

XIII. The Structure of Andalusite, Al_2SiO_5 .

By

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(With 3 figures.)

Introduction.

The three naturally-occurring forms of Al_2SiO_5 form an interesting series of crystals for analysis, since they may be expected to reveal some fundamental differences in the mode of arrangement of the positive ions in the interstices of the grouping of large oxygen ions which have such a powerful influence on the crystalline properties.

The structures of two members of the series, cyanite¹⁾ and sillimanite²⁾, have already been determined; the present paper describes the structure of andalusite, and summarizes the interesting points of similarity, in the three structures, as well as the features which differentiate them.

All the specimens of andalusite used in this work are from Brazil. The crystal used for the photographic work is a fragment of a clear dark-green crystal shewing some trace of pleochroism, and of density 3.44. I am indebted to L. J. Spencer, F.R.S., for the use of larger crystals (water worn specimens from the gem gravels of Brazil), which are clear and transparent, light green when viewed in a direction normal to the c -axis and red when viewed along the c -axis. The density was found to be 3.45.

The experimental data has been obtained from rotating crystal photographs taken with a small crystal and analysed by graphical methods; the relative blackness of the spots has been estimated by eye and from this the relative intensity of reflection by the different planes has been deduced. In the case of planes with indices of the types $(00l)$, $(h00)$, $(0k0)$, $(hk0)$, the data obtained in this way from photographs has been supplemented by qualitative measurements made on the ionisation spectrometer. These confirmed the photographic results in every case, and served to extend the range of the experimental data beyond the limits possible in the photographic method.

1) St. Náray-Szabó, W. H. Taylor, and W. W. Jackson — a recent paper in *Z. Krist.* 2) W. H. Taylor, *Z. Krist.* 68, 503, 1928.

Since the experimental data is entirely qualitative, the precise values of the parameters defining the atomic positions cannot be found with certainty. Experience has proved, however, that a structure obtained in the way to be described is sufficiently accurate to reveal all its essential features. As far as the final structure is concerned, the application of the quantitative method may be regarded as a refinement; the advantages of the quantitative method in the earlier stages of analysis have been described elsewhere¹).

The unit cell and space group.

Crystallographic data assign andalusite to the holohedral class of the orthorhombic system, the axial ratios being given by Des Cloiseaux²) as

$$a : b : c = 0,9864 : 1 : 0,7025.$$

The only X-ray examination of which I have any record is that of Mark and Rosbaud³), who also examined the other forms of Al_2SiO_5 . For andalusite they find a unit cell with dimensions

$$a = 7,90 \text{ \AA} \quad b = 7,90 \text{ \AA} \quad c = 5,55 \text{ \AA},$$

and they assign the space group V_h^{12} , their data being taken entirely from rotating-crystal photographs.

Measurements made on the ionisation spectrometer confirm fairly satisfactorily the values given above; the mean of several measurements on different crystal specimens leads to the following values for the axial lengths:

$$a = 7,76 \pm 0,03 \text{ \AA}, \quad b = 7,90 \pm 0,03 \text{ \AA}, \quad c = 5,56 \pm 0,02 \text{ \AA}.$$

The density being 3,4—3,2, the unit cell with these dimensions contains four molecules of Al_2SiO_5 . Analysis of a number of photographs determines the space group as V_h^{12} in agreement with Mark and Rosbaud's results.

The symmetry elements of V_h^{12} are as follows, the origin of co-ordinates being at a symmetry-centre at the centre of the unit cell⁴):

Symmetry-centres: $0\ 0\ 0, \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}; \frac{1}{2}\ 0\ 0, 0\ \frac{1}{2}\ \frac{1}{2}; 0\ 0\ \frac{1}{2}, \frac{1}{2}\ \frac{1}{2}\ 0; 0\ \frac{1}{2}\ 0, \frac{1}{2}\ 0\ \frac{1}{2}$.

Digonal Rotation Axes: $(001)_{00}, (001)_{\frac{1}{2}\frac{1}{2}}; (001)_{\frac{1}{2}0}, (001)_{0\frac{1}{2}}$.

Digonal Screw Axes: $(010)_{\frac{1}{2}\frac{1}{2}}, (010)_{-\frac{1}{2}\frac{1}{2}}, (010)_{\frac{1}{2}-\frac{1}{2}}, (010)_{-\frac{1}{2}-\frac{1}{2}};$
 $(100)_{\frac{1}{2}\frac{1}{2}}, (100)_{-\frac{1}{2}\frac{1}{2}}, (100)_{\frac{1}{2}-\frac{1}{2}}, (100)_{-\frac{1}{2}-\frac{1}{2}}$

Reflection Planes: $(001)_0, (001)_{\frac{1}{2}}$

1) W. L. Bragg and J. West, Z. Krist. **69**, 139, 1928. 2) Cf. Dana, Mineralogy, 496. 3) Mark and Rosbaud, N. J. Min. **54**, A, 127, 1926. 4) Cf. Niggli, Geom. Krist. d. Disk. 198.

Glide Planes: $(010)_{\frac{1}{2}}$ $(010)_{-\frac{1}{2}}$ with glide $\frac{a}{2} + \frac{c}{2}$

$(100)_{\frac{1}{2}}$ $(100)_{-\frac{1}{2}}$ with glide $\frac{b}{2} + \frac{c}{2}$.

An atom in the general position is converted into a group of eight equivalent atoms, by the operation of the symmetry elements, and if this group is represented by one member having the coordinates $(x y z)$ (measured from a centre of symmetry at the centre of the cell as origin of coordinates), then the contribution of the eight equivalent atoms to the reflection from the plane (hkl) is given by the expression

$$S = 8A \cos(\bar{h} + k + l\pi/2 + h\theta_1) \cos(\bar{h} + k + l\pi/2 + k\theta_2) \cos(l\theta_3)$$

in which A represents the contribution of a single atom, and

$$\theta_1 = 2\pi \frac{x}{a}, \quad \theta_2 = 2\pi \frac{y}{b}, \quad \theta_3 = 2\pi \frac{z}{c}.$$

If $(h + k + l)$ is even, the expression takes the form

$$S = 8A \cos h\theta_1 \cos k\theta_2 \cos l\theta_3.$$

If $(h + k + l)$ is odd, the expression takes the form

$$S = 8A \sin h\theta_1 \sin k\theta_2 \cos l\theta_3.$$

The "8A" in the expression for S is altered to $2A$ if the typical atom lies at a symmetry-centre, and to $4A$ if the typical atom lies on a reflection plane or on a digonal rotation axis.

The determination of the structure resolves itself, from this point, into finding positions for the four silicon atoms, eight aluminium atoms, and twenty oxygen atoms, in the unit cell, in accordance with the symmetry elements of the space group, which explain the observed diffraction data.

The determination of the structure.

(1) The length of the c -axis and the arrangement of reflection planes at heights $(001)_0$, $(001)_{\frac{1}{2}}$, in the unit cell, suggests that it will be easy to fix the atomic positions in the c -direction; for the distance between successive reflection planes ($2.78 \text{ \AA}$) is only slightly greater than the diameter of an oxygen atom ($2.7 \text{ \AA}$ approximately), so that an oxygen atom must either be on the reflection planes or almost exactly midway between.

There are only four silicon atoms in the cell; they must therefore be at two pairs of symmetry centres, or on digonal axes, or on reflection planes. If the silicon atom is to be surrounded by a tetrahedral group of oxygen atoms, it cannot be at a symmetry centre, and there is no room between successive reflection planes for an (SiO_4) group

placed on a digonal rotation axis. The silicon atoms must therefore be all of the same kind and lie on the reflection planes, and the tetrahedral group surrounding the silicon atom consists of two oxygen atoms lying on the reflection plane, together with a pair of oxygen atoms above and below the reflection plane and touching in that plane (Fig. 4). If we assume that the (SiO_4) groups in the structure are independent, the two oxygen atoms of the group which lie on the reflection planes must be members of different sets of four equivalent atoms; if the (SiO_4) groups are arranged in pairs which share one corner, the oxygen atom at this corner must be at a symmetry centre; if the tetrahedral groups are

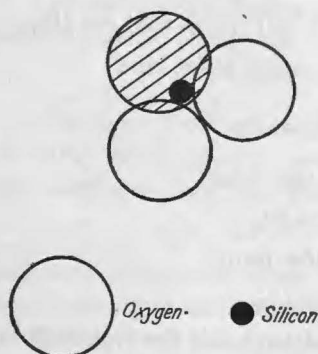


Fig. 4. Arrangement of tetrahedral O_4 group about a silicon atom lying on a reflection plane parallel to the plane of the diagram. The shaded oxygen atoms lie at distances $1.35 \text{ \AA}$ above and below the reflection plane, touching in it, and the unshaded oxygen atoms lie on the plane.

arranged in pairs which share an edge, the oxygen atoms held in common are members of the same set of four atoms. The last arrangement is highly improbable in a structure with the oxygen: silicon ratio five to one, and either of the other arrangements requires that eight oxygen atoms are placed on the reflection planes and eight midway between.

There remain four oxygen atoms and eight aluminium atoms to which parameters in the c -direction must be assigned. The oxygen atoms may be either on the reflection planes or on the rotation axes and midway between the planes, and the aluminium atoms may be either entirely on the reflection planes, or entirely on the rotation axes, or half on the planes and half on the axes, or in a general (eightfold) position. In any case, if the aluminium atoms are not on the reflection planes, they will be very nearly midway between; otherwise two such atoms would approach more closely than is reasonably probable, since the reflection planes are $2.8 \text{ \AA}$ apart.

In Table I the observed relative intensities of the $(00l)$ spectra are compared with the F -values calculated for the various arrangements which are possible according to the argument given above. Only two arrangements (those called A_1 and A_7) show satisfactory agreement, and the evidence is slightly in favour of A_7 , in which the aluminium atoms are partly on the reflection planes and partly on the rotation axes.

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(2) An attempt to arrange the atoms, in the unit cell, in accordance with parameters in the c -direction given in arrangement A_1 above, shows that it is impossible to obtain any atomic arrangement which looks at all reasonable or gives a uniform distribution of the ions.

Table I.

Comparison of observed and calculated intensities of $(00l)$ spectra.

Arrangement	Atoms on reflection planes	Atoms midway between planes	F values					
			002	004	006	008	0.0.10	0.0.12
A_1	$4 Si + 8 O$	$12 O + 8 Al$	-57	+140	-22	+40	-7	+16
A_2	$4 Si + 4 Al + 8 O$	$12 O + 4 Al$	+15	+140	+44	+40	+8	+16
A_3	$4 Si + 8 Al + 8 O$	$12 O$	+88	+140	+50	+40	+23	+16
A_4	$4 Si + 12 O$	$8 O + 8 Al$	-10	+140	-10	+40	-4	+16
A_5	$4 Si + 12 O$	$8 O + 8 Al$	-10	+140	-10	+40	-4	+16
A_6	$4 Si + 8 Al + 12 O$	$8 O$	+137	+140	+62	+40	+26	+16
A_7	$4 Si + 4 Al + 12 O$	$8 O + 4 Al$	+64	+140	+26	+40	+11	+16
Values of $\sin \theta$			0.128	0.255	0.383	0.511	0.639	0.766
Observed relative intensities			<i>vs</i>	<i>vs</i>	<i>mv</i>	<i>m</i>	<i>vw</i>	<i>w</i>

The relative intensities quoted are from ionisation spectrometer measurements.

The values of $\sin \theta$ correspond to MoK_α radiation with $\lambda = 0.71 \text{ \AA}$.

Taking the other arrangement (A_7 above), we have to determine the parameters in the a - and b -directions, for one group of four silicon atoms and one group of four aluminium atoms lying on the reflection planes, for one group of eight oxygen atoms in a general position midway between the reflection planes, and for twelve oxygen atoms lying on the reflection planes. The most probable arrangement of oxygen atoms around the aluminium atoms lying on rotation axes is suggested at once by the space group symmetry; each of these aluminium atoms is surrounded by an octahedron of oxygen atoms, successive octahedra sharing one edge — i. e. sharing two oxygen atoms which lie on a reflection plane.

So far as I am aware, the only silicate structure yet determined, in which the aluminium atom is not closely surrounded by an octahedron of oxygen atoms, is that of sillimanite¹⁾, in which one half the aluminium atoms lie on reflection planes and each of these atoms is surrounded by an oxygen group which may be regarded as a distorted octahedron but is more probably a slightly opened tetrahedral group of four atoms (see also a later section of this paper). We may therefore reasonably expect that the aluminium atoms lying on the reflection planes

1) W. H. Taylor, Z. Krist. 68, 503, 1928.

in andalusite will be surrounded by either six or four oxygen atoms; we have already assumed the existence of tetrahedral (SiO_4) groups, which will very probably be independent, or may possibly be arranged in pairs which share one corner, so that if these assumptions are correct it ought not to be difficult to find the correct atomic arrangement, by reason of the high symmetry of the space-group.

As a preliminary test, a set of reflections from planes with low indices of all types — such as (200), (020), (110), (120), (210), (220), (101), (011), (202), (022), (112), (122), (212), (222), — is chosen; any proposed structure must shew a rough correspondence between the observed intensities and the calculated F values. After many trials I have failed to find any structure, based on the assumptions detailed above, which satisfies the data selected for a preliminary test. There must then be something unjustified in the assumptions, and some other line of attack is needed.

In a recent paper¹⁾ a method of exclusion based on quantitative measurements of intensity of reflection has been applied, to fix limits within which the heavier atoms of the unit cell must be found. The same general method can be applied to this structure, although of course the results obtained from considerations of this kind are much less exact, and less reliable, when the data available is entirely qualitative. The result of this attempt is to indicate fairly definitely certain possible positions for the silicon and aluminium atoms lying on the reflection planes, so that it remains to find a grouping of the oxygen atoms about silicon and aluminium atoms supposed placed in the positions indicated, which will account for the observed intensities of reflection. The assumption that silicon atoms are surrounded by tetrahedral groups of oxygen atoms is probably the least open to objection, and may be used again as a guide; no assumption is made with regard to the oxygen grouping around the aluminium atoms on the reflection planes, but it does not seem possible to place any but an octahedral group around the aluminium atoms which are located on the rotation axes.

A few trials show that one arrangement of the atoms gives a very satisfactory agreement between observed and calculated intensities in the case of those reflections (with low indices) used as a preliminary test. It remains to be seen whether this structure, modified if necessary by the introduction of small changes in the values of the parameters, can explain satisfactorily the large mass of observational data available from the analysis of several rotation photographs.

1) B. Warren and W. L. Bragg, *Z. Krist.* **69**, 468, 1928.

(3) The curious and unexpected form of the group of oxygen atoms which surrounds each aluminium atom lying on the reflection planes (the oxygen grouping is discussed below), makes it desirable to carry out a thorough test of the proposed structure. About 160 planes have

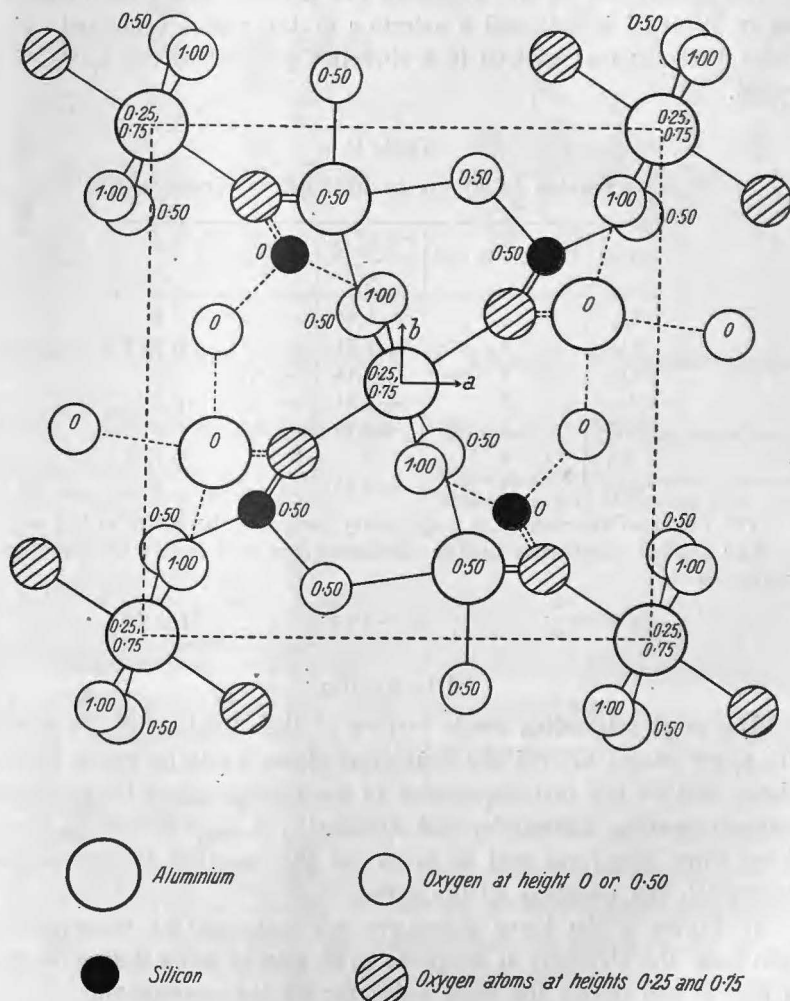


Fig. 2. The structure of andalusite viewed parallel to the c -axis. The figures give the heights of the atoms, as fractions of the c -axis above a base-plane in the plane of the diagram. The origin of coordinates used in Table II is a centre of symmetry at the centre of the unit cell, and so at height 0.50 in this diagram. The positive direction of the c -axis is normally upward from the plane of the diagram. The nature of the oxygen group which surrounds each positive ion is brought out clearly in this method of representation.

been examined, and no serious disagreement found anywhere; the striking features of the spectra are faithfully reproduced in the F^2 -values calculated, and it is therefore highly probable that the structure proposed is correct.

The coordinates of the atoms in the unit cell are given in Table II, and in Table III is collected a selection of the planes examined. Fig. 2 shows the structure viewed in a direction parallel to the c -axis of the crystal.

Table II.
Coordinates of atoms in unit cell of andalusite.

Atom	Number in cell	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$
O_A	4	+ 0,08	- 0,14	0
O_B	4	+ 0,04	- 0,17	+ 0,50
O_C	4	+ 0,14	+ 0,40	0
O_D	8	+ 0,24	+ 0,14	+ 0,25
Si	4	+ 0,28	+ 0,25	0
Al_I	4	0	0	+ 0,25
Al_{II}	4	- 0,14	+ 0,36	0

The origin of coordinates is a symmetry centre at the centre of the unit cell

The angular coordinates used in calculating structure factors are given by the expressions

$$\theta_1 = 2\pi \frac{x}{a}$$

$$\theta_2 = 2\pi \frac{y}{b}$$

$$\theta_3 = 2\pi \frac{z}{c}$$

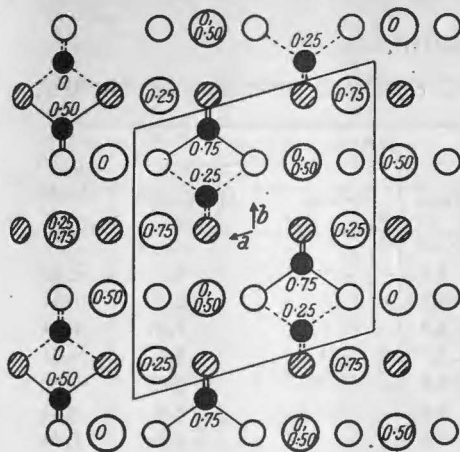
Discussion.

The most interesting single feature of the structure is the grouping of oxygen atoms around the aluminium atoms which lie on the reflection planes, but as the real importance of the analysis lies in the relationship between cyanite, sillimanite, and andalusite, it is proposed to compare these three structures and to point out the essential differences which distinguish the members of the series.

In Figure 3 the three structures are collected for comparison; in each case the structure is supposed to be viewed along the c -axis, which of course has nearly the same value for all the crystals-viz.

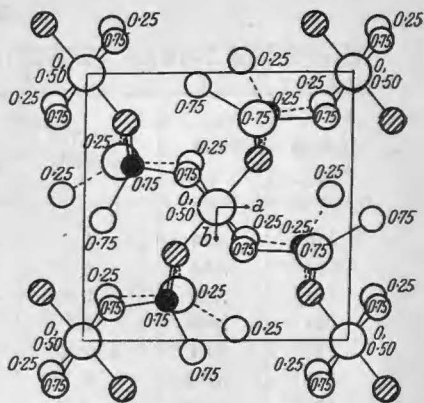
5,56 Å for cyanite, 5,74 Å for sillimanite, 5,56 Å for andalusite.

The structure of andalusite may best be understood if it is pointed out that passing through the corners of the unit cell, and through its centre, are columns of octahedra formed by oxygen atoms, and surrounding aluminium atoms. The octahedra form continuous chains parallel to the c -axis, for successive octahedra share two oxygen atoms which lie



- Aluminium ○ Oxygen atoms at heights 0.25, 0.75
 ● Silicon ⊗ Oxygen atoms at heights 0 and 0.50

The centre of symmetry at the centre of the unit cell is at height 0.50.
Cyanite.

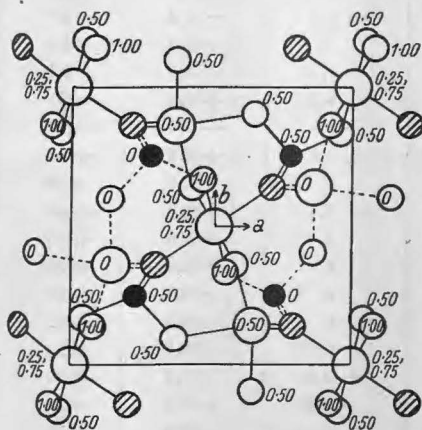


- Aluminium ○ Oxygen at height 0.25 or 0.75
 ● Silicon ⊗ Oxygen atoms at heights 0 and 0.50

There are reflection planes of symmetry parallel to (001) at heights 0.25, 0.75.
Sillimanite.

Fig. 3.

The structures of cyanite, sillimanite, and andalusite, viewed in a direction parallel to the c -axes in each case. The directions of the a - and b -axes are indicated and the unit cell is outlined, in each crystal. The figures give the heights of the atoms, as fractions of the c -axis, above the plane of the diagram taken as base plane.



- Aluminium ○ Oxygen at height 0 or 0.50
 ● Silicon ⊗ Oxygen atoms at heights 0.25 and 0.75

There are reflection planes of symmetry parallel to (001) at heights 0, 0.50, 1.00.
Andalusite.

Table III.

Comparison between observed and calculated intensities of reflection.

Indices	sin θ	Observed Intensity	Structure Factor			Approx. F -value
			Oxygen	Silicon	Aluminium	
110	.064	4	+ 3,4	0	+ 2,4	+ 52
044	.078	4	- 2,7	0	- 2,6	- 47
101	.079	5	+ 2,2	- 0,7	+ 2,6	+ 37
020	.090	2	- 2,7	- 4,0	+ 3,3	- 34
111	.091	2 or 3	+ 1,2	+ 3,9	- 2,3	+ 28
200	.092	2	- 1,9	- 3,8	+ 3,3	- 22
120	.101	3 or 4	+ 2,0	0	+ 3,0	+ 44
210	.102	3 or 4	+ 1,0	- 1,4	- 3,0	- 37
002	.128	5	+ 4,0	+ 4,0	0	+ 64
220	.129	5 or 6	- 1,2	+ 3,8	+ 4,1	+ 67
130	.142	2	- 8,0	0	+ 6,2	+ 10
221	.143	1	- 5,2	0	+ 3,9	+ 5
112	.143	3 or 4	+ 0,7	0	- 5,6	- 46
310	.144	5	+ 0,9	0	+ 6,2	+ 61
031	.149	2 or 3	+ 1,6	0	+ 3,5	+ 38
022	.156	5	0	- 4,0	- 4,7	- 76
202	.157	nil	+ 12,0	- 3,8	- 4,7	- 12
311	.158	3	+ 0,6	- 3,5	- 1,5	- 41
122	.163	3 or 4	- 13,2	0	+ 3,0	- 42
212	.163	3 or 4	- 5,0	- 1,4	- 3,0	- 63
040	.180	4	- 16,4	+ 4,0	+ 0,2	- 40
222	.181	nil	- 3,6	+ 3,8	- 3,9	- 12
400	.183	3	+ 0,8	+ 3,0	+ 0,2	+ 30
140	.186	1	- 3,1	0	- 1,0	- 21
410	.188	1 or 2	- 11,9	+ 2,6	+ 1,0	- 20
132	.191	2	- 4,4	0	- 1,8	- 33
330	.192	1	+ 0,8	0	+ 1,0	+ 11
312	.193	nil	+ 8,1	0	- 1,8	+ 20
013	.197	3	- 2,7	0	- 2,6	- 32
411	.199	1 or 2	+ 1,1	0	+ 2,4	+ 22
331	.203	1	- 0,1	+ 3,5	- 1,0	+ 20
042	.221	2 or 3	- 1,3	+ 4,0	- 7,8	- 30
402	.223	6	- 7,2	+ 3,0	- 7,7	- 58
142	.225	nil	+ 2,2	0	- 1,0	+ 1
412	.227	nil	- 1,4	+ 2,6	+ 1,0	+ 22
150	.229	3	+ 2,6	0	+ 4,9	+ 44
332	.231	3 or 4	- 4,1	0	- 7,0	- 62
510	.233	4	+ 4,6	0	+ 4,9	+ 49
051	.234	nil	+ 0,6	0	+ 1,4	+ 12
033	.234	1 or 2	+ 1,6	0	+ 3,5	+ 29
303	.236	2	- 5,9	+ 2,0	- 3,5	- 28

Table III (Continued).

Indices	$\sin \theta$	Observed Intensity	Structure Factor			Approx. F -value
			Oxygen	Silicon	Aluminium	
313	.240	3	+ 0,6	- 3,5	- 1,5	- 34
544	.242	6	- 0,8	+ 2,6	+ 2,9	+ 36
501			- 5,5	- 3,1	- 1,4	- 51
004	.255	8	+ 20,0	+ 4,0	+ 8,0	+ 140
440	.257	6	- 0,5	+ 3,0	+ 7,5	+ 70
152	.263	2	+ 4,0	0	- 3,1	- 10
512	.266	1 or 2	- 5,3	0	- 3,1	- 35
413	.269	1	+ 1,4	0	+ 2,4	+ 18
060	.270	3	+ 6,5	- 4,0	+ 6,0	+ 31
333	.272	2	- 0,1	+ 3,4	- 1,0	+ 17
531	.273	1	- 4,9	- 2,6	+ 1,9	- 19
160	.274	3	- 3,6	0	- 2,6	- 25
600	.274	3	- 1,9	- 2,0	+ 6,0	+ 19
610	.278	2	0	- 3,4	+ 2,6	- 8
442	.287	3	+ 7,0	+ 3,0	- 0,5	+ 34
062	.298	3 or 4	- 1,5	- 4,0	- 2,0	- 40
513	.302	3	- 0,8	+ 2,6	+ 2,9	+ 32
162	.302	nil	+ 9,9	0	- 2,6	+ 8
602	.303	4	- 1,9	- 2,0	- 2,0	- 29
612	.306	nil	- 12,3	- 3,4	+ 2,6	- 33
044	.312	1	- 16,4	+ 4,0	+ 0,2	- 10
404	.314	1	+ 0,8	+ 3,0	+ 0,2	+ 22
170	.318	1 or 2	+ 8,5	0	+ 1,5	+ 27
550	.321	1	- 2,4	0	+ 3,5	+ 14
015	.322	1	- 2,7	0	- 2,6	- 19
710	.323	? trace	- 11,2	0	+ 1,5	- 14
172	.343	1 or 2	+ 4,5	0	- 6,5	- 25
712	.348	2 or 3	- 1,2	0	- 6,5	- 35
731	.353	1	- 0,1	+ 1,4	+ 0,4	+ 10
080	.360	6	+ 7,9	+ 4,0	+ 7,1	+ 70
444	.362	3	- 2,8	+ 3,0	+ 7,5	+ 48
180	.362	nil	+ 5,9	0	+ 2,0	+ 20
800	.366	3 or 4	- 5,8	+ 0,7	+ 7,1	+ 28
810	.369	trace	- 4,7	+ 3,9	- 2,1	+ 4
006	.383	1 or 2	+ 4,0	+ 4,0	0	+ 26

The values of $\sin \theta$ correspond to the wave length $\lambda = 0,710 \text{ \AA}$ (MoK_{α}).

The observed intensities are arranged on an arbitrary scale in which 8 or 7 is very strong, 6 or 5 strong, 4 or 3 medium, 2 or 1 weak.

on a reflection plane. These chains, which include one half of the aluminium atoms in the unit cell, are bound together by the remaining positive ions; each silicon atom is surrounded by a tetrahedral group of oxygen atoms, and each aluminium atom (which lies on a reflection plane) is inside a symmetrical group of five oxygen atoms, three being arranged around it equatorially and one at each pole.

In sillimanite there are continuous chains of octahedra, parallel to the *c*-axis, containing one half of the aluminium atoms in the unit cell and located in almost exactly the same positions as in andalusite; the difference between andalusite and sillimanite lies in the different arrangement of the remaining positive ions which link together the chains of octahedra. In sillimanite each silicon atom is surrounded by a tetrahedron of oxygen atoms, and each aluminium atom (which lies on a reflection plane) by an oxygen grouping which may be regarded as either a very distorted octahedron or a slightly opened tetrahedron. It is very probable that the latter view represents the true state of affairs so that one half of the aluminium atoms are surrounded by tetrahedra of oxygen atoms, but in the work on sillimanite it was difficult to determine the precise form of this oxygen group.

The special feature of the cyanite structure is the arrangement of the oxygen atoms in cubic close packing, but the continuous columns of octahedra, surrounding half the aluminium atoms in the cell and parallel to the *c*-axis, are still to be distinguished. Each silicon atom is surrounded by a tetrahedron of oxygen atoms, and each of the remaining aluminium atoms by an octahedron of oxygen atoms, and these positive ions bind together the whole structure which would appear to be based, in the first place, on the columns of octahedra which are present in all three modifications of Al_2SiO_5 .

The relations existing between the three members of this series may then be summarized as follows: — Half the aluminium atoms in each crystal are contained in octahedra of oxygen atoms which form continuous columns parallel to the (short) *c*-axis of the crystal, the silicon atoms in each crystal are at the centres of tetrahedral groups which do not hold any oxygen atoms in common, while the remaining aluminium atoms are surrounded by symmetrical groups containing six, five, and four oxygen atoms in cyanite, andalusite and sillimanite respectively. The arrangement of continuous chains of octahedra in sillimanite and andalusite brings out clearly the pseudotetragonal aspect of the structure; the same feature also probably accounts for the fact that sillimanite sometimes occurs "associated in parallel growths with andalusite" (Dana).

The discovery that an aluminium atom may be surrounded by six, five, or four oxygen atoms, is of great interest. On theoretical grounds it has been predicted¹⁾ that the aluminium atom may have a coordination number either six or four, but the discovery of a group containing five oxygen atoms is unexpected. Of course, it may be said that one of these five oxygen atoms does not really "belong" to the aluminium atom, but since the positive ion is nearly equidistant from all the five surrounding oxygen atoms, there does not seem to be any justification for adopting this attitude.

Pauling²⁾ has recently given a most interesting rule which determines the distribution of valencies in ionic compounds, and has applied the rule to a number of crystals for which structures have already been determined. In accordance with this rule, the sum of the valency bonds between surrounding positive ions and a given oxygen ion, is equal to 2; in cyanite (which is close-packed) the rule is obeyed exactly, and in andalusite and sillimanite it is approximately true for any given oxygen ion, and of course true on the average for all the oxygen ions in the structure.

Mineralogists have related the axial ratios of andalusite to those of topaz; thus for andalusite

$$a:b:c = 0,9864 : 1 : 0,7025, \text{ so that } \frac{1}{2}b:a:\frac{2}{3}c = 0,5070 : 1 : 0,4749$$

while for topaz the crystallographic ratios³⁾ are

$$a:b:c = 0,5285 : 1 : 0,4770$$

I am unable to suggest any reason for this numerical relationship, beyond the fact that the absolute length of the c -axis of topaz bears a simple relation to the length of the c -axis in andalusite. Thus $c = 8,38 \text{ \AA}$ for topaz⁴⁾ and $c = 5,56 \text{ \AA}$ for andalusite; the ratio $\frac{8,38}{5,56} = \frac{3}{2}$ very nearly.

This arises from the arrangement of the oxygen atoms, in both crystals, in layers parallel to (001) which are approximately $1,4 \text{ \AA}$ apart. The andalusite cell contains four such layers, the topaz cell six. The relationship which exists between the ratio $a:b$ for topaz, and $\frac{1}{2}b:a$ for andalusite, is not an exact one, and does not appear to have any special significance.

1) Cf. L. Pauling, (following reference) for a discussion of this question.

2) I am indebted to Mr. L. Pauling for allowing me to see a full account of this work before publication.

3) Cf. Dana Mineralogy, 490.

4) N. A. Alston and J. West, Z. Krist. **69**, 449, 1928.

Summary.

The structure of andalusite, Al_2SiO_5 , has been determined by means of data obtained from qualitative measurements of relative intensities of reflection of X-rays.

The atomic arrangement is based on the space group V_h^{12} , and possesses a number of interesting features which relate it to the other minerals having the same composition. These relations are discussed in detail.

I have to thank Prof. W. L. Bragg, F.R.S., for advice and assistance throughout the course of the work. Some of the measurements were made on water-worn crystals of andalusite from the gem-gravels of Brazil; for the use of these specimens I am indebted to L. J. Spencer, F.R.S.

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