

The Crystal Structure of Aluminum Phosphate and Gallium Phosphate, Low-Cristobalite Type

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Crystals of the low-cristobalite phases of AlPO_4 and GaPO_4 have orthorhombic symmetry corresponding to the space group $C22_1$. The pseudo-tetragonal base-centered cell contains four formula weights of $M\text{PO}_4$. Parameters for each of the structures have been determined from the analysis of their X-ray powder diffraction patterns. Both structures are quite similar in arrangement to the analogous silica low cristobalite. Gallium is coordinated to four oxygens at a distance of 1.78 Å. Aluminum is coordinated to four oxygens at a distance of 1.70 Å. The angle, $M\text{-O-P}$, is 135° in GaPO_4 , and 145° in AlPO_4 . The analogous angle in silica low cristobalite, Si-O-Si , is 150° .

Introduction

As part of a systematic investigation of the structures of the phosphates of trivalent cations, an X-ray diffraction analysis of gallium phosphate was undertaken. The compound was prepared by Alvin Perloff, who also studied the phase changes of the crystalline material between room temperature and 1100°C . The details of this work have been reported elsewhere (Perloff, 1956). The results relevant to the present discussion are briefly the following. The form of gallium phosphate which is stable at ordinary temperatures was found to be isostructural with AlPO_4 , a well known low-quartz analogue. Two high-temperature modifications of GaPO_4 were observed. These are isostructural with two of the high-temperature phases of AlPO_4 , which are identified as the low-cristobalite and the high-cristobalite types because of their close resemblance to the corresponding silica modifications. These results are in agreement with the observations of other investigators (R. Roy, private communication).

This report is concerned with the structure determination of the low-cristobalite phases of GaPO_4 and AlPO_4 , based on an analysis of powder diffraction data. Though the existence of low-cristobalite AlPO_4 has been known for a long time (Gruener, 1945; Beck, 1949), apparently no serious effort has been made to determine its atomic coordinates. This is understandable, since its powder pattern is almost identical to that of silica low-cristobalite, for which structural parameters have been found (Nieuwenkamp, 1935). Similarly, the pattern of low-cristobalite GaPO_4 is distinguished from the isostructural AlPO_4 pattern only by the effects of a small contraction in cell dimensions, and by such intensity differences as may be attributed to the presence of the heavier metal atom. Clearly, a model of low-cristobalite silica on a gross scale should descriptively represent the structural arrangement of the other two crystals. Nevertheless,

the crystals cannot be identical in such interesting details as interatomic distances and bond angles. Though normally powder data would not be chosen for the elucidation of such details, the lack of single crystals of the compounds left no alternative. In this case, because of the simplicity of the structures, it seemed quite feasible to extract some dependable information from the powder patterns.

Experimental

Samples of the low-cristobalite phases of AlPO_4 and GaPO_4 were prepared in much the same way. Thoroughly ground samples of the low-quartz type were heated well above their high-cristobalite transition temperatures, and then allowed to air-cool quickly to room temperature. In both cases, the conversion to the low-cristobalite form is rapid and complete at the respective transition temperatures, and the phase persists unchanged at ordinary temperatures (Perloff, 1956). In order to avoid troublesome temperature effects, all of the diffraction patterns used for structure analysis were taken at room temperature. The material, which was fine-grained and well crystallized, yielded excellent powder patterns. All of the patterns were taken with filtered copper radiation by means of a wide-angle Geiger-counter spectrometer with a strip-chart recorder. Sets of patterns were taken with scaling ratios of two, four and eight. The instrumental constants used were: receiving slit width, 0.006 in.; horizontal divergence, 1° ; time constant, either 2 or 4 sec.; and scanning speeds, either $\frac{1}{4}^\circ$ or $\frac{1}{2}^\circ$ per minute; maximum counting rate, 180 per sec.

The patterns were indexed to a Bragg angle of about 75° , but the measurement of intensities was terminated at about 40° . At angles higher than this, excessive superposition of peaks made the measured intensities of doubtful value. In the useful range, numerical values of the relative intensities were obtained from measurement of peak areas, partially superposed peaks being

resolved whenever feasible. Intercomparison of values from a number of diffraction patterns showed only minor variations, so the observations were presumed to be a reasonably reliable basis for structure determination.

The relative intensity values were corrected for the polarization-Lorentz factor, and, at a subsequent stage of the work, scaled to the calculated intensities by an appropriate constant. The temperature factor was negligible, as far as could be judged from the ratios of the observed and calculated intensities within the range of the observations.

Scattering factors were taken from the *International Tables* (1935) for Al^{+3} , O^{-2} , P^{+5} , and slightly modified at low orders in the case of gallium to approximate the assumed state, Ga^{+3} . Atomic scattering factors might have been used without appreciable effects on the results.

Lattice type and space group

The unit cell of low-cristobalite silica, containing two formula weights of SiSiO_4 , is primitive tetragonal, with dimensions $a = b = 4.96$, $c = 6.92$ Å (Nieuwenkamp, 1935). The pattern of GaPO_4 , like that of AlPO_4 , can be indexed to correspond to a closely analogous cell containing two formula weights of $M\text{PO}_4$. For AlPO_4 , the dimensions are $a = b = 5.03$ Å, $c = 7.00$ Å, and for GaPO_4 , $a = b = 4.93$, $c = 6.87$ Å. In both cases, the line positions give no evidence of deviation from tetragonal axial symmetry, though a small difference between the a and b axes quite possibly could be masked by the superposition of reflections at the higher angles.

The diffraction patterns of low-cristobalite AlPO_4 and GaPO_4 strongly resemble the pattern of the analogous silica crystal in intensity distribution as well as in spacing. There is, however, a difference in the type of extinctions which occur in the patterns. The space group of SiO_2 low cristobalite is $P4_12_12-D_4^4$ so that planes $00L$ are absent unless $L = 4n$, and planes $H00$ are absent unless $H = 2n$. In AlPO_4 and GaPO_4 , there is only one extinction; that is, $00L$ is absent unless $L = 2n$. These observations support the inference that the sites which are occupied in SiO_2 by an identical set of silicon atoms are shared, in the analogue structures, between phosphorus and metal atoms in regular alternation. Consequently, the 4_1 and 2_1 axes of the silica structure are transformed, respectively, to 2_1 and 2 axes in the phosphate analogues so that only the systematic absence, $00L$, unless L is even, is required by their symmetry.

However, it is not necessary to predict a structure model, but only to assume the presence of discrete phosphate groups in order to deduce the space-group symmetry of the AlPO_4 and GaPO_4 low cristobalites. Only a few space groups are characterized by the single observed systematic absence, and simple considerations serve to eliminate all but two. In the tetragonal

system, three space groups fulfill the required extinction condition; namely, $P4_2$, $P4_2m$ and $P4_22_2$. In each case, the metal and phosphorus atoms would have to occupy twofold special positions such that they would contribute intensity only to particular sets of reflections. The observed intensities completely refute this possibility. Therefore, the observed extinction must be due to a 2_1 axis, and the crystal symmetry must be orthorhombic or lower, despite the tetragonal axial system.

Four space groups remain to be considered: in the orthorhombic system, $P22_2$ and $C22_2$ (with the necessary change in the choice of the unit cell); in the monoclinic system, $P2_1$ and $P2_1/m$. $P22_2$ can be eliminated on spatial considerations, and $P2_1/m$ on intensity considerations similar to those given for the tetragonal space groups. Only $C22_2$ and $P2_1$ remain as possibilities. Credible and, indeed, very similar arrangements may be based on either one. However, there is no reason to suspect that the coordination of the oxygens about the metal and phosphorus atoms is so irregular as to require the lower symmetry of $P2_1$ for its description; and subsequent detailed study of the intensities gave no indication of such a possibility. It appears, therefore, that the space-group symmetry of the low-cristobalite forms of AlPO_4 and GaPO_4 is $C22_2$, and that the true structural unit is not the small primitive cell heretofore used for comparison with that of low-cristobalite silica, but the larger base-centered cell, having as axes the diagonals of the original cell base, and containing four rather than two formula weights of $M\text{PO}_4$.

Crystallographic data

The crystallographic data for the low-cristobalite forms of AlPO_4 and GaPO_4 may now be summarized. The crystals are isomorphous. The base-centered cell, which is pseudo-tetragonal, contains four formula weights of $M\text{PO}_4$. The cell dimensions, determined from a small set of well resolved and moderately-high-angle lines, are given in the following table, along with the calculated cell volumes and densities. The corresponding values for low-cristobalite silica, referred to analogous axes, are included for comparison.

	$a (= b)$ (Å)	c (Å)	V (Å ³)	ρ (g.cm. ⁻³)
GaPO_4	6.967 ± 0.003	6.866 ± 0.003	333.3	3.26
AlPO_4	7.099 ± 0.003	7.006 ± 0.003	353.1	2.28
SiSiO_4^*	7.003	6.950	340.8	—

* Swanson & Tatge, 1953.

It is interesting to notice that the cell volume of GaPO_4 is the smallest of the three, being 5.5% less than that of AlPO_4 , and 2.2% less than that of SiSiO_4 .

The space group $C22_2$ has eightfold general positions and two sets of fourfold special positions on twofold axes. The sixteen oxygens per cell may then

be assigned to two sets of general positions, while the four Ga (or Al) and the four P atoms must lie on the twofold axes (in fourfold special positions). Following the *International Tables* (1935), the coordinates of the sets of equivalent positions are given by

$$[0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0] +$$

- | | | | |
|-----|---|---|----------------|
| (a) | 2 | $x, 0, 0; \bar{x}, 0, \frac{1}{2}$ | (4 P) |
| (b) | 2 | $0, y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}$ | (4 Ga or Al) |
| (c) | 1 | $x, y, z; x, \bar{y}, \bar{z};$
$\bar{x}, \bar{y}, \frac{1}{2} + z; \bar{x}, y, \frac{1}{2} - z$ | (8 O-1; 8 O-2) |

Thus, eight parameters are required to determine the structure.

Details of structure analysis for low-cristobalite AlPO_4

The eight parameters required to fix the atomic positions must be deduced from powder diffraction data. The chief disadvantage of this type of data, namely, the superposition of non-equivalent intensities, is materially increased in this case because of the strictly pseudo-tetragonal nature of the cell; that is, pairs of reflections, HKL and KHL , are always coincident in the diffraction pattern. Further, all of the constituents of the cell have about the same scattering power, so that the sure location of one set of atoms independent of the others is not feasible. Therefore, the procedure must be one of trial and error; that is, the assumption of a complete structure, and the subsequent testing of its credibility by means of intensity calculations. The close relation between the powder patterns of the AlPO_4 and the low-cristobalite forms of silica certainly indicates that only small changes in the values of the SiO_2 parameters should be sufficient to convert them into reasonable values for the AlPO_4 analogue. However, the exact nature and extent of these changes are not too easily postulated. Almost any model based on acceptable interatomic distances gives some semblance of agreement between the observed and calculated intensities. Without a prior knowledge of the best agreement attainable from the available data, it seemed necessary to explore systematically, and in some detail, the entire range of parameter sets which could be considered reasonable.

The scheme adopted for this purpose involved certain assumptions: first, that the phosphate group is a regular tetrahedron, with phosphorus to oxygen distances of 1.56 Å; second, that oxygens of neighboring phosphate groups are at least 2.55 Å apart; and finally, that the aluminum atom is equidistant from its four surrounding oxygens. On the basis of these assumptions, an extensive series of structure models was devised in the following way.

From the space-group symmetry it is known that phosphorus, the center of the phosphate tetrahedron, occupies a set of special positions ($x, 0, 0$, and related points) on twofold rotation axes of the crystal. Conse-

quently, a twofold axis of the tetrahedron must coincide with the crystal axis, but the orientation of the group as a whole about this axis is unrestricted by symmetry. The phosphorus parameter, x , fixes the position of the center of the group on the axis; a second parameter, φ , may be used to specify its orientation. If φ is taken as the angle between any convenient reference plane—in this case, the cell base—and a given mirror plane of the tetrahedron, values of φ between 0 and 45° describe all structurally unique orientations of the tetrahedron. Thus, the required parameters are reduced to three, x for the phosphorus, φ for the oxygens, and y for the aluminum.

All values of φ greater than 25° may be eliminated from consideration at once, because they produce unreasonably small separations between the oxygens of different tetrahedra. For any given value of φ less than 25°, there is a small range of x values, increasing with decreasing φ , for which the O-O distances are acceptable. On the assumption that the aluminum is centrally located with reference to its four nearest oxygens, the aluminum parameter may be calculated for particular values of x in the permitted range. Thus, for any particular angular orientation of the phosphate group, it is possible to derive hypothetical structure models having consecutive small differences in the x parameters of the phosphate group, in the aluminum parameter, and consequently in the aluminum to oxygen distances. A tabulation of such parameter sets, for a series of φ values taken at suitably small intervals, gives a convenient means for studying the whole range of structural arrangements which are possible within the restrictions imposed by the preliminary assumptions.

Fortunately, a large number of cases can be eliminated by the use of a few simple planes as criteria. Some reflections can be found which are highly dependent on the orientation of the tetrahedron; that is, on the y and z parameters of oxygen. For instance, the intensity calculated for 004 cannot be made to agree with the observed intensity unless the oxygen contribution is small and negative; the intensity of plane 222 depends completely on oxygen contributions, which must be fairly large. From these, and other less obvious examples, it appears that φ must be somewhere between 18° and 20°. For orientation parameters between 18° and 20°, the aluminum parameter may theoretically have values between 0.163 and 0.200 (unit-cell fractions). The corresponding Al-O distances range from 1.85 Å to 1.68 Å.

An attempt to use small groups of selected planes as criteria for narrowing the range of aluminum parameter values gave results which were not sufficiently decisive. Therefore, complete intensity calculations were made for model structures selected so as to sample the various combinations of parameter values as effectively as possible. A form of residual factor, $R_I = \Sigma[I_o - I_c] \div \Sigma I_o$, was used as an estimate of the over-all agreement between the observed and cal-

culated intensities. This factor was found to change appreciably, and in a regular manner, for small differences in the aluminum parameter, and in the orientation parameter, as shown in Table 1.

Table 1

Al(<i>y</i>)	P(<i>x</i>)	φ (°)	Al-O (Å)	R_I (%)
0.178	0.339	20	1.77	43
0.184	0.321	19	1.73	28
0.190	0.314	20	1.70	19
0.194	0.311	19.5	1.71	14.5
0.198	0.306	19	1.70	11

The minimum value of R_I attained was 11%; attempts to reduce it still further by small changes, including slight deformations of the tetrahedron, were fruitless. The set of parameters for AlPO_4 which gives the most satisfactory agreement with the data is shown in Table 2.

Table 2. *Low-cristobalite parameters of AlPO₄*

	<i>x</i>	<i>y</i>	<i>z</i>
Al	0	0.198	0.25
P	0.306	0	0
O ₁	0.179	0.058	0.172
O ₂	0.433	0.170	0.941

A comparison of observed and calculated intensities is given in Table 3. The agreement is quite good. The largest discrepancies occur for planes of low intensity, where the measurement is most subject to error.

The calculated intensities of the pairs of planes, *HKL* and *KHL*, have been given separately in the table, though they cannot be so observed in the powder pattern. They have, in general, quite different intensities, so that single-crystal patterns of this crystal would be easily distinguishable by cursory inspection from single crystal patterns of low-cristobalite silica.

As has been shown, the parameters of low-cristobalite AlPO_4 were determined by a method which made no use of the known parameters of SiO_2 . However, the set which gave the best agreement with the observed intensities is remarkably close to the set given by Nieuwenkamp (1935) for the silica crystal. His parameters, here referred to the base-centered rather than to the correct primitive cell for more direct comparison, are shown in Table 4.

The main difference between the structures is in the orientation of the oxygen tetrahedra; the parameter φ , which is 19° in low-cristobalite AlPO_4 , is about 23° in the silica crystal.

Details of structure analysis of low-cristobalite GaPO_4

The procedure used in the study of low-cristobalite GaPO_4 was essentially the same as that described for the analysis of the AlPO_4 crystal. The same preliminary assumptions were made, and a comprehensive series

Table 3. *Calculated and observed intensities, AlPO₄ (low-cristobalite type)*

$(\sin^2 \theta)_0$	<i>HKL</i>	$I_c/8$	I_o
0.0236	110	2	8
0.0357	111	2188	2020
0.0472	200 020	7 25	32 45
0.0485	002	7	11
0.0592	021 201	172 216	388 386
0.0721	112	689	621
0.0942	220	1080	1278 1391
0.0953	202 022	89 109	
0.1065	221	5	
0.1170	310 130	0 2	2 6
0.1301	311 131	152 189	354 411
0.1327	113	13	
0.1425	222	255	273
0.1562	203 023	487 307	794 760
0.1665	312 132	406 440	846 755
0.1885	400 040	46 58	104 114
0.1933	004	200	220
0.2002	401 041	13 12	602 540
0.2030	223	577	
0.2125	330	0	0
0.2168	114	111	114
0.2246	331	879	1097 1193
0.2264	133 313	102 116	
0.2365	240 420 042 402	95 58 27 72	
0.2401	024 204	0 23	23 20
0.2480	241 421	402 404	806 700
0.2606	332	1088	897
0.2843	242 422	338 251	589 700
0.2877	224	482	466
0.2978	043 403	258 250	508 553
0.3066	150 510	0 1	954 1056
0.3116	134 314	370 583	
0.3190	151 511 333	260 209 208	
0.3252	115	849	730

Table 3 (cont.)

$(\sin^2 \theta)_0$	<i>HKL</i>	$I_c/8$	I_0
0.3447	243	516	1279
	423	738	
0.3485	025	23	
	205	2	1167
0.3550	152	625	
	512	542	
0.3772	440	19	28
0.3819	044	155	285
	404	130	
0.3897	441	541	515
0.3960	225	80	81
0.4012	350	352	736
	530	361	
0.4055	334	23	
0.4128	351	108	2686
	531	152	
0.4152	153	332	
	513	299	2476
0.4194	135	424	
	315	402	
0.4244	060	139	290
	600	111	
0.4254	442	202	
0.4287	244	252	303
	424	257	
0.4341	006	8	
0.4377	061	168	290
	601	122	
0.4489	352	18	122
	532	104	

Table 4. *Low-cristobalite parameters of SiSiO₄*

	<i>x</i>	<i>y</i>	<i>z</i>
Si ₁	0	0.2	$\frac{1}{4}$
Si ₂	0.3	0	0
O ₁	0.173	0.073	0.175
O ₂	0.428	0.173	0.925

of hypothetical structures were derived in the same way.

Because the cell of low-cristobalite GaPO₄ is somewhat smaller than that of its AlPO₄ counterpart, the maximum value of φ must also be smaller in order to avoid unreasonably short distances between neighboring tetrahedra. The limiting value is 15° in GaPO₄, compared to 25° in AlPO₄. The possible values of gallium parameters over the whole angular range of φ fall between 0.150 and 0.200.

Because the scattering power of gallium is about twice as large as that of aluminum, there are no reflections from GaPO₄ which depend solely on the oxygen contributions, and few which are particularly sensitive to changes in the oxygen positions. Therefore, the orientation parameter cannot be limited to a small range of values at the outset, as was done in the case of low-cristobalite AlPO₄. On the other hand, many of the intensities are appreciably modified by small changes in the gallium position. By using groups of suitably

chosen reflections as criteria, it is possible to show clearly that the gallium parameter must be somewhere between 0.180 and 0.190.

In order to refine the gallium parameter, and to find the associated oxygen positions, complete intensity calculations were made for models having a wide range of φ parameters, and a gallium parameter between 0.180 and 0.190. The value of R_1 changes in a small but consistent way for differences as small as 0.001 in the gallium parameter, with φ kept constant. It goes through a minimum for values of the gallium parameter between 0.180 and 0.185, attaining its lowest value close to 0.183. On the other hand, R_1 is not too greatly affected by the oxygen orientation. Table 5 shows three cases, calculated from the optimum

Table 5

φ (°)	Ga(<i>y</i>)	P(<i>x</i>)	Ga-O (Å)	R_1 (%)
7	0.183	0.330	1.84	12.4
11	0.183	0.327	1.78	9
15	0.183	0.325	1.73	11.4

value of the gallium parameter and widely different orientations. Quite acceptable values of R_1 are obtained for values of φ at opposite ends of its range. However, the value of $R_1 = 9\%$ seems to be a minimum, and the corresponding set of parameters, given in Table 6, were taken as the best obtained from the data.

Table 6. *Low-cristobalite parameters of GaPO₄*

	<i>x</i>	<i>y</i>	<i>z</i>
Ga	0	0.183	$\frac{1}{4}$
P	0.327	0	0
O ₁	0.198	0.035	0.182
O ₂	0.456	0.179	0.965

The parameters of GaPO₄ differ appreciably from those of AlPO₄ and SiO₂ (low-cristobalite forms); and the orientation angle of its oxygen tetrahedra is considerably smaller: 11° compared to 19° and 23° for the AlPO₄ and SiO₂ compounds, respectively.

Table 7 shows the calculated and observed intensities to be in satisfactory agreement.

Discussion of the structures

Owing to the obvious deficiencies of the data, the accuracy of the parameters cannot be high. However, the final sets of positions in each case give agreement with the observations which seems close to the limit set by the data, in the sense that a change in the gallium position by as little as ± 0.01 Å, and of the other atoms by less than ± 0.05 Å appreciably increases the factor, R_1 .

The interatomic distances and bond angles calculated from the parameters of the low-cristobalite phosphate structures are compared with those of low-cristobalite silica in Table 8. The structure diagram

Table 7. *Calculated and observed intensities, GaPO₄ (low-cristobalite type)*

(sin ² θ) _o	HKL	I _c /8	I _o
0.0245	110	42	26
0.0369	111	3990	3175
0.0487	020 200	12 420	337
0.0502	002	146	120
0.0615	021 201	882 245	1242
0.0746	112	1813	1825
0.0979	220	2360	2675
0.0990	022 202	288 408	858
0.1103	221	610	607
0.1224	130 310	364 101	394
0.1347	131 311	398 1520	2160
0.1371	113	888	917
0.1481	222	370	377
0.1621	023 203	866 514	1500
0.1728	132 312	1840 68	2052
0.1952	040 400	94 497	568
0.2009	004	1030	1052
0.2084	041 401	302 7	252
0.2108	223	1470	1605
0.2201	330	192	226
0.2245	114	44	38
0.2327	331	557	703
0.2350	133 313	77 888	1050
0.2458	240 420 042 402	266 492 75 792	1540
0.2499	024 204	118 670	683
0.2571	241 421	1810 1090	2847
0.2702	332	4084	3634
0.2944	242 422	11 164	216
0.2986	224	1250	1272
0.3090	043 403	776 152	908
0.3184	150 510	116 108	192
0.3231	134 314	1170 848	1980
0.3311	151 511 333	589 1220 132	1680

Table 7 (cont.)

(sin ² θ) _o	HKL	I _c /8	I _o
0.3382	115	2130	2133
0.3568	243 423 025 205	2000 1650 110 45	3942
0.3684	152 512	2010 1004	3210
0.3955	440 044 404	34 39 450	494
0.4047	441	1040	918
0.4097	225	424	
0.4165	350 530	634 462	1630

Table 8. *Distances and bond angles in MXO₄ (low-cristobalite type)*

	M-O (Å)	X-O (Å)	O-O (Å)	M-O-X (°)
GaPO ₄	1.78	1.56	2 at 2.80 1 at 2.91 2 at 2.98 1 at 3.00 (2.91*)	135 (138, 132)
AlPO ₄	1.70	1.56	2 at 2.72 1 at 2.77 2 at 2.81 1 at 2.84 (2.78*)	145 (147, 143)
SiSiO ₄	1.59	1.59	3 at 2.57 3 at 2.63 (2.60*)	150

* Average.

of low-cristobalite GaPO₄ is shown in Fig. 1. With due allowance for such small differences as appear in the table, the same diagram could be used to illustrate the structural arrangement in AlPO₄ or SiO₂ (low-cristobalite forms). The fact that the three structures are quite similar can be inferred merely by inspection of their powder photographs. Therefore, the results of a structure analysis of GaPO₄ and AlPO₄ can have interest only in showing what differences exist between them.

In the low-cristobalite SiO₂, the oxygens form a practically regular tetrahedron about each silicon. In the two MPO₄ structures, the phosphate group has been assumed to be a regular tetrahedron, and the distances, M-O, have been assumed to be exactly equal. The resulting configuration of four oxygens about M is a somewhat distorted tetrahedron, as can be seen from the six shortest O-O distances, which form the tetrahedral edges. This distortion may, of course, be exaggerated by the preliminary assumptions, if, as is quite probable, it is shared between the gallium-oxygen and the phosphorus-oxygen configuration.

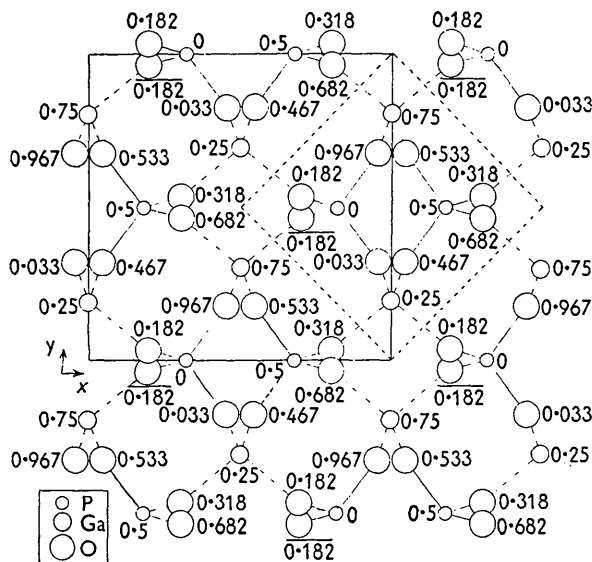


Fig. 1. Gallium phosphate, low-cristobalite type; [001] projection of the crystal structure. The true base-centered cell is indicated by full lines, and the pseudo-cell, comparable to that of low-cristobalite silica, by heavy broken lines.

In low-cristobalite SiO_2 the angle Si-O-Si is 150° . The analogous angle is smaller in the two phosphates, and decreases with the heavier metal: it is 145° for Al-O-P , and 135° for Ga-O-P . This difference in the orientation of the oxygen tetrahedra accounts for the facts that the AlPO_4 cell is not quite as large compared to that of SiO_2 as might be expected from spatial considerations; and that the structural unit of GaPO_4 can be accommodated in a smaller cell volume than that of AlPO_4 or even SiO_2 , despite its larger $M\text{-O}$ separation.

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A Note on the Debye-Waller Theory

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The effect of temperature on the Bragg reflexion from crystals is examined theoretically for a general crystal. It is shown that measurements of this effect can be used to obtain information about the vibrational spectrum of a crystal. A comparison is made of the existing data and the theoretical predictions.

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The effect of temperature on the reflexion of X-rays from crystals was first investigated by Debye (1914), and in the form due to Waller (1925) is part of standard X-ray theory. The theory shows that the intensity of X-rays reflected by a particular set of Bragg

No preliminary assumptions were made concerning the magnitude of the $M\text{-O}$ distances in the $M\text{PO}_4$ structures; a wide range of values were tested with various phosphate group positions. In the case of low-cristobalite AlPO_4 , the distance Al-O was found to be 1.70 \AA . This value has also been reported for four-coordinated Al-O in the crystal of AlAsO_4 (Machatski, 1935), which is structurally analogous to low-quartz. It is considerably smaller than would be deduced from the assumption of ionic radii. For instance, in Al_2O_3 (corundum) the average O-Al distance in six-coordination is 1.91 \AA (three at 1.89 , three at 1.93 \AA). Correction of this distance to four coordination gives about 1.79 \AA .

The value of 1.78 \AA was found for the Ga-O distance in low-cristobalite GaPO_4 . There are no available experimental data with which to compare it. For ionic radii, the distance for four coordination would be in the neighborhood of 1.85 \AA .

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planes varies with temperature in the form $\exp(-2M)$, where

$$M = 8\pi^2 \overline{u_z^2} \sin^2 \theta / \lambda^2, \quad (1)$$

θ being the Bragg angle, λ the wavelength of the X-rays and $\overline{u_z^2}$ an averaged mean square displacement in the direction z perpendicular to the planes. The