Cobalt(III) Lithium Oxide, CoLiO₂: Structure Refinement by Powder Neutron Diffraction

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Abstract. $M_r = 97.9$, hexagonal, $R\bar{3}m$, $a = 2.815$ (1), $c = 14.05$ (1) Å, $V = 96.4$ Å³, $Z = 3$, $D_x = 5.06$ g cm⁻³, $\lambda = 1.520$ Å, $\mu = 0.886$ cm⁻¹, $R_{wp} = 11.8\%$. The structure has been refined by profile analysis of room-temperature (298 K) powder neutron data using natural and isotopically enriched lithium samples. It is a completely ordered rock-salt structure with alternate planes of lithium and cobalt atoms.

Introduction. It has been shown recently that a phase Li_xCoO_2 ($0 < x \le 1$) can be prepared by electrochemical extraction of Li from parent $LiCoO_2$ (Mizushima, Jones, Wiseman & Goodenough, 1980; Mizushima, Goodenough & Wiseman, 1980), and that it can be used as a battery cathode material. Mobility of lithium ions within the structure is high, but appears to be much lower in other Li_xMO_2 phases. Critical structural parameters are the bottleneck sizes to lithium motion and the degree of ordering of the cations. The previously known end member, $LiCoO_2$, has only been subjected to a powder X-ray study (Johnston, Heikes & Sestrich, 1958).

Experimental. $LiCoO_2$ prepared by heating stoichiometric mixture of Li_2CO_3 and Co metal (Koch Light Laboratories) at 1073 K in air for 20 h, followed by repeated grinding and heating; powder X-ray pattern confirmed a single phase. Sample analysed for total cobalt by ethylenediaminetetraacetic acid titration, and the oxidizing power determined by reaction with excess potassium iodide and back-titration with standardized thiosulphate; found 59.6% Co^{III} (theoretical 60.2%). In view of the high neutron absorption coefficient of lithium a sample of $^7LiCoO_2$ was prepared and characterized by an analogous method using $^7Li_2CO_3$ as a starting material (Isotope Production Unit, AERE Harwell, >99.95% ^{7}Li).

Neutron powder profile for $LiCoO_2$ recorded (298 K, atmospheric pressure) on diffractometer PANDA at AERE Harwell, 2θ 11–108° in steps of 0.1°; sample (~10 g) contained in thin-walled vanadium can; neutron wavelength 1.520 Å, obtained by reflection from (511) planes of crushed-Ge monochromator with take-off angle 90°; neutron powder profile for $^7LiCoO_2$ recorded (298 K, atmospheric pressure) on the 10HPD diffractometer, AERE Harwell, 2θ 7–125°, wavelength

1.00 Å, (422) planes of Cu monochromator used at take-off angle 85°. Powder neutron profile for $LiCoO_2$ could be indexed in $R\bar{3}m$ as suggested by powder X-ray work; X-ray parameters used as trial coordinates in least-squares refinement (Rietveld, 1969); $M = \sum_i w_i \times [y_i(\text{obs}) - cy_i(\text{calc})]^2$ minimized, w_i is weighting function ($= 1/Y_i$, where Y_i is number of counts at $2\theta_i$ before correction for background), y_i is corrected number of counts at point $2\theta_i$ and c is scale factor; background determined in peak-free regions of profile, other values obtained by interpolation; contribution from a given reflection taken as one and a half times the full width at half height on either side of the peak centre; no regions of profile excluded from the refinement; scattering lengths $b(\text{Li}) = -2.14$, $b(^7\text{Li}) = -2.33$, $b(\text{Co}) = 2.5$, $b(\text{O}) = 5.8$ fm (Bacon, 1975); refinement of $LiCoO_2$ included scale factor, three half-width parameters, zero-point correction, lattice constants, O$_z$ positional parameter, three isotropic thermal parameters and one cation disorder parameter; corrections unnecessary for peak asymmetry and preferred orientation; $R_{wp} = 100\{\sum_i w_i[y_i(\text{obs}) - cy_i(\text{calc})]^2/\sum_i w_i[y_i(\text{obs})]^2\}^{1/2} = 11.8\%$, compared with 11.1% expected on purely statistical grounds; parameter shifts in last refinement cycle not greater than 5% of the e.s.d.; atom parameters are given in Table 1; e.s.d.'s calculated according to the original Rietveld formulation. Neutron profile of $^7LiCoO_2$ refined in an analogous manner, $R_{wp} = 7.3\%$ (expected 6.8%); atom parameters given in Table 2 and agreement between observed and calculated profiles shown in Fig. 1.* The structure is illustrated in Fig. 2 and, in an idealized form, in Fig. 3. In both refinements tetrahedral coordination of the lithium atoms led to a rapid rise in the R_{wp} value.

Discussion. The linear absorption coefficient for the natural isotopic material was calculated to be 0.886 cm⁻¹. This only results in an additional contribution to the thermal and scaling parameters (Hewat, 1979). For the isotopically enriched sample, $\mu =$

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* A list of numercial values of each measured point (minus background) for $^7LiCoO_2$ has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38909 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0·2 cm⁻¹. While the positional parameter is the same for both samples, a more precise fix of the occupancy parameter is obtained for the enriched sample. This is mainly due to the extra data afforded by working at a lower wavelength and it does not appear essential to work with enriched material. The following discussion refers to the parameters determined from the enriched study.

The ordering of lithium and cobalt atoms into alternate (111) planes of the cubic close-packed oxygen lattice of $LiCoO_2$ is essentially perfect. The octahedra are distorted, the negative deviation of the O_z parameter from 0·25 compresses the CoO_6 octahedra and elongates the LiO_6 octahedra. The Li—O and Co—O bond distances are 2·092 (5) and 1·921 (5) Å, respectively; they compare favourably with their ionic radii [octahedral Li⁺, 0·76 Å; three-coordinate O^{2-}, 1·36 Å; low-spin, octahedral Co^{3+}, 0·545 Å; Shannon (1976)]. The LiO_6 octahedra are described by two O—O bond distances, O(1)—O(2) = 2·815 (1) and O(1)—O(3) = 3·095 (14) Å; and by two O—Li—O bond angles, O(1)—Li—O(2) = 84·6 (1) and O(1)—Li—O(3) = 95·4 (1)°. Corresponding figures for the CoO_6 octahedra are 2·815 (1), 2·616 (13) Å, 94·2 (1) and 85·8 (1)°. The shortest O—O contact of 2·62 Å is suggestive of an O^{2-} radius in this compound of 1·31 Å. This reduced value is compatible with the high covalent character of the Co^{III}—O bond.

The structure of Li_xCoO_2 is closely related to that of $LiCoO_2$ (Thomas & Wiseman, 1984). It is, therefore, worth considering the geometry of the probable Li⁺-ion tunnel route assuming the presence of some Li⁺-ion intrinsic vacancies. This should occur within the lithium layer via empty adjacent face-shared tetrahedral sites (Fig. 4). The maximum radius of an ion that can pass through the common triangular face without requiring expansion of the face (the bottleneck radius) is given by $R = [d_1^2/2(d_1^2 - d_2^2)^{1/2}] - r(O^{2-})$, where d_1 and d_2 are the

Table 1. Atomic parameters for $LiCoO_2$ ($\lambda = 1·520$ Å)

		x	y	z	$B(Å^2)$	Number of atoms/ unit cell
Li(1)	3(a)	0·0	0·0	0·0	1·1 (4)*	2·84 (4)
Li(2)	3(b)	0·0	0·0	0·5	1·1 (4)	0·16 (4)
Co(1)	3(a)	0·0	0·0	0·0	0·1 (3)	0·16 (4)
Co(2)	3(b)	0·0	0·0	0·5	0·1 (3)	2·84 (4)
O	6(c)	0·0	0·0	0·2394 (9)	0·2 (1)	6·0

* E.s.d.'s in parentheses.

Table 2. Atomic parameters in ⁷$LiCoO_2$ ($\lambda = 1·00$ Å)

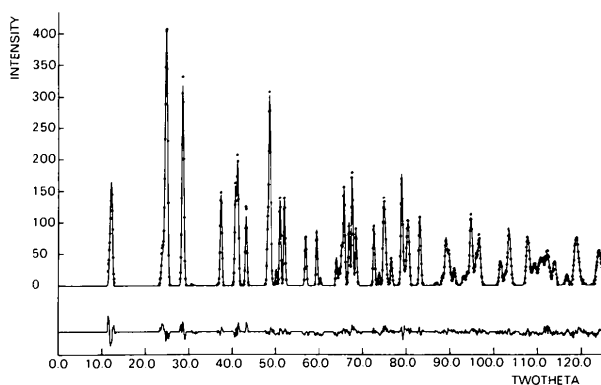|		x	y	z	$B(Å^2)$	Number of atoms/ unit cell
Li(1)	3(a)	0·0	0·0	0·0	0·93 (5)	3·00 (2)
Li(2)	3(b)	0·0	0·0	0·5	0·93 (5)	0·00 (2)
Co(1)	3(a)	0·0	0·0	0·0	0·16 (3)	0·00 (2)
Co(2)	3(b)	0·0	0·0	0·5	0·16 (3)	3·00 (2)
O	6(c)	0·0	0·0	0·2396 (6)	0·24 (1)	6·0

Fig. 1. Observed and calculated profile for ⁷$LiCoO_2$; filled circles, observed; line, calculated; lower trace, difference plot.
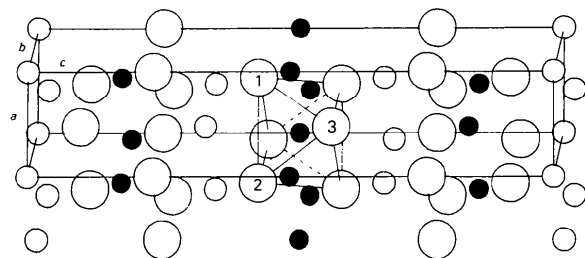

Fig. 2. $LiCoO_2$ structure; small filled circles, Co atoms; small empty circles, Li atoms; large empty circles, O atoms.
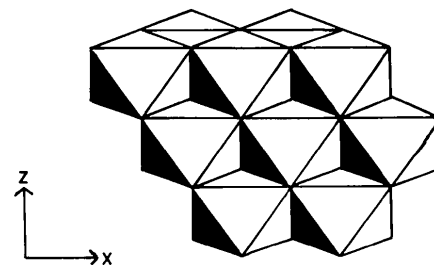

Fig. 3. Idealized $LiCoO_2$ structure; Co atoms in upper and lower sheets; Li atoms in middle sheet.
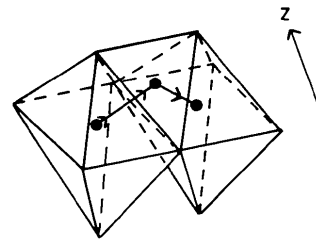

Fig. 4. Idealized tunnel route for Li⁺-ion migration.

long and short O–O distances of the LiO_6 octahedra and $r(O^{2-})$ is the ionic radius of the O^{2-} ion. For $r(O^{2-}) = 1.36$ Å, $R = 0.38$ (1) Å; for $r(O^{2-}) = 1.31$ Å, $R = 0.43$ (1) Å. The bottleneck radius is therefore quite small, although in four coordination the Li^+ ionic radius has dropped to 0.59 Å. The structural data suggest that fast Li^+-ion transport may be found even when the bottleneck to motion appears too small. The almost perfect cation ordering facilitates such motion because the presence of highly charged Co^{III} atoms in the lithium layer would impede the motion in a manner similar to that of interlayer Ti atoms in the CdI_2 structure of $Ti_{1+x}S_2$ (Whittingham & Gamble, 1975).

References

BACON, G. E. (1975). *Neutron Diffraction*, 3rd ed., pp. 39–41. Oxford Univ. Press.
HEWAT, A. W. (1979). *Acta Cryst.* A**35**, 248.
JOHNSTON, W. D., HEIKES, R. R. & SESTRICH, D. (1958). *J. Phys. Chem. Solids*, **7**, 1–13.
MIZUSHIMA, K., GOODENOUGH, J. B. & WISEMAN, P. J. (1980). US Patent No. 06/135222.
MIZUSHIMA, K., JONES, P. C., WISEMAN, P. J. & GOODENOUGH, J. B. (1980). *Mater. Res. Bull.* **15**, 783–789.
RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
THOMAS, M. G. S. R. & WISEMAN, P. J. (1984). In preparation.
WHITTINGHAM, M. S. & GAMBLE, R. R. (1975). *Mater. Res. Bull.* **10**, 363–371.

Dicesium Magnesium Bis(chromate) Hexahydrate, $Cs_2Mg(CrO_4)_2.6H_2O^*$

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Abstract. $M_r = 630.2$, monoclinic, $P2_1/a$, $a = 9.621$ (5), $b = 12.968$ (5), $c = 6.375$ (3) Å, $\beta = 106.17$ (4)°, $V = 763.9$ (5) Å^3, $Z = 2$, D_m(flotation) $= 2.70$, $D_x = 2.740$ Mg m^{-3}, $F(000) = 588$, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 6.35$ mm^{-1}, $T = 295$ K. The structure which is isomorphous with the corresponding diammonium nickel chromate has been determined by refinement of diffractometer data to a final R value of 0.069 for 1340 observed reflexions. The metal–water distances are 2.098 (3), 2.093 (3) and 2.057 (3) Å.

Introduction. In the continuing study of the variations of hexaaqua ions of the first transition group of elements (Montgomery, 1980), the structure of the title compound has been determined.

Experimental. Crystal $0.26 \times 0.19 \times 0.40$ mm from aqueous solution at room temperature, mounted along **c**, PDP-11-controlled Picker four-circle diffractometer, Zr-filtered Mo$K\alpha$ radiation; accurate cell dimensions by least-squares fitting of eight pairs of reflexions, $2\theta = 24$ to 41°; intensity measurements in the $\theta/2\theta$ scan mode, 60 steps of $0.04°$ in 2θ, counting 1 s/step and for 30s at each end of the scan; three standard reflexions recorded for every 50 observed reflexions; $2\theta \le 45°$, h −11 to 10, k 0 to 15, l 0 to 7, 1475 nonequivalent reflexions measured, 1340 observed at $3\sigma(I)$ level, corrected for Lorentz and polarization effects and for absorption by the method of Coppens, Leiserowitz & Rabinovich (1965). Initial atomic parameters taken from diammonium nickel chromate (Montgomery, 1979), least squares on $\sum w(|F_o| - |F_c|)^2$, $w = (A + B|F_o| + C|F_o|^2 + D|F_o|^3)^{-1}$, $A = 4.9272$, $B = 2.65394$, $C = -0.08266$, $D = 0.00183$; computer programs of Penfold (1969); scattering factors from *International Tables for X-ray Crystallography* (1974) and those for H from Stewart, Davidson & Simpson (1965), anomalous dispersion (real and imaginary) included for Cs, Mg and Cr; final pair of cycles run varying only the H-atom positions and individual isotropic temperature factors ($B = 5.0$ Å^2 initially);† final R 0.069, R_w 0.086; $(\Delta/\sigma)_{max} = 0.2$; difference-map excursions <0.3 e Å^{-3}; no correction for secondary extinction.

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* Tutton's Salts. XII.