Investigation of Thermal Stability of $LiCoO_2$ and $Li_{1-x}CoO_2$

DINA G. KELLERMAN, VERA V. KARELINA, VADIM S. GORSHKOV and YAKOV N. BLINOVSKOV

Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences,
Ul. Pervomayskaya 91, Ekaterinburg 620219 (Russia)

E-mail: kellerman@ihim.uran.ru

Abstract

Processes that occur during the heating of the stoichiometric and defect lithium cobaltite are investigated. This compound is usually considered as one of the most promising cathode materials for secondary lithium batteries. Analysis of thermal stability of chemically deintercalated $Li_{1-x}CoO_2$ showed that lithium cobaltite phases which are deficient with respect to lithium sublattice, obtained by chemical deintercalation of $LiCoO_2$, are thermally unstable and decompose forming stoichiometric $LiCoO_2$ and Co_3O_4 under heating. The process is accompanied by the evolution of oxygen. The results of investigations into the magnetic properties of cobaltites with various types of defects are reported.

INTRODUCTION

Layered compounds $LiMeO_2$, in which Me is a $3d$ transition metal, are considered as functional materials of new generation [1] because of the possibility to use them as positive electrodes for secondary lithium batteries [2, 3] to feed modern electronic devices. Most of all this relates to $LiCoO_2$, which combines high energy characteristics with the stability of crystal structure within a broad range of lithium concentrations. Secondary lithium batteries are mainly used in personal computers, mobile phones, *etc*. Such an application area explains strict requirements for the safety of the devices [4], so the problems of thermal stability of both the whole system and its parts receive a definite attention [5]. The present work deals with the investigation of processes which take part on heating the stoichiometric and defect-bearing lithium cobaltite.

SYNTHESIS AND INVESTIGATION PROCEDURES

High-temperature modification $HT-LiCoO_2$ was obtained by means of agglomeration of a mixture of Co_3O_4 and Li_2CO_3 in the air at the temperature of 850 °C for 25 h, followed by slow cooling. According to the X-ray data, $LiCoO_2$ has hexagonal structure with unit cell parameters $a = 2.813$ Å, $c = 13.973$ Å. The samples with oxygen non-stoichiometry were obtained by additional annealing of the initial cobaltite in helium atmosphere with fixed partial pressure of oxygen (log $p_{O_2} > -3.8$). The annealing temperature was 750 °C. X-ray phase analysis demonstrated that after the mentioned treatment all the samples were still exclusively composed of $LiCoO_{2-\delta}$.

Non-stoichiometric cobaltites $Li_{1-x}CoO_2$ were obtained by two methods: 1. By passing dry gaseous chlorine through $LiCoO_2$ prepared as a suspension in acetonitrile. 2. By treating the initial cobaltite in diluted H_2SO_4 solution. The initial $LiCoO_2$ was also taken in the high-temperature thermodynamically stable form (HT) with layered structure, and in the form of cubic spinel (LT) synthesized at 400 °C from a mixture of lithium and cobalt acetates.

Magnetic susceptibility within the temperature range 300–1000 K was measured using Faraday's procedure in a field up to 10 kOe and within the temperature range 4–300 K with SQUID Quantum Design magnetometer at 1000 Oe. Magnetization curves were recorded at the temperature of 4 K in a field up to 60 kOe.

Thermogravimetric curves were recorded with MOM thermoanalyzer within the temperature range 300–1200 K with heating rate of 5 K/min.

FORMATION OF OXYGEN DEFECTS IN LiCoO₂ ON HEATING

Investigations of thermal stability of the high-temperature modification of $LiCoO_2$ show that this phase is stable till ~1200 K. Above this point, cobaltite starts to decompose evolving oxygen and forming Co_3O_4 [6]. The fact that the stability limit depends on the partial pressure of oxygen is confirmed by the data shown in Fig. 1, which is the dependence of specific electric conductance s of $LiCoO_2$, measured at different temperatures, on p_{O_2}. A feature of this dependence is a sharp change in electric parameters when the oxygen partial pressure decreases below a definite value, which is an indication of the formation of the second phase (Co_3O_4) in the system [7]. At the temperature of 920 K, the critical value is p_{O_2} ~ 10^{-3} atm, while at p_{O_2} ~ 10^{-1} atm the system remains single-phase at 1170 K.

It is essential that in the single-phase region (T < 1200 K), too, definite changes take place in $LiCoO_2$, while mass loss is detected at lower temperature than that suggested by [6], but the mass loss is reversible and is the evidence
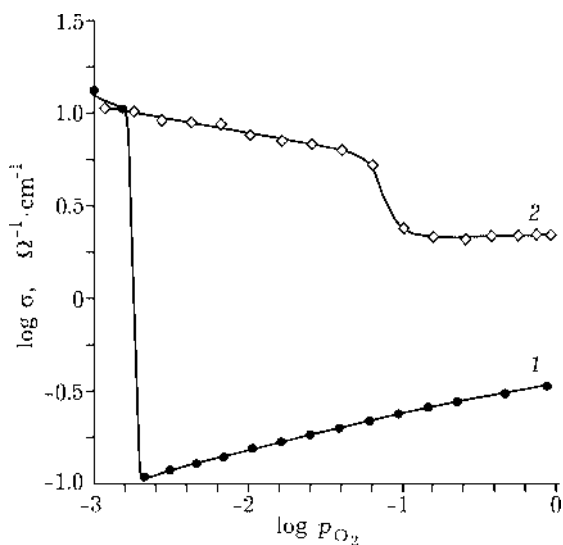

Fig. 1. Dependence of specific electric conductivity of $LiCoO_2$ on the partial pressure of oxygen. Temperature, K: 920 (*1*), 1170 (*2*).
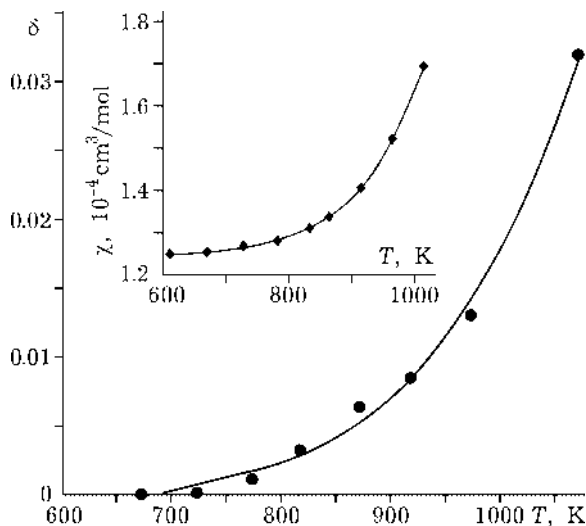

Fig. 2. Changes in non-stoichiometry of $LiCoO_{2-\delta}$ depending on the sample annealing temperature. The temperature dependence of magnetic susceptibility of $LiCoO_2$ is shown in the insertion.

of the formation of defects in the oxygen sublattice of $LiCoO_{2-\delta}$. The change in δ depending on sample annealing temperature is shown in Fig. 2. The temperature dependence of magnetic susceptibility of $LiCoO_2$, measured within the same temperature range as the previous measurements, is shown in the insertion. The behaviour of this curve is almost similar to the behaviour of the thermogravimetric curve. The reproducibility of results after multiple repeated cycling is the evidence of the reversible character of the process, which is depicted by Fig. 2.

Trivalent cobalt is known to be in the low-spin state in $LiCoO_2$ $(t_{2g}\uparrow)^3(t_{2g}\downarrow)^3(e_g)^0$, its magnetic moment is zero [8], therefore, magnetic susceptibility of the stoichiometric $LiCoO_2$ should be independent of temperature. However, the behaviour of its temperature dependence is the evidence that paramagnetic centres arise in $LiCoO_2$ when temperature rises. Divalent cobalt ions $(t_{2g}\uparrow)^3(t_{2g}\downarrow)^2(e_g)^2$ are likely to be these centres; they are formed as a result of partial reduction of $LiCoO_2$ according to the reaction $LiCoO_2 = LiCoO_{2-\delta} + \delta/2O_2$.

The temperature dependence of magnetic susceptibility is described by the modified Curie – Weiss law which takes into account the exponential change in the number of paramagnetic centres of Co_{Co}^I type in $LiCoO_{2-\delta}$:

$$\chi = A_0 + \frac{0.125 A_1 g^2 \mu_0^2 e^{-\frac{A_2}{T}}}{T} \qquad (1)$$

where A_0 is the temperature-independent para-magnetism; $A_1 = e^{\Delta S/k}$; $A_2 = \Delta H/k$. Entropy $\Delta S_{def} = 60.5$ J/(mol K) and enthalpy $\Delta H_{def} = 93.1$ kJ/mol of the process of defect formation were obtained from the analysis of the magnetic susceptibility data [9]. So, it may be concluded on the basis of the mentioned data that at elevated temperature the major defects in LiCoO₂ are Co²⁺ ions (Co_{Co}^{I}) and oxygen vacancies ($V_O^{\bullet\bullet}$). Temperature point above which the exchange with the gas phase becomes possible that leads to defect formation process (see Fig. 2) is ≈700 K.

In order to investigate the nature of defects in non-stoichiometric LiCoO₂₋δ, we used partially reduced samples obtained by annealing in the medium with decreased oxygen partial pressure. The data presented below demonstrate how the formation of defects affected the unit cell parameters:

log p_{O_2}	a, Å	c, Å
−1.85	2.8147(2)	14.039(3)
−2.8	2.8153(2)	14.047(2)
−3.8	2.8159(2)	14.049(2)

As a result of the performed electrochemical investigations, it was discovered that the capacitance losses decrease with cycling the samples [10]; some changes in photoelectron spectra were observed [11].

The annealing of LiCoO₂ in the atmosphere with reduced oxygen partial pressure is accompanied by the formation of oxygen vacancies; a definite part of them is conserved even after the sample is quenched. It is these vacancies that provide the paramagnetic contribution into the magnetic susceptibility of the partly reduced cobaltite shown in Fig. 3 (log p_{O_2} = −2.8). In the same Figure, for comparison, the data for the stoichiometric LiCoO₂ are presented. One can see that at low temperature magnetic susceptibility of the stoichiometric LiCoO₂ is almost independent of temperature, while for LiCoO₂₋δ its changes follow Curie − Weiss law:

$$\chi = A_0 + C/(T - \Theta) \qquad (2)$$

where A_0 is the temperature-independent part that includes the diamagnetic constituent and Van Vleck's paramagnetism; C is the Curie constant, Θ is the Weiss constant. The following parameters have been determined from the
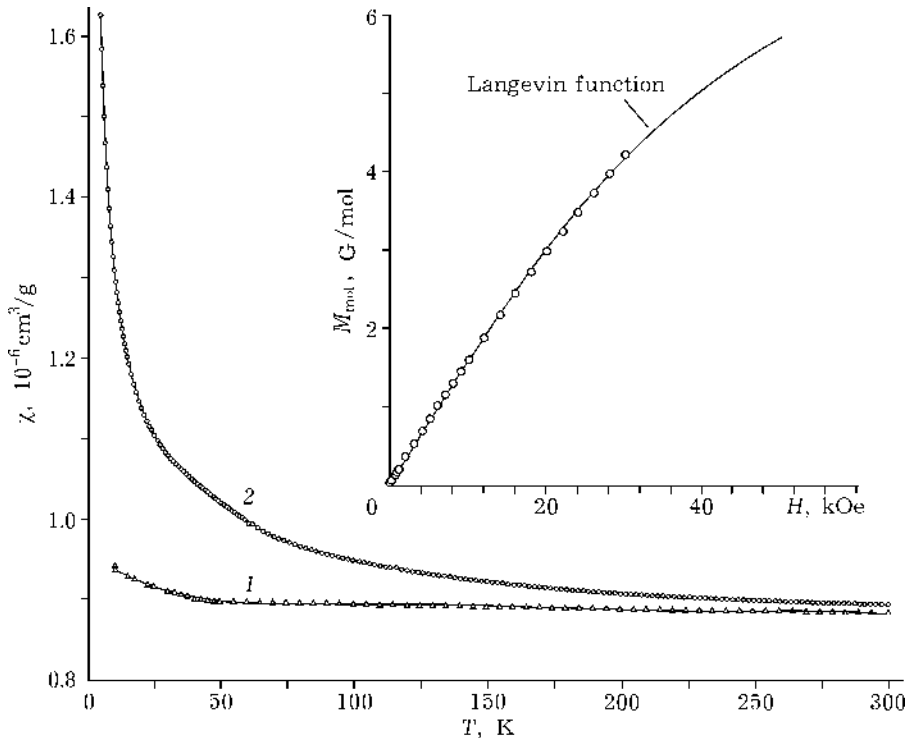

Fig. 3. Polyterms of magnetic susceptibility for LiCoO₂ (1) and LiCoO₂₋δ (2). Magnetization curve for LiCoO₂₋δ is shown in the insertion.

experimental dependence of magnetic susceptibility: $A_0 = 0.862 \cdot 10^{-4}$ cm³/mol, $C = 0.656 \cdot 10^{-3}$ cm³ K/mol, $\Theta = -5.5$ K.

Since Curie constant is connected with the concentration of paramagnetic centres n and magnetic moment μ per such a centre by the equation $C = N_A \mu_B^2 \mu^2 n /(3K)$ (N_A is the Avogadro number, μ_B is the Boron magneton, K is the Boltzmann constant) one cannot unambiguously determine the concentration of defects without knowing the spin state of Co²⁺ ions. If we assume that Co²⁺ is in high-spin state, then, $n = 0.04$ %; for the low-spin state, $n = 0.18$ %. The spin state of Co²⁺ ions was determined from the analysis of magnetization curve (see Fig. 3) obtained at 4 K. Non-linear dependence of magnetization on field *M(H)* depicts saturation at low temperature and high field strength, and can be well described by Langevin function:

$$M = N_A \mu_B \mu n L(x) \qquad (3)$$

where $x = \mu_B \mu H/(k_B T)$, and $L(x) = \text{cth}(x) - 1/x$.

The analysis of *M(H)* dependence allows separate determination of magnetic moment and concentration of paramagnetic centres. Thus, it was determined that the number of paramagnetic centres with the magnetic moment μ = 3.22μ_B per one formula unit of LiCoO₂ ₋ δ is $n = 0.0005$. This corresponds to high-spin state of Co²⁺ $(t_{2g}\uparrow)^3 (t_{2g}\downarrow)^2 (e_g)^2$ with three unpaired electrons. So, the concentration of metal defects in LiCoO₂ ₋ δ after annealing LiCoO₂ in the atmosphere with log $p_{O_2} = -2.8$ at 750 K is 0.05 %, which is close to the value obtained from the analysis of temperature dependence of magnetic susceptibility. Such a number of paramagnetic centres corresponds to δ = 0.00025.

THERMAL STABILITY OF Li₁ ₋ ₓCoO₂

While the stoichiometric lithium cobaltite remains stable till high temperature, thermal stability of Li₁ ₋ ₓCoO₂ with different deintercalation degrees is limited by the temperature of ~450 K. In Fig. 4 presenting the data for Li₀.₉₂CoO₂ one can see that at temperature rise above the room temperature, magnetic susceptibility undergoes substantial changes. A

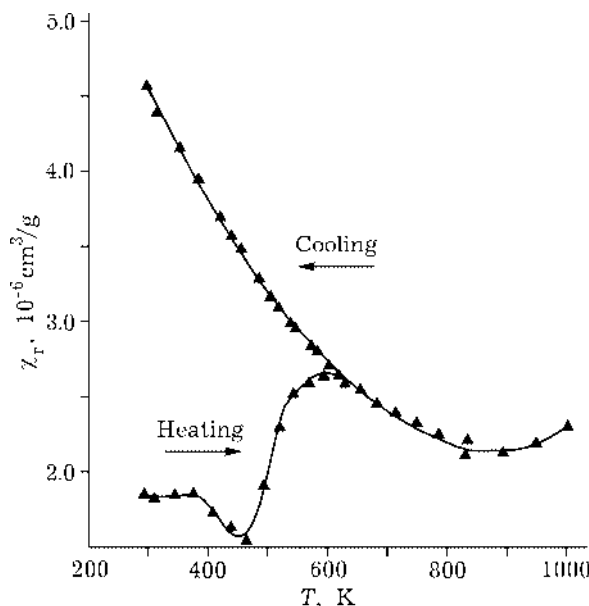Fig. 4. Changes in magnetic susceptibility during thermal decomposition of Li₀.₉₂CoO₂.

weak temperature dependence changes at first for a decrease, then for a sharp increase; at $T \sim 600$ K, a slow decrease starts again. Subsequent cooling causes an increase in magnetic susceptibility according to hyperbolic law, which stays unchanged also in repeated cycles of heating and cooling. Such a behaviour of Li₁ ₋ ₓCoO₂ is an evidence of thermal instability of deintercalated cobaltites. Really, X-ray phase analysis of the sample subjected to heating during the measurement of magnetic susceptibility revealed the presence of trace amount of Co₃O₄. It is the formation of Co₃O₄, with Co²⁺ ions containing unpaired electrons and thus possessing substantial magnetic moment, which causes an increase in magnetic susceptibility. The results of X-ray analysis of thermally treated samples point to the fact that the main phase does not undergo structural transformation and remains hexagonal.

It may be assumed that the decomposition of lithium cobaltite Li₁ ₋ ₓCoO₂ which is non-stoichiometric with respect to lithium sublattice occurs according to the reaction

$$\text{Li}_{1-x}\text{CoO}_2 \rightarrow (1-x)\text{LiCoO}_2 + x/3\text{Co}_3\text{O}_4$$
$$+ x/3\text{O}_2\uparrow$$
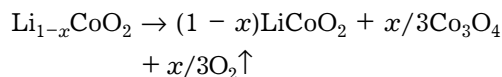
It follows from this fact that the transition of Li₁ ₋ ₓCoO₂ into the stable form should be accompanied by the evolution of oxygen. To
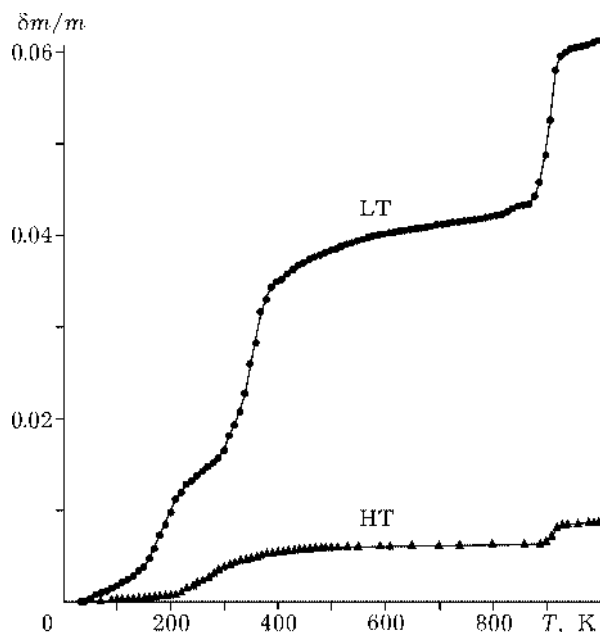
Fig. 5. Thermal curves for Li$_{1-x}$CoO$_2$ obtained by chemical deintercalation of HT- and LT-LiCoO$_2$ (0.4 M H$_2$SO$_4$, 40 min).

verify this assumption, we obtained thermogravimetric curves; their analysis is an evidence of mass loss within the range 500–750 K, coinciding with the region of a sharp change in magnetic susceptibility. The evolution of oxygen, detected by means of thermogravimetry, and the formation of Co$_3$O$_4$, which is well detected by the magnetic data, depict the extent of chemical deintercalation of lithium from LiCoO$_2$. This process occurs to a substantially higher extent in the low-temperature cubic phase than in the stable hexagonal one (Fig. 5). Mass loss at 1100 K is the evidence of the reduction of the formed Co$_3$O$_4$ to CoO.

The information on the nature of defects in the cobaltites which are non-stoichiometric with respect to lithium can be obtained from the examination of their magnetic properties. One can see in Fig. 6, *a* that the magnetic susceptibility of Li$_{1-x}$CoO$_2$ increases sharply with temperature decrease; its behaviour is well described by Curie – Weiss law (2). It is natural to assume that the paramagnetic centres in lithium-non-stoichiometric cobaltites are Co^{4+} ions, their formation being connected with charge compensation processes. Magnetic moments calculated for Li$_{1-x}$CoO$_2$ samples are close to each other and are ≈0.9μ$_B$. This value is

somewhat lower than those reported in [12] (1.157μ$_B$ for LiCoO$_2$, and 1.164μ$_B$ for Li$_{0.92}$CoO$_2$). Larger magnetic moments obtained in the cited work can be caused by small admixtures or by oxygen non-stoichiometry, which is mentioned by the authors of [12] themselves. For the Co^{4+} ion, three spin states are possible: $(t_{2g})^3(e_g)^2$, $(t_{2g})^4(e_g)^1$ and $(t_{2g})^5(e_g)^0$. The version of low-spin state with $S = 1/2$ in the case under consideration seems to be more probable because the former two states are characterized by larger magnetic moments; however, in this case, too, the obtained values are too small. Using the magnetic moment values calculated from susceptibility polyterms, we plotted theoretical dependencies of magnetization on field. In Fig. 6, *b* one can see the *M(H)* dependence for Li$_{0.92}$CoO$_2$ calculated both with the help of classical Langevin eq. (3) and with the help of Brillouin function:

$$M = N_A J g \mu_B n B(x) \qquad (4)$$

where $x = gJ\mu_B H/(k_B T)$,

$B(x) = (2J + 1)/2J \, \mathrm{cth}((2I + 1)x/2J)$

    $- 1/2J \, \mathrm{cth}(x/2J)$

A distinguishing feature of these dependencies is their non-linearity at large external field strength, which is an evidence of saturation. Experimental dependencies *M(H)* meas-
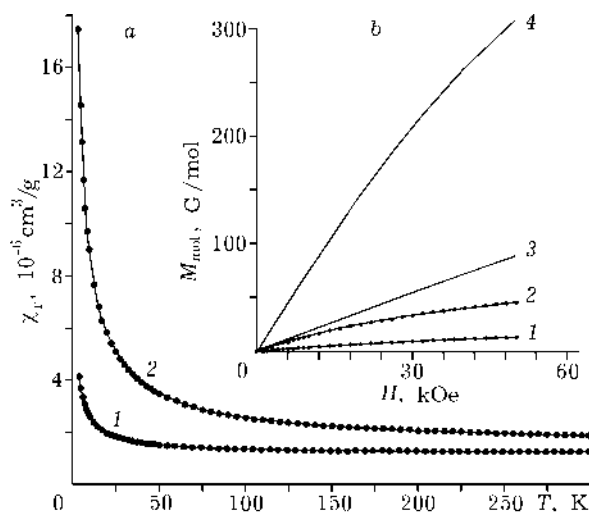

Fig. 6. Polyterms of magnetic susceptibility (*a*) and magnetization curves (*b*) for Li$_{1-x}$CoO$_2$. The *x* values: 0.02 (*1*), 0.08 (*2*); *3, 4* – Langevin functions (*n* = 0.08, μ = 0.85μ$_B$) and Brillouin functions (*n* = 0.08, *J* = 1/2), respectively.

ured for $Li_{0.98}CoO_2$ and $Li_{0.92}CoO_2$ at the temperature of 4 K are non-linear, too; one can see that both the magnetization level and the curvature of *M(H)* dependence correlate with the defects content. However, experimental results differ substantially from both theoretical dependencies. In our opinion, additional experiments are to be performed in order to explain the discovered discrepancies; however, it can be assumed that these discrepancies are due to the fact that the electron structure and spin state of the defects which are paramagnetic centres do not remain unchanged during magnetization. One more circumstance should be stressed: a method of charge compensation occurring during lithium deintercalation can differ from that discussed above. The examination of chemically deintercalated $LiCoO_2$ by means of X-ray absorption spectroscopy performed recently by the authors of [13, 14] showed that after the removal of lithium not the electron state of cobalt is changed ($Co^{3+} \rightarrow Co^{4+}$) but partial oxidation of oxygen ions occurs ($O^{2-} \rightarrow O^-$). The charge compensation processes leading to the formation of a hole in the oxygen band are similar to those observed in HTSC [15]. In this case, paramagnetic centres which provide the observed behaviour of magnetic susceptibility polyterms are either defects like $O_O^{\cdot}$ or some complexes containing these defects. The possibility of such a situation was discussed in [16], where, on the basis of investigation of the X-ray absorption spectra of $Li_xNi_{1-x}O$, a hypothesis was put forward that the magnetic properties of $LiNiO_2$ are determined by exchange-bound pairs ($Ni^{2+}-O^-$).

CONCLUSIONS

The analysis of the stability of $Li_xNi_{1-x}O$ phase shows that the cobaltite deficient with respect to lithium sublattice, obtained as a result of chemical deintercalation of $LiCoO_2$, is thermally unstable and decomposes when heated above 500 K with the formation of stoichi-

ometric $LiCoO_2$ and Co_3O_4. The process is accompanied by oxygen evolution. Both the evolution of oxygen, detected by means of thermogravimetry, and the formation of Co_3O_4, causing a sharp increase in magnetic susceptibility, depict the degree of chemical extraction of lithium from $LiCoO_2$. This process goes on to a substantially higher extent in the low-temperature cubic phase than in the stable hexagonal one. The possibility of the existence of defects like $O_O^{\cdot}$ in $Li_xNi_{1-x}O$ is discussed.

The formation of vacancies ($V_O^{\cdot\cdot}$) in the oxygen sublattice of $LiCoO_{2-\delta}$ and an equivalent number of Co^{2+} ions (Co_{Co}^I)in the high-spin state is detected by means of magnetic susceptibility measurements and thermogravimetry. The temperature point above which an exchange with the gas phase becomes possible, which causes defect formation process, is about 700 K.

REFERENCES

1 Yu. D. Tretyakov, O. A. Brylev, *Ros. khim. zhurn.,* 4 (2000) 10.
2 T. Nagaura, K. Tazawa, *Prog. Batteries Cells,* 9 (1990) 20.
3 J. R. Dahn, U. von Sacken, M. R. Jakow, H. Al-Janaby, *J. Electrochem. Soc.,* 137 (1991) 2207.
4 S.-I. Tobishima, K. Takei, Y. Sakurai, J.-I. Yamaki, *J. Power Sources,* 90 (2000) 188.
5 J. R. Dahn, E. W. Fuller, M. Obrovac, U. von Sacken, *Solid State Ionics,* 69 (1994) 265.
6 E. Antolini and M. Ferretti, *J. Solid State Chemistry,* 117 (1995) 1.
7 V. V. Karelina, D. G. Kellerman, V. S. Gorshkov *et al.,* *ZhFKh,* 75 (2001) 496.
8 M. Oku, *J. Solid State Chem*istry, 23 (1978) 177.
9 V. S. Gorshkov, D. G. Kellerman, V. V. Karelina, *ZhFKh,* 73 (1999) 1041.
10 R. Apostolova, P. Novak, E. Shembel *et al.,* Lithium Battery Discussion. Electrode Materials. Program. Extended abstr. Bordeaux − Arcachon, France, May 27 − June 1, 2001, No. 64.
11 V. P. Galakhov, V. V. Karelina, V. S. Gorshkov *et al.,* *FTT,* 44 (2002) 257.
12 N. Imanishi, M. Fujiyoshi, Y. Takeda *et al.,* Solid State Ionics, 118, (1999) 121.
13 L. A. Montoro, M. Abbate, J. M. Rosolen, *Electrochem. and Solid State Lett.,* 3 (2000) 410.
14 L. A. Montoro, M. Abbate, J. M. Rosolen, *J. Electrochem. Soc.,* 147 (2000) 1651.
15 N. Nucker, J. Fink, J. C. Fuggle *et al.,* *Phys. Rev.,* B37 (1988) 5158.
16 P. Kuiper, G. Kruizinga, J. Ghijsen *et al.,* *Phys. Rev. Lett.,* 62 (1989) 221.