NASA TECHNICAL TRANSLATION NASA TT F-14045

"CATION-RICH" OXIDES. THE CRYSTAL STRUCTURE OF $LiInO_3$.

F. Stewner and R. Hoppe

Translation of "Zeitschrift fur Anorganische und
Allgeine Chemie, Vol. 374, no. 3,
1970, pp. 239-258.

DEC 1971
RECEIVED
NASA STI FACILITY
INPUT BRANCH

N72-12768 (NASA-TT-F-14045) CATION-RICH OXIDES. THE CRYSTAL STRUCTURE OF LiInO3 F. Stewner, et al (Techtran Corp.) Dec. 1971 22 p CSCL 20B

Unclas G3/26
09836
(NASA CR OR TMX OR AD NUMBER) (CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 DECEMBER 1971

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

NASA TT F-14045

"CATION-RICH" OXIDES [*], [1]. THE CRYSTAL STRUCTURE OF Li_3InO_3 [2], [3]. /239

Frank Stewner and Rudolf Hoppe

ABSTRACT. Li_3InO_3 crystallizes trigonal, P3c1, with a = = 9.606_4, c = 10.42_0 Å, c/a = 1.064_7, Z = 12 and In_1 in 2(a), In_2: 4(d), In_3: 6(f), and O_1, O_2, O_3, Li_1, Li_2, Li_3 each in 12(g). According to $Li_2^{[4]} \wedge In_{2/3}^{[6]} \square_{1/3} \wedge O_2$, Li_3InO_3 is a "stuffed derivative" of a layer structure of the CdJ_2 type. Calculations of the MADELUNG Part of Lattice Energy (MAPLE) assure the localization of Li by x-ray work and explain why In_2, O_1, O_2 and O_3 depart from "ideal" positions.

The system Li_2O/In_2O_3 has already been widely studied. $LiInO_3$ is well known, a trigonal order variant (α-$LiFeO_2$-type) of the NaCl structure. According to studies on powder samples [5,6], there exist in the partial system $LiInO_2/Li_2O$ at least two further phases whose composition is still unknown. One of these was viewed as $LiInO_3$ [7].

An explanation of the apparently complicated relationship appear to be possible only by means of monocrystal investigations. By appropriate experiments we obtained monocrystals of Li_3InO_3, $Li_{31}In_{11}O_{32}$, as well as a third phase whose /240 composition is "$Li_7In_3O_8$".

These represent "cation-rich" oxides, i.e. representatives of a group of compounds about which we are still insufficiently informed.

We can differentiate three classes of ternary oxides, A_x, B_y, O_z, according to whether

a) none, b) only one or c) each of the partners A and B is a metal. There are at times present three subclasses, since there can be

$$\alpha)\ x + y < z,\ \beta)\ x + y = z\ ,\ \text{or}\ \gamma)\ x + y > z.$$

Oxides which correspond to the combination (c,γ) we call "cation-rich" oxides (of the metals).

Ternary oxides of this type were only recently investigated more closely. Only in exceptional cases do we know about their crystal structure through monocrystal studies [Li_8TbO_6 [8], Na_2HgO_2 [9], $Na_2Zn_2O_3$ [10], K_2ZnO_2 [11]. It is desirable to differentiate two groups for the "cation-rich oxides" of the alkali metals:

In the first case the partner B^{I} is monovalent or divalent [B : KCuO [12], KAgO [13], CsAuO [14], KTlO [15]; B^{II}: compare above]. Then all occurring phases are "cation-rich".

In the second case, B is trivalent or of higher valency. "Cation-rich" oxides may occur here (example: the sodium Li_2O/Al_2O_3 with $LiAl_5O_8$ [16], $LiAlO_2$ [17], Li_5AlO_4 [18,19]; analogous: Li_2O/Ga_2O_3 [19]), but there still apparently exist systems in which such phases are not formed in the usual pressure—temperature range (Li_2O/Sc_2O_3; Li_2O/Y_2O_3 [27]).

I. Preparation of Li_3InO_3

Amounts of "active" In_2O_3 (from $In_2(C_2O_4)_3 \cdot 6\ H_2O$ from In metal 99,99%, by thermal decomposition under vacuum) and Li_2O (from LiOH, purest Merck) give Li_3InO_3 as a colorless powder after beating (700°C, dry O_2 gas, 4 hrs.). Guinier exposures of such samples show the reflex origin of $LiInO_3$ when a sample is first adjusted to Li:In $\geq$ 3:1. /242

Relatively large monocrystals [$\emptyset \approx 0.3$ mm] are obtained from these powder samples when they are heated for long periods in a closed system (900-1100°C, 30 days) [9]. The crystals show six-cornered base line surfaces of trigonal appearance. The identity of the powder and monocrystal was established by the good agreement between I_o and I_c with the parameters from the intensity calculation carried out from the monocrystal investigation for the Guinier data, Table 1.

Li_3InO_3 is colorless and practically stable against atmospheric moisture; even water decomposes it only slowly.

TABLE 1. INTENSITY CALCULATIONS FOR "GUINIER REFLEXES" (Cu-K_α)

H	K	L	$\sin^2\theta \cdot 10^3$ Calculated	$\sin^2\theta \cdot 10^3$ Observed	Intensity Calculated	Intensity Observed
1	0	0	0.57		0	
0	0	2	21.86	21.85	1000	850
1	1	0	25.71	25.75	165	62
1	0	2	30.43		0	
0	1	2	30.43		7	
1	1	1	31.18	31.19	777	980
2	0	0	34.28	34.29	0	57
1	1	2	47.57	47.61	137	80
2	0	2	56.14		5	
0	2	2	56.14		2	
1	2	0	60.00		0	
2	1	0	60.00		0	
2	1	1	65.46		0	
1	2	1	65.46		0	
1	1	3	74.89	74.87	233	320
3	0	0	77.14	77.13	388	460
2	1	2	81.85		5	
1	2	2	81.85		5	
0	0	4	87.43	87.39	52	77
0	1	4	96.00	95.89	8	12
1	0	4	96.00		4	
0	3	2	99.00	99.02	175	1000
3	0	2	99.00		835	
2	2	0	102.85	102.94	23	25
2	2	1	108.32	108.35	135	250
1	2	3	109.18		0	
2	1	3	109.18		0	
3	1	0	111.42		0	
1	3	0	111.42		0	
1	1	4	113.14	113.03	33	12
1	3	1	116.89		0	
3	1	1	116.89		0	
0	2	4	121.71		3	
2	0	4	121.71		3	
2	2	2	124.71	124.72	39	30
1	3	2	133.28		2	
3	1	2	133.28		5	
4	0	0	137.14		0	
2	1	4	147.43		0	
1	2	4	147.43		14	
2	2	3	152.03	151.98	110	140
0	4	2	158.99		1	
4	0	2	158.99		1	
3	1	3	160.60		0	
1	3	3	160.60		0	
1	1	5	162.32	162.36	85	86
3	2	0	162.85		0	
2	3	0	162.85		0	
0	3	4	164.57	164.55	291	570
3	0	4	164.57		332	
3	2	1	168.31		0	
2	3	1	168.31		0	
4	1	0	179.99	179.76	13	30
1	4	0	179.99		13	
2	3	2	184.71		3	
3	2	2	184.71		3	
4	1	1	185.46	185.56	84	156
1	4	1	185.46		63	
2	2	4	190.28	190.19	21	7
1	2	5	196.60		0	
2	1	5	196.60		0	
0	0	6	196.71	196.63	46	57
3	1	4	198.85		7	
1	3	4	198.85		8	
4	1	2	201.05	201.72	25	25
1	4	2	201.05		17	
0	1	6	205.29		10	
1	0	6	205.29		3	
3	2	3	212.03		0	
2	3	3	212.03		0	
5	0	0	214.23		0	
1	1	6	222.43	222.58	9	10
0	4	4	224.56		5	
4	0	4	224.56		2	
4	1	3	229.17	229.18	65	100
1	4	3	229.17		50	
2	0	6	231.00		6	
0	2	6	231.00		4	
3	3	0	231.42	231.49	260	320
5	0	2	236.13		1	
0	5	2	236.13		1	
3	3	1	236.68		0	
2	2	5	239.46	239.38	59	81
2	4	0	239.99		0	
4	2	0	239.99		0	
4	2	1	245.45		0	
2	4	1	245.45		0	
1	3	5	248.03		0	
3	1	5	248.03		0	
3	2	4	250.28		3	
2	3	4	250.28		5	
3	3	2	253.27	253.36	266	165
1	2	6	256.71		14	
2	1	6	256.71		5	
3	4	2	261.85		1	
4	2	2	261.85		1	
1	5	0	265.70		0	
5	1	0	265.70		0	
1	4	4	267.42		11	
4	1	4	267.42		12	
1	5	1	271.17		0	
5	1	1	271.17		0	
0	3	6	273.85	273.92	174	160
3	0	6	273.85		85	

II. Measurements of the Elementary Cell, Space Groups

Revolving crystal, Weissenberg and precession exposures were prepared from an oval polished crystal. They show that Li_3InO_3 crystallizes trigonally. The lattice constants (Cu—K_{α_1}-radiation, λ = 1.54051 Å) are

$$a = 9.606_4 \text{ Å},\ c = 10{,}420 \text{ Å},\ c/a = 1{,}064_7. \quad \text{(Guinier exposure)}$$

There are 12 formula units per elementary cell. Li_3InO_3 (mol. vol. = 41.80 cm^3) is formed from the binary oxides without change in volume (sum of the mol. vol. from Li_2O and In_2O_3 corresponds to Li_3InO_3: 41.82 cm^3). The unusually good agreement shows that the coordination ratios do not change appreciably during the formation of Li_3InO_3 from Li_2O and In_2O_3.

The cancellations ((h 0.l) only with l = 2n) are characteristic for the space groups

No. 158: $P\bar{3}c1$—C_{3v}^3 (acentric) and No. 156: $P\bar{3}c1$—D_{3d}^4 (centric).

III. Clarification of Structure

The reflexes (h k.l) with k = 0—6 and l = 0—2 as well as (h h.l) were measured photometrically (integrated Weissenberg exposure, MoK_α radiation, Zeiss high-speed photometer). Intensities of weaker reflexes were evaluated visually. The centric space group $P\bar{3}c1$ was accepted for the interpretation of the Patterson projections after (00.l), (01.0), and (11.0). The projection after (00.l) yielded with the interpretation temporary parameters x and y, the two other projections z parameter for In^{3+} and O^{2-} as well as indications of the Li positions from the Li—In Pik. Table 2 reproduces the parameters thus obtained.

A. Parameter Refinement By Least Squares Calculation /243

The free parameters of In^{34}, O^{2-}, and Li^+ were refined with 1544 reflexes (h k.l) with k = 0—6; they are highlighted in Table 2. 106 other reflexes, for which the error caused by secondary extinction was too great, were not considered. The refinement ended with the parameter values given in Table 3. For this R = 0.10_7 (h 0.l), 0.11_7 (k 1.l), 0.11_0 (h 2.l), 0.08_4 (h 3.l), 0.09_4 (h 4.l), 0.09_0 (h 5.l), 0.07_9 (h 6.l), resp. for 1544 reflexes, total R = 0.098. The

observed and calculated structure factors are compared in Table 4. (the eliminated reflexes are provided with a *)

TABLE 2. POINT POSITIONS AND "IDEAL" PARAMETERS OF Li_3InO_3 AFTER THE INTERPRETATION OF PATTERSON PROJECTIONS

Atom	Point position	Parameter x	y	z
In_1	2 (a)	0	0	1/4
In_2	4 (d)	1/3	2/3	1/4
In_3	6 (f)	1/3	0	1/4
O_1	12 (g)	1/9	2/9	1/8
O_2	12 (g)	4/9	8/9	1/8
O_3	12 (g)	7/9	5/9	1/8
Li_1	12 (g)	1/9	2/9	7/16
Li_2	12 (g)	4/9	8/9	7/16
Li_3	12 (g)	7/9	5/9	7/16

TABLE 3. PARTICLE PARAMETERS
(Standard deviation in parantheses)

	x	y	z	B [Å²]
In_1	0	0	0,25	1,27 (4)
In_2	0,33333	0,66667	0,2683 (1)	0,24 (1)
In_3	0,3332 (2)	0	0,25	0,18 (1)
O_1	0,096 (2)	0,218 (1)	0,1267 (7)	0,4 (1)
O_2	0,439 (3)	0,879 (2)	0,1350 (9)	0,9 (1)
O_3	0,769 (2)	0,556 (1)	0,1259 (8)	0,5 (1)
Li_1	0,134 (5)	0,229 (5)	0,431 (3)	1,2 (4)
Li_2	0,431 (5)	0,911 (5)	0,443 (3)	2,8 (5)
Li_3	0,800 (5)	0,552 (5)	0,436 (3)	1,2 (5)

B. The Position of the Li^+ Particles

The position of Li^+ was determined by least square calculations (compare above) and also by a Difference Fourier Synthesis $F_0 - F_c$ for (InO_3), which distinguishes Li^+ by Piks at z = 1/4 subject to termination effects. Table 5 gives a comparison of the parameters determined in this way.

The arrangement of O^{2-} for Li_3InO_3 practically corresponds to an hexagonal close-packed structure (see below). Since for each elementary cell, 12 In^{3+} occupy 1/3 of the total 36 octohedra spaces, there are 3 possibilities of inserting 36 Li^+ in the available spaces (under consideration of point positions at $P\bar{3}c1$):

1. Occupation of 24 octohedra and 12 tetrahedra spaces

2. Occupation of 12 octohedra and 24 tetrahedra spaces, or
3. Occupation of 36 tetrahedra spaces.

For 1. and 2. the simultaneous occupation of octohedra and tetrahedra spaces leads to Li—Li- and Li—In-distances which are much too short (1.96 Å). At the same time the distance Li—O for Li^+ in octohedron spaces is clearly too great (2.28 Å against the expected 2.14 Å).

Inasmuch as there are a total of 72 tetrahedron spaces per elementary cell, whose center of mass is at times marked by the occupation of the point position 12 (g), there are 6 compositions independent of each other for each 12 related "tetrahedron spaces" indicated in the following with the number 1—6. (compare Table 6). When one considers the distances Li—) and Li—Li, or Li—In, resp. as they are given in Table 7, then it follows that only the tetrahedron spaces 2, 4, and 6 of Table 6 should be occupied; this also corresponds to x-ray results in Table 5.

IV. Description of the Li_3InO_3 Structure

There is a "filled" layer structure of CdI_2 basic type, where the basic structure, analogous to CdI_2, $(\wedge In_{2/3} \square_{1/3} \wedge O_2)^{2-}$ becomes "filled" by occupying all tetrahedra spaces of the shell unoccupied intermediate layers with Li^+, corresponding to $Li_2 \wedge In_{2/3} \square_{1/3} \wedge O_2 \equiv Li_3InO_3$.

The occupation of the octohedra spaces (In^{3+}) and the tetrahedra spaces (Li^+) alternately in layers parallel to the hexagonal base of the close-packed structure (Figure 1) is characteristic.

If the positions of In^{3+} and O^{2-} correspond to the ideal positions of the hexagonal close-packed structure, then a subcell would develop of the true elementary cell with $a_{sub} = 1/\wedge 3 \cdot a_{obs}$ ($Z = 4Li_3InO_3$). Compare Figure 2. /250

TABLE 4. OBSERVED STRUCTURE AMPLITUDES F_0 AND CALCULATED STRUCTURE AMPLITUDES F_c

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	0	0	7	0	-8	63	67	7	0	-16	75	-61	18	0	-12	60	60	0	1	10	81	-94
0	0	2	185	-493o	9	0	4	156	190o	11	0	12	56	55	0	0	26	41	-35	0	1	-10	70	69
1	0	2	94	31	0	0	-4	169	192o	3	0	18	97	-92	21	0	0	72	85	0	1	6	60	-61
1	0	-2	0	-29	0	0	12	120	132	3	0	-18	63	-93	21	0	2	81	-93	0	1	-6	54	50
2	0	0	0	-4	1	0	12	34	-45	4	0	-18	63	-98	21	0	-2	66	-83	7	1	4	51	60
2	0	2	0	-29	1	0	-12	68	86	15	0	0	136	140	18	0	14	46	-54	7	1	-4	46	56
2	0	-2	39	24	2	0	12	05	94	10	0	-14	56	-59	10	0	-14	46	-55	2	1	10	52	54
3	0	0	197	347o	2	0	-12	42	-46	0	0	16	61	64	21	0	4	08	89	2	1	-10	76	-62
0	0	4	161	256o	0	0	10	111	-131o	15	0	2	123	-131	21	0	-4	73	88	5	1	8	80	-60
1	0	4	00	-91	0	0	-10	192	-239o	15	0	-2	155	-167	21	0	6	52	-74	5	1	-8	65	60
1	0	-4	36	93	10	0	0	0	-12	5	0	18	52	-59	21	0	-6	70	-84	4	1	9	115	-127
3	0	2	231	-603o	3	0	12	194	200o	13	0	-10	52	-39	21	0	0	46	67	4	1	-9	107	123
3	0	-2	193	-343o	3	0	-12	172	199o	15	0	4	141	149	21	0	-0	53	68	7	1	5	134	-144
2	0	4	63	07	10	0	2	0	22	19	0	-4	157	154	18	0	10	47	53	7	1	-5	120	131
2	0	-4	40	-47	10	0	-2	0	2	12	0	12	123	122	21	0	10	48	-66	0	1	0	0	-6
4	0	0	0	-4	9	0	0	103	-228o	12	0	-12	119	113	21	0	-10	51	-50	0	1	2	45	32
4	0	2	60	40	9	0	-6	184	-219o	0	0	18	97	-49	1	1	0	70	135o	0	1	-2	0	-9
4	0	-2	0	-25	8	0	0	53	99	0	0	-18	102	-84	0	1	2	0	-29	3	1	10	91	-98
3	0	4	294	530o	0	0	-0	36	-95	9	0	16	112	106	0	1	-2	95	31	3	1	-10	53	53
3	0	-4	240	422o	4	0	12	70	-97	9	0	-16	123	106	2	1	0	27	-2	7	1	6	35	-37
0	0	6	218	-383o	4	0	-12	85	93	11	0	14	52	-97	1	1	1	153	-232o	7	1	-6	20	-37
1	0	6	55	94	10	0	4	44	-38	15	0	6	141	-149	1	1	2	71	-122o	1	1	11	107	110
1	0	-6	67	-88	10	0	-4	0	24	15	0	-6	109	-114	2	1	2	68	33	8	1	4	49	-41
5	0	0	0	0	7	0	10	48	47	0	0	20	62	36	1	1	3	144	207o	0	1	-4	0	23
4	0	4	50	-48	7	0	-10	73	-70	7	0	18	81	-64	2	1	-2	0	-28	0	1	8	60	60
4	0	-4	57	58	5	0	12	75	83	1	0	-20	47	50	0	1	4	35	53	6	1	-6	53	-54
2	0	6	58	-71	5	0	-12	41	-57	2	0	20	62	63	0	1	-4	63	-51	7	1	7	103	111
2	0	-6	78	73	9	0	8	191	224o	13	0	-12	98	48	3	1	0	32	-3	7	1	-7	105	-109
5	0	2	0	-21	9	0	-8	192	224o	10	0	-16	53	62	1	1	4	54	-90	9	1	0	0	-10
5	0	-2	33	28	10	0	0	42	42	3	0	20	90	81	3	1	2	20	-36	0	1	12	74	65
3	0	6	156	-213o	10	0	-0	42	-38	3	0	-20	71	-98	3	1	-2	45	27	0	1	-12	39	-45
3	0	-6	254	-461o	0	0	14	119	-116	19	0	0	112	112	2	1	4	88	-58	9	1	2	0	-2
5	0	4	33	39	1	0	-14	79	-86	15	0	-8	128	106	2	1	-4	48	62	9	1	-2	0	24
5	0	-4	61	-97	0	0	16	54	-69	12	0	14	85	-75	1	1	5	130	-175o	5	1	10	49	52
0	0	8	214	286o	6	0	12	160	173	12	0	-14	113	-106	4	1	0	64	99	5	1	-10	81	-85
0	0	2	208	-287o	6	0	-12	165	170	8	0	18	53	-58	4	1	1	147	-197o	0	1	6	51	43
6	0	-2	257	-423o	2	0	14	74	-83	4	0	-20	62	56	4	1	-1	121	150o	8	1	-6	53	-44
4	0	6	65	53	2	0	-14	38	43	11	0	16	47	49	3	1	4	30	51	4	1	11	111	125
4	0	-6	64	-77	3	0	14	103	-119	9	0	18	80	-70	3	1	-4	66	-47	4	1	-11	96	-105
0	0	8	231	360o	3	0	-14	162	-176	0	0	-18	91	-70	4	1	2	72	-100	2	1	12	55	-56
1	0	0	73	-69	10	0	0	53	-52	15	0	10	82	-84	4	1	-2	56	-79	2	1	-12	93	95
1	0	-8	89	101	10	0	-8	56	52	15	0	-10	120	-114	0	1	6	69	-88	9	1	4	43	21
2	0	8	76	84	7	0	12	40	-44	6	0	20	62	94	0	1	-6	61	54	9	1	-4	52	-42
2	0	-8	76	-67	7	0	-12	84	77	0	0	-20	88	73	1	1	6	38	-61	3	1	12	88	91
6	0	4	248	330o	4	0	14	53	40	13	0	-14	58	-49	4	1	3	147	178o	3	1	-12	47	-47
6	0	-4	270	396o	4	0	-14	92	-91	7	0	-20	52	55	4	1	-3	130	-163o	6	1	10	69	-67
9	0	6	58	-64	12	0	0	176	181	10	0	-18	52	-51	2	1	6	80	60	6	1	-10	53	-50
9	0	-6	59	59	9	0	18	160	-174	12	0	16	64	55	2	1	-6	77	-81	7	1	9	97	-100
7	0	0	0	-10	9	0	-10	160	-174	12	0	-16	77	65	5	1	0	26	-9	7	1	-9	98	102
3	0	8	181	236o	12	0	2	253	-223	0	0	22	57	-37	4	1	4	57	74	1	1	13	97	-106
3	0	-8	190	271o	12	0	-2	157	-170	1	0	-22	40	-44	4	1	-4	53	76	10	1	0	54	47
7	0	2	34	24	5	0	14	73	-84	2	0	22	47	-43	5	1	2	36	25	10	1	1	111	-109
7	0	-2	0	-23	12	0	4	193	209	15	0	12	80	89	5	1	-2	0	-18	10	1	-1	116	118
4	0	0	74	-58	12	0	-4	184	195	15	0	-12	98	96	1	1	7	127	165o	10	1	2	51	-46
4	0	-8	65	73	8	0	12	54	67	3	0	22	46	-32	3	1	6	59	-60	10	1	-2	53	-47
6	0	6	252	-354o	6	0	14	144	-156	3	0	-22	73	-64	3	1	-6	84	70	8	1	8	60	-53
6	0	-6	159	-198o	6	0	-14	104	-105	18	0	0	125	129	4	1	5	126	-155o	8	1	-8	63	57
7	0	4	57	-43	11	0	8	42	40	4	0	-22	46	-51	4	1	-5	141	172o	9	1	6	58	-45
7	0	-4	0	31	8	0	16	151	148	0	0	2	30	-15	5	1	4	52	-43	9	1	-6	51	43
0	0	10	206	-273o	10	0	10	42	50	18	0	2	122	-116	5	1	-4	47	46	10	1	3	102	97
0	0	0	0	-12	10	0	-10	55	-55	18	0	-2	114	-114	0	1	8	91	101	10	1	-3	109	-106
1	0	10	67	69	1	0	-16	77	89	11	0	18	40	-45	0	1	-8	71	-69	10	1	4	41	27
1	0	-10	83	-94	12	0	6	134	142	13	0	-16	46	44	6	1	0	20	-7	10	1	-4	30	31
5	0	8	68	79	12	0	-6	190	-199	18	0	4	102	97	1	1	8	30	36	5	1	-12	75	82
5	0	-8	50	-50	2	0	16	63	76	18	0	-4	101	97	4	1	6	38	-40	0	1	14	79	-66
0	0	-2	46	38	3	0	16	77	73	9	0	20	56	32	4	1	-6	34	-56	10	1	5	95	-94
2	0	10	85	-103	3	0	-16	93	94	0	0	22	71	-58	6	1	2	0	-13	10	1	-5	80	86
2	0	-10	53	53	9	0	12	102	101	6	0	-22	50	-30	6	1	-2	40	34	4	1	13	82	-90
7	0	6	72	61	9	0	-12	108	101	18	0	6	100	-99	2	1	0	64	-57	4	1	-13	80	103
7	0	-6	52	-43	7	0	14	77	-65	18	0	-6	105	-100	2	1	-8	76	85	9	1	8	66	56
3	0	10	190	-277o	4	0	16	84	71	15	0	14	76	-84	4	1	7	129	138	9	1	-8	55	-51
3	0	-10	119	-138o	11	0	10	49	-45	15	0	-14	55	-62	4	1	-7	120	-142	2	1	14	42	42
0	0	4	27	31	12	0	0	128	131	12	0	10	63	-62	6	1	4	44	41	2	1	-14	101	-94
0	0	-4	35	-40	12	0	-0	140	142	12	0	-10	45	-40	6	1	-4	91	-42	11	1	0	0	-14
0	0	8	189	229o	9	0	16	62	71	18	0	8	102	102	3	1	0	80	81	7	1	11	183	105
0	0	-8	175	203o	9	0	14	58	-63	18	0	-8	101	102	3	1	-8	60	-59	7	1	-11	105	-107
4	0	10	09	53	10	0	-12	49	51	0	0	24	60	49	5	1	0	61	61	6	1	12	76	69
4	0	-10	78	-78	0	0	16	85	87	3	0	-24	43	34	5	1	-6	48	-54	6	1	-12	94	-93
9	0	8	255	336o	0	0	-16	84	60	18	0	10	82	-83	1	1	9	129	-143	11	1	2	0	26
9	0	2	290	-254o	9	0	14	87	-92	18	0	-10	88	-82	7	1	0	54	60	11	1	-2	0	0
9	0	-2	210	-252o	9	0	-14	105	-92	15	0	16	59	55	7	1	1	116	-119	0	1	10	56	54
0	0	0	33	-42	8	0	10	101	-09	15	0	-16	46	-48	7	1	-1	137	142	0	1	-10	67	-64
0	0	-6	33	40	1	0	-10	71	-72	9	0	22	41	-32	7	1	2	48	-56	3	1	14	74	-77
9	0	10	72	-74	12	0	10	138	-147	12	0	20	61	53	7	1	-2	53	-67	3	1	-14	30	42
9	0	-10	47	51	12	0	-10	104	-102	0	0	24	40	32	7	1	3	131	134	10	1	7	110	107
7	0	0	40	-58	2	0	10	72	-71	10	0	12	98	08	7	1	-3	127	-141	10	1	-7	101	-100

NOT REPRODUCIBLE

(continued)

TABLE 4. OBSERVED STRUCTURE AMPLITUDES F_0 AND CALCULATED STRUCTURE AMPLITUDES F_c (continued)

/245

H K L	FO	FC	H K L	FO	FC	H K L	FO	FC	H K L	FO	FC	H K L	FO	FC	H K L	FO	FC
11 1 4	43	-38	0 1-18	97	-56	1 2 6	72	-81	7 2 8	65	55	0 2-16	73	64
11 1 -4	0	15	12 1 14	39	-44	1 2 -6	76	80	7 2 -8	59	-51	10 2 12	61	56
1 1 19	95	95	1 1 21	62	-64	4 2 2	0	-14	-1 2 13	93	106	10 2-12	43	-42
9 1 20	01	-97	9 1-20	97	98	4 2 -2	47	28	3 2 12	43	-46	2 2 16	39	56
9 1-20	44	90	7 1 19	60	64	-1 2 7	140	-169	3 2-12	78	82	5 2 17	60	75
11 1 0	45	45	7 1-19	94	-69	2 2 6	46	-98	9 2 4	35	-37	5 2-17	78	-81
11 1 -0	47	-31	16 1 9	79	-74	4 2 4	43	37	9 2 -4	41	25	11 2 11	80	-79
9 1-14	03	-73	16 1 -9	83	47	4 2 -4	49	-47	0 2 7	100	-101	11 2-11	88	84
12 1 0	0	-14	13 1 13	88	-59	5 2 0	72	85	0 2 -7	116	113	3 2-18	65	-67
12 1 2	0	-4	13 1-13	69	09	5 2 1	131	149	6 2 10	47	48	0 2 15	67	-69
12 1 -2	0	26	10 1 17	69	-66	5 2 -1	160	-172	6 2-10	70	-64	8 2-15	82	83
10 1 9	99	-94	10 1-17	65	70	5 2 2	63	-69	5 2 11	01	-95	9 2-14	65	-57
10 1 -9	102	100	11 1-10	94	49	5 2 -2	72	-83	5 2-11	104	105	14 2 1	76	79
0 1 16	87	09	9 1 10	94	-53	3 2 6	54	48	2 2 13	96	106	14 2 -1	93	-85
4 1 15	04	83	6 1 20	44	52	3 2 -6	62	-69	4 2 12	69	74	7 2 16	64	57
4 1-15	08	-93	4 1 21	54	-61	2 2 7	133	-143	4 2-12	42	-44	-1 2 19	59	-73
7 1 13	03	-95	4 1-21	55	65	-1 2 0	30	36	10 2 0	0	-14	14 2 3	67	-63
7 1-13	79	98	14 1-12	47	48	9 2 3	139	-139	9 2 6	54	49	14 2 -3	84	73
8 1-12	62	61	16 1 7	62	59	9 2 -3	148	153	9 2 -6	48	-34	4 2 18	66	-65
12 1 4	0	13	10 1 -7	72	-94	0 2 8	76	-67	10 2 2	0	0	12 2-10	44	-42
12 1 -4	46	-34	15 1 10	44	-20	0 2 -8	79	04	10 2 -2	0	27	13 2 8	40	34
6 1 14	70	-00	0 1 22	98	-44	1 2 8	76	89	-1 2 14	35	35	2 2 19	60	-73
2 1-16	71	74	2 1-22	53	-51	1 2 -8	97	-97	0 2 14	28	43	14 2 5	72	70
11 1 8	48	-42	12 1 16	53	43	5 2 4	48	54	0 2-14	80	-83	14 2 -5	70	-60
11 1 -8	92	40	16 1 9	56	-51	5 2 -4	42	57	7 2 10	77	-71	10 2 14	73	-59
3 1 16	72	71	16 1 -9	64	58	4 2 6	59	-65	7 2-10	92	48	11 2 13	72	77
12 1 6	0	-22	13 1 15	96	53	4 2 -6	54	49	1 2 14	87	-94	11 2-13	68	-74
12 1 -6	41	42	13 1-15	68	-66	6 2 0	0	-6	1 2-14	49	42	-1 2 20	42	-61
9 1 12	58	54	0 1-20	39	42	2 2 8	29	24	10 2 4	33	21	6 2-18	67	-54
9 1-12	50	-38	15 1 12	95	37	6 2 2	38	27	10 2 -4	40	-36	14 2 7	79	-79
13 1 0	30	32	14 1-14	92	-39	6 2 -2	0	-13	8 2 9	100	105	14 2 -7	75	69
13 1 1	100	-94	7 1 21	92	-63	-1 2 9	134	143	8 2 -9	104	-95	0 2-20	69	63
13 1 -1	83	75	7 1-21	03	59	5 2 5	137	137	9 2 0	48	-51	1 2 20	45	57
1 1 17	84	-84	11 1-18	46	-42	5 2 -5	111	-121	9 2 -8	50	44	13 2 10	44	-37
10 1 11	73	72	1 1 23	41	38	3 2 8	64	-63	6 2 12	48	-52	12 2-12	50	43
10 1-11	77	-79	10 1 19	42	52	3 2 -8	72	81	6 2-12	78	73	9 2-16	55	51
13 1 3	92	89	10 1-19	49	-57	5 2 6	42	-46	3 2-14	81	-77	8 2 17	70	73
13 1 -3	80	-74	16 1 11	59	58	6 2 4	65	-48	-1 2 15	81	-95	8 2-17	59	-64
5 1-16	64	66	16 1-11	70	-64	6 2 -4	40	29	5 2 13	87	94	5 2 19	49	-62
11 1 10	38	41	12 1 18	55	-46	2 2 9	118	126	5 2-13	86	-88	5 2-19	71	68
11 1-10	54	-43	15 1 14	50	-41	-1 2 15	0	-6	10 2 6	51	-35	7 2 18	64	-59
12 1 8	36	35	13 1-17	47	50	7 2 0	0	-12	10 2 -6	47	43	3 2-20	49	49
12 1 -8	38	-42	13 1 17	62	-59	0 2 10	55	53	11 2 0	38	26	14 2 9	71	67
0 1-14	59	-62	14 1-16	46	37	0 2-10	96	-103	11 2 1	87	81	14 2 -9	83	-76
13 1 5	82	-73	16 1 13	56	-60	4 2 8	85	81	11 2 -1	99	-90	4 2 20	49	46
13 1 -5	92	09	16 1-13	63	56	4 2 -8	71	-61	11 2 2	42	-31	-1 2 21	49	64
7 1 15	75	80	19 1 1	96	-54	7 2 2	0	-15	11 2 -2	42	-34	10 2 16	53	49
7 1-15	66	-72	19 1 -1	65	60	7 2 -2	41	27	11 2 3	106	-97	11 2 15	62	-61
6 1 16	69	65	19 1 3	50	45	5 2 7	129	-139	11 2 -3	106	102	11 2-15	62	56
4 1 17	70	-82	19 1 -3	62	-51	5 2 -7	126	131	4 2 14	72	-76	13 2 12	49	36
4 1-17	65	75	19 1 5	52	-50	1 2 10	74	-82	2 2 15	80	-89	2 2 21	50	66
0 1 18	72	-72	19 1 -5	44	44	1 2-10	52	54	11 2 4	35	34	12 2-14	60	-43
1 1 18	55	55	15 1 16	33	36	6 2 6	55	55	7 2 12	76	71	14 2 11	49	-53
2 1-18	63	-62	19 1 7	92	97	6 2 -6	55	-52	7 2-12	47	-41	14 2-11	73	61
13 1 7	74	70	19 1 -7	50	-51	7 2 4	39	29	8 2 11	92	-96	6 2-20	49	49
13 1 -7	91	-83	12 1 20	47	41	7 2 -4	57	-40	8 2-11	73	81	9 2-18	49	-50
9 1 14	08	-60	13 1 19	47	55	5 2 8	31	27	11 2 5	109	101	8 2-22	46	-43
9 1-14	35	32	16 1 15	44	48	-1 2 11	105	-119	11 2 -5	99	-95	8 2 19	50	-65
10 1 13	80	-74	19 1 9	45	-50	3 2 10	63	65	10 2 8	62	38	8 2-19	44	55
10 1-13	70	69	19 1 -9	55	55	3 2-10	83	-86	10 2 -8	47	-45	1 2 22	40	-51
3 1 10	70	-71	0 2 0	0	-4	8 2 0	64	59	-1 2 16	33	-47	5 2-21	44	-55
12 1 10	49	-47	-1 2 2	67	-122*	8 2 1	142	136	9 2 10	44	45	7 2 20	59	52
11 1-10	66	92	0 2 2	41	24	8 2 -1	113	-109	9 2-10	62	-55	13 2 14	50	-41
3 1 10	70	73	0 2 -2	12	-29	8 2 2	58	-57	0 2-16	68	74	17 2 1	72	67
13 1 0	90	-79	1 2 0	0	-2	8 2 -2	48	-41	1 2 16	69	74	17 2 -1	59	-54
13 1 -0	76	67	-1 2 3	125	-207*	2 2 11	122	-123	2 2 16	36	-48	10 2 18	52	-41
0 1-10	67	69	1 2 2	0	-28	8 2 3	125	-122	6 2 14	41	39	11 2 17	52	52
9 1-18	02	-65	1 2 -2	56	33	8 2 -3	111	105	6 2-14	80	-75	11 2-17	43	-55
7 1 17	67	-65	2 2 0	101	103	7 2 6	45	-39	11 2 7	77	-79	17 2 3	65	-64
7 1-17	69	71	2 2 1	137	190*	7 2 -6	65	53	11 2 -7	83	76	17 2 -3	53	51
12 1 12	48	50	-1 2 4	87	90	5 2 9	114	119	3 2-16	76	80	12 2-16	51	45
0 1 10	91	-53	0 2 4	92	-47	5 2 -9	126	-126	5 2 15	81	-91	14 2 13	49	57
6 1 19	60	73	0 2 -4	62	67	4 2 15	79	-79	5 2-15	76	82	14 2-13	58	-50
6 1-19	56	-67	2 2 2	72	-102	4 2-15	63	61	-1 2 17	73	84	17 2 5	51	50
9 1 16	70	63	1 2 4	47	62	6 2 8	54	-40	10 2 10	59	-45	17 2 -5	69	-62
10 1 15	76	77	1 2 -4	70	-58	6 2 -8	75	65	10 2-10	46	42	2 2 23	50	-55
10 1-15	72	-70	2 2 3	148	-192*	8 2 4	57	39	4 2 16	76	79	17 2 7	50	-50
0 1 20	57	50	-1 2 5	134	175*	8 2 -4	48	37	8 2 13	68	75	17 2 -7	69	63
11 1-14	07	-95	3 2 0	0	-5	-1 2 12	0	-18	8 2-13	80	-85	13 2 16	49	45
1 1 20	44	-61	3 2 2	98	40	8 2 12	33	-46	7 2 14	62	-61	14 2 15	48	-62
13 1 11	70	76	3 2 -2	0	-28	8 2-12	95	94	9 2 12	42	-37	11 2 19	51	-55
13 1-11	05	-62	2 2 4	00	91	1 2 12	87	95	9 2-12	65	59	17 2 9	59	60
2 1-20	51	57	-1 2 0	36	-61	1 2-12	64	-58	2 2 17	69	79	17 2 -9	54	-49
3 1 20	60	62	0 2 6	02	73	0 2 5	91	100	11 2 9	70	71	17 2 11	47	-55
10 1 1	72	-57	0 2 -6	63	-71	0 2 -5	122	-121	11 2 -9	73	-74	17 2-11	34	44
10 1 -1	74	04	2 2 5	146	182*	9 2 0	0	-17	-1 2 18	38	55	13 2 18	45	-39
10 1-10	54	-36	4 2 0	0	-4	9 2 2	0	23	5 2-18	72	-71	14 2 17	44	51
10 1 3	77	00	3 2 4	98	-45	9 2 -2	0	-1	12 2 0	47	-43	0 3 0	167	347*
10 1 -3	05	-74	3 2 -4	32	42	0 2 -6	40	-35	1 2 18	98	-82	-1 3 -2	45	33

NOT REPRODUCIBLE

(continued)

TABLE 4. OBSERVED STRUCTURE AMPLITUDES F_0 AND CALCULATED STRUCTURE AMPLITUDES F_c (continued)

/246

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	0	2	194	-343	1	3	22	47	-47	12	3	10	123	-118	-1	4	6	81	70	3	4	12	64	69
0	0	-2	267	-603	1	3-12		89	91	12	3-10		119	-117	-1	4	-6	49	-60	-1	4-14		72	-77
0	0	0	0	-3	0	3	-4	90	-47	9	3	18	63	-59	1	4	9	182	-172	6	4	10	72	-67
0	0	2	42	27	0	3	4	0	13	0	3	16	63	57	1	4	-5	143	150	6	4-10		30	45
0	0	-2	0	-36	2	3	12	71	82	-1	3	20	96	97	3	4	0	0	-6	6	4	14	59	-61
-2	0	4	43	62	2	3-12		46	-46	10	3-14		91	-40	2	4	4	55	-67	7	4	9	90	-95
-2	0	-4	64	-58	9	3	10	72	-72	0	3	20	65	98	2	4	-4	49	37	7	4	-9	67	60
0	0	0	0	-9	9	3-10		31	40	0	3-20		96	01	0	4	6	69	-77	8	4	-0	52	42
0	0	4	241	422	0	3	0	101	199	1	3-20		66	62	3	4	2	0	-7	9	4	12	47	-44
0	0	-4	274	538	3	3	12	109	121	6	3	18	89	-78	3	4	-2	33	22	5	4-12		79	72
2	0	2	0	-28	9	3	2	170	-191	6	3-18		51	-46	-2	4	7	143	143	2	4-14		79	-76
2	0	-2	54	40	9	3	-2	215	-253	15	3	0	128	122	1	4	6	41	-56	-2	4	15	78	69
0	0	4	49	-47	7	3	8	92	-49	9	3	16	80	70	1	4	-6	34	-40	4	4	13	91	-88
0	0	-4	41	51	7	3	-8	95	47	9	3-16		68	58	3	4	4	46	38	9	4	6	39	-33
0	0	0	307	555	0	3	6	44	-37	12	3	12	80	77	3	4	-4	56	-46	10	4	0	44	29
0	0	4	34	42	0	3	-6	47	49	12	3-12		89	77	4	4	1	159	-152	10	4	1	86	-78
0	0	-4	53	-45	6	3	10	194	-205	15	3	2	137	-141	4	4	2	55	-73	10	4	-1	96	94
0	0	2	235	-354	6	3-10		114	-124	15	3	-2	120	-114	2	4	0	55	49	10	4	2	40	-27
-2	0	0	68	-81	9	3	4	205	218	7	3-18		49	-47	2	4	-6	61	-65	10	4	-2	40	-33
-1	0	-4	66	60	9	3	-4	214	236	15	3	4	140	132	1	4	7	150	142	10	4	3	96	89
0	0	6	269	-461	4	3-12		67	69	15	3	-4	129	129	1	4	-7	133	-130	10	4	-3	103	-98
0	0	-6	154	-213	-1	3	14	86	-94	15	3	6	105	-102	4	4	3	144	139	3	4	14	83	-75
1	0	0	79	70	0	3-14		159	-176	15	3	-6	127	-127	-1	4	0	64	-59	1	4	15	87	93
1	0	-0	58	-60	0	3-14		124	-119	10	3-16		51	45	-1	4	-6	73	81	1	4-15		71	-63
4	0	0	0	-6	0	3	0	52	53	0	3	18	56	-49	4	4	4	57	50	6	4	12	70	66
0	0	4	176	236	0	3	-8	37	-42	5	3	20	49	53	3	4	0	62	-68	7	4	11	96	97
4	0	2	28	22	1	3	14	33	42	16	3	0	0	-11	3	4	-6	49	47	7	4-11		83	-83
4	0	-2	0	-7	1	3-14		78	-77	12	3	14	81	-71	5	4	0	0	-10	10	4	5	102	-100
2	0	0	63	-69	10	3	0	0	-13	12	3-14		81	-72	5	4	2	40	28	10	4	-5	91	80
2	0	-6	45	48	9	3	0	214	-223	0	3	22	77	-64	5	4	-2	0	-9	9	4	0	43	36
4	0	4	62	-46	9	3	-6	142	-154	0	3	20	79	67	-2	4	9	111	-126	8	4-10		62	-56
4	0	-4	34	38	5	3	12	71	74	6	3-20		62	51	4	4	5	112	-116	-1	4-16		63	71
-1	0	0	69	85	7	3	10	53	47	15	3	8	83	92	2	4	8	69	-61	0	4	16	60	71
-1	0	-0	52	-57	7	3-10		66	-57	15	3	-8	106	97	2	4	-8	81	81	5	4-14		78	-74
5	0	0	0	-15	2	3	14	75	-77	9	3	18	55	-41	4	4	6	29	-34	10	4	7	85	81
0	0	0	106	271	3	3	14	112	-107	9	3-18		76	-67	5	4	4	51	-42	10	4	-7	79	-74
0	0	-8	175	236	4	3	12	158	168	7	3-20		47	46	5	4	-4	29	32	2	4-16		90	79
3	0	6	208	-304	0	3-12		152	192	15	3	10	94	-98	1	4	9	125	-123	4	4	15	79	66
5	0	2	0	-6	0	3	0	150	158	15	3-10		79	-77	1	4	-9	108	127	-2	4	17	72	-75
5	0	-2	0	20	0	3	-8	142	149	10	3-18		51	-48	6	4	8	0	-12	8	4	10	49	-44
1	0	0	62	-59	0	3	10	53	-53	12	3	16	85	75	-1	4	10	52	53	3	4	16	83	78
1	0	-0	71	81	4	3-14		76	-75	12	3-16		87	75	-1	4-10		92	-98	7	4	13	81	-77
5	0	4	46	41	11	3	0	0	-10	15	3	12	86	84	3	4	8	78	77	7	4-13		85	-85
5	0	-4	45	-38	7	3	12	42	-49	15	3-12		80	79	3	4	-8	68	-61	6	4	14	65	-59
2	0	0	73	81	7	3-12		78	69	0	3-22		68	-54	6	4	2	0	-15	8	4-12		65	58
2	0	-0	62	-63	-1	3	16	72	74	0	3-20		61	57	6	4	-2	31	25	1	4	17	71	-75
4	0	0	57	47	0	3	16	93	94	18	3	0	92	96	4	4	7	129	132	1	4-17		79	82
4	0	-6	60	-60	0	3-16		78	73	7	3-22		53	-43	5	4	6	56	51	10	4	9	71	-70
6	0	0	199	249	5	3	14	72	-71	18	3	2	87	-90	5	4	-6	54	-51	10	4	-9	71	75
6	0	2	239	-336	1	3-16		70	71	18	3	-2	103	-107	6	4	4	0	24	-1	4-10		69	-71
6	0	-2	190	-245	10	3	-0	46	41	12	3	18	67	-53	6	4	-4	55	-40	0	4	18	73	-58
3	0	0	215	294	9	3	10	108	-107	12	3-18		65	-53	-2	4	11	113	123	5	4-16		64	61
-1	0	10	72	-82	9	3-10		157	-162	18	3	4	89	97	2	4	10	65	61	9	4	12	60	55
-1	0-10		39	54	2	3	16	63	80	18	3	-4	92	99	2	4-10		80	-79	4	4	17	73	-77
9	0	0	49	-51	6	3	14	94	-95	15	3	14	62	-56	7	4	0	55	51	10	4	11	78	73
9	0	-0	56	59	6	3-14		143	-148	15	3-14		74	-72	7	4	1	126	-127	10	4-11		84	-83
0	0	10	110	-138	8	3	12	91	96	18	3	6	92	-96	7	4	-1	97	99	2	4-13		71	-65
0	0-10		203	-277	12	3	0	195	198	18	3	-6	79	-81	1	4	11	99	108	7	4	15	71	65
6	0	4	235	320	3	3	16	139	131	18	3	8	75	78	1	4-11		106	-120	7	4-15		79	-70
6	0	-4	284	278	12	3	8	174	-168	10	3	-9	62	79	7	4	2	53	-59	8	4-14		54	-52
1	0	10	51	53	12	3	-2	156	-166	15	3-16		53	49	7	4	-2	49	-36	13	4	1	82	-76
1	0-10		07	-98	12	3	4	131	133	18	3	10	59	-63	7	4	3	119	119	13	4	-1	84	81
4	0	0	67	-61	12	3	-4	131	134	18	3-10		65	-76	7	4	-3	103	-106	6	4	16	56	55
4	0	-0	74	77	4	3-16		89	78	-1	4	0	8	-3	6	4	6	37	-36	-2	4	19	69	73
7	0	0	0	-9	10	3-10		57	-49	-2	4	2	71	-102	6	4	-6	60	55	13	4	3	62	64
7	0	2	0	35	7	3-14		76	-68	-1	4	2	44	27	3	4	10	67	-76	13	4	-3	71	-69
7	0	-2	0	-9	0	3	12	125	123	-1	4	-2	0	-36	4	4	9	109	-121	3	4	18	74	-63
2	0	10	81	-86	9	3-12		135	132	0	4	0	0	-4	3	4-10		56	59	1	4	19	58	67
2	0-10		57	65	12	3	0	136	-143	-2	4	3	166	192	5	4	8	52	-50	1	4-19		65	-73
0	0	6	163	-182	12	3	-6	146	-143	0	4	-2	65	40	5	4	-8	60	57	13	4	5	60	-65
6	0	-0	206	-294	5	3	16	73	62	1	4	0	73	99	7	4	4	40	38	13	4	-5	65	60
7	0	0	0	-30	-1	3	10	59	-62	1	4	-1	162	-158	7	4	-4	34	40	9	4	14	65	-57
7	0	-4	44	28	0	3	10	61	-53	1	4	-1	182	197	-1	4	12	37	-47	10	4	13	70	-75
9	0	0	01	66	0	3-10		102	-92	-2	4	4	89	91	-1	4-12		81	91	10	4-13		69	62
9	0	-0	96	-68	13	3	0	0	-16	-1	4	4	65	-47	0	4	12	80	93	5	4-16		59	-51
0	0	10	193	-228	1	3-10		78	-71	-1	4	-4	37	51	7	4	5	110	-104	13	4	7	60	76
0	0	0	0	-5	0	3	14	64	-68	1	4	2	62	-79	7	4	-5	123	123	13	4	-7	72	-71
-1	0	12	04	95	2	3	10	76	-67	1	4	-2	71	-100	6	4	0	64	56	-1	4-20		62	62
-1	0-12		50	-58	6	3	16	69	65	0	4	4	65	58	6	4	-6	50	-40	0	4	20	53	56
0	0	2	0	-5	6	3-16		87	08	0	4	-4	50	-40	-2	4	13	93	-106	0	4-16		64	56
0	0	-2	0	20	12	3	0	144	150	1	4	3	160	163	2	4	12	36	-44	7	4	17	59	-60
4	0	10	57	59	12	3	-6	154	150	1	4	-3	172	-178	2	4-12		70	74	7	4-17		51	60
4	0-10		69	-76	10	3-12		96	93	-2	4	5	100	-102	7	4	7	90	95	4	4	19	55	63
0	0	12	100	199	3	3	10	92	-82	2	4	6	0	-4	7	4	-7	107	-103	6	4	18	69	-59
0	0-12		179	200	9	3	14	119	-116	2	4	2	40	28	5	4	10	46	48	13	4	9	72	-69
9	0	0	47	44	0	3-14		96	-80	2	4	-2	0	-16	5	4-10		62	-60	13	4	-9	75	73
9	0	-0	92	-47	7	3-16		60	57	1	4	4	94	76	4	4	11	91	93	-2	4	21	59	-64
0	0	0	203	279	4	3-10		74	-63	1	4	-4	47	74	1	4	13	97	-103	9	4	16	53	40
0	0	-0	101	108	14	3	0	0	-20	-2	4	0	55	-50	1	4-13		65	98	10	4	19	69	64

NOT REPRODUCIBLE

(continued)

TABLE 4. OBSERVED STRUCTURE AMPLITUDES F_0 AND CALCULATED STRUCTURE AMPLITUDES F_c (continued)

/247

H	K	L	FO	FC
10	4	11	62	93
10	4	-11	68	-57
0	4	-10	90	-51
7	4	10	61	65
-2	5	0	0	-5
-1	5	0	76	99
-1	5	1	135	198o
-1	5	-1	153	-197o
-2	5	2	14	-28
-2	5	-2	47	48
-3	5	2	66	-79
-1	5	-2	69	-100
0	5	0	0	8
-1	5	3	145	-163o
-1	5	-3	149	178o
0	5	2	43	28
0	5	-2	0	-21
-2	5	4	39	42
-2	5	-4	52	-45
1	5	0	0	-9
-1	5	4	59	76
-1	5	-4	52	74
1	5	2	0	-18
1	5	-2	35	25
0	5	4	09	-97
0	5	-4	34	39
-1	5	5	169	172
-1	5	-5	145	-156
2	5	0	73	85
2	5	1	159	172
2	5	-1	152	-149
1	5	4	47	46
1	5	-4	54	-43
2	5	2	73	-83
2	5	-2	51	-69
-2	5	0	65	-69
-2	5	-6	51	48
-1	5	6	49	-56
-1	5	-6	36	-48
2	5	3	160	-153
2	5	-3	144	139
0	5	0	72	59
0	5	-6	61	-64
3	5	0	0	-15
2	5	4	48	57
2	5	-4	46	54
3	5	2	24	20
3	5	-2	0	-6
-1	5	7	152	-142
-1	5	-7	140	138
1	5	-6	64	61
2	5	5	123	121
2	5	-5	144	-137
3	5	4	41	-38
3	5	-4	41	41
-2	5	8	75	81
-2	5	-8	63	-63
4	5	0	0	-10
2	5	6	29	-34
2	5	-6	38	-46
4	5	2	0	-9
4	5	-2	39	28
0	5	0	59	-50
0	5	-8	73	79
2	5	7	131	-131
2	5	-7	132	139
4	5	4	39	32
4	5	-4	49	-42
1	5	0	72	69
1	5	-0	96	-60
3	5	0	61	59
3	5	-6	47	-51
-1	5	9	118	123
-1	5	-9	114	-127
5	5	1	122	115
5	5	2	49	-54
5	5	3	131	-129
-2	5	10	75	-86
-2	5	-10	63	65
4	5	6	62	-51
4	5	-6	55	51
0	5	-10	74	-74
3	5	0	69	-60
3	5	-8	55	60
2	5	9	137	126
2	5	-9	116	-110
5	5	5	136	120
0	5	8	0	-13
12	0	-10	50	46

H	K	L	FO	FC
6	5	2	40	35
0	5	-2	0	-9
1	5	10	86	-85
1	5	-10	51	52
-1	5	11	102	-108
-1	5	-11	108	120
6	5	4	43	-39
0	5	-4	32	23
4	5	0	58	57
4	5	-8	45	-50
5	5	7	100	-101
7	5	0	0	-10
-2	5	12	77	82
-2	5	-12	49	-46
7	5	-2	35	27
3	5	10	39	48
3	5	-10	72	-72
6	5	6	33	30
6	5	-6	44	-39
2	5	11	104	-105
2	5	-11	90	95
0	5	12	50	-57
0	5	-12	84	83
7	5	4	40	-40
1	5	12	89	82
4	5	10	71	-60
4	5	-10	39	48
5	5	9	92	92
-1	5	13	96	103
-1	5	-13	92	-90
0	5	8	46	44
0	5	1	96	97
0	5	-1	116	-114
0	5	2	41	-31
0	5	-2	50	-43
6	5	8	50	-52
6	5	-8	53	40
7	5	6	43	-35
7	5	-6	45	42
8	5	3	87	-86
8	5	-3	105	102
8	5	-4	40	28
3	5	-12	70	74
-2	5	14	71	-77
0	5	9	104	96
0	5	-9	73	-81
2	5	13	86	80
2	5	-13	86	-94
7	5	0	63	50
7	5	-8	53	-48
0	5	-14	75	-84
5	5	11	104	-100
4	5	12	82	72
4	5	-12	40	-49
6	5	10	56	54
6	5	-10	62	-60
1	5	14	80	-73
0	5	7	186	-101
0	5	-7	87	88
-1	5	15	82	-93
-1	5	-15	69	83
7	5	10	68	-52
7	5	-10	46	48
3	5	-14	76	-71
0	5	9	94	84
0	5	-9	96	-96
-2	5	16	75	80
2	5	15	83	-82
2	5	-15	80	91
5	5	13	94	90
0	5	-12	63	59
4	5	14	83	-74
0	5	-16	67	71
1	5	16	84	66
7	5	12	62	51
11	5	1	104	91
11	5	-1	75	-74
-1	5	17	71	75
-1	5	-17	72	-82
0	5	11	59	-68
0	5	-11	81	80
11	5	3	95	-83
11	5	-3	68	68
3	5	-16	71	62
0	5	-14	62	-57
11	5	5	64	66
11	5	-5	92	-82
5	5	15	72	-71
9	6	20	94	40

H	K	L	FO	FC
2	5	17	80	81
2	5	-17	67	-75
4	5	16	65	61
-2	5	18	69	-67
0	5	-18	61	-59
11	5	7	78	-69
11	5	-7	90	83
7	5	14	68	-55
8	5	13	72	73
8	5	-13	70	-64
-1	5	19	69	-67
-1	5	-19	73	73
11	5	9	85	79
11	5	-9	76	-86
6	5	-16	79	58
3	5	-18	66	-59
5	5	17	60	64
4	5	18	55	-51
2	5	19	50	-68
2	5	-19	49	82
7	5	16	70	59
8	5	15	70	-76
0	5	-15	62	64
11	5	11	80	-70
11	5	-11	62	57
14	5	1	49	55
14	5	-1	54	-58
14	5	3	70	-69
14	5	-3	76	72
6	5	-18	66	-53
5	5	19	34	-65
14	5	5	66	70
14	5	-5	73	-67
11	5	13	58	54
11	5	-13	62	-64
8	5	17	58	60
8	5	-17	65	-68
7	5	18	62	-50
14	5	7	51	-55
14	5	-7	43	52
14	5	9	45	49
14	5	-9	45	-51
11	5	-15	64	65
14	5	11	50	-59
14	5	-11	54	61
14	5	13	53	58
14	5	-13	51	-56
17	5	1	45	51
17	5	-1	58	-59
17	5	3	33	-42
17	5	-3	47	51
-2	6	0	0	-4
-3	6	2	132	-354o
-2	6	2	39	28
-2	6	-2	0	-16
-1	6	0	0	-9
-1	6	2	0	-18
-1	6	-2	28	25
0	6	0	153	286o
3	6	4	152	236o
-2	6	4	50	-47
-2	6	-4	43	37
0	6	2	180	-423o
0	6	-2	167	-287o
-1	6	4	44	46
-1	6	-4	49	-43
1	6	0	0	-7
1	6	2	51	34
1	6	-2	0	-13
4	6	4	204	396o
4	6	-4	190	330o
-3	6	6	188	-304o
-2	6	6	54	49
-2	6	-6	54	-65
2	6	0	0	-6
1	6	4	55	-42
1	6	-4	37	41
-1	6	6	46	-54
-1	6	-6	60	61
2	6	2	0	-13
2	6	-2	29	27
0	6	6	160	-198o
0	6	-6	9	-354o
2	6	4	38	29
2	6	-4	60	-48
3	6	0	101	249o
3	6	2	172	-245o
3	6	-2	211	-338o

H	K	L	FO	FC
1	6	6	56	50
1	6	-6	57	-61
-3	6	8	202	294o
-2	6	8	66	-61
-2	6	-8	74	81
-1	6	8	67	68
-1	6	-8	52	-65
3	6	4	207	278o
3	6	-4	212	320o
2	6	6	52	-52
2	6	-6	34	55
4	6	0	0	-12
0	6	8	171	203o
0	6	-8	177	229o
4	6	2	33	25
4	6	-2	0	-15
1	6	8	55	-54
1	6	-8	55	60
3	6	6	207	-294o
3	6	-6	176	-162o
4	6	4	52	-40
4	6	-4	27	24
-3	6	10	188	-228
5	6	0	0	-13
-2	6	10	57	61
-2	6	-10	69	-79
2	6	8	68	65
2	6	-8	42	-40
5	6	2	0	-9
5	6	-2	31	35
-1	6	10	79	-86
-1	6	-10	40	52
4	6	6	58	55
4	6	-6	34	-36
0	6	10	199	-235
0	6	-10	120	-131
5	6	4	25	23
5	6	-4	31	-39
3	6	8	192	198
3	6	-8	154	179
1	6	10	39	50
1	6	-10	67	-67
6	6	0	226	287o
6	6	2	206	-225o
5	6	6	51	-35
5	6	-6	32	39
2	6	10	60	-64
2	6	-10	35	48
4	6	8	50	-48
4	6	-8	55	56
6	6	4	160	174
-3	6	12	114	121
-2	6	12	31	-44
-2	6	-12	67	74
-1	6	12	73	82
3	6	10	119	-124
3	6	-10	197	-205
7	6	0	0	-13
0	6	12	173	178
0	6	-12	162	173
7	6	2	8	23
7	6	-2	0	2
6	6	8	190	-194
5	6	8	56	48
5	6	-8	40	-52
1	6	12	48	-53
1	6	-12	77	80
4	6	10	33	45
4	6	-10	71	-67
2	6	12	72	73
2	6	-12	34	-52
6	6	8	193	199
7	6	-6	39	-32
-3	6	14	108	-107
-2	6	-14	73	-76
5	6	10	61	-60
5	6	-10	45	54
3	6	12	154	152
3	6	-12	147	160
-1	6	14	71	-73
0	6	14	104	-105
0	6	-14	149	-156
7	6	-8	54	46
4	6	-12	70	68
1	6	-14	83	-80
9	6	0	149	165
6	6	10	154	-155
9	6	2	185	-200

H	K	L	FO	FC
9	6	-2	147	-155
2	6	14	70	-75
9	6	4	173	187
9	6	-4	168	177
5	6	12	56	59
3	6	14	147	-140
3	6	-14	98	-95
-3	6	16	132	131
7	6	-10	90	-49
-2	6	-16	83	79
9	6	6	130	-132
9	6	-6	179	-179
-1	6	16	66	66
0	6	16	77	69
0	6	-16	90	87
6	6	12	95	94
4	6	-14	56	-59
1	6	-16	71	65
9	6	8	123	121
9	6	-8	120	130
2	6	16	66	64
5	6	14	59	-57
12	6	2	123	-122
12	6	-2	155	-154
7	6	-12	47	47
3	6	16	90	80
3	6	-16	72	65
6	6	14	86	-86
-3	6	18	87	-82
-2	6	-18	67	-65
9	6	10	142	-134
9	6	-10	88	-95
-1	6	18	72	-65
4	6	-16	61	55
0	6	18	96	-84
0	6	-18	63	-49
12	6	0	138	130
7	6	-14	60	-53
1	6	-18	58	-53
5	6	16	62	58
12	6	4	142	138
12	6	-4	145	142
9	6	12	119	112
9	6	-12	99	104
3	6	18	59	-46
3	6	-18	88	-78
6	6	16	104	97
12	6	6	139	-137
12	6	-6	104	-107
4	6	-18	69	-59
-1	6	20	55	58
7	6	-16	59	56
0	6	20	89	73
0	6	-20	67	54
12	6	8	106	105
12	6	-8	104	99
9	6	14	76	-70
9	6	-14	115	-98
5	6	18	53	-53
6	6	18	69	-65
12	6	10	77	-80
12	6	-10	107	-106
3	6	20	63	51
3	6	-20	82	67
4	6	-20	56	51
7	6	-18	85	-48
9	6	16	61	52
9	6	-16	73	61
12	6	12	85	83
12	6	-12	102	89
8	6	-22	69	-50
15	6	0	118	120
15	6	2	117	-108
15	6	-2	115	-107
15	6	4	85	92
15	6	-4	84	92
3	6	22	61	-54
15	6	6	88	-93
15	6	-6	86	-94
12	6	14	80	-78
12	6	-14	63	-59
9	6	18	66	-58
9	6	-18	44	-38
15	6	8	91	95
15	6	-8	93	95
15	6	10	79	-78
15	6	-10	75	-77
12	6	16	57	52

NOT REPRODUCIBLE

TABLE 5. PARAMETERS OF Li PARTICLES /248

LSQU = Least Squares Calculations
FOUR = Difference Fourier synthesis
TET = Tetrahedron center of mass in InO_3 structure.

		LSQU	FOUR	TET
Li_1	x	0,134	0,12	0,125
	y	0,229	0,23	0,224
	z	0,431	0,444	0,438
Li_2	x	0,431	0,47	0,450
	y	0,911	0,91	0,899
	z	0,443	0,440	0,443
Li_3	x	0,800	0,80	0,780
	y	0,552	0,56	0,550
	z	0,436	0,434	0,437

TABLE 6. TETRAHEDRA CENTER OF MASS IN THE InO_3 STRUCTURE /249

TET		O_1	O_2	O_3	O_4	Li	Li-O in Å
1	x	0.213	0.218	-0.096	0.096	0.1255	1.95_1
	y	0.444	0.096	0.122	0.218	0.2242	
	z	0.3741	0.3733	0.3733	0.1267	0.3123	
2	x	0.213	0.218	-0.096	0.122	0.1252	1.96_3
	y	0.444	0.096	o.122	0.218	0.2237	
	z	0.3741	0.3733	0.3733	0.6267	0.4334	
3	x	0.560	0.556	0.231	0.439	0.4557	1.94_7
	y	1.121	0.769	0.787	0.879	0.8932	
	z	0.3641	0.3741	0.3741	0.1359	0.3222	
4	x	0.560	0.556	0.231	0.440	0.4587	2.02_4
	y	1.121	0.769	0.787	0.879	0.8987	
	z	0.3641	0.3741	0.3741	0.6359	0.4425	
5	x	0.878	0.879	0.561	0.769	0.7826	1.93_0
	y	0.782	0.439	0.440	0.556	0.5642	
	z	0.3733	0.3641	0.3641	0.1259	0.3108	
6	x	0.878	0.879	0.561	0.787	0.7800	1.97_4
	y	0.782	0.439	0.440	0.556	0.5589	
	z	0.3733	0.3641	0.3461	0.6259	0.4366	

TABLE 7. RELATIONS BETWEEN THE SHORTEST DISTANCES AND COMPARISON WITH THE IDEAL HEXAGONAL CLOSE-PACKED STRUCTURE ("OKT and TET" respectively = Center of mass of Octohedra and Tetrahedra, respectively) /250

Distance (spacing)	Li_3InO_3 distance [Å]	Relation	Close-packed structure
OKT – O^{2-}	2,21	1	1
TET – O^{2-}	1,96	0,89	0,866
OKT – OKT	3,30	1,45	1
TET_1 – TET_1	2,29	1,04	1
TET_1 – TET_2	1,29	0,59	0,577
OKT – TET_1	2,74	1,24	1,190
OKT – TET_2	1,96	0,89	0,866

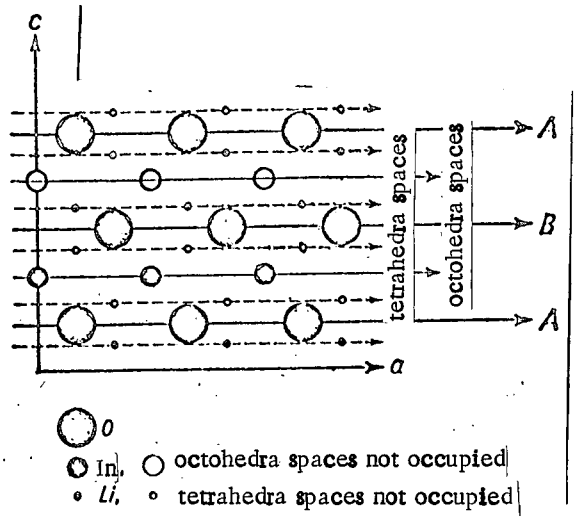

Figure 1. Schematic Representation of the Hexagonal Close-packed Structure (of, for example O^{2-}) the available spaces in it.

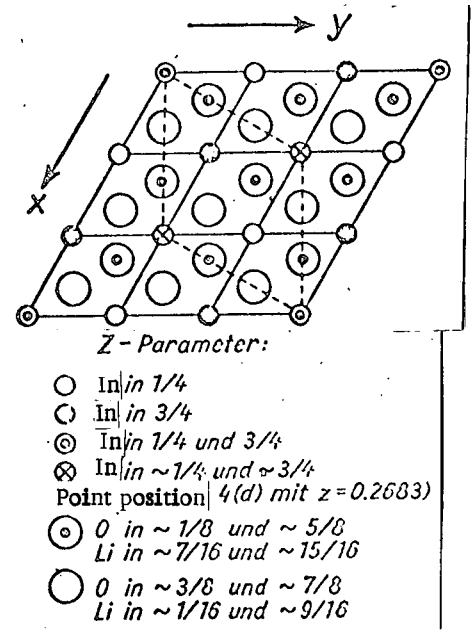

Figure 2. Li_3InO_3 of the Particles According To (00.1) (the sub-cell By Broken Lines)

Inasmuch as 1/3 of the Cd positions of the CdI_2 type remain empty, the structural geometric equivalence of the occupied octahedra spaces becomes lost: even though each In^{3+} in the same layer contains three other In^{3+} neighbors (d = 3.202 Å), in the direction (00.1) however, In^{3+} or In_2^{3+} , respectively has two other In^{3+} neighbors (d = 5.210 Å), but In_3^{3+} on the other hand does not. In_2^{3+} deviates from the ideal position (z = 1/4 instead of the z = 0.2683 formed), whereby the true cell forms from the subcell. /252

Moving out of In_2 subjects the O^{2-} part to further deviations and leads to this that the distances In-O and Li-O, respectively are somewhat increased (see Table 8). The merely slight angle distortion of the coordination polyhedron around In^{3+} is covered by the data in Table 9. The average distance d(Li-O) = 1.99 Å agrees completely with the expected value (compare Table 10). Analogously d(In-O) = 2.21 Å is in good agreement with the result for $LiInO_2$ (2.19 Å), In_2O_3, respectively.

V. Calculations of the Madelung Parts of the Lattice Energy (MAPLE) on Li_3InO_3 /253

Since the position parameters of the particles are known for both modifications of In_2O_3 by newer determinations, it seemed attractive to compare the MAPLE values of the binary oxides with those of the ternary oxides $LiInO_2$ and Li_3InO_3. The relevant values are summarized in Table 11.

The values in Table 11 show: /254

1. As expected the two In_2O_3 modifications don't differ very much (30 kcal/mol.)

2. $LiInO_3$ with ΔH_0° = 11.9 kcal/mol. would be unstable to decomposition into Li_2O and In_2O_3 if MAPLE represented the total lattice energy.

3. In analogous manner Li_3InO_3 would be unstable to decomposition into Li_2O and $LiInO_2$ with ΔH_0° = +46.7 k/cal mol.

These values show that the MAPLE values above do not decide the stability of the individual phases in the system Li_2O-In_2O_3, as for example Li_3InO_3. This is really understandable. As may be seen from the crystal structures, or the coordination of O^{2-}, respectively:

a) the induced dipole moment (i.D.M.) of O^{2-} in the cubic In_2O_3 is certainly low [27]; since a tetrahedron is unfolded approximately from 4 In^{34};

b) the i.D.M. is somewhat greater in rhombohedral In_2O_3 [28], because O^{2-} occupies only 4 of the 6 corner positions of a trigonal prisma, whereby partial compensation takes place;

c) the i.D.M. is by far at its greatest in Li_3InO_3, because here the In^{3+} (out of necessity in cis-position) occupies only 2 of the 6 corner positions of a trigonal prism.

TABLE 8. ALL INTERATOMIC DISTANCES UP TO 4.5 Å (Li_3InO_3). /251

	PARTNER								
	Li_1	Li_2	Li_3	In_1	In_2	In_3	O_1	O_2	O_3
Li_1	2.27(2) 3.23(2) 3.95 4.25 4.44	3.04 3.35 3.83 3.88	2.23 3.05 3.30 4.31	2.71 3.75	4.09	2.76 3.68	1.96 1.97(2) 3.25 3.75(3) 4.46	3.71 3.75 3.85 3.91 4.44	1.96 3.61 3.90 4.50
Li_2	3.04 3.35 3.83 3.88	2.07 3.35(2) 4.36	2.22 2.34 3.08 3.18 4.01 4.36 4.43	--	2.66 3.90	2.76 3.64 4.18	3.63 3.72 3.77 3.89	2.02(2) 3.21 3.75 3.82 4.50	2.03(2) 3.55 3.78 3.86
Li_3	2.23 3.05 3.30 4.31 4.35	2.22 2.34 3.07 3.18 4.01 4.35 4.43	3.25(2) 3.90(2)	4.15	2.85 3.60	2.68 3.74 4.19	1.97 3.63 3.85 4.45	1.98(2) 3.72 3.87 3.88	1.97 3.24 3.67 3.75 3.81 3.82
In_1	2.71(6) 3.75(6)	--	4.15(6)	--	--	3.20(3)	2.23(6) 4.33(6)	--	3.91(6)
In_2	4.09(3)	2.66(3) 3.90(3) 4.23(3)	2.85(3) 3.60(3)	--	--	3.21(3)	4.02(3)	2.24(3) 3.91(3) 4.22(3)	2.16(3) 4.50(3)
In_3	2.76(2) 3.68(2) 4.10(2)	2.76(2) 3.64(2) 4.18(2)	2.68(2) 3.74(2) 4.19(2)	3.20	3.21(2)	--	2.18(2) 4.00(2) 4.39(2)	2.23(2) 3.85(2) 4.45(2)	2.19(2) 3.99(2) 4.36(2)
O_1	1.96 1.97(2)	3.63 3.72	1.97 3.63	2.23 4.33	4.02	2.18 4.00 4.39	3.03 3.15(2) 3.21(2) 3.27 4.45 4.49	3.17 3.30 4.40	3.03 3.19 3.24 3.37
O_2	3.75 3.71 3.85 3.91 4.44	2.02(2) 3.21 3.75 3.82 4.50	1.98(2) 3.72 3.87 3.88	--	2.24 3.91 4.22	2.23 3.85 4.45	3.17 3.30 4.40	3.06(2) 3.12 3.48	3.03 3.12 3.19 3.24 3.31 3.36 4.39
O_3	1.96 3.61 3.90 4.50	2.03(2) 3.55 3.78 3.86	1.97 3.24 3.67 3.75 3.81 3.82	3.91	2.15 4.50	2.19 3.99 4.36	3.03 3.19 3.24 3.37	3.03 3.12 3.19 3.24 3.31 3.36 4.39	3.21(2) 4.39

TABLE 9. BOND ANGLES WITHIN THE InO_6-OCTAHEDRON.

	In_1	In_2	In_3		
O –	O^u_1	O^u_1	O^u_1	O^u_2	O^u_2
$O-In-O^u_1$	90,0	86,1	92,0		
$O-In-O^u_2$	90,0	86,1	92,1	87,8	
$O-In-O^o_1$	94,7	90,3	88,6	174,2	86,3
$O-In-O^o_2$	85,6	87,0	96,3	93,7	177,8
$O-In-O^o_3$	173,6	172,4	174,2	88,0	93,7
O –	O^o_1	O^o_2	O^o_1	O^o_2	
$O-In-O^o_2$	90,0	92,2	92,2		
$O-In-O^o_3$	90,0	92,2	92,1	87,8	

O^u = O^{2-} below
O^o = O^{2-} above
} from In^{34} along (00.1)

TABLE 10. Li-O DISTANCES FOR A FEW METALLATES.

compound	distance [A]	literature
$LiBO_2$	1,945 – 2,007	[20])
γ-$LiAlO_2$	1,93 – 2,08	[21])
γ-$LiAlO_2$	1,948 – 2,059	[22])
Li_2CO_3	1,96 – 2,00	[23])
Li_2O	2,00	[24])
β-$LiGaO_2$	1,949 – 2,001	[25])
α-Li_5GaO_4	2,00	[5])[6])
Li_4GeO_4	1,91 – 2,08	[26])

TABLE 11. MAPLE VALUES FOR $LiInO_2$, Li_3InO_3, AND In_2O_3 (KCAL/MOL).

		binary	ternary	Δ	total parts
Li_2O	Li^+	145,9	163,5	+17,6	+17,6
	O^{2-}	542,4	535,0	– 7,4	– 3,7
In_2O_3	In^{3+}	1122,5*	1087,8	–34,7	–34,7
	O^{2-}	529,1	535,0	+ 5,9	+ 8,9
Li_3InO_3					–11,9

		binary	ternary	Δ	Δ total
Li_2O	Li^+	145,9	157,3*	+11,4	+34,2
	O^{2-}	542,4	540,4*	– 2,0	– 3,0
In_2O_3	In^{3+}	1122,5*	1015,7*	–106,8	–106,8
	O^{2-}	529,1	540,4*	+11,3	+17,0
					–58,6

single MAPLE in InO_3 (kcal/mol)

	cubic	rhombohedral
In_1^{3+}	1136,0	1082,4
In_2^{3+}	1108,9	1082,4
O^{2-}	529,1	545,4
Σ	3832,0	3801,0

* average value

Undoubtedly it is the ion dipole interacting part of the lattice energy which stabilizes Li_3InO_3 against decomposition, for example into $LiInO_2 + Li_2O$, or $3Li_2O + In_2O_3$, respectively.

More favorable are the calculations with the same compounds of very similar forms [29]. Such calculations were carried out here in order to A) determine whether here also the deviations from the ideal axial ratios c/a and ideal positions would increase the MAPLE value and B) in order to control the Li positions.

A) MAPLE of Li_3InO_3 was calculated for the following cases:

(1) Real case: a = 9.6064, c = 10,420 Å; c/a = 1.0847; for parameters of particles see Table 3.

(2) Ideal case A: cell volumes equal to (1) with $c/a = 4/9 \cdot \sqrt{6} =$ = 1.08866 (Ideal values), i.e. a = 9.5947, c = 10.4454 Å and idea parameters (see Table 2).

(3) Ideal case B: Real cell dimensions as for (1), ideal parameters of particles as for (2).

(4) Ideal case C: as for (2), however all $z_0 = 0.13375$ and all $z_{Li} =$ = 0.4416, whereby all In-O distances are 2.21 Å (average value of (1)) and all Li-O distances are 2.007 Å.

(5) Ideal case D: cell dimensions as for (1); parameters corresponding to (4), but here $z_0 = 0.13338$ and $z_{Li} = 0.4412$.

The results are summarized in Table 12.

Table 12 shows:

The MAPLE values of corresponding structural models (compare line 2, Table 12) are practically independent of whether one inserts the real lattice constants or the calculated values for the same mol volumes and "ideal" ration c/a = $= 4/9 \sqrt{6} = 1.08866$ (No. 2/3, or No. 4/5, respectively).

Changing of the models with ideal parameters to those in which furthermore the "ideal" position of In the O^{2-} layers are sometimes shifted to the In layers in the (00.1) direction, on the whole brings only an insignificant improvement of MAPLE, as shown by the comparison, for example, of 2 with 4.

TABLE 12. MAPLE VALUES OF Li_3InO_3 AND FOR DIFFERENT STRUCTURAL MODELS (COMPARE TEXT); IN KCAL/MOL /255

Li_3InO_3	MAPLE Li_3InO_3	$\overline{Li^+}$	$\overline{In^{3+}}$	$\overline{O^{2-}}$	d° [Å] Li – O	In – O
(1)	3108,7	157,3	1015,7	540,4	1,959	2,138
(2)	3055,0	164,8	957,0	534,2	1,958	2,262
(3)	3054,7	164,8	957,0	534,2	1,954	2,260
(4)	3059,1	149,0	1012,1	533,3	2,007	2,210
(5)	3059,2	148,8	1012,8	533,3	2,007	2,210

	partial MAPLE values								
	Li_1^+	Li_2^+	Li_3^+	In_1^{3+}	In_2^{3+}	In_3^{3+}	O_1^{2-}	O_2^{2-}	O_3^{2-}
(1)	164,2	145,4	162,2	994,8	1022,5	1018,1	543,2	528,7	549,3
(2)	164,9	164,8	164,8	955,4	955,1	960,5	534,2	534,3	534,2
(3)	164,9	164,8	164,8	955,4	955,1	960,5	534,2	534,3	534,2
(4)	149,0	149,0	149,0	1009,6	1009,3	1014,8	533,3	533,4	533,3
(5)	148,9	148,8	148,8	1010,4	1010,0	1015,5	533,3	533,4	533,3

d° = shortest distance

The change to the real case, for which additionally In_2 leaves the ideal position and corresponding shifts of O and Li set in, brings ≈ 50 kcal/mol gain in total value of MAPLE (Li_3InO_3).

Table 12 shows further interesting details. Here it will only be mentioned that the gain by going from (4) or (5) to (1) is not achieved by MAPLE (In^{3+}), but by the MAPLE contributions of Li^+ and O^{2-}. This is all the more noteworthy in that the average distance Li-O, or In-O, respectively -t (5) correspond to the average distances for the real case (1). Apparently, the In-In-interactions are decisive.

B) The question law to arrange most favorably the 36 Li^+ elementary cell electrostatically on the existing 72 tetrahedron spaces, could be best answered by MAPLE calculations.

There are altogether 20 possibilities, 3 each of the 6 compositions of each of the 12 common tetrahedron spaces (compare p. 248) to be used for the formation of Li_3InO_3. However, simultaneous combinations of the compositions /256
1/2, or 3/4, or 5/6 should be excluded. Since then Li-Li distances of 1.29 Å would appear. In order to avoid such absurdly short distances, only one of each of these double groups can be used. There thus still remain 8 possibilities, compare Table 13.

TABLE 13. MAPLE CALCULATIONS FOR 8 PARTS POSSIBILITIES OF 3 Li^+ IN THE InO_2 STRUCTURE (FOR NOMENCLATURE, SEE TABLE 6).

	246	236	245	146	136	235	145	135
Li_1	461,2	170,3	177,2	94,5	88,7	183,2	77,1	71,6
Li_2	145,4	105,3	170,2	151,8	99,9	86,7	176,7	81,3
Li_3	162,2	185,1	117,4	176,6	199,5	96,8	101,8	81,3
In_1	994,8	986,8	964,1	723,4	715,1	956,0	692,7	684,7
In_2	1022,5	875,4	905,8	1006,8	859,5	758,8	889,9	712,8
In_3	1018,1	929,6	909,9	928,8	840,3	821,4	820,6	732,1
O_1	543,2	542,4	549,0	546,2	545,3	548,2	552,6	551,1
O_2	528,7	539,6	535,6	530,9	541,8	546,5	537,9	548,7
O_3	549,3	559,3	550,9	549,7	559,7	560,9	551,3	561,3
Li_3	471,8	460,7	464,7	422,0	388,0	366,7	355,9	231,1
In	1015,7	921,1	917,6	920,5	825,9	823,0	822,4	727,8
O_3	1621,2	1641,2	1635,5	1626,8	1646,8	1655,6	1641,1	1661,2
Li_3InO_3	3108,7	3022,9	3017,0	2970,2	2860,7	2815,3	2819,4	2623,1

NOT REPRODUCIBLE

The corresponding MAPLE values were calculated for these and are summarized in Table 13.

The result is unmistakable: The combination 2/4/6 of the tetrahedron spaces is on the whole higher by 86 kcal/mol in MAPLE value than the next most favorable arrangement 2/3/6. This result confirms the x-ray finding.

VI. The Structure Systematology of Cation-Rich Ternary Oxides

Li_3InO_3 is only a special case of a general series of compounds of the formula $A^1_x + B^n_y + O^{2-}_{(x + ny)/2}$. One can differentiate two cases for these, according to whether the O^{2-} forms a close-packed structure approximately or exactly, respectively, or does not. Li_3InO_3 belongs to the first group. Three classes are possible here, since O^{2-} can exhibit

a) an hexagonal close-packed structure,

b) a cubic close-packed structure and

c) a closed-packed interchangeable structure

Li_3InO_3 belongs to case a). Table 14 shows how various limiting formulas result in relation to the valence n+ of the metal partner according to whether the components A^{1+} occupy only tetrahedra spaces or also vacant octohedra spaces. Many arbitrary combinations are possible because of the possibility of only partially occupying the available spaces in the hexagonal close-packed O^{2-} /257

structure. It is important for its understanding that a complete occupation of all tetrahedra spaces for this O^{2-} is not possible, in contradistinction to the cubic close-packed structure (Example: Li_2O). The only definitely known structure of compounds of the type Li_8MO_6 also belong here: for Li_8TbO_6 [8], all tetrahedra spaces are occupied with Li^+, according to $Li_2(Tb^{4+}_{1/3}Li^+_{2/3})O_2$, the octohedra spaces are theoretically occupied up to 1/3 with TB^{4+}, up to 2/3 with Li^+. It was also reported recently about Li_8SnO_6, etc. [30]. Undoubtedly many of the compounds of type $A^I_8B^{IV}O_6$, $A^I_7B^VO_6$, and $A_6B^{VI}O_6$ first mostly prepared by Scholder [31] also belong here. See 14A.

TABLE 14. LIMITING FORMULAS WITH MAXIMUM CATION/OXYGEN RATIOS FOR THE HEXAGONAL CLOSE-PACKED OXYGEN STRUCTURE

n	tetrahedron & octohedron	only tetrahedron
2	A_8BO_3	A_3BO_2
3	A_5BO_4	A_3BO_3
4	A_6BO_5	A_4BO_4
5	$A_{11}BO_8$	A_5BO_5
6	$A_{14}BO_{10}$	A_6BO_6
7	$A_{17}BO_{12}$	A_7BO_7

A cubic close-packed structure on the other hand, is present in Li_2O and the structure variants derived from it, as α-Li_5GaO_4, α-Li_5AlO_4, β-Li_5GaO_4, β-Li_5AlO_4 [19], as well as in Na_2CdO_2 [32], where all cations necessarily have to have tetrahedra surroundings, since more cations than anions could otherwise not be distributed in the cubic close-packed structure. In this connection mention should be made of Li_4GeO_4 [26].

VII. Concluding Remarks

It was assumed that of the two possible space groups, the centric is present. Later we also screened the case of the acentric space group P3c1. Exclusive calculations [33], which will not be gone into further at this time, showed the following:

1) A significant R-value improvement of 10.03% after 9.30% was found for (InO_3) according to Hamilton [34]

2). However, the discussion of the distances and MAPLE values shows, according to our view, that the available I_0 information is insufficiently certain to be able to decide between the two space groups. /258

We will shortly report about further cation-rich oxides in the system Li_2O/Tl_2O_3 [35].

The computations were carried out at the DRZ, Dormstadt. We used our own programs as well as those of Professor Zemann, which were modified.

We thank the German Research Association and the Federation of German Industry (Funds for Chemistry) for support also in this work.

Giesseu, Institute for Inorganic and Analytical Chemistry of the Justus-Liebig University.

Received at the editorial office 3 October 1969.

BIBLIOGRAPHY

* Preliminary Report: *Z. anorg. allg. Chem.*, Vol. 371, p. 338, 1969.

1. Hoppe, R., "The Alkali Metals", Spec. Publ. No. 22, p. 452, The Chemical Society, London, 1967.
2. Part of the thesis of F. Stewner, D26 Giessen, 1969.
3. Stewner, F. and R. Hoppe, *Jahrestagung der Deutschen Mineralogischen Gesellschaft*, Cologne, p. 60, 1968.
4. Hoppe, R. and B. Schepers, *Z. anorg. allg. Chem.*, Vol. 295, p. 233, 1958.
5. Hoppe, R. and F. Stewner, Thesis F. Stewner, Giessen, 1966.
6. Scholder R. and C. Keller, unpublished, [7].
7. Schwarz H. and D. Bommert, *Z. anorg. allg. Chem.*, Vol. 345, p. 246, 1966.
8. Paletta E. and R. Hoppe, Dissertation E. Paletta, Munster, 1966, [1].
9. Hoppe, R. and H. J. Rohrborn, *Z. anorg. allg. Chem.*, Vol. 329, p. 110, 1964.
10. Hoppe, R. and E. Vielhaber, *Naturwissenschaften*, Vol. 51, p. 103, 1964.
11. Vielhaber, E. and R. Hoppe, *Z. anorg. allg. Chem.*, Vol. 360, p. 7, 1968.
12. Hestermann, K. and R. Hoppe, *Z. anorg. allg. Chem.*, Vol. 360, p. 113, 1968.
13. Sabrowsky, H. and R. Hoppe, *Z. anorg. allg. Chem.*, Vol. 359, p. 241, 1968.
14. Wasel-Nielen, H. D. and R. Hoppe, *Z. anorg. allg. Chem.*, Vol. 359, p. 36, 1968.
15. Sabrowsky, H., *Z. anorg. allg. Chem.*, Vol. 365, p. 146, 1969.
16. Kordes, E., *Z. Kristallogr., Mineralog. Petrogr.*, Section A, Vol. 92, p. 139, 1935.
17. Weyberg, Z., *Zbl. Mineralog.*, Vol. 1906, p. 645.
18. Lehmann, H. A. and H. Hesselbarth, *Z. anorg. allg. Chem.*, Vol. 315, p. 14, 1962
19. Stewner, F. and R. Hoppe, *Naturwissenschaften*, Vol. 55, p. 297, 1968.
20. Zachariasen, W. H., *Acta crystallogr.*, Copenhagen, Vol. 17, p. 749, 1964.
21. Bertaut. E. F., *Bull. Soc. franc. Mineralog. Cristallogr.*, Vol. 88, p. 103, 1965.
22. Marezio, M., *Acta crystallogr.*, Copenhagen, Vol. 18, p. 481, 1965.
23. Zemann, J., *Acta crystallogr.*, Copenhagen, Vol. 10, p. 664, 1957.
24. Wyckoff, R. W. G., *Crytsal structurs*, Interscience Publ., New York-London, Vol. 1, 1963.
25. Marezio, M., *Acta crystallogr.*, Copenhagen, Vol. 19, p. 396, 1965.
26. Vollenkle, H. and A. Wittmann, *Naturwissenschaften*, Vol. 54, p. 441, 1967.
27. Marezio, M., *Acta crystallogr.*, Copenhagen, Vol. 20, p. 273, 1966.
28. Christenssen, M., N. C. Broch, O. V. Heidenstam and A. Nilsson, *Acta Chem. scand.*, Vol. 21, p. 1046, 1967.
29. Compare R. Hoppe, *Z. anorg. allg. Chem.*, Vol. 364, p. 263, 1969.
30. Tromel, M. and J. Hauck, *Z. Naturforsch*, Vol. 23b, p. 110, 1968.
31. According to R. Scholder and H. Glaser, *Z. anorg. allg. Chem.*, Vol. 327, p. 15, 1960.
32. Vielhaber, E. and R. Hoppe, *Rev. Chim. minérale*, Vol. 6, p. 169, 1969.
33. Upon inquiry we shall gladly provide details to those interested.
34. Hamilton, W. C., *Acta crystallogr.*, Copenhagen, Vol. 18, p. 502, 1965.
35. Hoppe, R. and P. Panek, Thesis P. Panek, Giessen, 1970.

Translated for the National Aeronautics and Space Administration under contract No. NASw-2037 by Techtran Corporation, P. O. Box 729, Glen Burnie, Maryland, 21061, translator: Dr. Mark Plunguian.