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LETTER TO THE EDITOR

Synthesis and Structure Refinement of $LiCoO_2$ Single Crystals

Junji Akimoto,[1] Yoshito Gotoh, and Yoshinao Oosawa

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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Single crystals of $LiCoO_2$ have been successfully synthesized for the first time in a sealed gold tube by a flux method at 1173 K. A single-crystal X-ray diffraction study confirmed the trigonal $R\bar{3}m$ space group and the lattice parameters $a = 2.8161(5)$ Å and $c = 14.0536(5)$ Å. No superstructure could be observed in the single-crystal X-ray diffraction photographs. The crystal structure has been refined to the conventional values $R = 3.1\%$ and $wR = 3.5\%$ for 217 independent observed reflections. The refined oxygen parameter z is 0.23951(15), which is in good agreement with the previous result by powder neutron diffraction method. The short O–O contact distance of 2.614(2) Å in the CoO_6 octahedron is confirmed by the present structure refinement.
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INTRODUCTION

Lithium cobalt oxide, $LiCoO_2$, has the trigonal α-$NaFeO_2$ structure and is used industrially as the cathode material of lithium-ion rechargeable batteries. Since electrochemical deintercalation was first reported in $LiCoO_2$ by Mizushima *et al.* (1), the preparation method and the structural, physical, and electrochemical properties for $LiCoO_2$ and Li_xCoO_2 ($0 < x \leq 1$) have been widely investigated (2–7).

The crystal structure of $LiCoO_2$ was originally reported by Johnston *et al.* (2). The powder neutron diffraction technique has been applied to some $LiCoO_2$ samples (3, 6) to clarify the cationic distribution that affects the charge–discharge process. Indeed, using powder neutron difraction data, Orman and Wiseman (3) revealed that the ordering of lithium and cobalt atoms into alternate (111) planes of the cubic close-packed oxygen lattice of $LiCoO_2$ was essentially perfect. Moreover, Gummow *et al.* (4–6) recently investigated the spinel-like structure of $LiCoO_2$ synthesized at 400°C. However, the powder technique does not fully solve the problem, because it only provides a structure refinement using the starting model structure.

To clarify the true crystal symmetry, the precise crystal structure, and the anisotropic nature of the physical properties of cathode materials such $LiCoO_2$ and $LiMn_2O_4$, sizeable, well-characterized single crystal specimens are highly desirable; however, the corresponding single crystals have not yet been synthesized. In the pressent study, we report the synthesis of single crystals by a flux method and the X-ray structure refinement of the first single crystal of $LiCoO_2$.

EXPERIMENTAL

$LiCoO_2$ single crystals were grown by a flux method. The $LiCoO_2$ powder (Cell Seed C, Nippon Chemical Industrial Co., Ltd., Japan) was mixed with Li_2O (99.9%) and LiCl (99.9%) to form flux material in the nominal weight ratio of $LiCoO_2 : Li_2O : LiCl = 1:4:4$. The flux growth was conducted in a vertical resistance furnace. The mixture was heated to 1173 K for 10 h in a sealed gold tube, gradually cooled to 973 K at a rate of 5 K/h, and then cooled naturally. The products were easily separated from the frozen flux by rinsing the gold tube in water for several minutes. The crystals thus obtained were investigated by SEM–EDX analysis, inductive coupled plasma spectroscopy (ICP), and atomic absorption spectroscopy. The crystal symmetry and structural data were examined by the single-crystal X-ray diffraction method.

RESULTS AND DISCUSSION

Single Crystal Synthesis

Black, hexagonal platelet crystals of about $2 \times 2 \times 0.3$ mm^3 (maximum) were obtained, as shown in Fig. 1. The grown single crystals were found at the bottom of the frozen flux. They were easily separated in air because of the deliquescence of the flux material. EDX analysis showed that the crystals were free from gold contamination from the

[1]To whom correspondence should be addressed.

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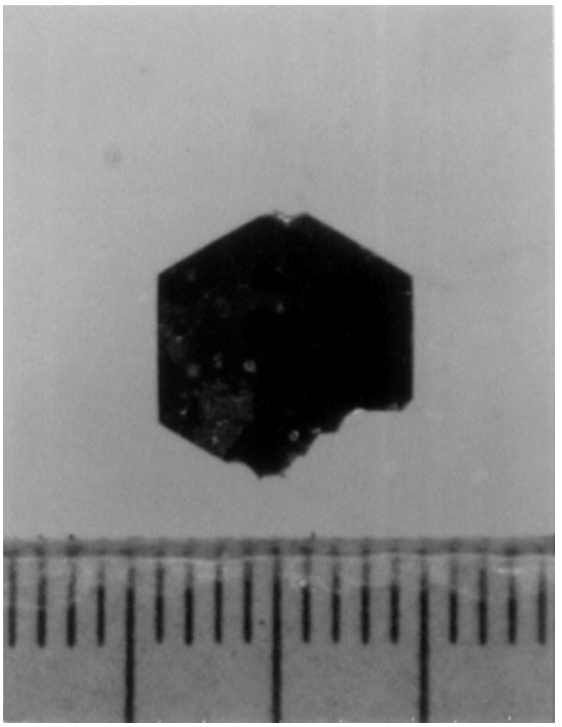

FIG. 1. The photograph of hexagonal platelet $LiCoO_2$ single crystal. (1 grid unit = 0.1 mm).

tube. The chemical formula, analyzed by ICP for the Co content and by atomic absorption spectroscopy for the Li content, using the pulverized sample, was $Li_{1.0}Co_{1.0}O_2$, which is consistent with the results of the present structure refinement.

TABLE 1
Experimental and Crystallographic Data for $LiCoO_2$

Formula	$LiCoO_2$
Crystal system	Trigonal
Space group	$R\bar{3}m$
a (Å)	2.8161(5)
c (Å)	14.0536(5)
V (Å^3)	96.52(3)
Z	3
D_x (g/cm^3)	5.051
Crystal size (μm)	$250 \times 150 \times 20$
Temperature (K)	300
Scan type	2θ–ω
Scan speed (°/min)	1
Maximum 2θ	120
Absorption correction	Gaussian integration
Transmission factors	
Min.	0.242
Max.	0.864
Observed reflections ($> 3\sigma$)	217
Number of variables	9
R	0.031
wR [w $= 1/\sigma^2 F$]	0.035
Extinction parameter g	296(17)

TABLE 2
Atomic Coordinates, Displacement Parameters,[a] and Site Occupancy Factors

Atom	Position	x	y	z	U_{eq}	U_{33}	U_{12}	s.o.f.
Li	3a	0	0	0	0.017(4)	0.009(4)	0.010(2)	1
Co	3b	0	0	1/2	0.00255(15)	0.00322(17)	0.00111(7)	1
O	6c	0	0	0.23951(15)	0.0045(4)	0.0045(6)	0.0023(2)	1

[a] $U_{11} = U_{22} = 2U_{12}$, $U_{23} = U_{13} = 0$.

Crystals were examined with an X-ray precession camera (Mo$K\alpha$ radiation) in order to check on crystal quality and to determine the lattice parameters, systematic extinctions, and possible superstructures. X-ray Laue (Fig. 2) and precession photographs (Fig. 3) confirmed the trigonal symmetry, space group $R\bar{3}m$ or $R3m$, and the lattice parameters. We could not find any superstructures in this study. The lattice parameters, determined by least-squares refinement using 2θ values of 25 strong reflections in the range 51.72°–68.22° and Mo$K\alpha_1$ radiation ($\lambda = 0.70926$ Å) on an automated Rigaku AFC-5S four-circle diffractometer, are $a = 2.8161(5)$ Å, $c = 14.0536(5)$ Å, $V = 96.52(3)$ Å^3, and $c/a = 4.990$. These values agree quite well with the reported powder data for $LiCoO_2$; e.g., $a = 2.8179(1)$ Å, $c = 14.0597(8)$ Å, and $c/a = 4.99$ (4).

Structure Refinement

A small hexagonal platelet crystal, $0.25 \times 0.15 \times 0.02$ mm in size, was used for the intensity data collection. The intensity data were collected in the 2θ–ω scan mode at a scan rate of 1°/min at 300 K on a four-circle diffractometer (operating conditions: 40 kV, 30 mA), using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The

TABLE 3
Selected Bond Distances (Å) and Angles (°)

	Present study	Orman and Wiseman (3)
	LiO_6 octahedron	
Li–O	2.0934(14)	2.092(5)
O–O	2.8161(5)	2.815(1)
O–O′	3.098(3)	3.095(14)
O–Li–O	84.54(5)	84.6(1)
O–Li–O′	95.46(5)	95.4(1)
	CoO_6 octahedron	
Co–O	1.9213(12)	1.921(5)
O–O	2.8161(5)	2.815(1)
O–O′	2.614(2)	2.616(13)
O–Co–O	94.25(5)	94.2(1)
O–Co–O′	85.75(5)	85.8(1)

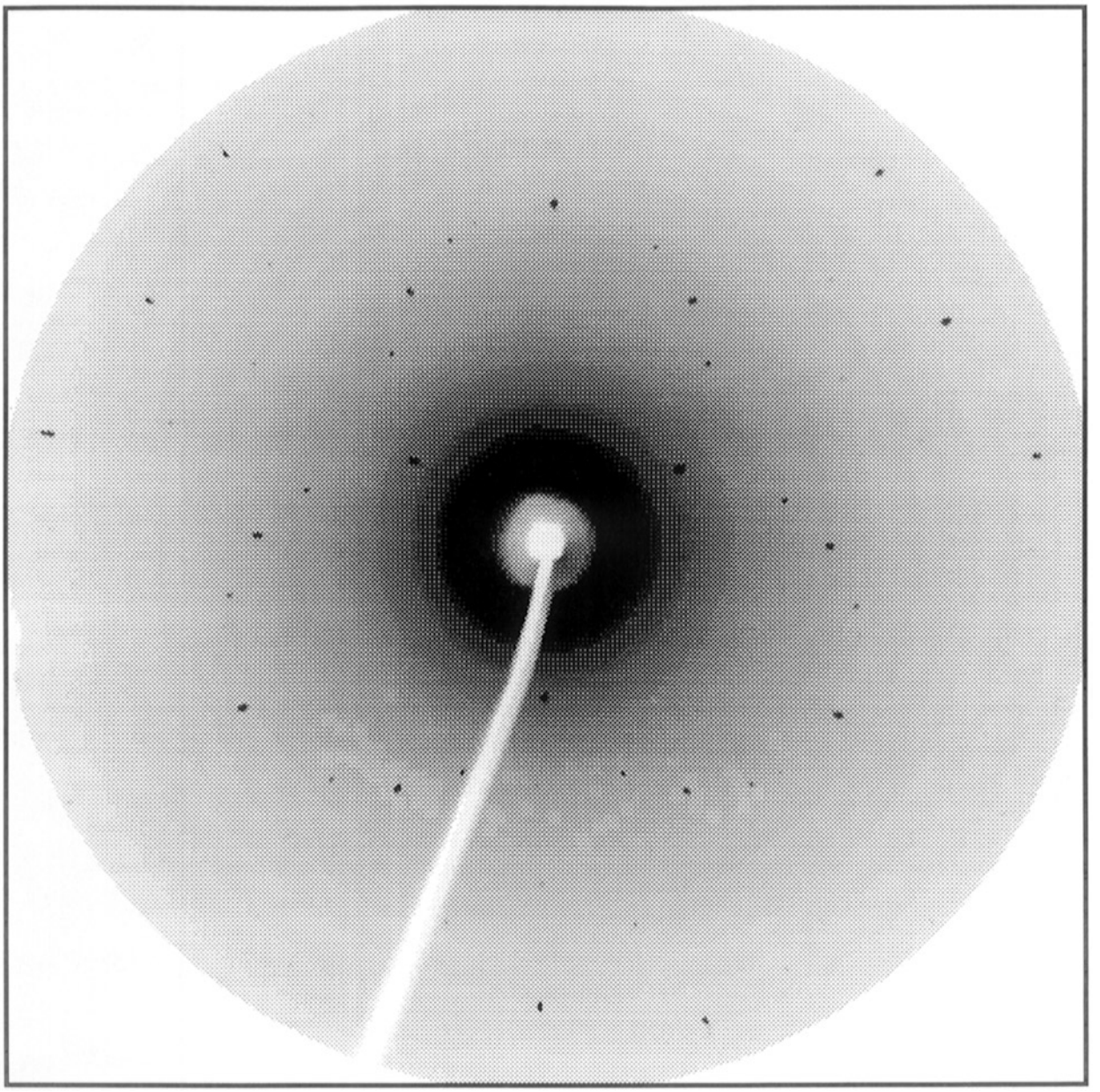

FIG. 2. X-ray transmission Laue photograph of $LiCoO_2$ single crystal, taken using the precession camera (Mo$K\alpha$ radiation). The incident beam direction is parallel to the crystallographic c-axis. Threefold symmetry is clearly observed.

fluctuation of intensities, monitored by examining a set of three standard reflections ((015), (110), (009)) and taken after every 50 observations, was within 0.67%. A total of 217 independent reflections were obtained within the limit of $2\theta \leq 120°$, all of which meet the criterion of $|F_0| > 3\sigma(|F_0|)$. Absorption and extinction corrections were performed. All calculations were carried out using the XTAL3.4 program (8).

In the structure analysis that followed, the space group of highest symmetry, $R\bar{3}m$, confirmed by successful refinement, was adopted. The refinement was initiated with the atomic coordinates specified by Orman and Wiseman (3). The R value using isotropic displacement parameters was 6.6%, showing that the structure model adopted was reasonable. At this stage, site-population refinements were applied, using three structural models as follows: (I) the 100% Li occupation model at the 3a site, (II) the Li-site deficiency model at the 3a site, (III) the Li/Co substitutional model at the 3a and 3b sites. The structural model (II), however, did not significantly improve either the R value or the

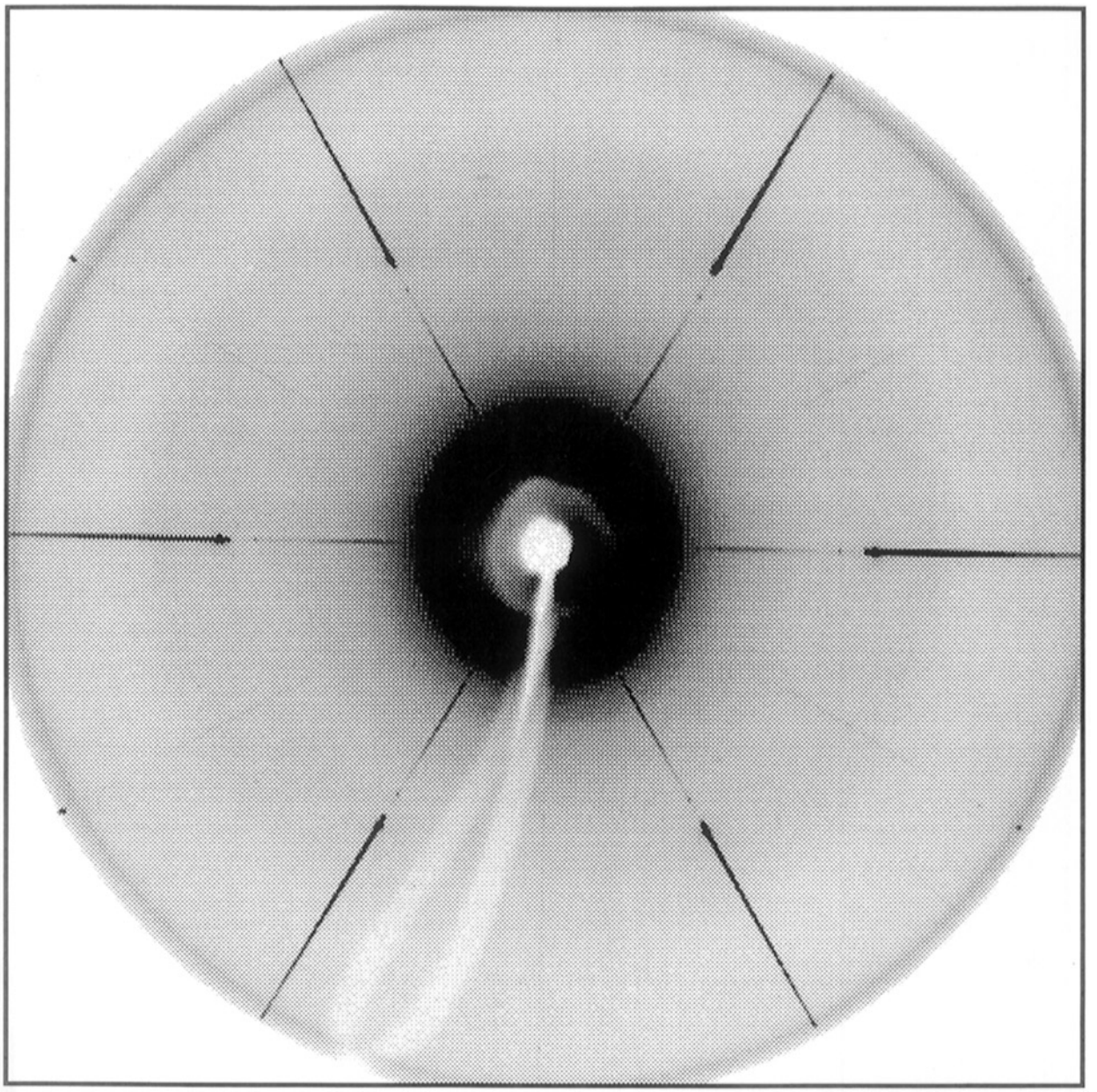

FIG. 3. The $\{hk0\}^*$ precession photograph of the $LiCoO_2$ single crystal using Mo$K\alpha$ radiation filtered by Zr.

difference-Fourier map, compared to model (I). Furthermore, the structural model (III) led to a negative occupancy value for the Co ions at the 3*a* site and for the constrained Li ions at the 3*b* site, respectively. These results clearly indicate that the Li ions are located with 100% occupancy in the 3*a* site, as reported by Orman and Wiseman (3). A difference-Fourier synthesis, using the final atomic parameters, showed no significant residual peak. Finally, the structure was refined to $R = 3.1\%$ and $wR = 3.5\%$ for 217 reflections, with a shift/error for all nine parameters less than 0.001. The crystallographic and experimental data are summarized in Table 1. The final atomic coordinates and displacement parameters are given in Table 2.

The refined oxygen parameter z is 0.23951(15), which is in good agreement with the previous result of $z = 0.2396(6)$ from Orman and Wiseman (3), based on powder neutron diffraction data. Accordingly, the negative deviation of the z parameter from the ideal value of 0.25 compresses the

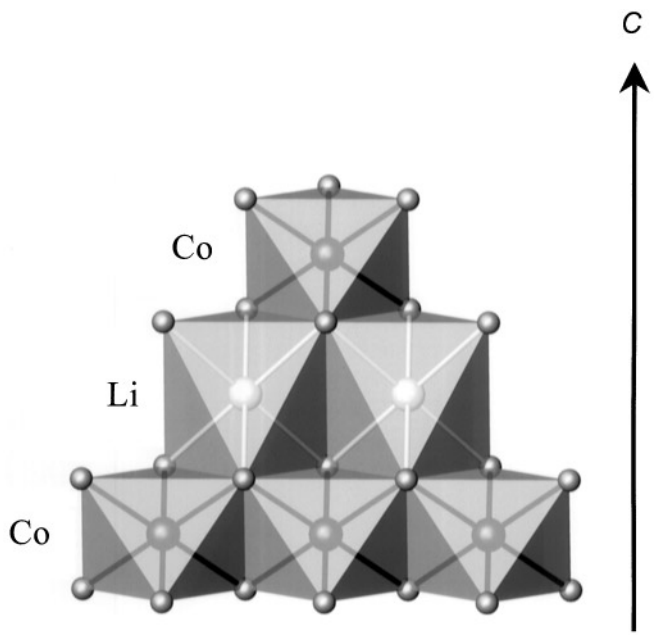

FIG. 4. The stacking representation of the compressed CoO_6 octahedra and the elongated LiO_6 octahedra along the *c*-axis direction in $LiCoO_2$, drawn with ATOMS by Shape Software.

CoO_6 octahedra and elongates the LiO_6 octahedra, as shown in Fig. 4 and Table 3. The bond distances and angles are essentially consistent with the previous results, but with higher accuracy. The short O–O contact distance of 2.614(2) Å in the CoO_6 octahedron is confirmed by the present single-crystal X-ray structure refinement.

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