26	20.14	176.25	25.76
82.01	20.15	177.99	25.80
83.76	20.52	179.74	25.94
85.50	20.69	181.48	26.06
87.26	20.77	183.22	26.11
88.99	20.94	184.97	26.22
90.73	21.05	186.73	26.22
92.46	21.28	188.47	26.40
94.19	21.42	190.23	26.55
95.94	21.39	191.99	26.68
97.66	21.69	193.75	26.89
99.32	22.00	195.52	26.95
101.40	22.13	197.28	27.16
103.06	22.32	199.04	27.27
105.14	22.44	200.81	27.37
107.63	22.67	202.57	27.55
109.30	22.87	204.34	27.58
111.37	22.91	206.11	27.70
112.53	23.18	207.88	27.84
114.23	23.27	209.65	27.92
115.94	23.32	211.42	28.03
117.63	23.49	213.20	28.18
119.34	23.61	214.97	28.29
121.05	23.47	216.74	28.36
122.76	23.62	218.51	28.44
124.47	23.64	220.28	28.40
126.19	23.64	222.06	28.53
127.90	23.85	223.84	28.62
129.62	24.04	225.61	28.67
131.34	24.10	227.39	28.72
133.06	24.06	229.17	28.79
134.77	24.14	230.94	28.72
136.48	24.17	232.72	28.85
138.21	24.30	234.50	28.87
139.92	24.36	236.28	28.91
141.64	24.34	238.07	28.84
143.36	24.44	239.85	28.94
145.08	24.43	242.06	28.89
146.80	24.54	243.13	28.93
148.52	24.66	243.96	29.00
150.25	24.68	246.04	28.91
151.97	24.77		

Table 4
The results of heat capacity measurements for sample 3

Temperature (K)	C_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Temperature (K)	C_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
64.28	19.67	146.90	23.43
65.19	18.84	148.81	23.69
66.10	19.01	150.73	23.62
67.01	19.36	152.65	23.88
67.92	19.62	154.57	23.92
68.83	19.72	156.49	24.09
69.73	20.08	158.41	24.19
70.63	19.50	160.33	23.98
71.54	19.71	162.26	24.13
72.46	20.00	164.18	24.53
73.36	20.01	166.10	24.52
74.27	20.43	168.03	24.74
75.18	19.87	169.96	24.95
76.09	19.93	171.88	24.93
77.00	20.11	173.81	24.84
77.91	20.19	175.71	24.94
78.81	20.59	177.64	25.49
79.72	20.74	179.57	25.67
80.63	20.06	181.51	25.65
81.54	20.23	183.43	26.12
82.45	20.48	185.36	26.08
83.35	20.73	187.29	26.57
84.26	20.85	189.21	26.60
85.67	20.56	191.15	26.76
87.58	20.79	193.07	27.03
89.49	21.18	195.00	27.39
91.40	21.00	196.92	27.46
93.31	21.26	198.85	27.94
95.21	21.13	200.79	27.78
97.12	21.38	202.71	28.22
99.04	21.69	204.64	28.72
100.95	21.45	206.56	28.82
102.87	21.79	208.49	29.04
104.78	22.03	210.41	29.25
106.70	21.72	212.34	29.65
108.61	22.02	214.27	30.02
110.52	21.85	216.20	30.16
112.44	22.15	218.12	30.52
114.35	22.39	220.04	30.69
116.26	22.12	221.97	31.08
118.18	22.36	223.89	31.31
120.09	22.16	225.81	31.76
122.00	22.44	227.74	31.67
123.92	22.65	229.66	31.99
125.83	22.41	231.55	32.24
127.74	22.67	233.46	32.83
129.66	22.84	235.38	32.75
131.57	22.74	237.29	32.85
133.49	22.99	239.20	33.25
135.40	22.85	241.12	33.55
137.32	23.04	243.05	33.58
139.23	23.26	244.96	33.88
141.15	23.21	246.89	33.75
143.06	23.39	248.81	34.04
144.98	23.56	250.74	33.91

Table 5
The results of heat capacity measurements for sample 4

Temperature (K)	C_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	Temperature (K)	C_p ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
61.05	17.71	149.16	23.97
61.94	17.90	151.08	24.01
62.85	18.09	153.00	24.13
63.74	18.54	154.91	24.29
64.65	18.26	156.83	24.27
65.55	17.99	158.74	24.41
66.45	18.37	160.66	24.40
67.34	18.79	162.57	24.53
68.26	18.81	164.49	24.70
69.16	18.86	166.40	24.71
70.06	18.68	168.32	24.89
70.96	18.75	170.24	24.87
71.88	19.02	172.16	25.04
72.79	19.17	174.08	25.21
73.67	19.57	176.00	25.25
74.58	19.46	177.92	25.45
75.48	19.16	179.84	25.62
76.38	19.38	181.75	25.64
77.29	19.37	183.68	25.87
78.20	19.67	185.60	25.98
79.10	19.86	187.52	26.20
80.51	19.93	189.44	26.45
82.41	20.13	191.37	26.54
84.31	20.45	194.22	27.01
86.22	20.35	194.62	26.83
88.13	20.66	196.53	26.83
90.04	20.63	198.44	27.04
91.94	20.91	198.52	27.30
93.85	21.17	200.35	27.34
95.75	21.14	200.43	27.30
97.66	21.41	202.27	27.65
99.56	21.68	202.35	27.59
101.47	21.62	204.19	27.73
103.38	21.86	204.26	27.85
105.28	21.79	206.13	27.76
107.19	22.01	206.18	27.97
109.10	22.22	208.10	28.23
111.00	22.16	210.02	28.41
112.90	22.38	211.89	28.62
114.81	22.59	213.82	28.92
116.71	22.52	215.75	29.03
118.62	22.72	217.67	29.28
120.52	22.67	219.60	29.63
122.43	22.84	221.52	29.71
124.33	23.03	223.44	29.91
126.24	22.99	225.36	30.22
128.15	23.14	227.28	30.49
130.05	23.09	229.20	30.75
131.96	23.29	231.12	30.88
133.87	23.43	233.05	31.14
135.78	23.37	234.97	31.34
137.69	23.50	236.88	31.45
139.60	23.65	238.80	31.74
141.51	23.61	240.72	31.64
143.42	23.76	242.63	31.77
145.34	23.68	244.55	31.67
147.25	23.84	246.48	31.76

From the data on temperature dependence of heat capacity, the thermal part of enthalpy and Gibbs function were calculated (Table 6). The data were extrapolated up to 300 K.

The values of heat capacity listed in Tables 3–5 were averaged in 60–250 K region. The root-mean square deviation of the values was about 2% between 60 and 200 K and slightly higher between 200 and 250 K. The resulting curves $C_p(T)$ and $C_p(T)/T$ are shown in Figs. 2 and 3 respectively.

Abnormal character of dependence of C_p/T value in 45–65 K region can be observed in Fig. 3. In this region the values were corrected by polynomial regression fitting in order to obtain a smooth curve. Such a procedure gives less than 1% error to the standard entropy value.

Regarding the following reaction:

$$\mathrm{Cu} + 0.39\mathrm{H_2} \rightarrow \mathrm{CuH_{0.78}} \qquad (1)$$

one can calculate the entropy of formation of copper hydride as follows:

$$\Delta S_{\mathrm{form}} = S_{\mathrm{CuH_{0.78}}} - S_{\mathrm{Cu}} - 0.39 S_{\mathrm{H_2}} \qquad (2)$$

where $S_{\mathrm{CuH_{0.78}}} = 130.8\,\mathrm{J\,K^{-1}\,mol^{-1}}\,(\mathrm{H_2})$, $S_{\mathrm{Cu}} = 33.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $S_{\mathrm{H_2}} = 130.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$, and $\Delta S_{\mathrm{form}} = -85.1\,\mathrm{J\,K^{-1}\,mol^{-1}}\,(\mathrm{H_2})$.

In paper [7] the decomposition enthalpy value of CuH was obtained for temperature 398 K assuming full stoichiometry of copper hydride and was found to be $-27.5\,\mathrm{kJ\,mol^{-1}}$ (CuH) or $-55.1\,\mathrm{kJ\,mol^{-1}}$ ($\mathrm{H_2}$). The knowledge of temperature dependence of heat capacity gives the possibility to calculate the decomposition enthalpy, previously determined by direct calorimetric measurements, under the standard conditions, i.e. 298.15 K. Based on our data the value of $H^\circ(T) - H^\circ(0)$ was evaluated and standard enthalpy of decomposition of $\mathrm{CuH_{0.78}}$ was determined. Making use of the $H^\circ(T) - H^\circ(0)$ value for copper [14]

Table 6
Thermodynamic functions of copper hydride ($CuH_{0.78}$)

T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	$S°(T)$ ($J\,K^{-1}\,mol^{-1}$)	$H°(T) - H°(0)$ ($kJ\,mol^{-1}$)	$-[G°(T) - H°(0)]$ ($kJ\,mol^{-1}$)
0	0	0	0	0
5	0.0358	0.0298	0.0001	0.00005
10	0.3625	0.1214	0.0008	0.0004
15	1.354	0.4358	0.0049	0.0016
20	2.994	1.076	0.0162	0.0053
25	5.263	2.036	0.0380	0.0129
30	7.571	3.206	0.0703	0.0259
35	9.092	4.509	0.1126	0.0452
40	11.48	5.888	0.1644	0.0711
45	13.04	7.318	0.2252	0.1041
50	14.70	8.780	0.2946	0.1444
60	17.46	11.71	0.4562	0.2464
70	19.01	14.55	0.6406	0.3779
80	19.97	17.18	0.8372	0.5372
90	20.91	19.60	1.042	0.7220
100	21.77	21.85	1.256	0.9290
110	22.40	23.95	1.477	1.158
120	22.84	25.92	1.703	1.407
130	23.30	27.77	1.934	1.676
140	23.75	29.51	2.169	1.962
150	24.02	31.16	2.408	2.266
160	24.46	32.73	2.651	2.586
170	25.09	34.23	2.900	2.919
180	25.69	35.68	3.153	3.269
190	26.52	37.10	3.415	3.634
200	27.65	38.49	3.686	4.012
210	28.67	39.86	3.967	4.404
220	29.63	41.22	4.259	4.809
230	30.51	42.56	4.560	5.229
240	31.30	43.88	4.870	5.661
250	32.00	45.17	5.187	6.106
260	32.57	46.43	5.510	6.562
270	33.04	47.67	5.838	7.033
280	33.39	48.88	6.170	7.516
290	33.63	50.06	6.506	8.011
298.15	33.75	51.00	6.775	8.431
300	33.76	51.20	6.843	8.517

and $H°(T)$ for hydrogen [15] the decomposition enthalpy was calculated to be equal to $-55.1\,kJ\,mol^{-1}$ (H_2), indicating lack of the temperature dependence of enthalpy in this temperature region.

Using the equation

$$\frac{C_p(T)}{T} = \gamma + \frac{12\pi^4}{5} R \frac{T^2}{\Theta^3} \qquad (3)$$

where γ is the electronic heat capacity coefficient, R the gas constant, Θ the Debye temperature; the Debye temperature of copper hydride was determined by fitting procedure to the experimental data in 3–7 K temperature region (Fig. 4). This value is equal to $196 \pm 5\,K$. The electronic heat capacity coefficient is around $1.1\,mJ\,K^{-2}\,mol^{-1}$.

4. Discussion

With respect to the value of entropy of hydride formation ($\Delta S_{form} = -85.1\,J\,K^{-1}\,mol^{-1}$ (H_2)) copper hydride occupies a specific place among hydrides

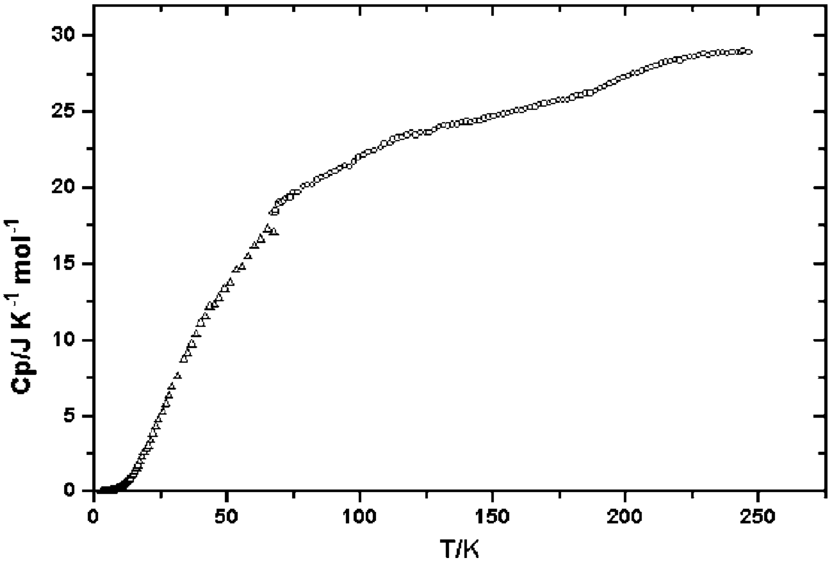

Fig. 2. Temperature dependence of heat capacity of copper hydride (triangles and circles correspond to two different measurement regions—see text).

family. For metallic hydrides the typical entropy of formation is about $-104.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (H_2) [16] and for saline hydrides is equal to about $-130\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (H_2) [16]. Copper hydride can be compared with the aluminium and magnesium hydrides assuming similar covalent bonding. But both of them show the value of entropy of formation similar to saline hydrides ($-130\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (H_2) [17] and

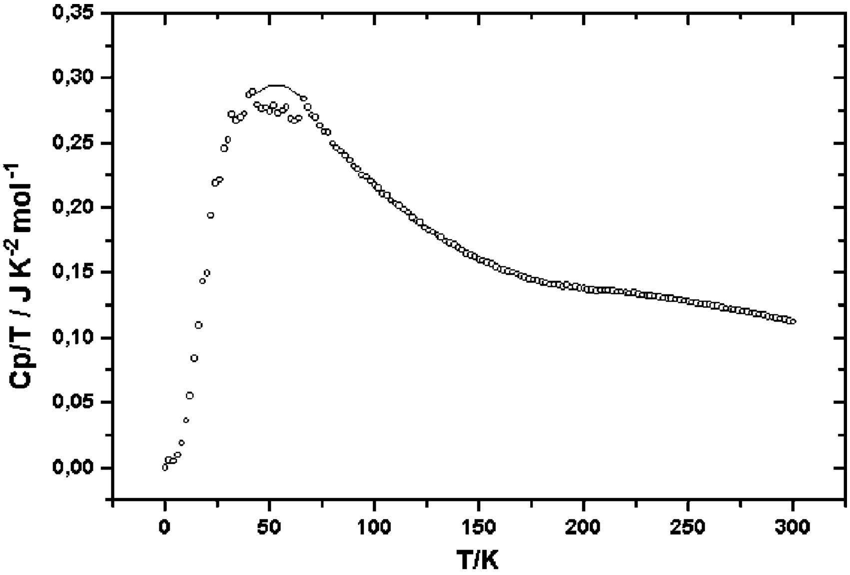

Fig. 3. Plot of C_p/T against temperature.

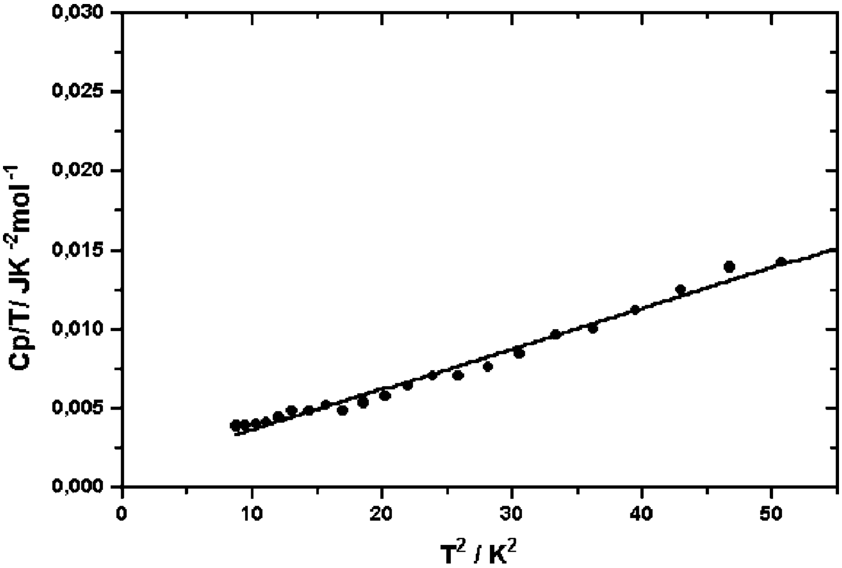

Fig. 4. Plot of C_p/T against T^2.

$-135\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (H_2) [16], respectively). In the light of the above-mentioned facts copper hydride with the formation entropy value $-85.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$ (H_2) cannot be classified to any of three groups of hydrides in respect to their entropies.

For reaction (1) assuming $\Delta H_{\mathrm{form}} = -\Delta H_{\mathrm{decomp}}$ and knowing the standard entropy of formation of copper hydride one can calculate the standard free energy of formation according to the equation

$$\Delta G_{\mathrm{form}} = \Delta H_{\mathrm{form}} - T\,\Delta S_{\mathrm{form}} \qquad (4)$$

It is equal to $80.5\,\mathrm{kJ\,mol^{-1}}$ (H_2). The knowledge of Gibbs energy gives us possibility to calculate the hydrogen pressure for equilibrium condition in copper–hydrogen system. The free energy of formation of $CuH_{0.78}$ can be written in terms of chemical potential of hydrogen and volume changes during transition from copper to copper hydride in form

$$\Delta G_{\mathrm{form}} = 0.39\,RT\ln f - \int_{p_0}^{p} (V_{\mathrm{CuH}} - V_{\mathrm{Cu}})\,\mathrm{d}p \qquad (5)$$

According to the well-known relation between hydrogen pressure and fugacity and data on pressure dependence of volume for copper [18] and copper hydride [19] the equilibrium hydrogen pressure was found to be 31 GPa. The decomposition pressure for copper–hydrogen system was recently determined experimentally in diamond anvil cell as equal to 8.4 GPa [20]. It is much lower than the pressure calculated from the calorimetric data. The possible reason of obtaining so high value is the great value of Gibbs free energy and its enthalpy component in particular. Due to the unusual stability of copper hydride one can expect that the value of enthalpy of decomposition involves not only the energetic effect of breaking copper–hydrogen bonding but also additional effects that are responsible for the stabilisation of CuH. Therefore the real value of enthalpy may be lower than the measured one, resulting in a lower equilibrium pressure calculated.

As for the Debye temperature, the value obtained in this work is lower than that for pure copper [14]. Such a behaviour is observed in some metal hydrides, and the lower stability of the hydride results in a lower Debye temperature [21]. The same tendency follows from the Madelung relationship since the bulk modulus for copper hydride is significantly lower than that for pure copper [19].

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