Regarding the compatibility of this hydrogen bond with others, the 3·15 Å distance is in the range of hydrogen bonds involving nitrogen. Layers of glycine molecules (Albrecht & Corey, 1938) are hydrogen bonded across a distance of 3·0 Å. Robertson (1940) refers to the glycine case in a general discussion wherein he makes note of the longer hydrogen bond to be expected between nitrogen and oxygen, as compared with oxygen to oxygen, owing to the lesser electronegativity of nitrogen. A recent analysis of the crystal structure of *p*-nitroaniline (Abrahams & Robertson, 1948) includes a hydrogen bond of about 3·1 Å between nitrogens, linking an amino-nitrogen with a nitro-nitrogen atom.

Bond lengths and other spacings are given in Table 4 and Fig. 4.

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Structural Interpretation of the Diaspore–Corundum and Boehmite–γ-Al_2O_3 Transitions[*]

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Transitions from hydrated to anhydrous compounds are treated as transformations *in situ*, with special attention to effects of the limited opportunity for atomic rearrangement which accompanies such transformations. The diaspore–corundum group is characterized by oxygen atoms in hexagonal close-packing as distinct from the boehmite–γ-Al_2O_2 group which is based on oxygens in cubic close-packing. Detailed microscopic and X-ray data are cited to show that corundum preserves the structural orientation of the diaspore crystals from which it is produced by dehydration.

The new group of γ-Al_2O_2-type structures is discussed, and it is suggested that the supposition of 'order–disorder' phenomena in the γ-Al_2O_3 structure provides a reasonable explanation for the existence of the new forms.

Introduction

Aluminum oxide exists in two forms, γ-Al_2O_3 and corundum, whose properties contrast to a high degree. The same contrast is carried over to the two forms of the monohydrate of aluminum oxide, boehmite and diaspore, with boehmite resembling γ-Al_2O_3 and diaspore resembling corundum. Thermal dehydration of either of the trihydrates, gibbsite and bayerite, or of hydrous alumina gel yields only boehmite followed by γ-Al_2O_3, while diaspore dehydrates to corundum and is formed only under hydrothermal conditions. These facts led Haber and others to designate the group composed of gibbsite, bayerite, boehmite and γ-Al_2O_3 as the γ series and the group diaspore and corundum as the α series. In this paper it is shown that there are structural relationships between the compounds in each series which account for the similarities in their properties and the reluctance of members of one series to transform to the other. The structural basis is also employed to explain the recent finding of several additional forms of anhydrous aluminum oxide which are of great practical importance as activated aluminas.

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Dehydration *in situ*

When crystals are produced from the vapor phase, from the melt or from solution, their form is usually well developed and they often grow to large size if grown slowly. The important condition favoring good growth in these cases is the presence of a fluid phase containing a substantial concentration of the compound crystallizing. Crystal formation in the absence of such a fluid phase often leads to unusual effects because of the limited opportunity provided for atomic rearrangement. This is the case when new phases are formed by dehydration. The change from hydrated phase to dehydrated phase, with evolution of water, takes place *in situ*.

One of the most noticeable results of this behavior is the formation of the dehydrated phase as pseudomorphs after the hydrated phase, that is, the gross external form of the hydrated phase is often preserved in the dehydrated phase. However, the preservation of form and structure may go much deeper than external macroscopic appearance. Study of dehydration of boehmite to γ-Al_2O_3 and of diaspore to corundum shows that the basic pattern of the atomic arrangement in the crystal hydrates is almost undisturbed in changing to the anhydrous crystal.

Cubic and hexagonal packing in the aluminas

First, the published structures of the compounds involved must be reviewed. The structures of boehmite, diaspore, γ-Al_2O_3 and corundum have been directly determined and found to be completely analogous to the corresponding iron compounds, lepidocrocite, goethite, γ-Fe_2O_3, and hematite, respectively. For the present purpose, the structures are best considered as oxygen-ion networks with metal cations in the interstices, following the treatment of Wells (1945). Thus the corundum structure consists of oxygen ions in *hexagonal* close-packing with aluminum ions filling two-thirds of the octahedral interstices.

γ-Alumina has been shown (Brill, 1932; Barlett, 1932; Hägg & Soderhölm, 1935; Verwey, 1935*a*, 1935*b*) to have the spinel structure, but with vacant cation sites, the unit cell containing only $21\frac{1}{3}$ aluminum ions statistically distributed over the twenty-four cation sites. The important feature of the structure is that the oxygen ions are in *cubic* close-packing.

Boehmite and diaspore, each with the formula AlOOH, are both orthorhombic and in closely related space groups. Other properties differ markedly, however, because of fundamental differences in structure. The structures have been described by Ewing (1935), Reichertz & Yost (1946) and Hoppe (1940). The oxygen atoms in diaspore are nearly equivalent, each being joined to one other oxygen atom by way of a hydrogen atom. In boehmite, on the other hand, there are two distinct types of oxygen atoms, one which is joined to two others via hydrogen and is thus hydroxyl ions, and the other type which is not joined with hydrogen at all and so is clearly oxygen ions. But again the important difference lies in the nature of the packing of the oxygen atoms. In diaspore the oxygens are arranged in *hexagonal* close-packing. In boehmite the structure as a whole is not close-packed but consists of layers which do not fit with each other in position of closest packing because of directed hydroxyl bonds. Within the layers, however, the oxygens are in *cubic* close-packing. These relations may be perceived by study of the diagrams given by Ewing (1935) and reproduced by Wells (1945).

These observations provide a reasonable basis for the distinction between the α and γ series of compounds mentioned earlier. As shown above, the α series (diaspore and corundum) is based on oxygens in hexagonal close-packing while the γ series (boehmite and γ-Al_2O_3) is based on oxygens in cubic close-packing. The two series exist because the transition from hydrated to dehydrated phase occurs *in situ*, and under such conditions the fundamental architecture of a structure tends to be preserved. As will be seen later, the same principles also lead to a reasonable interpretation of the nature of the new series of anhydrous aluminas referred to above. But, before considering these, it will be instructive to consider first the diaspore–corundum transition because it is simpler, and the better crystal development has permitted more elaborate evidence to be obtained.

The diaspore–corundum transition

Deflandre (1932) first demonstrated that when a crystal of diaspore is heated so as to drive off all of its water, corundum is formed without destruction of the external form of the crystal, and the resulting corundum behaves as a single crystal whose axes are lined up with the old axes of diaspore, as determined by the rotating-crystal method of X-ray analysis. The correspondence of axes was as follows:

Diaspore
[100] = 4·40 Å [010] = 9·38 Å [001] = 2·83 Å
Dehydrated diaspore
[100] = 12·91 — [001] = 8·23
Corundum
3-fold axis = 12·97 2-fold axis = 4·75 $[11\bar{2}]$ = 8·20

On further study, Deflandre found that because of the polar character of the two-fold axis of corundum, the dehydrated crystal actually behaved as two crystals or two sets of crystallites with their two-fold axes parallel but in reverse orientation. At about the same time, Schwiersch (1933) showed optically that when corundum formed from diaspore *in situ*, its *c* axis had the same orientation as the former *a* axis of diaspore. Natural occurrences of corundum associated with diaspore with similar orientation have also been reported. The literature on dehydration of diaspore was reviewed by Fricke & Huttig (1937).

Some laboratory observations made by the author provide further confirmation of the orientation of corundum from diaspore. The experiments consisted of heating small diaspore samples for short periods at high temperature. A sample of natural diaspore from Chester, Mass., was used, and also samples of artificial diaspore prepared by the author hydrothermally (Ervin, 1949). Heating either artificial or natural diaspore for 1 sec. at 1400° C. or 5 sec. at 1200° C. resulted in partial conversion to corundum. Some grains were completely converted; others became a mosaic of interlocking grains of corundum and diaspore. Microscopically the converted areas showed up because of much lower birefringence and because of their mottled or ribbed appearance. The clearest demonstration of the conversion was the change of a grain or crystal from length slow to length fast owing to the change in orientation of axes. This was best shown by the artificial disapore which was predominantly in the form of laths elongated on the *c* axis. Since in diaspore $c=\alpha$, these crystals were all length fast. The corundum which formed from these laths was in tiny crystallites whose *c* axis corresponded with the former *a* axis of diaspore at right angles to the length of the laths. These crystallites took the form of a minute ribbing of the laths at right angles to the length. Since corundum is uniaxial negative, crystals elongated on the *c* axis were length fast so that the laths became length slow. Thus a partially converted grain under crossed nicols with its length parallel to the slow ray of a gypsum plate was a mosaic of blue and yellow, blue for the corundum areas and yellow for the diaspore areas.*

X-ray data on these samples supplied additional evidence for the correspondence of the axes of corundum with the axes of the diaspore from which it forms. For this purpose advantage was taken of the effect of preferred orientation of crystals in the X-ray specimen to produce intensification of certain reflections. To enhance this effect, relatively coarse powder was used, mounted on a glass slide, to obtain patterns with a Norelco spectrometer. For natural diaspore, with excellent cleavage parallel to (010), the (020), (040) and (060) lines were greatly intensified by comparison with intensities of these lines in a normal pattern free from orientation effects. The next step was to calcine samples of this same coarse diaspore to convert it to corundum. Then, without further crushing, the calcined diaspore was X-rayed as before so that the particles had the same preferred orientation; a complete corundum pattern was obtained, but a very abnormal pattern, in that one line was very strong and all the others very weak. The one strong line was the $(10\bar{1})$ reflection at 2·375 Å. This corresponds to the (040) reflection of diaspore at 2·355 Å which, as already noted, was greatly intensified in the diaspore pattern. [The (020) and (060) reflections disappear in corundum because of symmetry.] Thus the corundum showed a preferred-orientation effect imposed on it by the diaspore from which it formed *in situ*. Ordinary corundum crystals do not show such an effect because there is no cleavage on $(10\bar{1})$.

To present the structural basis for the orientation of corundum with respect to diaspore, it will be convenient to compare three types of unit cell: hexagonal close-packing of a single kind of atom such as oxygen, the disapore cell, and the hexagonal corundum cell (the true cell of corundum is a rhombohedron).

Deflandre showed that the unit cell for a structure composed of oxygen atoms in hexagonal close-packing would be $a=4{\cdot}40$ Å (twice the distance between close-packed layers), $b=4{\cdot}68$ Å (two octahedron face diagonals), and $c=2{\cdot}7$ Å (an octahedron edge), while the corresponding diaspore dimensions are $a=4{\cdot}40$ Å, $b=9{\cdot}38$ Å ($2\times4{\cdot}69$), and $c=2{\cdot}83$ Å. The difference in the *c* axis is due to distortion while the *b* axis is doubled because of the alignment of aluminum atoms in double strips perpendicular to this axis. The *a* axis of diaspore is therefore perpendicular to the close-packed layers; the *c* axis is in the plane of the layers parallel to the octahedron edges; while the *b* axis is in the same plane at right angles to the octahedron edges (and to the *c* axis).

The hexagonal cell of corundum has its *c* axis perpendicular to the close-packed layers and three *a* axes in the plane of the layers at 120° to each other and at right angles to the octahedron edges. Thus when diaspore converts to corundum *in situ*, the hexagonal close-packing of oxygens is retained, and the *a* axis of diaspore necessarily becomes the *c* axis of corundum because these axes are perpendicular to the close-packed layers. Likewise, the *b* axis of diaspore becomes the *a* axis of corundum because these are both at right angles to the octahedron edges. The *c* axis of diaspore becomes the $[010]_H$ or $[11\bar{2}]_R$ direction of corundum because these directions are parallel to the octahedron edges.

The lengths of the axes change in small integer ratios, modified by distortion effects, because of symmetry changes. The axial length of simple hexagonal close-packing and of diaspore at right angles to the layers is the thickness of two layers because the layers are stacked in only two different ways which alternate. The aluminum atoms in corundum are distributed in three different ways which, superimposed on the two different oxygen layers, makes a repeat distance of six layers, or three times the axial length of diaspore. Similar considerations will show that the corundum

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* According to Schwiersch (1933) the refractive index of diaspore crystals *decreased* rather sharply as conversion to corundum proceeded, in contradiction to the fact that the refractive indices of corundum are substantially higher than those of diaspore. The effect was confirmed in these experiments although it was evidently a false appearance, probably due to a film or coating such as water adsorbed in the micropores of the grains. The grains showed a cloudiness which increased with heat treatment. After 24 hr. at 1400° C. even the thinnest fragments were completely opaque.

a axis is half the diaspore *b* axis, while the corundum $(010)_H$ or $(11\bar{2})_R$ planes have three times the spacing of the (001) planes of diaspore.

Dehydration of diaspore requires removal of one-fourth of the oxygen atoms and all of the hydrogen atoms. On the basis of the optical and X-ray evidence the loss of water occurs without destruction of the original form and orientation of the diaspore lattice.

Order–disorder forms of γ-Al_2O_3

It will now be shown that the dehydration of boehmite to γ-Al_2O_3, although more complex, is analogous to the dehydration of diaspore to corundum, in that the change occurs *in situ*, and the architectural motif of the structure, cubic close-packed oxygen atoms, is preserved, just as in the diaspore–corundum case the motif of hexagonal close-packed oxygen atoms is maintained. There is no optical evidence of orientation effects in this case because boehmite crystals of even microscopic size have been unavailable* and because γ-Al_2O_3 is isotropic.

In the boehmite structure, half of the oxygen atoms are in the interior of the complex layers and half are on the surfaces, and it is only the latter which are associated with hydrogen. Since dehydration requires the loss of one-fourth of the oxygen atoms, it is to be expected that half of the surface oxygens would be lost and that those in the interior of the layers would be unaffected. After this loss the layers would come together to make a cubic close-packed oxygen network, but the aluminum atoms would then be in some arbitrary configuration and would have to diffuse through the oxygen framework to reach stable positions.

A substantial contribution to our knowledge of γ-Al_2O_3 structures has been made by investigators at the Aluminum Company Research Laboratories. Recent reports of their work (Frary, 1946; Stumpf, Russell, Newsome & Tucker, 1950) indicate that boehmite does not dehydrate simply to γ-Al_2O_3, but that a whole series of dehydrated phases are produced. The evidence for this was the X-ray patterns obtained on products formed in sequence by increasing heat treatment of various hydrated aluminas. Even though boehmite was always an intermediate stage in dehydration, the sequence of dehydrated (nearly anhydrous) forms varied, depending on the starting material (gibbsite, bayerite, or boehmite). The authors considered each of these X-ray patterns to represent a distinct modification of anhydrous alumina—six in addition to corundum. None of the structures of these six was worked out, but χ-alumina was indexed as simple cubic while η-alumina was indexed as cubic with a spinel lattice. The lack of definite transition temperatures and the dependency on the nature of the hydrate used as starting material was unexplained. A serious criticism of their work is the lack of evidence that their patterns correspond to single phases and not mixtures of two or more phases.

The patterns reported by Stumpf are shown in Table 1, omitting for brevity the relatively weak lines at low *d* values. Examination of these patterns shows that all are markedly similar, having one strong line (1·395–1·405 Å) in common, other lines being usually much weaker. It is natural to speculate that this line is due to some dominant structural feature which all these preparations possess. With oxygens in cubic close-packing, this line corresponds to the oxygen ion radius and is indexed as the (440) line for the spinel unit cell. Planes giving rise to this reflection have the unique property of passing through the centers of all the oxygen positions as well as the centers of all the possible cation positions, i.e. both octahedral and tetrahedral interstices. Thus in *any* structure consisting of anions in cubic close-packing this line will be strong; furthermore, its spacing and intensity will be unaffected by the cation arrangement as long as the cations are restricted to the octahedral and tetrahedral interstices. By inference, therefore, all of the preparations listed in Table 1 have oxygens in cubic close-packing and aluminum ions in the interstices of the network. They differ only in the arrangement of the aluminum ions in these interstices, which differences affect the weaker lines but not the one strong line which all display at 1·395–1·405 Å.

The above reasoning may be carried one step further to account for the line at 1·985–2·03 Å which is fairly strong in most of the patterns. It is the (400) line of the spinel pattern, and it may be shown that planes causing this reflection pass through all the anion positions and the octahedral cation positions but not the tetrahedral cation positions. Its intensity could be affected only by the relative distribution of cations between these two types of positions.

A reasonable picture to account for these data is that when boehmite loses water, the oxygen network forms readily but that the aluminum ions, which have to reach their stable positions by diffusion through the oxygen framework, achieve this end to varying degrees depending on the heat treatment. It would be expected that the initial or lowest-heat-treatment form would have a random distribution of aluminum ions in the octahedral and tetrahedral interstices or have some degree of order imposed on them by the structure of the hydrate which is its parent. Random distribution would result in a cubic cell of length about half that for the spinel structure. Such a structure was not found by Stumpf but has been reported (Verwey, 1935*a*) as a low-temperature oxidation product of aluminum metal. In Stumpf's work the low-temperature products of the hydrates were η-Al_2O_3,

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* Now that a method for synthesing large microscopic crystals under pressure has been demonstrated (Ervin, 1949) it would be possible to study the dehydration in somewhat more detail, although the isotropic character of γ-Al_2O_3 is still a limiting factor.

χ-Al_2O_3 or γ-Al_2O_3, all showing a low degree of order for the aluminum ions, i.e. the spinel structure alone or with one or two additional lines. The higher-temperature modifications all show more complex symmetry in addition to that of spinel, attributable to increasing order in the aluminum ion arrangement. Thus the low-temperature forms may be regarded as 'disordered' modifications of γ-Al_2O_3. The completely 'ordered' or most stable form is achieved only at the maximum heat treatment below that required to produce corundum. (For it must be realized that even the most stable γ-Al_2O_3 is unstable with respect to corundum and that at a high enough temperature or under steam pressure the cubic close-packed oxygen framework itself rearranges to the hexagonal close-packed framework of corundum.)

The above picture is consistent with the results of others such as Jellinek & Fankuchen (1945) who found changes in the γ-Al_2O_3 pattern with increasing heat treatment but did not consider that there was evidence for distinct phases.

In a paper which came to the author's attention subsequent to submitting this paper for publication, Tertian (1950) has published a brief report of what appears to be the first complete structure determination of a γ-Al_2O_3-type product. The determination was based on a Laue pattern obtained by the ingenious method of dehydrating a large single crystal of gibbsite, which resulted in a composite crystal consisting of crystallites of the dehydrated material retaining the orientation of the original gibbsite and thus giving the Laue pattern of a single crystal of γ-Al_2O_3. Tertian states that the structure of θ-Al_2O_3 (the best crystallized form of γ-Al_2O_3) has aluminum atoms in the same configuration as in corundum but inscribed in a face-centered cubic oxygen network (cubic close-packing) instead of the hexagonal oxygen network of corundum. Tertian's paper gives only the Laue photograph and the lattice constants, $a = 8{\cdot}40$, $c = 13{\cdot}65$ Å with eighteen Al_2O_3 molecules in the unit cell.

To compare Tertian's results with the patterns of Stumpf, the author has calculated d values from Tertian's lattice constants, and these are given in the second column of Table 1. [To make the best fit with the other patterns, the following types of absences

Table 1. *X-ray data for γ-aluminas*

Calculated from lattice constants of Tertian		Patterns reported by Stumpf *et al.* (1950)														
		θ-Alumina		δ-Alumina		γ-Alumina		κ-Alumina		η-Alumina			χ-Alumina			
hkl	*d.* (Å)	*I*, rel.	*d.* (Å)	*I*, rel.	*d.* (Å)	*I*, rel.	*d.* (Å)	*I*, rel.	*d.* (Å)	*I*, rel.	*hkl*	*d.* (Å)	*I*, rel.	*hkl*	*d.* (Å)	
—	—	—	—	?	5·76	—	—	*w*	6·2	—	—	—	—	—	—	
—	—	*w*	5·25	?	5·26	—	—	—	—	—	—	—	—	—	—	
—	—	—	—	*w*	5·05	—	—	—	—	—	—	—	—	—	—	
003	4·55	*m*	4·55	*w*	4·58	—	—	*vw*	4·52	*w*	111	4·6	*vw*	111	4·8	
110	4·20	—	—	*vw*	4·10	—	—	*vvw*	4·5	—	—	—	—	—	—	
200	3·64	*vw*	3·56	?	3·55	—	—	—	—	—	—	—	—	—	—	
113	3·09	—	—	?	3·05	—	—	*mw*	3·06	—	—	—	—	—	—	
203	2·84	*ms*	2·87	*mw*	2·89	—	—	*m*	2·81	*vvw*	220	2·8	—	—	—	
—	—	*ms*	2·74	*ms*	2·75	*vw*	2·75	*vw*	2·72	—	—	—	—	—	—	
—	—	*w*	2·58	*w*	2·60	—	—	*ms*	2·59	—	—	—	—	—	—	
—	—	*ms*	2·45	*m*	2·45	*m*	2·43	*w*	2·43	*m*	311	2·4	*mw*	311	2·4	
—	—	*m*	2·325	*mw*	2·30	*m*	2·295	*mw*	2·34	—	—	—	—	—	—	
006	2·27	*m*	2·26	—	—	—	—	*vvw*	2·28	*vw*	222	2·29	*vw*	222	2·29	
—	—	?	2·17	?	2·175	*vvw*	2·20	*vvw*	2·18	—	—	—	—	—	—	
220	2·10	*vvw*	2·13	—	—	?	2·09	*ms*	2·125	—	—	—	*w*	321	2·13	
—	—	—	—	—	—	—	—	*w*	2·07	—	—	—	—	—	—	
310	2·02	*ms*	2·03	*ms*	2·005	*s*	2·00	*mw*	2·00	*ms*	400	1·985	*vw*	400	2·00	
116	2·00	—	—	*w*	1·96	*m*	1·965	*vw*	1·96	—	—	—	—	—	—	
206	1·927	*mw*	1·92	*vw*	1·92	—	—	—	—	—	—	—	—	—	—	
223	1·905	—	—	?	1·86	—	—	*m*	1·88	—	—	—	—	—	—	
313	1·842	—	—	—	—	—	—	*w*	1·835	—	—	—	—	—	—	
400	1·818	*w*	1·81	*vw*	1·81	—	—	—	—	—	—	—	—	—	—	
—	—	*vvw*	1·745	—	—	—	—	*vw*	1·755	—	—	—	—	—	—	
403	1·689	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
—	—	*vw*	1·625	?	1·625	—	—	*m*	1·646	—	—	—	—	—	—	
226	1·543	*m*	1·55	*mw*	1·55	*vw*	1·55	*vvw*	1·55	—	—	—	—	—	—	
009	1·515	—	—	*w*	1·515	—	—	—	—	*vvw*	333	1·53	*vvw*	333	1·54	
316	1·508	*mw*	1·495	*vw*	1·498	—	—	*w*	1·495	—	—	—	—	—	—	
—	—	*mw*	1·461	*w*	1·46	—	—	*w*	1·46	—	—	—	—	—	—	
119	1·424	*vvw*	1·435	—	—	—	—	*ms*	1·440	—	—	—	—	—	—	
406	1·420	*m*	1·41	*m*	1·41	—	—	—	—	—	—	—	—	—	—	
330	1·400	*s*	1·395	*s*	1·40	*s*	1·403	*s*	1·396	*s*	440	1·405	*ms*	440	1·40	
209	1·399	—	—	—	—	—	—	—	—	—	—	—	—	—	—	

Code:
s—strong
ms—medium strong
m—medium
mw—medium weak
w—weak
vw—very weak
vvw—very, very weak

due to symmetry were assumed: (1) *hkl* odd, (2) *h*00 with *h* odd, and (3) *hkl* with *l* not divisible by 3. The last indicates a *c* axis one-third the length of Tertian's or that all such reflections are very weak.] Agreement with Stumpf's θ-Al_2O_3 (and with some of the other forms) is fairly good except for a group of strong lines between 2·26 and 2·87 Å. All of these lines appear in the δ, γ and κ forms as well as the θ form. The indication is that Stumpf's θ-Al_2O_3 is either a mixture of Tertian's θ-Al_2O_3 and another phase, or that it is a different phase with the same basic network but more complex symmetry.

Tertian's results are good confirmatory evidence for the ideas expressed in the preceding paragraphs. His hexagonal cell is based on a cubic close-packed oxygen network of the same dimensions as Stumpf's cubic cell but with the *c* axis of the hexagonal cell (perpendicular to the close-packed oxygen planes) inclined to the axes of the cubic cell. The cell constants therefore have the following simple geometrical relationship:

$$c_H=\sqrt{3}\,a_C \quad \text{and} \quad a_H=\frac{3}{2\sqrt{2}}a_C.$$

Furthermore, the *d* values for the hexagonal cell correspond to certain lines of the cubic cell, 111_C to 003_H and 440_C to 330_H, but with additional lines because of the more complex symmetry. Thus Tertian's results make it clear that the more complex higher-temperature forms have the same oxygen network as the low-temperature forms but with a higher degree of order in the aluminum atom arrangement.

There is a straightforward analogy between γ-Al_2O_3 structures and the order-disorder structures in metallic alloys. In certain quenched alloys the distribution of two different kinds of metal atoms over the available lattice positions is completely random. This is the 'disordered' structure. When the alloy is annealed, atoms of different kinds migrate to definite positions to form a 'superlattice' or 'ordered' structure with more complex symmetry. In γ-Al_2O_3, aluminum ions and vacant spaces are the two different kinds of units whose distribution over the available cation sites is random or 'disordered' for low-temperature dehydration (corresponding to quenched alloys) and 'ordered' for higher temperature dehydration (corresponding to annealed alloys). The occurrence of a multiplicity of forms of γ-Al_2O_3, instead of just two, must be attributed to the existence of intermediate stages between the completely random cation distribution and the completely ordered distribution. A detailed study, and possibly a complete structure analysis of the various γ-Al_2O_3 preparations is needed before it can be decided if each is a distinct structure or if the transition from disorder to order is continuous.

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