Table 1. CsCl *structure type*(a)

	a (Å)		*a* (Å)
YCu	3·4757 (2)(b)	YbAu	3·5634 (7)
YCu(c)	3·477	YIn	3·806 (2)
YCu(d)	3·474	LaIn	3·985 (1)
EuCu	3·479 (3)	PrIn	3·955 (4)
YAg	3·6196 (7)	TmIn	3·739 (1)
YAg(c)	3·617	YbIn	3·8138 (5)
YAg(e)	3·619	TmTl	3·670 (2)
YbAg	3·6787 (4)	TmTl(f)	3·711 (3)

Efforts to prepare YCo resulted in no such compound being formed.

(*a*) *Strukturbericht*, **1**, 74 (1931).
(*b*) Calculated standard deviations are given in parentheses.
(*c*) Dwight (1959).
(*d*) Domagala, Rausch & Levinson (1961).
(*e*) Bruzzone & Ferro Ruggiero (1962–63).
(*f*) Iandelli & Palenzona (1965).

Table 2. $MgCu_2$ *structure type*(a)

	a (Å)
$TmPt_2$	7·556 (2)(b)
$YbPt_2$	7·381 (4)
$TbFe_2$	7·368 (3)
$TbFe_2$(c)	7·369

Efforts to prepare $YbFe_2$, $EuFe_2$, $YbMn_2$, $EuMn_2$, $SmMn_2$, $EuCo_2$, and $EuNi_2$ resulted in no such compounds being formed.

(*a*) *Strukturbericht*, **1**, 490 (1931).
(*b*) Calculated standard deviations are given in parentheses.
(*c*) Krip'yakevich, Teslyuk & Frankevich (1965).

Table 3. $MoSi_2$ *structure type*(a)

	a (Å)	*c* (Å)
$YbAu_2$	3·6274 (7)(b)	8·889 (6)
$YbAg_2$	3·624 (2)	8·88 (2)

(*a*) *Strukturbericht*, **1**, 741 (1931).
(*b*) Calculated standard deviations are given in parentheses.

Table 4. $AuCu_3$ *structure type*(a)

	a (Å)		*a* (Å)
$YbAl_3$	4·2036 (3)(b)	$PrPt_3$	4·0650 (4)
$YbAl_3$(c)	4·202	$NdPt_3$	4·0590 (8)
$TbIn_3$	4·5896 (3)	$SmPt_3$	4·0633 (7)
$TbIn_3$(d)	4·588	$TbPt_3$	4·0839 (6)
$TmIn_3$	4·561 (1)	$TmPt_3$	4·0423 (4)
$TmIn_3$(d)	4·554	$YbPt_3$	4·0455 (1)
$YbIn_3$	4·6164 (4)	La_3In	5·075 (1)
$YbIn_3$(d)	4·620	La_3In(e)	5·07
$EuTl_3$	4·718 (5)	Ce_3In	5·0006 (7)
$TbTl_3$	4·679 (1)	Ce_3In(f)	4·9610 (5)
$TmTl_3$	4·6554 (3)	Pr_3In	4·9636 (8)
$LaPt_3$	4·0745 (8)	Pr_3In(g)	4·93
$CePt_3$	4·162 (1)	Nd_3In	4·9296 (6)

(*a*) *Strukturbericht*, **1**, 486 (1931).
(*b*) Calculated standard deviations are given in parentheses.
(*c*) van Vucht & Buschow (1964).
(*d*) Kuz'ma & Markiv (1964).
(*e*) McMasters & Gschneidner (1964).
(*f*) Dariel (1966).
(*g*) Iandelli (1947).

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Reinvestigation of the crystal structure of lithium iodate.

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Discussion of the structure

From their early X-ray study of lithium iodate Zachariasen & Barta (1931) concluded that the iodine atoms were regularly surrounded by six oxygen atoms. Irregular coordination polyhedra were observed, however, in iodates which were investigated more accurately later on ($NaIO_3$, MacGillavry & Panthaleon van Eck, 1943; $Ce(IO_3)_4$, Cromer & Larsson, 1956; $Ce(IO_3)_4.H_2O$, Ibers, 1956; Ibers & Cromer, 1958). During the present reinvestigation of the crystal structure of lithium iodate we found that the symmetry of the crystals is lower than was assumed by Zachariasen & Barta (Table 1). The hexagonal close packing *ABABAB* with the iodine atoms in the centres of regular octahedra is distorted. Fig. 1 clearly shows that in the structure separate IO_3 groups with symmetry 3 are present; the I–O distance is 1·809 Å, the angle O–I–O 99·5°. The oxygen atoms of the IO_3 groups are coordinated to iodine atoms of neighbouring IO_3 groups at distances, 2·892 Å, which are much (approximately 0·7 Å) shorter than the sum of the van der Waals radii. Owing to the strong interaction between neighbouring IO_3 groups a firm three-dimensional network is formed, in which the atoms have a small thermal motion (Table 4). The short and the long I–O distances may be compared with corresponding distances in $NaIO_3$, 1·80, 1·83 Å and 2·84, 3·30 Å respectively. The lithium ions are regularly surrounded by six oxygen atoms. The two independent Li···O distances, 2·11 and 2·13 Å, are equal within experimental error.

Table 1. *Crystallographic data and special positions of the atoms*

	Present work*	Z. & B. (1931)
Space group	$P6_3$	$P6_322$
a	5·478, s.d. 0·003 Å	5·469 Å
c	5·170, s.d. 0·002	5·155
Z	2	2
Li	$0,0,z;\ 0,0,z+\frac{1}{2}$	$0,0,\frac{1}{4};\ 0,0,\frac{3}{4}$
I	$\frac{1}{3},\frac{2}{3},\frac{1}{4};\ \frac{2}{3},\frac{1}{3},\frac{3}{4}$	$\frac{1}{3},\frac{2}{3},\frac{1}{4};\ \frac{2}{3},\frac{1}{3},\frac{3}{4}$
O	*x*,*y*,*z etc.*	*x*,0,0 *etc.*

* The space group $P6_3/m$ was excluded by geometrical considerations. The polar *z* coordinate of the iodine atom was fixed at $z=\frac{1}{4}$.

Experimental

The cell constants and intensities were obtained with an automatic Nonius single-crystal diffractometer. The crystals used were of nearly hexagonal shape with symmetry 6/*m*, somewhat elongated in the **c** direction and bounded by {100}, {101} and {001}. The cell constants were determined from 64 θ values of high order reflexions ($48 \le \theta \le 59°$, $\lambda(\text{Mo } K\alpha_1)=0·70926$, $\lambda(\text{Mo } K\alpha_2)=0·71354$ Å) of a small crystal (diameter $\varphi \simeq 0·06$ mm, height $h=0·10$ mm). Two larger crystals were used for the collection of the intensities, crystal I with $\varphi \simeq 0·14$ mm, $h=0·17$ mm and crystal II with $\varphi \simeq 0·20$ mm, $h=0·26$ mm. For both crystals all independent reflexions *hkl* with $\theta \le 56°$ were measured with zirconium-filtered Mo radiation by the moving-crystal moving-counter method. Deviations from linearity of the (scintillation) counting equipment were kept below 1% by the use of attenuation filters. The intensities were corrected for Lorentz and polarization effects and for absorption ($\mu=117$ cm^{-1}). The absorption corrections were calculated according to the Busing & Levy (1957) scheme; for each crystal 6×6×6 volume fragments and 20 bounding planes were considered. Reflexions with strong extinction or low statistical weight were not taken into account during the refinement. 576 reliable reflexions were available for crystal I, and 567 for crystal II.

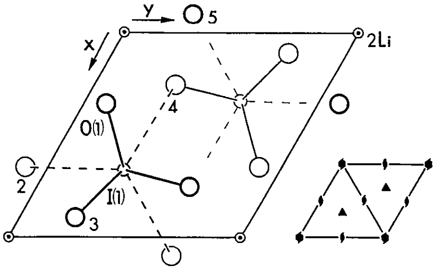

Fig. 1. The crystal structure of $LiIO_3$ viewed along the *c* axis.

It was not difficult to find the position of the oxygen atoms from Fourier maps. In the latter stages of refinement *z*(Li) could be determined from the difference density *D*(0,0,*z*). This density showed two independent peaks at positions related by a pseudo centre (inversion centre of the iodine atoms) in the structure, *viz.* a maximum of 5·6 $e.Å^{-3}$ at $z=0·67$ and a maximum of 5·3 $e.Å^{-3}$ at $z=0·33$. The former position was accepted since the latter is too close to the oxygen atoms at $z=0·42$.

The structure was refined independently for the two crystals. The calculations were done on a TR4 computer with an anisotropic least-squares program written by Palm and Peterse according to Cruickshank's scheme (Cruickshank, 1961). The temperature factor of the lithium atom was assumed to be isotropic with $B=1$ $Å^2$. The non-anomalous parts of the scattering factors were represented by analytical functions (Moore, 1963), for lithium $f(Li^+)$ was used, for oxygen $\frac{1}{4}f(O^-)+\frac{3}{4}f(O)$. For iodine the anomalous scattering was taken into account with $\Delta f'=-0·5$ and $\Delta f''=2·4$. During the final refinement cycles the weighting scheme was $w=250\ [250+(15-|F_o|)^2]^{-1}$ for both crystals. The index *R* decreased to 0·022 for the reliable reflexions of crystal I, and to 0·023 for those of crystal II.

The atomic coordinates are listed in Table 2, together with the standard deviations as calculated by the least-squares program (c.s.d.). Except for *z*(O) for which a difference of 0·024 Å was observed, the values obtained for the two crystals agree within the calculated standard deviations. The average values of corresponding coordinates were taken as final coordinates. Estimated values for their standard deviations (e.s.d.) were obtained by considering the atomic shifts due to changes in the weighting scheme, the differences observed for the two crystals and the c.s.d. The atomic distances and valence angles are listed in Table 3; their standard deviations were obtained from the e.s.d. in Table 2.

The thermal parameters are listed in Table 4. The values obtained for the two crystals show systematic differences,

Table 2. *Atomic coordinates and standard deviations* (*see text*)

	Crystal I	Crystal II	c.s.d.	Final coordinate	e.s.d.
z(Li)	0·662	0·661	0·004	0·661	0·005
x(0)	0·3420	0·3430	0·0006	0·3425	0·0008
y(0)	0·0940	0·0941	0·0007	0·0940	0·0008
z(0)	0·9175	0·9129	0·0008	0·9152	0·0025

Table 3. *Atomic distances* (Å) *and angles* (°)

The e.s.d.'s are given in brackets

I(1) –O(1)	1·809 (0·008)	O(2)–O(3)	3·082 (0·003)
I(1) –O(2)	2·892 (0·009)	O(2)–O(4)	4·012 (0·007)
Li––O(1)	2·13 (0·019)	O(1)–I(1)–O(2)	94·73 (0·2)
Li––O(4)	2·11 (0·019)	O(1)–I(1)–O(3)	99·54 (0·5)
O(1)–O(2)	3·535 (0·006)	O(1)–I(1)–O(4)	78·24 (0·2)
O(1)–O(3)	2·763 (0·007)	O(2)–I(1)–O(4)	87·85 (0·3)
O(1)–O(5)	2·908 (0·007)	O(3)–I(1)–O(4)	165·73 (0·4)

Table 4. *Thermal parameters of the temperature factor*

$$\exp\{-\tfrac{1}{4}[h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2hla^*c^*U_{13}]\}$$

Crystal I	U_{11}	U_{22}	$2U_{12}$	U_{33}	$2U_{13}$	$2U_{23}$
I	0·53	0·53	0·53	0·46	0	0
O	0·71	1·11	0·55	0·99	0·35	0·44
Crystal II						
I	0·50	0·50	0·50	0·43	0	0
O	0·64	0·99	0·46	0·96	0·38	0·44

all atoms in the larger crystal II having smaller thermal parameters than the corresponding atoms in crystal I. This systematic difference is presumably largely caused by the extinction in crystal II being larger than that in crystal I; to a smaller extent systematic errors in the absorption corrections may play a part (Jellinek, 1958).

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The crystal structure of niobium monoxide.*

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The crystal structure of niobium monoxide has been described as cubic, space group *Pm*3*m*, with three niobium atoms in 3(*c*) $(0\frac{1}{2}\frac{1}{2};\ \frac{1}{2}0\frac{1}{2};\ \frac{1}{2}\frac{1}{2}0)$ and three oxygen atoms in 3(*d*) $(\frac{1}{2}00;\ 0\frac{1}{2}0;\ 00\frac{1}{2})$, (Brauer, 1941; Andersson & Magnéli, 1957) on the basis of X-ray powder diffraction data. However, only the niobium positions could be determined with certainty because of the relatively small X-ray scattering power of oxygen. We have now confirmed the oxygen positions by neutron diffraction.

Niobium monoxide was prepared by heating a stoichiometric mixture of niobium and Nb_2O_5 powders for 1 hour at 1700° under vacuum of 5×10^{-6} torr or better. A lattice constant of $4{\cdot}2101\pm0{\cdot}0003$ Å was determined from X-ray powder diffraction data (copper $K\alpha$, $\lambda=1{\cdot}54051$ Å). The neutron-diffraction data were obtained at the Los Alamos Omega West reactor with a monochromatic beam, $\lambda=1{\cdot}1357$ Å and with a step increment of 0·2° in 2θ. The sample was contained in a parallel-sided holder made from a null-matrix alloy (Ti–Zr) (Sidhu, Heaton, Zauberis & Campos, 1956), and was placed in the symmetrical transmission position. The neutron and X-ray diffraction traces are shown in Fig. 1.

The observed neutron intensities were determined by least-squares analysis of the diffraction data (Bowman, Wallace, Yarnell, Wenzel & Storms, 1965), and were fitted to the trial structure by least-squares solution of the equation (Bacon, 1962)

$$I=K\frac{\exp(-\mu t\sec\theta)}{\sin^2 2\theta}\exp\left(-2B\frac{\sin^2\theta}{\lambda^2}\right)jF^2\,,$$

with $K=0{\cdot}265\pm0{\cdot}002$, $B=0{\cdot}34\pm0{\cdot}02$, $R=0{\cdot}025$, where $R=\Sigma\, w|I_o-I_c|/\Sigma\, wI_o$. Neutron scattering lengths of $0{\cdot}691\times10^{-12}$ cm for niobium and $0{\cdot}577\times10^{-12}$ cm for oxygen were used. The observed and calculated neutron diffraction intensities are compared in Table 1. The excellent agreement fully confirms the previously assigned oxygen positions.

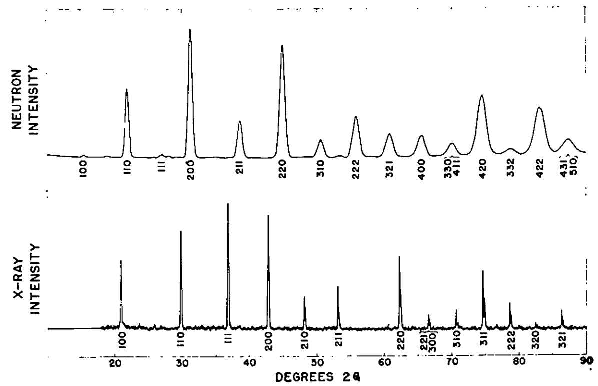

Fig. 1. Neutron ($\lambda=1{\cdot}1357$ Å) and X-ray ($\lambda=1{\cdot}54051$ Å) diffraction patterns of NbO.

Table 1. *Summary of experimental data*

hkl	*d*	*I* (obs)	*I* (calc)
100	4·210	<0·3	0·3
110	2·977	31·6	31·2
111	2·431	1·4	1·0
200	2·105	71·0	71·1
210	1·833	<0·3	0·2
211	1·719	22·4	21·4
220	1·489	73·9	73·7
221 300	1·403	<0·3	0·2
310	1·331	12·5	13·4
311	1·269	<0·3	0·9
222	1·215	33·2	34·2
320	1·168	<0·3	0·1
321	1·125	20·6	20·0
400	1·053	20·4	20·3
410	1·021	<0·3	0·1
411 330	0·992	11·8	12·4
331	0·966	<0·3	0·6
420	0·941	68·1	68·9
421	0·919	<0·3	0·1
332	0·898	5·5	7·2
422	0·859	62·7	61·8
500 430	0·842	<0·3	0·0
510 431	0·826	20·3	19·8

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