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The structure of lithium oxalate.

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Introduction

The dimensions of the oxalate ion have been determined by a number of workers (Table 1), but these results are not sufficiently accurate for a reliable comparison to be made with the dimensions of the oxamate ion (Beagley & Small, 1963*a*). The carbon–carbon bond of the oxamate ion was found to be rather long ($1·564 \pm 0·002$ Å) and in addition residual electron density occurred at its centre. It has been reported (Beagley & Small, 1963*b*) that the carbon–carbon in lithium oxalate has similar properties and this paper describes the structure determination in detail. The lithium salt was chosen for the study because it has the advantage that nearly all the scattering which takes place is from the oxalate ion.

Crystal data

Lithium oxalate crystallizes with difficulty from water and forms platey crystals elongated along the [*a*] axis. Wyckoff (1960) records that the crystals are orthorhombic, but this was not found to be so. From systematic absences the crystals were found to have the monoclinic space group $P2_1/n$.

Using approximate cell parameters obtained from Weissenberg photographs as a guide, the Bragg angles of the $h00$, $0k0$, $00l$, $h0l$ and $h0\bar{l}$ reflexions were measured accurately with a three-circle goniometer (Small & Travers, 1961) and Cu $K\alpha$ radiation. To eliminate the zero error of the θ-circle and any mis-setting of the φ-circle when measuring a reciprocal lattice row, the observed interplanar spacings, d_{obs}, were plotted against cot θ, and the linear graph extrapolated by least squares to cot $\theta = 0$ to give the corrected interplanar spacing, d. The measurements produced the following unit-cell parameters and estimated standard deviations:

$$a_0 = 3·400 \pm 0·001,\quad b_0 = 5·156 \pm 0·002,\quad c_0 = 9·055 \pm 0·003 \text{ Å}$$
$$\beta = 95° \ 36' \pm 1'$$

The density, D_x, calculated for two formula units of $Li_2C_2O_4$ in the unit cell, is 2·142 g.cm^{-3}. *The Handbook of Chemistry and Physics* (1962–1963) gives $D_m = 2·121$ g.cm^{-3} at 17·5 °C. Each oxalate ion is therefore situated at a centre of symmetry and the possibility that the two ends of the ion are twisted with respect to each other is excluded.

Determination of the structure

Three-dimensional intensity data were collected by the semi-automatic three-circle diffractometer developed by Small & Travers (1961) which employs a xenon-filled proportional counter. The details of the procedure adopted for the use of this instrument are described elsewhere (Beagley & Small, 1963*a*), although one important modification to the described system was in use during the study of lithium oxalate. The improvement, which was possible because of the acquisition of a highly stabilized X-ray generator, was that the duration of the counting periods was controlled by an oscillator producing a 600 c.p.s. square wave, instead of by a monitoring counter operating from the primary X-ray beam. One crystal only (dimensions $0·02 \times 0·02 \times 0·02$ cm) was used throughout this study for both the measurement of the cell parameters and the intensity measurements. The intensity of every one of the 345 unique reflexions with $\theta < 80°$ was measured; it was necessary in only two cases (excluding those of the systematically absent reflexions) to adopt a value of zero for an intensity.

Preliminary atomic coordinates for the carbon and oxygen atoms were rapidly determined from sharpened Patterson projections on (100) and (010) and a value of 1·2 Å^2 was adopted for the overall isotropic temperature constant, B. Using the phases derived from the positions of the oxygen and carbon atoms only, an F_o Fourier

Table 1. *Results of some earlier investigations of the oxalate ion*

Compound	C–C	Mean C–O	OCO	Twist	Reference
Sodium oxalate	1·54 Å	1·23 Å	124°	0°	Jeffrey & Parry (1954)
e.s.d.	0·04	0·02	—	—	
Ammonium oxalate monohydrate (i)	1·58	1·24	129	28	Hendricks & Jefferson (1936)
e.s.d.	0·01	0·02	2	—	
(ii)	1·56	1·24	125	28	Jeffrey & Parry (1952)
e.s.d.	0·02	—	—	—	
(iii)	1·569	1·258	—	26·6	Robertson (1961)
e.s.d.	0·014	0·014	—	0·4	
Silver oxalate	1·53	1·20	118	0	Griffith (1943)
e.s.d.	—	—	—	—	
$Cu(NH_4)_2(C_2O_4)_2.2H_2O$	1·58, 1·61	1·28	120	11, 15	Viswamitra (1962*a*)
e.s.d.	0·02	0·02	2	—	
$CuK_2(C_2O_4)_2.2H_2O$	1·56, 1·57	1·29	124	12, 24	Viswamitra (1962*b*)
e.s.d.	—	—	—	—	

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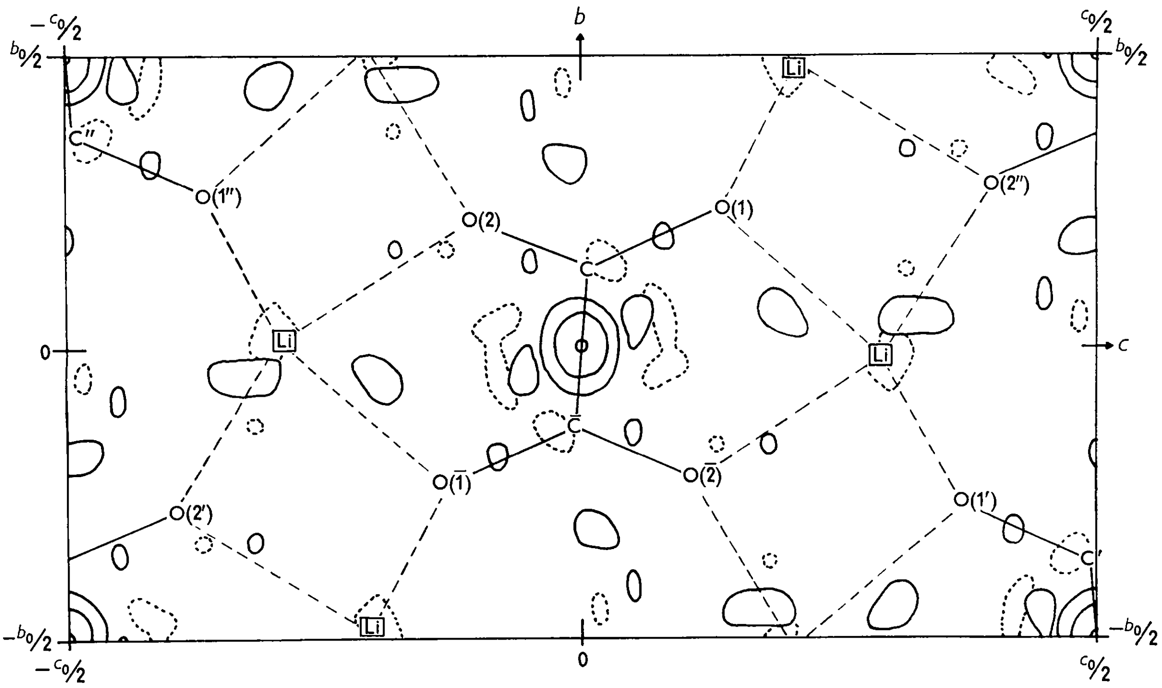

Fig. 1. Three-dimensional difference Fourier synthesis. F_o-F_c matrix weighted as in the least-squares refinement. All atoms subtracted. Plane of projection (100).

synthesis for each projection was calculated. The Fourier syntheses indicated the position of the lithium atom.

The atomic parameters were refined, using the whole of the three-dimensional data, on the MERCURY electronic computer of the University of Oxford, by means of the least-squares program written by Dr. J. S. Rollett (1960) which produces ellipsoidally anisotropic vibrational parameters. The weighting scheme used throughout the refinement was

$$\sqrt{w} = \sqrt{\frac{1}{1+[(|F_o|-4K)/4K]^2}}$$

where K, the scale factor, is approximately 0·68. For carbon, the atomic scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used; for oxygen, as $O^{\frac{1}{2}-}$, scattering factors were derived from those of Freeman (1959); and for lithium, as Li^+, those of Womack, Silverman & Matsen (1961) were used.

Refinement ceased at $R_{hkl} = 0·060$, when $\bar{\mathscr{S}}$, the mean of the estimated standard deviations of the atomic coordinates of the carbon and oxygen atoms was $16·7 \times 10^{-4}$ Å.

A three-dimensional F_o-F_c Fourier synthesis was computed at this point; the coefficients were weighted as in the least-squares refinement. A suitable projection of this is shown in Fig. 1. Contours are drawn at intervals of 3σ, where σ is the root mean square deviation of electron density averaged over the whole cell; the zero contour is omitted and the dotted contour is -3σ. A peak of electron density, of height about 10σ, can be seen at the centre of the carbon–carbon bond. A similar peak was observed in the case of ammonium oxamate (Beagley & Small, 1963*a*) and thus, although the lithium oxalate peak lies at a centre of symmetry, there is a strong indication that a significant region of electron density exists at the centre of the carbon–carbon bond. Smaller peaks ($< 4·5\sigma$) can be seen, notably at or near the centres of the carbon–oxygen bonds, and negative regions as low as -5σ occur, but there is doubt as to the significance of these features. As in the case of ammonium oxamate, an empirical correction was applied making allowance for the electron density in the carbon–carbon bond. Experience with ammonium oxamate suggested that a somewhat larger proportion of a hydrogen atom than one

Table 2. *Final fractional atomic coordinates*

Atom	x/a_0	y/b_0	z/c_0
C	0·10582	0·13418	0·00738
O(1)	0·13313	0·23698	0·13379
O(2)	0·23847	0·22028	−0·10649
Li^+	−0·05670	−0·01344	0·29179

Table 3. *Final vibrational parameters*

$$f = f_o[2^{-(h^2b_{11}+k^2b_{22}+l^2b_{33}+klb_{23}+lhb_{31}+hkb_{12})}]$$

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
C	0·04370	0·01649	0·00560	0·00124	0·00564	−0·00200
O(1)	0·07504	0·02191	0·00553	−0·00414	0·00848	−0·01896
O(2)	0·06320	0·02119	0·00608	0·00200	0·01508	−0·00832
Li^+	0·10810	0·02654	0·00693	−0·00285	0·00312	0·03937

Table 4. *Observed structure amplitudes and calculated structure factors*

hkl	$50\|F_o\|$	$50\,F_c$	hkl	$50\|F_o\|$	$50\,F_c$	hkl	$50\|F_o\|$	$50\,F_c$	hkl	$50\|F_o\|$	$50\,F_c$	hkl	$50\|F_o\|$	$50\,F_c$
0 0 2	721	877	1 1 0	695	803	1 4 $\bar{3}$	419	-431	2 2 $\bar{4}$	373	-348	3 1 $\bar{7}$	293	-291
0 0 4	1102	-1052	1 1 1	2049	-2212	1 4 $\bar{4}$	312	-321	2 2 $\bar{5}$	235	-215	3 1 $\bar{8}$	108	-121
0 0 6	183	201	1 1 2	114	137	1 4 $\bar{5}$	631	-634	2 2 $\bar{6}$	155	141			
0 0 8	810	807	1 1 3	283	266	1 4 $\bar{6}$	18	-6	2 2 $\bar{7}$	404	-407	3 2 0	138	-150
0 0 10	375	399	1 1 4	417	450	1 4 $\bar{7}$	170	166	2 2 $\bar{8}$	72	-68	3 2 1	578	565
			1 1 5	916	697	1 4 $\bar{8}$	118	121	2 2 $\bar{9}$	188	-192	3 2 2	126	-127
0 1 1	794	890	1 1 6	54	41	1 4 $\bar{9}$	40	41	2 2 $\overline{10}$	82	71	3 2 3	104	105
0 1 2	126	-124	1 1 7	365	-367							3 2 4	273	-267
0 1 3	513	565	1 1 8	23	19	1 5 0	104	95	2 3 0	238	237	3 2 5	279	-259
0 1 4	526	544	1 1 9	644	-642	1 5 1	185	-212	2 3 1	269	269	3 2 6	208	-200
0 1 5	82	-95	1 1 10	119	116	1 5 2	52	-59	2 3 2	104	114	3 2 $\bar{1}$	172	-186
0 1 6	27	22	1 1 $\bar{1}$	1393	-1277	1 5 3	216	222	2 3 3	117	-87	3 2 $\bar{2}$	229	-231
0 1 7	432	445	1 1 $\bar{2}$	44	81	1 5 4	46	51	2 3 4	364	-361	3 2 $\bar{3}$	468	-468
0 1 8	538	-545	1 1 $\bar{3}$	1162	1035	1 5 5	509	502	2 3 5	270	-273	3 2 $\bar{4}$	334	-308
0 1 9	114	116	1 1 $\bar{4}$	249	239	1 5 6	107	-121	2 3 6	216	-212	3 2 $\bar{5}$	43	-30
0 1 10	203	-209	1 1 $\bar{5}$	451	403	1 5 $\bar{1}$	58	-55	2 3 7	122	113	3 2 $\bar{6}$	268	-260
0 1 11	136	129	1 1 $\bar{6}$	382	368	1 5 $\bar{2}$	308	-315	2 3 8	32	-30	3 2 $\bar{7}$	449	455
			1 1 $\bar{7}$	468	-481	1 5 $\bar{3}$	409	414	2 3 $\bar{1}$	55	-46	3 2 $\bar{8}$	144	-155
0 2 0	1737	-1836	1 1 $\bar{8}$	146	153	1 5 $\bar{4}$	268	-260	2 3 $\bar{2}$	469	-462			
0 2 1	129	132	1 1 $\bar{9}$	194	-200	1 5 $\bar{5}$	207	200	2 3 $\bar{3}$	94	-100	3 3 0	198	204
0 2 2	413	-419	1 1 $\overline{10}$	235	222	1 5 $\bar{6}$	39	39	2 3 $\bar{4}$	757	-721	3 3 1	263	-280
0 2 3	106	105	1 1 $\overline{11}$	50	46	1 5 $\bar{7}$	132	-132	2 3 $\bar{5}$	344	-337	3 3 2	151	146
0 2 4	1393	1409							2 3 $\bar{6}$	128	128	3 3 3	194	-193
0 2 5	41	-41	1 2 0	705	-824	1 6 0	198	-190	2 3 $\bar{7}$	35	-19	3 3 4	137	133
0 2 6	131	116	1 2 1	466	-455	1 6 1	17	-4	2 3 $\bar{8}$	322	333	3 3 5	134	131
0 2 7	212	-222	1 2 2	424	-436	1 6 2	47	56	2 3 $\bar{9}$	32	-32	3 3 $\bar{1}$	87	-76
0 2 8	590	-605	1 2 3	198	193	1 6 3	178	171				3 3 $\bar{2}$	102	-102
0 2 9	174	-181	1 2 4	28	23	1 6 $\bar{1}$	133	-118	2 4 0	200	-214	3 3 $\bar{3}$	121	-115
0 2 10	30	-16	1 2 5	196	-207	1 6 $\bar{2}$	173	152	2 4 1	261	256	3 3 $\bar{4}$	112	-121
			1 2 6	180	-176	1 6 $\bar{3}$	237	228	2 4 2	402	-415	3 3 $\bar{5}$	99	-89
0 3 1	817	-836	1 2 7	133	132	1 6 $\bar{4}$	283	261	2 4 3	71	80	3 3 $\bar{6}$	208	197
0 3 2	34	39	1 2 8	299	-302				2 4 4	312	307	3 3 $\bar{7}$	34	-23
0 3 3	127	122	1 2 9	80	77	2 0 0	528	-460	2 4 5	43	32			
0 3 4	305	-310	1 2 10	224	-229	2 0 2	839	-762	2 4 6	222	217	3 4 0	110	-115
0 3 5	136	-145	1 2 $\bar{1}$	630	-594	2 0 4	800	765	2 4 $\bar{1}$	34	25	3 4 1	167	-172
0 3 6	204	-201	1 2 $\bar{2}$	213	-226	2 0 6	382	379	2 4 $\bar{2}$	78	70	3 4 2	16	-12
0 3 7	142	-153	1 2 $\bar{3}$	1026	950	2 0 8	338	-295	2 4 $\bar{3}$	236	-231	3 4 3	39	28
0 3 8	299	303	1 2 $\bar{4}$	40	46	2 0 $\bar{2}$	504	488	2 4 $\bar{4}$	37	35	3 4 $\bar{1}$	62	66
0 3 9	336	-351	1 2 $\bar{5}$	276	242	2 0 $\bar{4}$	586	549	2 4 $\bar{5}$	70	46	3 4 $\bar{2}$	87	77
0 3 10	58	68	1 2 $\bar{6}$	55	-53	2 0 $\bar{6}$	196	189	2 4 $\bar{6}$	123	-121	3 4 $\bar{3}$	497	462
			1 2 $\bar{7}$	414	-416	2 0 $\bar{8}$	30	-21	2 4 $\bar{7}$	225	228	3 4 $\bar{4}$	125	127
0 4 0	654	686	1 2 $\bar{8}$	172	-175	2 0 $\overline{10}$	183	171				3 4 $\bar{5}$	26	-15
0 4 1	34	-21	1 2 $\bar{9}$	427	-433				2 5 0	87	-102			
0 4 2	403	-420	1 2 $\overline{10}$	84	-91	2 1 0	1083	-1051	2 5 1	216	-214	4 0 0	150	-142
0 4 3	201	-218				2 1 1	42	23	2 5 2	100	97	4 0 2	162	-156
0 4 4	796	-808	1 3 0	157	-142	2 1 2	748	-706	2 5 3	97	79	4 0 $\bar{2}$	59	-55
0 4 5	25	-28	1 3 1	821	865	2 1 3	123	89	2 5 4	287	298	4 0 $\bar{4}$	166	-164
0 4 6	290	-289	1 3 2	521	-586	2 1 4	40	39	2 5 $\bar{1}$	215	-204			
0 4 7	194	208	1 3 3	478	-506	2 1 5	76	22	2 5 $\bar{2}$	379	355	4 1 0	11	17
0 4 8	84	87	1 3 4	83	-95	2 1 6	80	-70	2 5 $\bar{3}$	187	181	4 1 1	41	-44
0 4 9	87	101	1 3 5	748	-781	2 1 7	126	79	2 5 $\bar{4}$	454	419	4 1 2	245	263
			1 3 6	102	-110	2 1 8	196	-193	2 5 $\bar{5}$	48	21	4 1 3	109	-131
0 5 1	140	141	1 3 7	10	6	2 1 9	147	-146				4 1 $\bar{1}$	127	-141
0 5 2	104	-112	1 3 8	10	3	2 1 $\bar{1}$	209	-164	3 0 1	692	-612	4 1 $\bar{2}$	363	-422
0 5 3	235	-247	1 3 9	262	258	2 1 $\bar{2}$	317	325	3 0 3	312	-294	4 1 $\bar{3}$	60	-71
0 5 4	200	213	1 3 $\bar{1}$	283	265	2 1 $\bar{3}$	420	387	3 0 5	146	149	4 1 $\bar{4}$	206	-220
0 5 5	444	-429	1 3 $\bar{2}$	190	-195	2 1 $\bar{4}$	632	580	3 0 7	10	-3	4 1 $\bar{5}$	113	-130
0 5 6	119	122	1 3 $\bar{3}$	785	-800	2 1 $\bar{5}$	36	19	3 0 $\bar{1}$	24	-85			
0 5 7	59	70	1 3 $\bar{4}$	33	20	2 1 $\bar{6}$	560	-568	3 0 $\bar{3}$	742	721	4 2 0	30	20
			1 3 $\bar{5}$	363	-342	2 1 $\bar{7}$	180	160	3 0 $\bar{5}$	148	-142	4 2 1	23	-3
0 6 0	167	-159	1 3 $\bar{6}$	284	-282	2 1 $\bar{8}$	737	-728	3 0 $\bar{7}$	479	-519	4 2 $\bar{1}$	110	-116
0 6 1	86	97	1 3 $\bar{7}$	186	187	2 1 $\bar{9}$	64	51	3 0 $\bar{9}$	20	-25	4 2 $\bar{2}$	34	-46
0 6 2	9	-1	1 3 $\bar{8}$	439	-457	2 1 $\overline{10}$	58	48				4 2 $\bar{3}$	190	-211
0 6 3	128	126	1 3 $\bar{9}$	96	95				3 1 0	72	-52			
0 6 4	370	352	1 3 $\overline{10}$	72	-32	2 2 0	676	695	3 1 1	99	88			
						2 2 1	499	-485	3 1 2	247	-226			
1 0 1	1372	1376	1 4 0	412	417	2 2 2	319	319	3 1 3	77	-70			
1 0 3	451	457	1 4 1	32	-31	2 2 3	425	-398	3 1 4	0	14			
1 0 5	108	106	1 4 2	151	150	2 2 4	303	-300	3 1 5	404	-399			
1 0 7	322	319	1 4 3	216	-231	2 2 5	189	-202	3 1 6	119	-114			
1 0 9	205	-200	1 4 4	246	-252	2 2 6	437	-463	3 1 7	211	-216			
1 0 $\bar{1}$	1082	1076	1 4 5	210	-218	2 2 7	195	-186	3 1 $\bar{1}$	194	-193			
1 0 $\bar{3}$	285	-212	1 4 6	100	-97	2 2 8	262	261	3 1 $\bar{2}$	17	19			
1 0 $\bar{5}$	450	-432	1 4 7	26	21	2 2 9	149	-145	3 1 $\bar{3}$	301	-274			
1 0 $\bar{7}$	1172	1127	1 4 8	219	230	2 2 $\bar{1}$	348	-323	3 1 $\bar{4}$	37	-33			
1 0 $\bar{9}$	592	610	1 4 $\bar{1}$	91	-96	2 2 $\bar{2}$	394	-392	3 1 $\bar{5}$	207	-206			
1 0 $\overline{11}$	144	-151	1 4 $\bar{2}$	66	74	2 2 $\bar{3}$	120	-113	3 1 $\bar{6}$	0	-3			

half should be placed at the position of the peak and accordingly, two-thirds of McWeeny's (1951) scattering factors for hydrogen were used. The anisotropic vibrational parameters of the carbon atom were also applied. The result of making the correction was that further refinement reduced the value of R_{hkl} to 0·057 and $\mathscr{S}$ to $15{\cdot}9\times10^{-4}$ Å; there was no significant change in the length of the carbon–carbon bond but there were changes in the vibrational parameters. An attempt was made to correct for the smaller peaks in the carbon–oxygen bonds, but this resulted in increases of R_{hkl} and $\mathscr{S}$.

Tables 2 and 3 list the final fractional atomic coordi-

Table 5(*a*). *The r.m.s. displacements* (Å) *of the atoms along the directions of their ellipsoid axes*

	After allowing for interatomic electron density			Before allowing for interatomic electron density		
Atom	$(\overline{u_1^2})^{\frac{1}{2}}$	$(\overline{u_2^2})^{\frac{1}{2}}$	$(\overline{u_3^2})^{\frac{1}{2}}$	$(\overline{u_1^2})^{\frac{1}{2}}$	$(\overline{u_2^2})^{\frac{1}{2}}$	$(\overline{u_3^2})^{\frac{1}{2}}$
C	0·1350	0·1283	0·1181	0·1365	0·1311	0·1191
O(1)	0·1824	0·1366	0·1182	0·1817	0·1371	0·1211
O(2)	0·1683	0·1435	0·1113	0·1696	0·1447	0·1116
Li+	0·2233	0·1457	0·1309	0·2243	0·1434	0·1331

Table 5(*b*). *Direction cosines*, g'_{ij}, *relating the ellipsoid axes*, *i*, *to orthogonal axes* (*a*, *b*, *c**), *j*

Key			
	g'_{11}	g'_{12}	g'_{13}
	g'_{21}	g'_{22}	g'_{23}
	g'_{31}	g'_{32}	g'_{33}

Atom	After allowing for interatomic electron density			Before allowing for interatomic electron density		
	0·844	−0·020	0·536	0·883	0·009	0·470
C	0·339	−0·756	−0·561	0·154	−0·950	−0·270
	−0·416	−0·655	0·631	−0·444	−0·311	0·840
	0·870	−0·435	0·234	0·869	−0·437	0·233
O(1)	−0·494	−0·775	0·394	−0·494	−0·797	0·348
	0·010	−0·458	−0·889	0·034	−0·417	−0·908
	0·861	−0·183	0·475	0·850	−0·155	0·504
O(2)	0·028	−0·914	−0·404	0·065	−0·918	−0·391
	−0·509	−0·361	0·782	−0·523	−0·365	0·770
	0·895	0·445	−0·042	0·896	0·437	−0·084
Li+	0·302	−0·533	0·790	0·321	−0·503	0·803
	−0·329	0·720	0·611	−0·308	0·746	0·591

nates and anisotropic vibrational parameters of each atom. Table 4 lists the values of the observed structure amplitudes, corrected with the refined scale factor, and the corresponding calculated structure factors.

Analysis of the anisotropic vibrational parameters

With the use of the computer program written by R. Sparks, which follows the procedure of Rollett & Davies (1955), the final anisotropic vibrational parameters produced by the refinement were converted to give the root mean square displacements, $(\overline{u_i^2})^{\frac{1}{2}}$, of the atoms along the directions of their principal ellipsoid axes and the direction cosines, g'_{ij}, relating the ellipsoid axes, *i*, to the orthogonal axes (*a*,*b*,*c**), *j*. For comparison, similar calculations were performed with the vibrational parameters from the point in the refinement before the correction was made for the electron density in the bond. The results of these calculations are given in Table 5. The most striking changes caused by making the correction occur in the parameters for the carbon atom; these changes are further considered below.

As the oxalate ion proved to be planar, the following 'molecular' axes were chosen: *L*, along the carbon–carbon bond; *M*, perpendicular to *L* and in the best least-squares plane of the ion; *N*, perpendicular to *L* and *M*. The mean-square displacements of the atoms in the directions of these axes were calculated and are listed in Table 6(*a*); the analysis of the motion of the ion was based on these displacements. In addition it was possible to calculate the displacements of the carbon atom in the bond directions, both before and after the peak in the bond had been considered; these parameters are given in Table 6(*b*). It can be seen from Table 6(*b*) that with the correction for the peak in the bond included in the refinement, the carbon atom appears to be vibrating less along the carbon–carbon bond. Considered in conjunction with the results obtained for ammonium oxamate, where the carbon–carbon bond length increased from 1·561 to 1·564 Å when the peak in the bond was considered, it appears, as would be expected, that the atomic parameters of the carbon atoms tend to assimilate the electron density in the carbon–carbon bond during the least-squares refinement. These matters have been discussed elsewhere (Beagley & Small, 1963*b*).

Table 6(*a*). *Mean square displacements* (Å^2) *of atoms in the directions of the axes L*,*M*,*N*

	Atom	$\overline{u_L^2}$	$\overline{u_M^2}$	$\overline{u_N^2}$
After allowing for interatomic electron density	C	0·0153	0·0153	0·0177
	O(1)	0·0173	0·0148	0·0332
	O(2)	0·0181	0·0138	0·0269
Before allowing for interatomic electron density	C	0·0169	0·0147	0·0182

Table 6(*b*). *Mean square displacements* (Å^2) *of the carbon atom along the directions of the bonds*

After allowing for interatomic electron density	Bond direction	Before allowing for interatomic electron density
0·0153	C–$\bar{\text{C}}$	0·0169
0·0165	C–O(1)	0·0160
0·0142	C–O(2)	0·0142

Detailed vibrational motion can be investigated by the setting up of groups of equations describing the motion in the directions of the three 'molecular' axes (Beagley, 1962). The motion of the oxalate ion can be described in terms of mean-square translational displacements,

Table 7(*a*). *Interatomic distances*

	Length (Å)		Estimated standard deviations (Å)			
	Uncorrected for libration	Corrected for libration	Atomic coordinates	Cell parameters	Librational correction	Combined e.s.d.
C–$\bar{\mathrm{C}}$*	1·559	1·561	0·0036	0·0005	0·0016	0·0040
C–O(1)	1·257	1·264	0·0023	0·0004	0·0013	0·0027
C–O(2)	1·247	1·252	0·0023	0·0003	0·0013	0·0027
Li^+ · · · O(1)	2·076	2·071	0·0042	0·0005	0·0014	0·0045
Li^+ · · · O($\bar{2}$)	2·033	2·030	0·0042	0·0005	0·0013	0·0044
Li^+ · · · O(1′)	1·999	1·996	0·0042	0·0005	0·0012	0·0044
Li^+ · · · O(2″)	1·935	1·931	0·0042	0·0005	0·0013	0·0044

* 1·559 Å before allowing for the interatomic electron density.

Table 7(*b*). *Angles*

	Angle		Estimated standard deviations			
	Uncorrected for libration	Corrected for libration	Atomic coordinates	Cell parameters	Librational correction	Combined e.s.d.
O(1)–C–O(2)	127·1°	127·3°	11′	5′	14′	18′
O(1)–C–$\bar{\mathrm{C}}$	116·4	116·3	12	4	14	19
O(2)–C–$\bar{\mathrm{C}}$	116·5	116·4	12	3	14	19
O(1) · · · Li^+ · · · O($\bar{2}$)	81·2	81·5	10	2	5	11
O(1) · · · Li^+ · · · O(1′)	111·8	111·6	12	3	6	14
O(1) · · · Li^+ · · · O(2″)	89·6	89·3	10	2	5	11
O($\bar{2}$) · · · Li^+ · · · O(1′)	95·3	95·1	11	3	5	12
O($\bar{2}$) · · · Li^+ · · · O(2″)	135·1	135·0	13	5	9	17
O(1′) · · · Li^+ · · · O(2″)	128·6	128·8	13	4	6	15

t_L^2, t_M^2, t_N^2 (Å^2), in the directions L, M, N, and mean-square angular displacements, $\omega_{L01}^2, \omega_{L02}^2, \omega_M^2, \omega_N^2$ (radians^2), about the directions L,M,N; individual angular displacements about the L axis can be assigned for atoms 0(1) and 0(2). Solution of the equations by inspection, and formally, led to the following results, to which estimated uncertainties have been assigned:

$$\begin{aligned} t_L^2 &= 0{\cdot}015 \pm 0{\cdot}001\ \text{Å}^2; & \omega_{L01}^2 &= 0{\cdot}012 \pm 0{\cdot}001 \text{ radians}^2 \\ t_M^2 &= 0{\cdot}015 \pm 0{\cdot}001\ \text{Å}^2; & \omega_{L02}^2 &= 0{\cdot}007 \pm 0{\cdot}001 \\ t_N^2 &= 0{\cdot}018 \pm 0.001\ \text{Å}^2; & \omega_M^2 &= 0 \\ & & \omega_N^2 &= 0{\cdot}002 \pm 0{\cdot}002 \end{aligned}$$

A number of factors contribute to the large uncertainty in ω_N^2; not only is there uncertainty in the refined vibrational parameters and in the choice of the best 'molecular' axes, but also there are errors which arise because of the existence of interatomic electron density. The uncertainties in the case of the oxalate ion are increased even further by the small number of equations from which the unknown displacement must be obtained.

Bond lengths and angles corrected for librational motion were calculated with the use of the angular displacements quoted above.

Results and discussion

Interatomic distances and angles and their estimated standard deviations are given in Table 7. As with ammonium oxamate, three sources of error were considered: errors due to uncertainties (i) in the fractional atomic coordinates produced by the refinement, (ii) in the cell parameters and (iii) in the librational correction.

The equation of the plane through the six atoms of the oxalate ion was calculated by the method of least squares, using atomic coordinates which had been corrected for libration. The equation, referred to orthogonal axes a, b, c^* is:

$$0{\cdot}8488x' - 0{\cdot}4698y' + 0{\cdot}2425z' = 0.$$

The deviations of the atoms from this plane are: C, 0·009; O(1), 0·002; O(2), 0·002; Li^+, 0·288 Å.

As can be seen from the results which have been quoted, each lithium ion is surrounded by four oxygen atoms arranged at the corners of an irregular tetrahedron. The Li^+....O distances vary between 1·931 and 2·071 Å, in approximate agreement with the range 1·86 to 2·05 Å given for a tetrahedrally coordinated lithium atom in *International Tables for X-ray Crystallography* (1962).

In contrast with the behaviour of the oxalate ion in ammonium oxalate monohydrate where the two ends of the ion are twisted 27° with respect to each other (Table 1), the ion in lithium oxalate is planar. Planar oxalate ions are also found in sodium and probably silver oxalates. Jeffrey & Parry (1954) explain the difference in configuration of the two oxalate ions in terms of their respective environments.

The length of the carbon–carbon bond (1·561 ± 0·004 Å) is greater than any value which has yet been considered for a single bond between trigonally hybridized carbon atoms, although it compares very favourably with the bond in ammonium oxamate (1·564 ± 0·002 Å, Beagley & Small, 1963*a*). The lengthening suggests that the total bond order is less than unity. The origin of the lengthening is uncertain, but it is unlikely to be due to repulsion of the *cis*-related oxygen atoms because this would be more likely to result in a twist of 90° between the two ends of the ion. The lengthening may be due in some way to participation of lone pair electrons from the oxygen atoms in molecular orbitals embracing the whole ion; such a hypothesis would also explain the planarity.

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Photoelastic constants of magnesium oxide.

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The photoelastic behaviour of magnesium oxide was studied by West & Makas (1948), Burstein & Smith (1948) and Giardini & Poindexter (1958). These data show discrepancies with regard to the strain-optical constants p_{11} and p_{12}. Burstein & Smith reported that $p_{11} = -0{\cdot}32$ and $p_{12} = -0{\cdot}08$, whereas according to Giardini & Poindexter $p_{11} = -0{\cdot}21$ and $p_{12} = +0{\cdot}04$. Thus there is disagreement with regard even to the sign of p_{12}. Hence, in view of the interesting optical and photoelastic behaviour of magnesium oxide, it is thought desirable to redetermine the photoelastic constants and clear the discrepancy.

The experimental technique used in this investigation is the same as that reported earlier (Krishna Rao & Krishna Murty, 1961). The stress-optical constants $(q_{11}-q_{12})$ and q_{44} are determined by Filon's method and the ratio of the strain-optical constants, p_{12}/p_{11}, is obtained by Mueller's (1938) ultrasonic method. Combining these results, the absolute strain-optical constants p_{11} and p_{12} have been evaluated using the elastic constants reported by Susse (1961). The results obtained in the present investigation along with those reported earlier are shown in Table 1.

It can be seen from Table 1 that there is a good agreement between the values obtained by different investigators except for the constants q_{12} and p_{12}. The values of both the constants and the sign of p_{12} reported by Giardini & Poindexter differ from the values obtained in the present investigation as well as from those reported by Burstein & Smith. The value of q_{12} reported by Giardini & Poindexter is very large and as a consequence p_{12}, which is evaluated from q_{12}, becomes positive. The sign of p_{12}/p_{11}, obtained in the present investigation by the ultrasonic method, is positive, whereas it should be negative if p_{12} is positive. Hence, it may be concluded that the value of q_{12} reported by Giardini & Poindexter is in error.

The specimen used in this investigation is a flawless synthetic crystal kindly lent to us by Dr T. S. N. Murty of our Laboratory.

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Table 1. *Photoelastic constants of magnesium oxide*

	$(q_{11}-q_{12})$ (units of 10^{-13} C.G.S.)	q_{11}	q_{12}	$(p_{11}-p_{12})$	p_{12}/p_{11}	p_{11}	p_{12}	q_{44} (units of 10^{-13} C.G.S.)
West & Makas	$-1{\cdot}24$	—	—	$-0{\cdot}25$*	—	—	—	$-0{\cdot}62$
Burstein & Smith	—	$-1{\cdot}11$*	$+0{\cdot}09$*	$-0{\cdot}24$	—	$-0{\cdot}32$	$-0{\cdot}08$	—
Giardini & Poindexter	$-1{\cdot}25$	$-0{\cdot}90$	$+0{\cdot}30$	$-0{\cdot}25$	—	$-0{\cdot}21$	$+0{\cdot}04$	$-0{\cdot}66$
Authors	$-1{\cdot}24$	$-1{\cdot}12$	$+0{\cdot}12$	$-0{\cdot}25$	$+0{\cdot}21$	$-0{\cdot}31$	$-0{\cdot}07$	$-0{\cdot}68$

* Calculated by the authors from the elastic constants reported by Susse.