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# Single-crystal synthesis, structure refinement and electrical properties of $\text{Li}_{0.5}\text{CoO}_2$

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Received 28 May 2007, in final form 6 August 2007

Published 26 September 2007

Online at [stacks.iop.org/JPhysCM/19/436202](http://stacks.iop.org/JPhysCM/19/436202)

## Abstract

Single crystals of  $\text{Li}_{0.5}\text{CoO}_2$  were synthesized for the first time by means of a chemical lithium-ion deintercalation process using  $\text{LiCoO}_2$  single crystals as a parent compound. A single-crystal x-ray diffraction study revealed an ordered superstructure with monoclinic symmetry, that could be assigned to the space group  $P2/m$ . The crystal structure, including anisotropic displacement parameters for each atom, was refined to the conventional values  $R1 = 3.1\%$ ,  $wR2 = 10.9\%$ , and  $S = 1.16$  using 2385 independent reflections in the range  $\sin\theta/\lambda < 1.3 \text{ \AA}^{-1}$ . The lithium-ion and vacancy ordering structure in  $\text{Li}_{0.5}\text{CoO}_2$  was clearly revealed in the electron density distribution analyzed by the maximum entropy method (MEM) using the single-crystal x-ray diffraction data. The in-plane electrical resistivity in  $\text{Li}_{0.5}\text{CoO}_2$  measured using the single-crystal specimen was around  $2 \text{ m}\Omega \text{ cm}$  and approximately temperature independent, suggesting metallic conduction. These findings were very consistent with those obtained by the FLAPW calculations.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Lithium cobalt dioxide,  $\text{LiCoO}_2$ , has the layered  $\alpha\text{-NaFeO}_2$  structure. This compound is used industrially as the positive electrode material for lithium-ion rechargeable batteries. The structural, physical, and electrochemical properties of  $\text{LiCoO}_2$  and  $\text{Li}_{1-x}\text{CoO}_2$  ( $0 < x < 1$ ) have been widely investigated following the initial report of the electrochemical deintercalation in  $\text{LiCoO}_2$  by Mizushima *et al* [1–9]. In particular, since the electrical conductivity of electrode materials is an important characteristic for the design of high-performance batteries, there have been a number of reports measuring the conductivity [10–18]. In most of the experimental

studies reported to date, sintered or pressed powder samples [10–15, 18] or the corresponding polycrystalline thin films [16, 17] have been used. However, much of the information on the anisotropy is lost in experiments using such samples, and in conductivity measurements in particular, the intrinsic properties of the material are sometimes masked by those of the grain boundaries or the impurities. Recently, the insulator–metal transition upon lithium deintercalation from  $\text{LiCoO}_2$  has been intensively investigated both experimentally [15, 18] and theoretically [19–21]. However, the true metallic conductivity for  $\text{Li}_{1-x}\text{CoO}_2$  has not been reported to date.

The in-plane ordering of lithium ions and vacancies in  $\text{Li}_{0.5}\text{CoO}_2$  was first proposed by Reimers and Dahn [4]. The monoclinic structure model and the corresponding space group have been examined by an electron diffraction study [22]. In addition, the  $\text{Co}^{3+}/\text{Co}^{4+}$  charge-ordering structure at room temperature has been predicted by theoretical calculations [20]. However, the precise structural parameters, including the anisotropic thermal displacement parameters, have not been revealed experimentally.

To clarify the structural and electrical properties in detail, well-characterized single-crystal specimens are highly desirable. In our recent study, we succeeded in growing  $\text{LiCoO}_2$  single crystals by a flux method and determined the crystal structure by a single-crystal x-ray diffraction method [23, 24]. Using these single-crystal specimens, we have clarified the anisotropy in electrical resistivity below room temperature [25]. In addition, we have determined the precise crystal structures of  $\text{Li}_{1-x}\text{CoO}_2$  by the single-crystal x-ray diffraction method using electrochemically and chemically deintercalated  $\text{Li}_{1-x}\text{CoO}_2$  single-crystal samples [26, 27]. In this paper, we report the x-ray structure refinement of the first single crystal of chemically deintercalated monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  and demonstrate the insulator–metal transition upon lithium deintercalation by the in-plane electrical resistivity measurements. We also calculate the electronic structure of monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  using full-potential linearized augmented plane-wave (FLAPW) methods, and compare the results with the experimental ones.

## 2. Experimental details

### 2.1. Single-crystal synthesis

Single crystals of  $\text{LiCoO}_2$  were grown by a flux method as described previously [23–25]. The as-prepared  $\text{LiCoO}_2$  powder (Cell Seed C; Nippon Chemical Industrial Co., Ltd, Japan) was mixed with  $\text{Li}_2\text{O}_2$  (99.9%) and  $\text{LiCl}$  (99.9%) to form flux material in the nominal weight ratio  $\text{LiCoO}_2:\text{Li}_2\text{O}_2:\text{LiCl} = 1:4:4$ . The mixture was heated to 1173 K for 10 h in a sealed gold tube, gradually cooled to 873 K at a rate of  $5 \text{ K h}^{-1}$ , and then cooled naturally. The single crystals produced were easily separated from the frozen Li–O–Cl system flux by rinsing the gold tube in water for several minutes.

Chemical analyses of selected as-grown single crystals were carried out by scanning electron microscopy-energy dispersive x-ray analysis (SEM-EDX, JEOL JSM-5400) and inductively coupled plasma (ICP) spectroscopy. EDX analysis showed that the crystals were free from gold contamination from the crucible. The chemical composition was analyzed by ICP spectroscopy using a pulverized sample (about 20 mg), and determined to be  $\text{Li}:\text{Co}:\text{O} = 1.0:1.0:2$ , which is consistent with the previous reports [25]. It should be noted that single crystals of the recently reported ‘lithium overstoichiometric’  $\text{Li}_{1.1}\text{CoO}_2$  compounds [28–30] could not be synthesized in the present study.

The  $\text{Li}_{0.5}\text{CoO}_2$  single crystals were prepared by a combined Li-ion extraction/chemical oxidation process. Selected  $\text{LiCoO}_2$  single crystals were placed in 1 M HCl solution for several hours. No stirring or heating was performed. We previously succeeded in the chemical

preparation of Li-deficient  $\text{Li}_{1-x}\text{CoO}_2$  single-crystal samples with  $0 < x < 0.65$  [27]. In the present experiments, the  $\text{Li}_{0.5}\text{CoO}_2$  single crystals were prepared with a reaction time of 26 h. The obtained crystals were washed carefully with ethanol, and then one was subjected to single-crystal x-ray diffraction analysis. The chemical formula of this oxidized crystal was determined by the present single-crystal x-ray structure analysis.

## 2.2. Structure and electron density analysis

The selected  $\text{Li}_{0.5}\text{CoO}_2$  single crystal was mounted on a glass fiber for single-crystal x-ray diffraction studies. The crystal was examined with an x-ray precession camera (Mo  $K\alpha$  radiation) in order to check the crystal quality and to determine the lattice parameters, systematic extinctions, and possible superstructures. Integrated intensity data were collected in the  $2\theta$ - $\omega$  scan mode at a scan rate of  $1.0^\circ \text{ min}^{-1}$  at 296 K on a Rigaku AFC-7S four-circle diffractometer (operating conditions: 45 kV, 35 mA) using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The corrections for absorption and Lorentz and polarization effects were performed using the XTAL3.4 program [31]. The lattice parameters of the rhombohedral  $\text{LiCoO}_2$  and monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  were determined by least-squares refinement using  $2\theta$  values of 25 strong reflections in the range  $20^\circ$ - $30^\circ$  and Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) on the four-circle diffractometer. The line-scan profiles in the single-crystal x-ray diffraction reciprocal space of  $\text{Li}_{0.5}\text{CoO}_2$  along some crystallographic directions ( $[hhl]$ ,  $[h00]$ ,  $[00l]$ ) at 296 K were measured with the use of the four-circle diffractometer. The temperature dependence of the lattice parameters for  $\text{LiCoO}_2$  and  $\text{Li}_{0.5}\text{CoO}_2$  single crystals between 100 and 360 K was investigated on the four-circle diffractometer using a nitrogen gas flow cryostat.

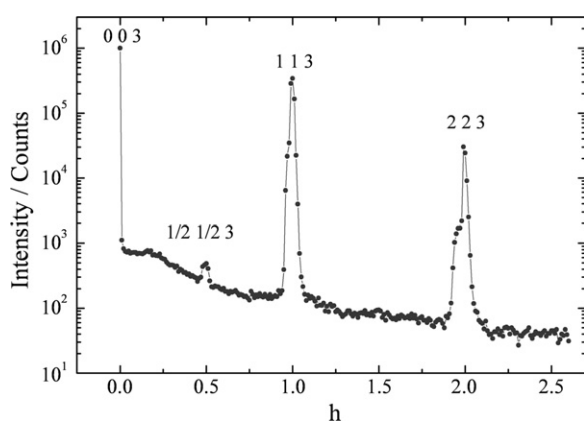
The electron density analyses of rhombohedral  $\text{LiCoO}_2$  and monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  were performed by the maximum entropy method (MEM) with the computer program PRIMA [32]. The three-dimensional electron density distributions obtained were visualized with the program VENUS developed by Dilanian and Izumi [33].

## 2.3. Electrical resistivity measurements

The in-plane resistivity ( $\rho_a$ ) in the direction perpendicular to the  $c$ -axis was measured by the conventional direct current four-probe method from 4 to 300 K. The single-crystal specimens measured were plane-shaped, with dimensions  $150 \times 200 \mu\text{m}^2$  for the large surface, and with  $10 \mu\text{m}$  thickness along the  $c$ -axis direction. We measured several specimens to check the reproducibility of these results.

## 2.4. Theoretical calculations

The electronic structure of monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  was calculated using the full-potential linearized augmented-plane-wave (FLAPW) method with the computer program WIEN2k package [34]. The generalized gradient approximation (GGA) in the formulation of Perdew, Burke and Ernzerhof was used for the exchange and correlation terms [35]. The atomic muffin-tin sphere radii used were 1.6 au for the Li atom, 1.9 au for the Co atom and 1.7 au for the O atom, respectively. The plane-wave cutoff was  $R_{\text{MT}} \times K_{\text{max}} = 7.0$ , where  $R_{\text{MT}}$  is the smallest atomic sphere radius in the unit cell and  $K_{\text{max}}$  is the magnitude of the largest  $k$  vector. The self-consistency was carried out on a 400  $k$ -points mesh in the full Brillouin zone. The energy criterion for self-consistency was set to less than 0.001 eV/f.u. Structural parameters for monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  determined by the present structure analysis were used in the calculations. The electronic structure for rhombohedral  $\text{LiCoO}_2$  was also calculated using the structural data [23, 25].



**Figure 1.** Single-crystal x-ray diffraction reciprocal space line scan of  $\text{Li}_{0.5}\text{CoO}_2$  along the  $[hh3]$  direction at 296 K assuming the original hexagonal lattice of  $\text{LiCoO}_2$ .

### 3. Results and discussions

#### 3.1. Structure analysis

Figure 1 shows a line-scan profile in the single-crystal x-ray diffraction reciprocal space of  $\text{Li}_{0.5}\text{CoO}_2$  along the  $[hh3]$  direction at 296 K assuming the original hexagonal lattice of  $\text{LiCoO}_2$ . A very weak superlattice spot, at  $\frac{1}{2} \frac{1}{2} 3$  of the original hexagonal lattice, is clearly visible in this figure. It is well known that in-plane lithium and vacancy ordering leads to a monoclinic distortion for polycrystalline  $\text{Li}_{0.5}\text{CoO}_2$  samples [4, 20, 22]. However, such a lattice distortion could not be observed in the present  $\text{Li}_{0.5}\text{CoO}_2$  single crystal. All of the superlattice spots can be successfully indexed to  $2a \times 2a \times 2c$ -type hexagonal lattice ( $a = 2 \times 2.809 \text{ \AA}$  and  $c = 2 \times 14.389 \text{ \AA}$ ), as recently reported for the electrochemically delithiated  $\text{Li}_{0.48}\text{CoO}_2$  single crystal [27]. However, such a superstructure could not be explained by the above-mentioned in-plane lithium/vacancy ordering model. On the other hand, the formation of a nanosized microstructure has been reported in the literature [22]. The superlattice structure observed in the present single-crystal study should be explained using a twinned monoclinic lattice with the space group  $P2/m$  [20]:  $a = 4.865(3) \text{ \AA}$ ,  $b = 2.809(3) \text{ \AA}$ ,  $c = 5.063(3) \text{ \AA}$ ,  $\beta = 108.68(5)^\circ$ , which are identical with the parameters of the hexagonal lattice in terms of geometry. In this twin model, all of the superlattice spots can be also indexed to the monoclinic lattice using a twin matrix of  $-\frac{1}{2} \quad -\frac{3}{2} \quad 0 / \frac{1}{2} \quad -\frac{1}{2} \quad 0 / \frac{1}{2} \quad \frac{1}{2} \quad 1$ . In the present study, further structural properties, including a structure refinement of the monoclinic form, were examined using the twinned x-ray intensity data. The refinement was initiated using the theoretically predicted space group  $P2/m$  and atomic coordinates by Hartree–Fock methods [20]. Finally, the crystal structure was refined to the conventional values  $R1 = 3.1\%$ ,  $wR2 = 10.9\%$ , and  $S = 1.16$  for 2385 independent reflections using the SHELX-97 program [36]. Difference-Fourier syntheses using the final atomic parameters showed no significant residual peaks. The experimental and crystallographic data are summarized in table 1. The final atomic coordinates and anisotropic displacement parameters are given in tables 2 and 3.

The crystal structure of monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  with the space group  $P2/m$  was clarified experimentally for the first time, as shown in figure 2. The lithium-ion and vacancy ordering arrangements along the  $a$ -axis in  $\text{Li}_{0.5}\text{CoO}_2$  are clearly visible in figure 2. Selected bond distances are listed in table 4. The mean octahedral Li–O distance is determined to be  $2.147 \text{ \AA}$ , which is much longer than the value of  $2.093(1) \text{ \AA}$  determined for  $\text{LiCoO}_2$  [23]. On the other hand, the value is slightly shorter than the (Li,  $\square$ )–O distance ( $2.1499(9) \text{ \AA}$ )

**Table 1.** Experimental and crystallographic data for  $\text{Li}_{0.5}\text{CoO}_2$  at 296 K. (Note: Definition of  $R$  indices:  $R1 = \Sigma||F_{\text{obs}}| - |F_{\text{calc}}||/\Sigma|F_{\text{obs}}|$ ;  $wR2 = \{\Sigma[w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2]/\Sigma[w(F_{\text{obs}}^2)^2]\}^{1/2}$ .)

|  |  |
|--|--|
| Structural formula                     | $\text{Li}_{0.5}\text{CoO}_2$                              |
| Crystal system                         | Monoclinic   |
| Space group                            | $P2/m$   |
| $a$ (Å)                                | 4.865(3)   |
| $b$ (Å)                                | 2.809(3)   |
| $c$ (Å)                                | 5.063(3)   |
| $\beta$ (°)                            | 108.68(5)  |
| $V$ (Å <sup>3</sup> )                  | 65.55(9)   |
| $Z$                                    | 2  |
| Crystal size ( $\mu\text{m}$ )         | $150 \times 200 \times 10$                                 |
| Maximum $2\theta$ (°)                  | 130  |
| Index ranges                           | $-12 \leq h \leq 12, -7 \leq k \leq 7, -12 \leq l \leq 12$ |
| Absorption correction method           | Gaussian integration                                       |
| Max. and min. transmission             | 0.510 and 0.041  |
| Measured reflections                   | 2499   |
| Observed reflections                   | 2385   |
| Number of variables                    | 26   |
| Goodness-of-fit $S$                    | 1.159  |
| Final $R$ indices [ $I > 2\sigma(I)$ ] | $R1 = 0.0307, wR2 = 0.1086$                                |
| $R$ indices (all data)                 | $R1 = 0.0315, wR2 = 0.1091$                                |

**Table 2.** Structural parameters for monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ .

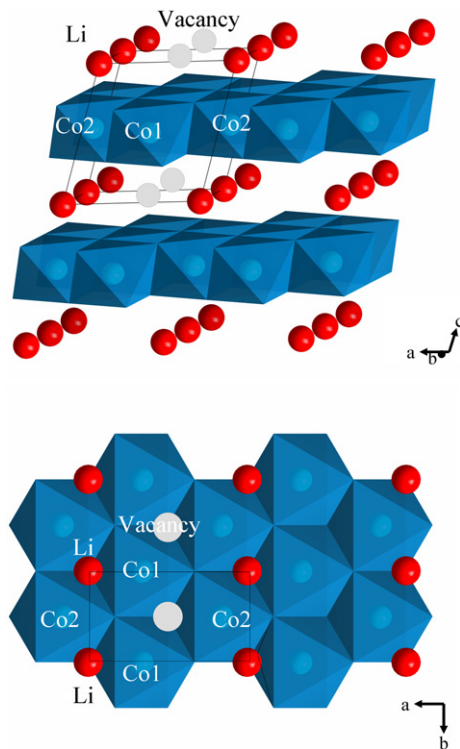
| Atom | Site | $x$       | $y$ | $z$       | $U_{\text{eq}}$ (Å <sup>2</sup> ) |
|------|------|-----------|-----|-----------|-----------------------------------|
| Li   | 1a   | 0         | 0   | 0         | 0.024(3)                          |
| Co1  | 1g   | 0.5       | 0   | 0.5       | 0.0051(2)                         |
| Co2  | 1f   | 0         | 0.5 | 0.5       | 0.0052(3)                         |
| O1   | 2m   | 0.2336(6) | 0   | 0.7065(7) | 0.0067(9)                         |
| O2   | 2n   | 0.7354(6) | 0.5 | 0.7057(8) | 0.0085(10)                        |

**Table 3.** Anisotropic displacement parameters for monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ .

| Atom | $U_{11}$   | $U_{22}$   | $U_{33}$  | $U_{12}$ | $U_{13}$    | $U_{23}$ |
|------|------------|------------|-----------|----------|-------------|----------|
| Li   | 0.033(10)  | 0.028(9)   | 0.014(5)  | 0        | 0.014(8)    | 0        |
| Co1  | 0.0054(4)  | 0.0048(3)  | 0.0056(6) | 0        | 0.0024(4)   | 0        |
| Co2  | 0.0027(3)  | 0.0034(3)  | 0.0098(7) | 0        | 0.0023(4)   | 0        |
| O1   | 0.0074(13) | 0.0021(9)  | 0.009(2)  | 0        | -0.0005(10) | 0        |
| O2   | 0.0064(14) | 0.0115(16) | 0.010(3)  | 0        | 0.0058(14)  | 0        |

in electrochemically deintercalated  $\text{Li}_{0.48}\text{CoO}_2$  [27], which was analyzed using the original trigonal symmetry.

Both the Co1 and Co2 atoms are octahedrally coordinated by six oxygen atoms. The coordination environments of oxygen atoms around the Co1 and Co2 atoms are very similar. The mean Co–O distances are 1.902 Å and 1.896 Å for Co1 and Co2, respectively. The  $\text{Co}^{3+}/\text{Co}^{4+}$  ratio in  $\text{Li}_{0.5}\text{CoO}_2$  is required to be 1:1 by charge compensation. Recently, the charge ordering of  $\text{Co}^{3+}/\text{Co}^{4+}$  at room temperature was theoretically predicted [20]. However, the present structure analysis of  $\text{Li}_{0.5}\text{CoO}_2$  suggests that both of the Co sites are randomly occupied by  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  cations at room temperature.



**Figure 2.** Crystal structure of monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  with the space group  $P2/m$ .

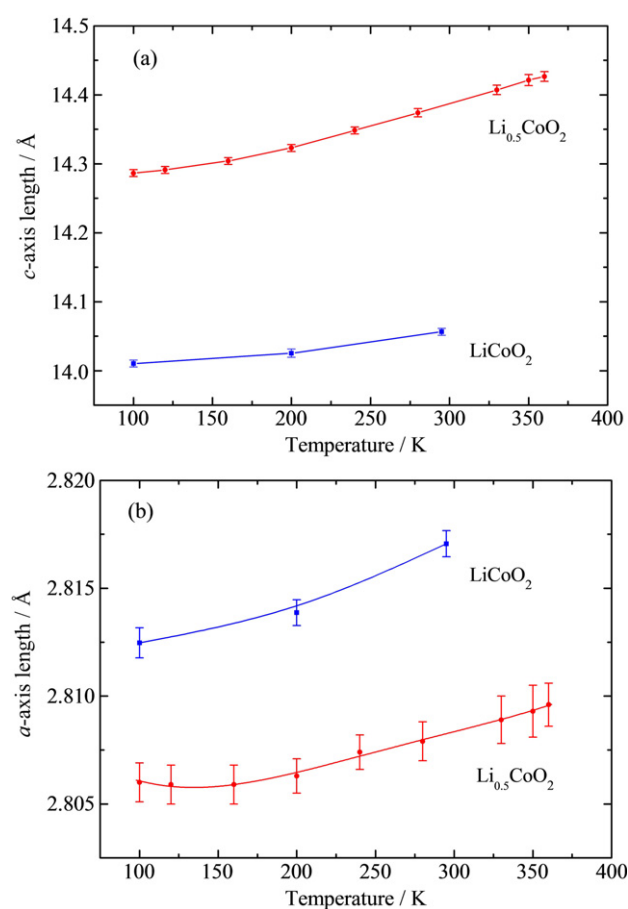
**Table 4.** Selected bond distances ( $\text{\AA}$ ) for monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ .

|        |                     |        |                     |
|--------|---------------------|--------|---------------------|
| Li–O1  | $2.141(3) \times 2$ |        |                     |
| Li–O2  | $2.150(3) \times 4$ |        |                     |
| Mean   | 2.147               |        |                     |
| Co1–O1 | $1.908(3) \times 2$ | Co2–O1 | $1.896(2) \times 4$ |
| Co1–O2 | $1.899(3) \times 4$ | Co2–O2 | $1.897(3) \times 2$ |
| Mean   | 1.902               | Mean   | 1.896               |

Figure 3 presents the temperature dependence of the lattice parameters of  $\text{LiCoO}_2$  and  $\text{Li}_{0.5}\text{CoO}_2$  assuming the original hexagonal lattice, respectively. It is indicated that the  $c$ -axis length gradually decreases with decreasing temperature in both  $\text{LiCoO}_2$  and  $\text{Li}_{0.5}\text{CoO}_2$ . However, the  $a$ -axis length shows a minimum value around 150 K in  $\text{Li}_{0.5}\text{CoO}_2$ . This fact may suggest a novel phase transition below 150 K, such as the  $\text{Co}^{3+}/\text{Co}^{4+}$  charge ordering. A further study on the structural and magnetic properties below 150 K should be performed in the future.

### 3.2. Electron density analysis

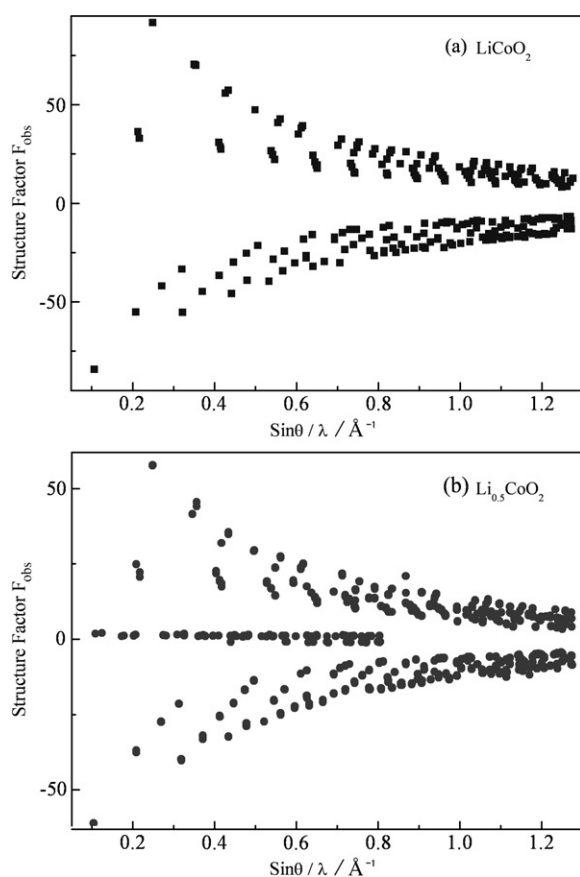
The electron density distributions in  $\text{Li}_{0.5}\text{CoO}_2$  were revealed by MEM analysis using the present single-crystal x-ray data. In the present MEM analysis, the total number of electrons in the unit cell was fixed at  $F(000)$  for monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ (89), and the unit cell was divided into  $100 \times 100 \times 100$  pixels for  $\text{Li}_{0.5}\text{CoO}_2$ , respectively, to ensure good spatial resolution. The



**Figure 3.** Temperature dependence of the lattice parameters of rhombohedral  $\text{LiCoO}_2$  and monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  assuming the hexagonal lattice.

number of independent reflections used was 703 for  $\text{Li}_{0.5}\text{CoO}_2$  in the range  $\sin \theta / \lambda < 1.3 \text{ \AA}^{-1}$ . The reliability factor of the MEM,  $R_{\text{MEM}}$ , was 3.25% for  $\text{Li}_{0.5}\text{CoO}_2$ . Figure 4 shows the values of the structure factors,  $F_{\text{obs}}$ , for monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  using the present MEM analysis, in comparison with those for rhombohedral  $\text{LiCoO}_2$  [23, 27]. It can be clearly seen that there are many reflections with small structure factors in the range  $\sin \theta / \lambda < 0.8 \text{ \AA}^{-1}$  in  $\text{Li}_{0.5}\text{CoO}_2$ . These data are considered to be very important in clarifying the crystal structure and electron density distributions in monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  precisely. The three-dimensional electron density distributions,  $\rho(r)_{\text{obs}}$ , of  $\text{Li}_{0.5}\text{CoO}_2$  at 296 K are shown in figure 5. The iso-surface density level is equal to  $0.6 \text{ \AA}^{-3}$ . From the MEM analysis, a strong covalent bonding feature is clearly found between the Co and O atoms, while no bonding is observed between the Li and O atoms for both structures. It is considered that the covalent bonding of Co–O is due to the Co 3d and O 2p interaction. Furthermore, the ordered arrangement of the Li ions in monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  is clearly visible in figure 5. The electron density heights at the saddle point between the Co1 and O atoms are experimentally determined to be  $0.94 \text{ \AA}^{-3}$  and  $0.70 \text{ \AA}^{-3}$  for Co1–O1 and Co1–O2, respectively. These values are in good agreement with those between the Co2 and O atoms, i.e.,  $0.84 \text{ \AA}^{-3}$  and  $0.74 \text{ \AA}^{-3}$  for Co2–O1 and Co2–O2, respectively. These values are very similar to those in  $\text{NaCoO}_2$  ( $0.78 \text{ \AA}^{-3}$ ) [37] and  $\text{Na}_{0.74}\text{CoO}_2$  ( $0.81 \text{ \AA}^{-3}$ ) [38], suggesting the good quality of the analysis in these compounds. From these results, it is suggested that





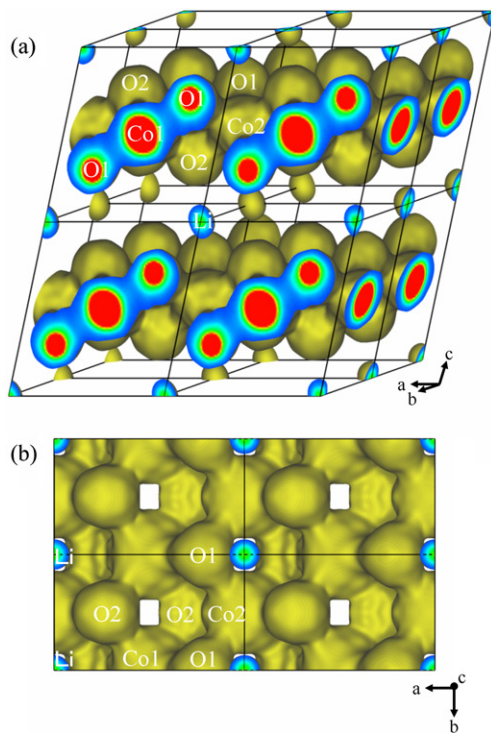
**Figure 4.** Structure factors,  $F_{\text{obs}}$ , of (a) rhombohedral  $\text{LiCoO}_2$  and (b) monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ .

both of the Co sites in  $\text{Li}_{0.5}\text{CoO}_2$  are randomly occupied by the  $\text{Co}^{3+}$  and  $\text{Co}^{4+}$  cations at room temperature. Accordingly, the predicted charge-ordering state of  $\text{Co}^{3+}/\text{Co}^{4+}$  at room temperature [20] could not be observed by the present electron density analysis using the single-crystal x-ray diffraction data.

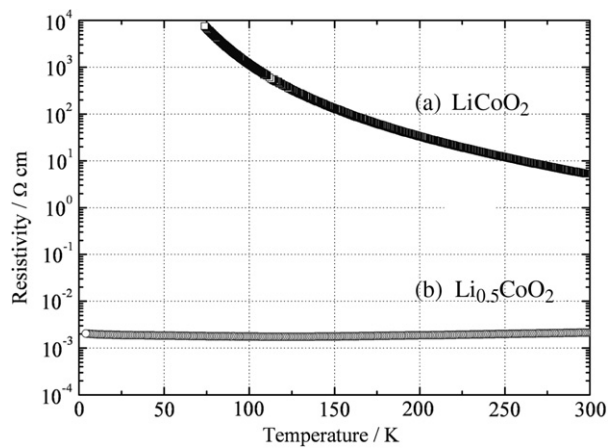
### 3.3. Electrical resistivity

Figure 6 shows the temperature dependence of the in-plane electrical resistivity in  $\text{LiCoO}_2$  and  $\text{Li}_{0.5}\text{CoO}_2$ , respectively. As previously reported,  $\text{LiCoO}_2$  is semiconductive, and the value of  $\rho_a$  is about  $5 \Omega \text{ cm}$  at 300 K. On the other hand, the resistivity in  $\text{Li}_{0.5}\text{CoO}_2$  is around  $2 \text{ m}\Omega \text{ cm}$  and approximately temperature independent, suggesting metallic conduction. This fact is comparable to those in metallic cobaltites, e.g.,  $0.2 \text{ m}\Omega \text{ cm}$  at 300 K in  $\text{NaCo}_2\text{O}_4$  [39], and  $16 \text{ m}\Omega \text{ cm}$  at 100 K in  $\text{Na}_{0.35}\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$  [40]. The metallic conductivity in  $\text{Li}_{0.5}\text{CoO}_2$  has been clarified for the first time, because the grain boundary resistance became significant using the polycrystalline samples in the previous study.

Figure 7 shows the magnified temperature dependence of the in-plane electrical resistivity in monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ . The accuracy of the resistivity data in this figure was within  $0.02 \text{ m}\Omega \text{ cm}$ . It is clearly observed that the electrical resistivity has a minimum value at around 125 K. This fact may suggest that a novel phase transition occurs at low temperature, such as the  $\text{Co}^{3+}/\text{Co}^{4+}$  charge ordering. The result is in good agreement with the temperature dependence



**Figure 5.** Three-dimensional electron density distribution,  $\rho(r)_{\text{obs}}$ , of monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  at 296 K. The iso-surface density level is equal to  $0.6 \text{ \AA}^{-3}$ .

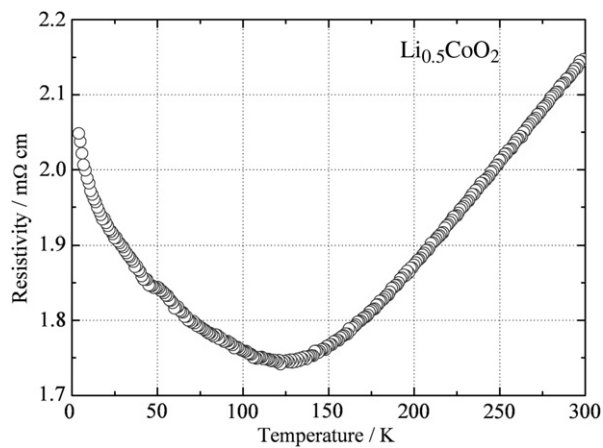


**Figure 6.** Temperature dependence of the in-plane electrical resistivity in (a) rhombohedral  $\text{LiCoO}_2$  and (b) monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ .

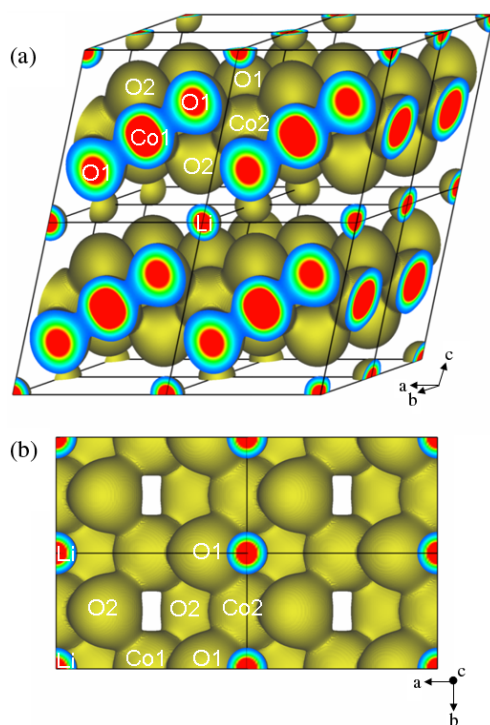
of the lattice parameters, as mentioned above (figure 3). Furthermore, a similar feature was previously reported for a  $\text{Li}_{0.55}\text{CoO}_2$  polycrystalline sample at 150 K [18]. We are now trying to measure some physical properties at low temperatures using larger  $\text{Li}_{0.5}\text{CoO}_2$  single-crystal samples.

### 3.4. First-principles calculations

Figure 8 shows the electron density distribution of monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  obtained by the FLAPW calculations. The iso-surface density level is equal to  $0.5 \text{ \AA}^{-3}$ . The electron density



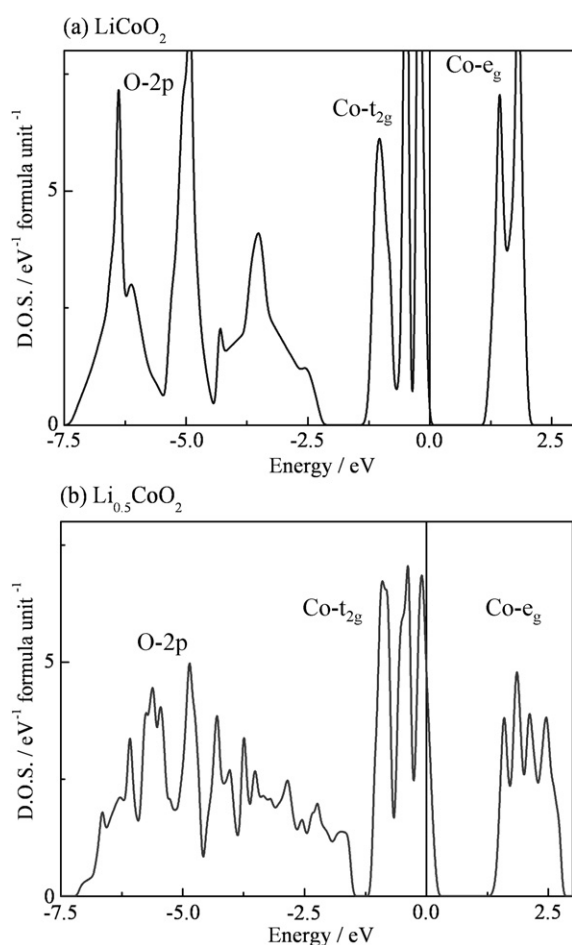
**Figure 7.** Temperature dependence of the in-plane electrical resistivity in monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ .



**Figure 8.** Three-dimensional electron density distribution of monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  calculated by the FLAPW method. The iso-surface density level colored light yellow is equal to  $0.5 \text{ \AA}^{-3}$ .

distributions obtained theoretically were qualitatively in good agreement with the experimental observations by the MEM, as shown in figure 5.

Figure 9 shows the total densities of states for rhombohedral  $\text{LiCoO}_2$  and monoclinic  $\text{Li}_{0.5}\text{CoO}_2$ . The origin of energy is at the Fermi level. The density of states of rhombohedral  $\text{LiCoO}_2$  agrees well with those reported previously [19, 20]. The valence band of rhombohedral  $\text{LiCoO}_2$  in the range from  $-7.5$  to  $-2.1$  eV consists of the O 2p orbital hybridized with the Co 3d orbital, which corresponds to the strong covalent bonding between the Co and O atoms. The energy states ranging from  $-1.4$  to  $0.1$  eV and  $1.1$  to  $2.2$  eV are attributed to the  $t_{2g}$  states and the  $e_g$  states of the Co 3d orbital, respectively. On the other hand, the valence



**Figure 9.** The total densities of states for (a) rhombohedral  $\text{LiCoO}_2$  and (b) monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  calculated by the FLAPW method.

band of monoclinic  $\text{Li}_{0.5}\text{CoO}_2$  in the range from  $-7.3$  to  $-1.4$  eV consists of the O 2p orbital hybridized with the Co 3d orbital. The energy states ranging from  $-1.2$  to  $0.4$  eV and  $1.2$  to  $2.9$  eV are attributed to the  $t_{2g}$  states and the  $e_g$  states of the Co 3d orbital, respectively. The density of states near Fermi energy ( $E_F$ ) descends toward the edge of the Co  $t_{2g}$  bands in these compounds. It can be clearly seen that  $E_F$  in  $\text{Li}_{0.5}\text{CoO}_2$  approaches closer to the edge of the Co  $t_{2g}$  bands than  $E_F$  in  $\text{LiCoO}_2$ . These results indicate that  $\text{LiCoO}_2$  behaves as an insulator, whereas metallic conductivity is predicted in  $\text{Li}_{0.5}\text{CoO}_2$ , as previously reported. These features are in good agreement with the present resistivity data in figure 6.

#### 4. Summary

$\text{Li}_{0.5}\text{CoO}_2$  single crystals were synthesized for the first time by means of a chemical lithium-ion deintercalation process using  $\text{LiCoO}_2$  single crystals as a parent compound. A single-crystal x-ray diffraction study revealed an ordered superstructure with monoclinic symmetry that could be assigned to the space group  $P2/m$ . The lithium-ion and vacancy ordering structure in  $\text{Li}_{0.5}\text{CoO}_2$  was determined experimentally for the first time. The electron density distributions in  $\text{Li}_{0.5}\text{CoO}_2$  were analyzed by the maximum entropy method (MEM) using the single-crystal x-ray diffraction data. Strong covalent bonding features were found between the Co and

O atoms. The in-plane electrical resistivity measurements revealed metallic conductivity in single-crystal samples of  $\text{Li}_{0.5}\text{CoO}_2$ . These experimental results were in good agreement with the theoretical calculations. A novel phase transition around 125 K was found in  $\text{Li}_{0.5}\text{CoO}_2$ , suggesting that the  $\text{Co}^{3+}/\text{Co}^{4+}$  charge ordering occurs at low temperatures.

## References

- [1] Mizushima K, Jones P C, Wiseman P J and Goodenough J B 1980 *Mater. Res. Bull.* **15** 783
- [2] Orman H J and Wiseman P J 1984 *Acta Crystallogr. C* **40** 12
- [3] Gummow R J, Thackeray M M, David W I D and Hull S 1992 *Mater. Res. Bull.* **27** 327
- [4] Reimers J N and Dahn J R 1992 *J. Electrochem. Soc.* **139** 2091
- [5] Ohzuku T and Ueda A 1994 *J. Electrochem. Soc.* **141** 2972
- [6] Amatucci G G, Tarascon J M and Klein L C 1996 *J. Electrochem. Soc.* **143** 1114
- [7] Uchimoto Y, Sawada H and Yao T 2001 *J. Synchrotron Radiat.* **8** 872
- [8] Graetz A, Hightower A, Ahn C C, Yazami R, Rez P and Fultz B 2002 *J. Phys. Chem. B* **106** 1286
- [9] Shao-Horn Y, Croguennec L, Delmas C, Nelson E C and O'Keefe M A 2003 *Nat. Mater.* **2** 464
- [10] Honders A, der Kinderen J M, Van Heeren A H, de Witt J H W and Broers G H J 1984 *Solid State Ion.* **14** 205
- [11] Kikkawa S, Miyazaki S and Koizumi M 1986 *J. Solid State Chem.* **62** 35
- [12] Hewston T A and Chamberland B L 1987 *J. Phys. Chem. Solids* **48** 97
- [13] Molenda J, Stoklosa A and Bak T 1989 *Solid State Ion.* **36** 53
- [14] Tukamoto H and West A R 1997 *J. Electrochem. Soc.* **144** 3164
- [15] Imanishi N, Fujiyoshi M, Takeda Y, Yamamoto O and Tabuchi M 1999 *Solid State Ion.* **118** 121
- [16] Shibuya M, Nishina T, Matsue T and Uchida I 1996 *J. Electrochem. Soc.* **143** 3157
- [17] Nishizawa M, Yamamura S, Itoh T and Uchida I 1998 *Chem. Commun.* 1631
- [18] Ménétrier M, Saadoune I, Levasseur S and Delmas C 1999 *J. Mater. Chem.* **9** 1135
- [19] Van der Ven A, Aydinol M K, Ceder G, Kresse G and Hafner J 1998 *Phys. Rev. B* **58** 2975
- [20] Catti M 2000 *Phys. Rev. B* **61** 1795
- [21] Marianetti C A, Kotliar G and Ceder G 2004 *Nat. Mater.* **3** 627
- [22] Shao-Horn Y, Levasseur S, Weill F and Delmas C 2003 *J. Electrochem. Soc.* **150** A366
- [23] Akimoto J, Gotoh Y and Oosawa Y 1998 *J. Solid State Chem.* **141** 298
- [24] Takahashi Y, Kijima N and Akimoto J 2005 *J. Solid State Chem.* **178** 3667
- [25] Takahashi Y, Gotoh Y, Akimoto J, Mizuta S, Tokiwa K and Watanabe T 2002 *J. Solid State Chem.* **164** 1
- [26] Akimoto J, Takahashi Y, Gotoh Y and Mizuta S 2000 *Intercalation Compounds for Battery Materials*, PV99-24, ed G A Nazri, M M Thackeray and T Ohzuku (Princeton, NJ: Electrochemical Society) p 81
- [27] Takahashi Y, Kijima N, Dokko K, Nishizawa M, Uchida I and Akimoto J 2007 *J. Solid State Chem.* **180** 313
- [28] Levasseur S, Ménétrier M, Suard E and Delmas C 2000 *Solid State Ion.* **128** 11
- [29] Imanishi N, Fujii M, Hirano A, Takeda Y, Inaba M and Ogumi Z 2001 *Solid State Ion.* **140** 45
- [30] Levasseur S, Ménétrier M, Shao-Horn Y, Gautier L, Audemer A, Demazeau G, Largeteau A and Delmas C 2003 *Chem. Mater.* **15** 348
- [31] Hall S R, King G S D and Stewart J M (ed) 1995 *Xtal3.4 User's Manual* (Lamb, Perth: University of Western Australia)
- [32] Izumi F and Dilanian R A 2002 *Recent Research Developments in Physics* vol 3, Part II (Trivandrum, India: Transworld Research Network) p 699
- [33] Izumi F and Dilanian R A 2005 *Commission on Powder Diffraction Newsletter* No 32 International Union of Crystallography, p 59
- [34] Blaha P, Schwarz K, Madsen G, Kvasnicka D and Luitz J 2001 *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Vienna, Austria: Technische Universität Wien)
- [35] Perdew P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [36] Sheldrick G M 1997 *SHELX-97* (Germany: University of Göttingen)
- [37] Takahashi Y, Gotoh Y and Akimoto J 2003 *J. Solid State Chem.* **172** 22
- [38] Takahashi Y, Akimoto J, Kijima N and Gotoh Y 2004 *Solid State Ion.* **172** 505
- [39] Terasaki I, Sasago Y and Uchinokura K 1997 *Phys. Rev. B* **56** R12685
- [40] Takada K, Sakurai H, Takayama-Muromachi E, Izumi F, Dilanian R A and Sasaki T 2003 *Nature* **422** 53