Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 833–839

LOW TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS OF $LiCoO_2$

H. Kawaji[1*], *M. Takematsu*[1], *T. Tojo*[1], *T. Atake*[1], *A. Hirano*[2] *and R. Kanno*[3]

[1]Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8503 Japan
[2]Department of Chemistry for Materials, Faculty of Engineering, Mie University, Tsu, 514-8507 Japan
[3]Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8502 Japan

(Received June 6, 2001; in revised form January 22, 2002)

Abstract

The sample of $LiCoO_2$ was synthesized, and the heat capacity was measured by adiabatic calorimetry between 13 and 300 K. The smoothed values of the heat capacity were calculated from the data. The thermodynamic functions, standard enthalpy, entropy and Gibbs energy, of $LiCoO_2$ were calculated from the heat capacity and the numerical values are tabulated at selected temperatures from 15 to 300 K. The heat capacity, enthalpy, entropy, and Gibbs energy at T=298.15 K are 71.57 J K^{-1} mol^{-1}, 9.853 kJ mol^{-1}, 52.45 J K^{-1} mol^{-1}, –5.786 kJ mol^{-1}, respectively.

Keywords: heat capacity, $LiCoO_2$, thermodynamic functions

Introduction

The ternary oxide $LiCoO_2$ is one of the most promising materials for use in lithium-ion rechargeable batteries. In fact, it has been widely used as insertion electrodes in 4 volt rechargeable lithium ion battery [1, 2]. Therefore, the properties of $LiCoO_2$ have been studied extensively by electrochemical experiments [1, 4], X-ray diffraction [3], Li NMR [5, 6], and so on. The crystal has a layered structure composed of alternate layers of Li ions and of two dimensional CoO_6 octahedrals, making up a rhombohedral structure of $R\bar{3}m$ space group [3]. The cobalt ion is in low spin state (S=0) in the crystal, and $LiCoO_2$ shows no remarkable magnetic properties. Although the thermodynamic data are required for evaluating the chemical and thermal behav-

---

[*] Author for correspondence: Tel.: (81)-45-924-5313; Fax: (81)-45-924-5339; E-mail:kawaji@thermo.rlem.titech.ac.jp

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ior of the material, no precise heat capacity data of $LiCoO_2$ have been published so far. In the present study, the precise heat capacity measurements were made by adiabatic calorimetry between 13 and 300 K for $LiCoO_2$ crystals, and the thermodynamic functions, standard enthalpy, entropy and Gibbs energy, were determined.

Experimental

The sample of $LiCoO_2$ was synthesized by a solid state reaction method. The powders of Li_2CO_3 and CoO were weighed in the stoichiometric ratio and mixed in an agate mortar, and then the mixture was heated at 800°C for 48 h in flowing high purity oxygen gas. After that, the sample was slowly cooled down to room temperature in the furnace. The obtained sample was identified with $LiCoO_2$ by powder X-ray diffraction. The powder X-ray diffraction patterns showed that the sample was free from impurities.

For the heat capacity measurements, powdered sample of 4.6629 g (0.04764 mol) was loaded into the calorimeter vessel (gold-plated copper), which was evacuated and then sealed after adding a small amount of helium (5 kPa at room temperature) for the purpose of thermal uniformity within the calorimeter vessel. The heat capacity measurements were carried out using a home-made adiabatic calorimeter between 13 and 300 K. The temperature was measured with an iron–rhodium resistance thermometer (Tinsley, 5187U) calibrated at NPL (UK) below 27.1 K and Oxford Instruments Ltd. above 27.1 K on the basis of the international temperature scale (ITS-90). The adiabatic control system gave the temperature stability of the calorimeter vessel within 0.00001 K min^{-1}. The performance of the calorimeter had been confirmed by measuring the standard reference material SRM 720 (synthetic sapphire) provided by NIST (USA), which gave about the accuracy of the heat capacity value of 0.1% at 100 K. The precision of the data was better than 0.05%. The heat capacity of the present sample was obtained by subtracting that of the calorimeter vessel from the total heat capacity. The contribution of the sample to the total heat capacity including that

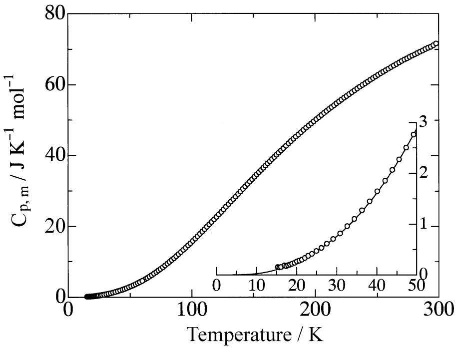

Fig. 1 Measured molar heat capacity of $LiCoO_2$. The inset shows the low-temperature data on an expanded scale. Solid line shows the fit of the data to the equation described in text

of the calorimeter vessel was about 5, 14 and 32% at 20, 100 and 300 K, respectively. The details of the method of the measurements were described elsewhere [7, 8].

Results and discussion

The measured molar heat capacity without curvature corrections is plotted in Fig. 1, and the numerical results are given in Table 1.

Table 1 Measure molar heat capacity $C_{p,m}$ of $LiCoO_2$

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}
Series 1		125.86	24.77	198.86	49.64
56.84	3.982	127.81	25.50	200.96	50.25
58.59	4.295	129.79	26.22	203.05	50.84
60.38	4.633	131.76	26.95	205.13	51.43
62.22	4.996	133.70	27.66	207.19	52.03
64.02	5.376	135.65	28.37	209.24	52.57
65.78	5.748	137.62	29.10	211.28	53.14
67.61	6.157	139.57	29.82	213.31	53.69
69.48	6.592	141.50	30.52	215.33	54.21
71.36	7.045	143.40	31.22	217.34	54.76
73.10	7.476	145.29	31.91	219.34	55.28
74.79	7.905	147.16	32.58	221.37	55.79
76.61	8.379	149.01	33.25	223.43	56.32
78.45	8.879	150.85	33.92	225.49	56.81
80.30	9.388	152.67	34.57	227.60	57.33
82.10	9.900	154.47	35.22	229.77	57.87
83.88	10.41	156.26	35.86	231.93	58.38
85.70	10.93	158.04	36.47	234.09	58.91
87.53	11.50	159.80	37.08	236.23	59.42
89.39	12.08	161.54	37.71	238.36	59.91
91.30	12.67	163.28	38.30	240.48	60.39
93.23	13.28	165.05	38.93	242.60	60.88
95.18	13.91	166.86	39.54	244.70	61.37
97.10	14.54	168.65	40.15	246.79	61.83
99.02	15.18	170.43	40.75	248.88	62.30
100.96	15.83	172.30	41.37	250.95	62.76

Table 1 Continued

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}
102.90	16.51	174.30	42.02	253.02	63.20
104.82	17.18	176.36	42.69	255.08	63.64
106.73	17.84	178.40	43.37	257.13	64.07
108.61	18.50	180.42	44.01	259.25	64.48
110.49	19.17	182.43	44.65	261.43	64.95
112.37	19.85	184.43	45.27	263.61	65.40
114.26	20.53	186.47	45.91	265.77	65.83
116.16	21.20	188.56	46.56	267.93	66.25
118.10	21.92	190.64	47.18	270.08	66.67
120.08	22.65	192.70	47.80	272.23	67.08
122.03	23.36	194.75	48.43	274.36	67.44
123.96	24.08	196.79	49.02	276.49	67.82
278.61	68.19	17.46	0.1704	34.42	1.101
280.72	68.54	17.92	0.1885	36.34	1.271
282.83	68.93	18.41	0.1995	38.24	1.446
284.98	69.29	18.94	0.2163	40.16	1.641
287.17	69.64	19.52	0.2346	42.12	1.850
289.35	70.04	20.12	0.2604	43.92	2.062
291.52	70.40	20.73	0.2777	45.60	2.269
293.68	70.70	21.38	0.2960	47.39	2.501
295.84	71.11	22.11	0.3321	49.27	2.758
297.99	71.62	22.93	0.3715	51.08	3.028
Series 2		23.87	0.4115	52.84	3.301
14.53	0.1447	24.98	0.4677	54.55	3.581
14.94	0.1434	26.23	0.5284	56.28	3.876
15.34	0.1500	27.59	0.6114	58.05	4.192
15.75	0.1477	29.15	0.7058	59.93	4.542
16.17	0.1519	30.90	0.8142		
17.01	0.1834	32.65	0.9588		

The temperature increment of each measurement is about 2 K. No abnormal relaxation or hysteresis phenomenon was observed during the experiments. After each heat input was over, thermal equilibrium of the whole calorimeter vessel including the sample was attained in a few minutes below 20 K and about 10 min above 100 K.

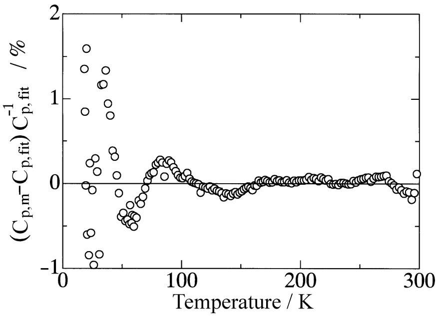

Fig. 2 Deviation plots of the measured heat capacity from the equation

In order to calculate the smoothed heat capacity and thermodynamic function, the following equations were used:

$$C_{V,\,fit}=3RD(\Theta_D/T)+xRE_1(\Theta_{E1}/T)+(9-x)RE_2(\Theta_{E2}/T)+yRE_3(\Theta_{E3}/T)$$
$$C_{p,\,fit}=C_{V,\,fit}+AC_{V,\,fit}^2T$$

where R, $D(\Theta_D/T)$ and $E(\Theta_E/T)$ are gas constant, Debye function and Einstein function, respectively. Debye term with $3N_A$ degrees of freedom corresponds to the heat capacity contribution from acoustic like lattice vibration modes, and the Einstein terms $E_1(\Theta_{E1}/T)$, $E_2(\Theta_{E2}/T)$, and $E_3(\Theta_{E3}/T)$ are the contribution from the other modes. $AC_{v,m}^2T$ term constitutes an approximation to $C_{p,m}-C_{V,m}$ correction similar to Nernst–Lindemann relation ($C_{p,m}-C_{V,m}=AC_{p,m}^2T$). The coefficients were determined by the least square method. The obtained coefficients for the equation are given in Table 2. The fitting value of the total degrees of freedom for Debye and Einstein functions, that is $12+y=12.044192$, exceeds the theoretical value 12. This may be caused by using the simplified model to express the real complex lattice vibration spectrum of LiCoO$_2$. Figure 2 shows the deviation plots of the measured heat capacity from the smoothed values. The standard thermodynamic functions calculated from the equation are given in Table 3.

Table 2 Coefficients determined by fitting the measured heat capacity to the equation given in the text

Parameters	Coefficients
Θ_D/K	447.748
x	6.67334
Θ_{E1}/K	625.450
Θ_{E2}/K	997.015
y	0.044192
Θ_{E3}/K	92.5083
A/mol J^{-1}	$11.8076\cdot10^{-7}$

Table 3 Thermodynamic functions of $LiCoO_2$. $C^{\circ}_{p,m}$: standard molar heat capacity, $\Delta^{T}_{\circ}H^{\circ}_{m}$:the standard molar enthalpy, $\Delta^{T}_{\circ}S^{\circ}_{m}$:the standard molar entropy, $\phi^{\circ}_{m}=\Delta^{T}_{\circ}S^{\circ}_{m}-\Delta^{T}_{\circ}H^{\circ}_{m}/T$

T/K	$C^{0}_{p,m}$/J K^{-1} mol^{-1}	$\Delta^{T}_{0}H^{0}_{m}$/J mol^{-1}	$\Delta^{T}_{0}S^{0}_{m}$/J K^{-1} mol^{-1}	Φ^{0}_{m}JK^{-1} mol^{-1}
15	0.1025	0.3455	0.0299	0.0069
20	0.2518	1.203	0.0782	0.0181
30	0.7599	6.016	0.2665	0.0659
40	1.611	17.55	0.5923	0.1537
50	2.876	39.62	1.080	0.2873
60	4.578	76.53	1.748	0.4724
70	6.718	132.6	2.609	0.7138
80	9.283	212.3	3.669	1.015
90	12.23	319.6	4.929	1.378
100	15.50	458.0	6.384	1.804
110	18.99	630.3	8.024	2.294
120	22.63	838.4	9.832	2.845
130	26.32	1083	11.79	3.457
140	30.01	1365	13.87	4.126
150	33.64	1683	16.07	4.849
160	37.18	2037	18.35	5.621
170	40.59	2426	20.71	6.439
180	43.86	2849	23.13	7.299
190	46.98	3303	25.58	8.196
200	49.95	3788	28.07	9.127
210	52.76	4302	30.57	10.09
220	55.42	4843	33.09	11.08
230	57.92	5409	35.61	12.09
240	60.29	6001	38.12	13.12
250	62.52	6615	40.63	14.17
260	64.62	7251	43.12	15.24
270	66.59	7907	45.60	16.32
280	68.46	8582	48.06	17.41
290	70.21	9275	50.49	18.50
298.15	71.57	9853	52.45	19.41
300	71.87	9986	52.90	19.61

The heat capacity is smaller than that of Dulong–Petit classical limit value of 100 J K^{-1} mol^{-1} even at room temperature. Debye characteristic temperature calculated from the heat capacity assuming $12N_A$ degrees of freedom is shown in Fig. 3.

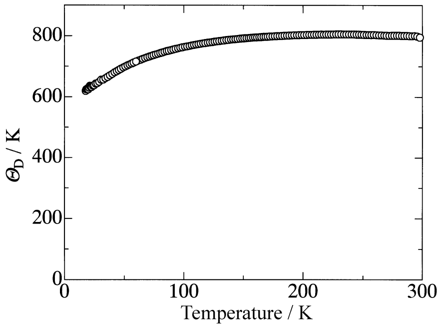

Fig. 3 Debye characteristic temperature calculated from the measured heat capacity of $LiCoO_2$ assuming $12N_A$ degrees of freedom

Debye characteristic temperature decreases rapidly with decreasing the temperature below about 150 K. This indicates that the heat capacity below about 100 K is larger than that expected from Debye model. $LiCoO_2$ has an anisotropic layer crystal structure [3], and Li ions can migrate in the 2-dimensional layer even at room temperature. Such a large heat capacity at low temperatures, thus, may be caused by the 2-dimensional layer structure of $LiCoO_2$. It is worth comparing the present data with the heat capacity of $LiNiO_2$, which has the same crystal structure, and it will be discussed elsewhere [9].

* * *

A part of this study was supported by Grant-in-Aid for Scientific Research on Priority Areas (B)(No. 740) 'Fundamental Studies for Fabrication of All Solid State Ionics Devices' from Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

1 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, Mat. Res. Bull., 15 (1980) 783.
2 K. Ozawa, Solid State Ionics, 69 (1994) 212.
3 W. D. Jonston, R. R. Heikes and D. Sestrich, J. Phys. Chem. Solids, 7 (1958) 1.
4 T. Ohzuku, A. Ueda and M. Nagayama, J. Electrochem. Soc., 140 (1993) 1862.
5 B. Garcia, P. Barboux, F. Ribot, A. Kahn-Harai, L. Mazerolles and N. Baffier, Solid State Ionics, 80 (1995) 111.
6 M. P. J. Peeters, M. J. van Bommel, P. M. C. Neilen-ten Wolde, H. A. M. van Hal, W. C. Keur and A. P. M. Kentgens, Solid State Ionics, 112 (1998) 41.
7 T. Atake, H. Kawaji, A. Hamano and Y. Saito, Rep. Res. Lab. Eng. Mater., Tokyo Inst. Technol., 15 (1990) 13.
8 T. Tanaka, T. Atake, H. Nakayama, T. Eguchi and K. Saito I. Ikemoto, J. Chem. Thermodyn., 26 (1994) 1231.
9 H. Kawaji, T. Oka, T. Tojo, T. Atake, A Hirano and R. Kanno, to be published.