

volve the use of any organic solutions containing perchloric acid. Any remote danger of violent reaction resulting from the use of such solutions is eliminated.

Gooch filtering crucibles with asbestos mats can be used wherever platinum-sponge filtering crucibles are mentioned in this paper.

Summary

1. The correct drying temperature of the insoluble alkali perchlorates has been found to be 350°.
2. The occlusion of perchloric acid by these salts has been studied.
3. Previous procedures for the perchloric acid separation of the alkali metals by extraction are shown to be faulty and an improved method is described.

URBANA, ILLINOIS

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THE CRYSTAL STRUCTURES OF HEMATITE AND CORUNDUM

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Introduction

Hematite, Fe_2O_3 , and corundum, Al_2O_3 , form crystals which have been assigned,¹ on the basis of observed face development, to the holohedral class of the rhombohedral system, with the rhombohedral angle α equal to 85° 42' and 85° 42 $\frac{2}{3}$ ', respectively. Spectrometric measurements have been made² of the reflection of X-rays from three faces of ruby, Al_2O_3 , and two of hematite. Utilizing the hypothesis that in ruby each aluminum atom is equidistant from six oxygen atoms, and each oxygen atom equidistant from four aluminum atoms, a possible structure has been devised³ which is not incompatible with these spectrometric observations. This structure has been used in a theoretical consideration of the influence of atomic arrangement on birefringence,⁴ and in the explanation of the observed variation with temperature of the intensity of reflection of X-rays from faces of crystals of ruby and sapphire.⁵ An exact knowledge of the arrangement of the constituent atoms in ruby would make the arguments of these papers much more convincing.

Powder photographic data from aluminum and ferric oxides prepared

¹ Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1908, Vol. 1, p. 105.

² W. H. and W. L. Bragg, "X-Rays and Crystal Structure," G. Bell and Sons, London, 1915, p. 171.

³ W. H. and W. L. Bragg, "X-Rays and Crystal Structure," 4th edition, G. Bell and Sons, London, 1924, p. 183.

⁴ W. L. Bragg, *Proc. Roy. Soc.*, **106**, 346 (1924).

⁵ I. Backhurst, *ibid.*, **102**, 340 (1922).

under different conditions have been published;⁶ but no attempt has been made to deduce their structures from them. The dimensions of units of structure of aluminum, ferric, and chromic oxides which are said to agree with unpublished powder photographic data have been reported.⁷

We have, therefore, made a thorough X-ray study of crystals of hematite and of corundum, utilizing the results of the theory of space groups to interpret the data obtained from Laue and spectral photographs and considering all possible structures. Well-formed natural crystals of hematite, transparent faintly blue crystals of Ceylon corundum,⁸ and sections cleaved from massive corundum were used. The X-ray data were obtained by the usual photographic methods described by Wyckoff.⁹ The investigation was aided financially by a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

The Structure of Hematite

Photographic Data.—The data obtained from spectral and Laue photographs are presented in the usual way in Tables I and II, respectively.

The Unit of Structure.—A spectral photograph of the K-radiation of molybdenum reflected from the face (100)' of hematite (planes denoted by primes refer to the axes used by Groth) gave, as shown in Table I, the value $3.682 \pm 0.010 \text{ \AA.}$ for d/n . If n is one, this corresponds to a unit of structure with $a = 3.70 \text{ \AA.}$, and $\alpha = 85^\circ 42'$. With one Fe_2O_3 in this unit, the density calculated from the X-ray data is 5.25, in good agreement with the observed values,¹ which range from 5.15 to 5.30.

TABLE I
SPECTRAL PHOTOGRAPHIC DATA FROM (110) OF HEMATITE

Line ^a	Order	Angle of reflection	$\frac{d_{110}}{n}$	Intensity of reflection ^b
β	n	$4^\circ 54'$	3.693 \AA.	w
α	n	$5 31$	3.700	m
γ	$2n$	$9 41$	3.683	vw
β	$2n$	$9 52$	3.678	m
α_1	$2n$	$11 5$	3.686	s
α_2	$2n$	$11 9$	3.681	ms

^a In Tables I and III, γ indicates $\text{MoK}\gamma$, $\lambda = 0.6197 \text{ \AA.}$; β , $\text{MoK}\beta$, $\lambda = 0.6311$; α_1 , $\text{MoK}\alpha_1$, $\lambda = 0.7078$; α_2 , $\text{MoK}\alpha_2$, $\lambda = 0.7121$; α , mean of α_1 and α_2 , $\lambda = 0.710$.

^b The abbreviations signify: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak.

⁶ Hedvall, *Z. anorg. Chem.*, **120**, 327 (1922).

⁷ Davey and Hoffman, *Phys. Rev.*, **15**, 333 (1920). Davey, *ibid.*, **21**, 716 (1923).

⁸ We wish to thank Professor Charles Palache of Harvard University for the Ceylon corundum.

⁹ Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, 1924, pp. 109-116 and 161-164.

TABLE II
LAUE PHOTOGRAPHIC DATA FROM HEMATITE

Incident beam normal to (110). Structure factors calculated for $u = 0.292$,
 $w = 0.1050$.

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	S_1	S_2	S_3
032	1.415	0.34	1	1.16	1.16	1.16
$\bar{1}31$	1.215	.32	2	1.88	1.88	1.88
$\bar{3}\bar{1}\bar{5}$	0.971	.44	2.5	1.88	1.88	1.88
$\bar{3}2\bar{2}$.932	.28	0.4	1.59	1.59	1.59
053	.927	.32	1.3	1.36	1.98	2.60
154	.909	.30	6	5.33	6.42	7.51
$\bar{3}2\bar{6}$.870	.38	0.03	0.61	0.61	0.61
456	.862	.42	.06	2.44	2.44	2.44
405	.808	.30	.2	1.84	1.84	1.84
567	.732	.43	2.5	2.17	3.06	3.95
275	.717	.43	8	5.63	6.76	7.89
174	.678	.41	0.05	1.16	1.09	1.02
578	.636	.30	.6	3.32	4.25	5.18
678	.623	.40	.1	2.44	2.44	2.44
$\bar{1}72$.586	.33	.2	1.73	2.35	2.97
497	.567	.42	.6	2.61	3.54	4.47
$\bar{4}3\bar{5}$.560	.40	1.3	2.94	3.73	4.52
789	.559	.39	1.6	5.94	7.08	8.22
$\bar{4}1\bar{7}$.552	.43	1.5	3.64	4.73	5.82
$\bar{1}81$.534	.42	0.3	1.87	2.49	3.11
194	.527	.39	1.5	5.26	6.39	7.52
3.10.7	.504	.34	0.4	5.89	6.82	7.75
$\bar{5}2\bar{7}$.497	.35	.3	3.78	4.87	5.96
$\bar{5}3\bar{6}$.495	.32	.05	1.02	1.64	2.26
$\bar{3}6\bar{2}$.493	.35	.04	2.54	2.54	2.54
9.9.10	.489	.42	.4	4.76	5.83	6.90
$\bar{5}0\bar{9}$.488	.35	.6	5.70	6.83	7.96
$\bar{5}.\bar{1}.\bar{1}0$.469	.33	.04	3.14	3.63	4.12
$\bar{4}.\bar{3}.\bar{1}\bar{1}$.461	.33	.1	3.76	4.65	5.54
$\bar{6}1\bar{9}$.439	.28	.04	1.96	3.09	4.22

Upon assigning indices to the spots on a Laue photograph and calculating values of $n\lambda$ on the basis of this unit, a number of forms, including $\{5\bar{3}\bar{1}\}'$, $\{\bar{7}3\bar{1}\}'$ and $\{9\bar{1}\bar{1}\}'$, were found to have $n\lambda$ less than 0.24 Å., the lower wave-length limit of X-rays present in the incident radiation. This unit is accordingly eliminated.

The corresponding hexagonal unit, as well as any hexagonal unit with the same value of $d_{00.1}$, is also eliminated by these data. However, the hexagonal unit with twice this value for $d_{00.1}$ does account for the Laue data. Similarly the rhombohedral unit containing two Fe_2O_3 obtained by taking new axes along the diagonals of the faces (100)', (010)' and (001)', accounts for all the Laue data, and is the smallest rhombohedral unit that does this. The hexagonal unit is improbable, for all planes of the large

class for which $2H + I + L$, $-H + I + L$, and $-H - 2I + L$ are not all divisible by three are found to give only third-order reflections, and it is difficult to explain the absence of first- and second-order reflections. Accordingly, the rhombohedral unit with $\alpha = 55^\circ 17'$ and $a = 5.42 \pm 0.01$ Å., containing two Fe_2O_3 , is taken to be correct. Indices (hkl) used in this paper refer to the axes of this unit.

The Space Group.—Laue photographs show the symmetry of point group D_{3d} ; the structure is, accordingly, isomorphous with one of the point groups C_{3v} , D_3 and D_{3d} . The only space groups fulfilling this requirement and based on a rhombohedral lattice are C_{3v}^6 , C_{3v}^5 , D_3^7 , D_{3d}^6 and D_{3d}^5 . Each of these space groups provides one or more arrangements of two Fe_2O_3 in the unit of structure.¹⁰ Those afforded by C_{3v}^6 , D_3^7 and D_{3d}^5 are improbable because they do not account for the observed absence of all planes of the type (hhl) with l odd, many of which were in positions favorable to reflection. Of the two remaining space groups C_{3v}^5 and D_{3d}^6 the latter is taken as correct, for the crystallographic data strongly indicate the structure to be isomorphous with point group D_{3d} .

The Atomic Arrangement.—The possible arrangements allowed by D_{3d}^6 are

Fe at (a) $000, \frac{1}{2}\frac{1}{2}\frac{1}{2}$ and (b) $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{3}{4}$,
 or at (c) $www, \bar{w}\bar{w}\bar{w}, \frac{1}{2}-w \frac{1}{2}-w \frac{1}{2}-w, w+\frac{1}{2} w+\frac{1}{2} w+\frac{1}{2}$,
 with O at (d) $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{3}{4}\frac{1}{4}$,
 or at (e) $u\bar{u}0, \bar{u}0u, 0u\bar{u}, \frac{1}{2}-u u+\frac{1}{2} \frac{1}{2}, u+\frac{1}{2} \frac{1}{2} \frac{1}{2}-u, \frac{1}{2} \frac{1}{2} -u u+\frac{1}{2}$.

Any arrangement with oxygen atoms at (d) requires that there be no first-order reflections from planes with $h + k + l$ odd. The presence of such reflection on Laue photographs eliminates such arrangements.

For oxygen atoms at (e) and iron atoms at (a) and (b), first-order reflections from planes with $h + k + l$ odd are due entirely to oxygen atoms, and the range of possible values of the oxygen parameter u can be limited by a consideration of their intensities. This consideration does not involve any assumption regarding the relative reflecting powers of different atoms. The structure factor S for these planes is given by the equation $S = 2\bar{O}[\sin 2\pi(h-k)u + \sin 2\pi(k-l)u + \sin 2\pi(l-h)u]$. The value of S for a plane reflecting in the first order more strongly than another plane with the same or larger interplanar distance must be greater than that for the second plane. Reference to Fig. 1 shows that the intensity relations $(\bar{1}31) > (032)$ and $(456) > (\bar{3}2\bar{6})$ observed on Laue photographs (Table II) are effective in limiting u to the region between 0.286 and 0.40.

Within this region the comparison $(\bar{3}6\bar{2}) > (\bar{3}2\bar{6})$ is also effective, requiring that u be less than 0.360. For this range of values of u , from 0.286 to 0.364, S for (154) is less than S for (053) if iron atoms are at

¹⁰ Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Pub.*, No. 318, pp. 153-157 (1922).

(a) and (b); the observation that (154) reflects much more strongly than (053) accordingly eliminates this arrangement.

For planes with $h + k + l$ even,

$$S = 4\sqrt{F}e \cos 2\pi(h + k + l)w + 2\sqrt{O} [\cos 2\pi(h - k)u + \cos 2\pi(k - l)u + \cos 2\pi(l - h)u]$$

In calculating values of S we have taken the relative reflecting powers of iron and oxygen atoms approximately proportional to 23 and 10, the

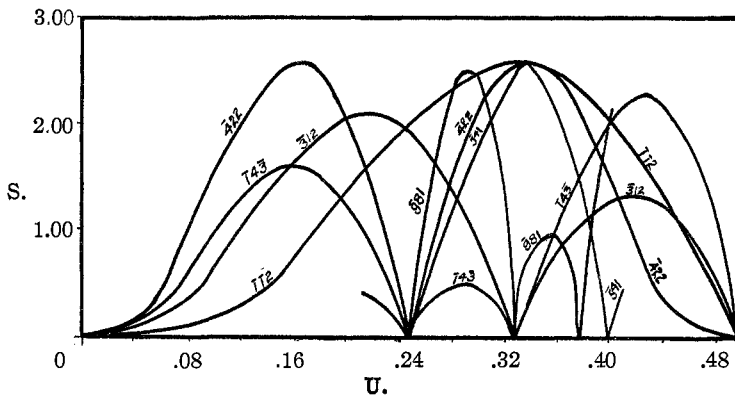


Fig. 1.—Curves showing values of the structure factor S for planes with $h + k + l$ odd; the numbers on each curve signify values of $h - k$, $k - l$ and $l - h$; for example, $\bar{4}22$ gives values of S for all planes with $h + k + l$ odd and with $h - k = -4$, $k - l = 2$, and $l - h = 2$.

electron-numbers of the ionized atoms. The second-order reflection from (110) (Table I) is stronger than the first-order reflection; w is

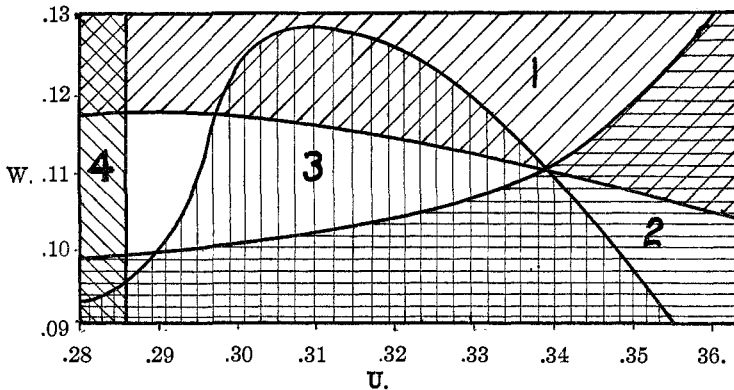


Fig. 2.—The shaded areas represent values of the parameters u and w for hematite excluded by the following comparisons: 1, (154) > (053); 2, (194) > ($\bar{4}3\bar{5}$); 3, ($\bar{4}1\bar{7}$) > ($\bar{4}3\bar{5}$); 4, comparisons from planes with $h + k + l$ odd.

accordingly restricted to the range between 0.07 and 0.17. With the range of values of u previously obtained, the following intensity

inequalities observed on Laue photographs restrict w to the region between 0.095 and 0.120: $(275) > (567)$; $(154) > (053)$; $(789) > (\bar{4}3\bar{5})$; $(\bar{4}3\bar{5}) > (174)$; $(\bar{5}0\bar{9}) > (\bar{5}2\bar{7})$; $(\bar{4}1\bar{7}) > (\bar{4}3\bar{5})$; $(9.9.10) > (\bar{1}81)$; and $(194) > (\bar{4}3\bar{5})$. Moreover, as shown in Fig. 2, these data further limit u to the region between 0.287 and 0.297, and w to between 0.098 and 0.115. By means of the intensity relations $(4.3.11) > (5.1.10)$, $(578) > (\bar{4}05)$, $(\bar{4}3\bar{5}) > (497)$, and $(497) > (678)$, w is still further restricted to between 0.1040 and 0.107.

It is probable that the reflecting power of an atom compared with that of another atom with a smaller electron number is somewhat greater than the value calculated assuming proportionality with the first power of the electron number. We have considered the effect on the calculated values of S of increasing the relative reflecting power of iron, and have found that the assumption that an iron atom reflects as much as 50% more strongly than indicated by its electron number does not invalidate the above limitation of the parameters u and w . For Table II the structure factor S_1 is calculated on the assumption of direct proportionality between reflecting power and electron number, S_2 involves an increase of 25% in the reflecting power of iron, and S_3 an increase of 50%. The observed data are not well explained on the assumption of direct proportionality, and the consequent increase in the reflecting power of iron, in conjunction with the comparisons used above, requires a decrease of the upper limit of w to about 0.106.

TABLE III
SPECTRAL PHOTOGRAPHIC DATA FOR CORUNDUM

Line	Order of reflection	Angle of reflection	$\frac{d_{hkl}}{n}$	Estimated intensity
DATA FROM (111), CEYLON CORUNDUM				
Å.				
γ	n	8° 13'	2.170	vwv
β	n	8 22	2.170	w
α_1	n	9 22.7	2.172	m
α_2	n	9 25.7	2.175	mw
γ	$2n$	16 38	2.165	vw
β	$2n$	16 56	2.168	m
DATA FROM (110), MASSIVE CORUNDUM				
$\frac{d_{hkl}}{n}$				
γ	n	5° 8.6'	3.454	vw
β	n	5 13.3	3.468	mw
α_1	n	5 51	3.480	ms
α_2	n	5 53	3.475	m
γ	$2n$	10 17.3	3.473	w
β	$2n$	10 28.3	3.474	m
α_1	$2n$	11 45.2	3.479	s
α_2	$2n$	11 49.7	3.478	ms

We accordingly adopt for the oxygen parameter u the value 0.292 \pm 0.007, and for the iron parameter w the value 0.1050 \pm 0.0010.

The Structure of Corundum

Photographic Data.—The observations obtained by the spectrographic and the Laue methods are presented in Tables III and IV, respectively.

TABLE IV

LAUE PHOTOGRAPHIC DATA FROM CEYLON CORUNDUM

Incident beam at small angles with the normal to (111). Structure factors calculated for $u = 0.303$, $w = 0.1050$.

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	S_1	S_2	S_3
02 $\bar{1}$ ^a	1.582	0.39	0.4	0.87	0.87	0.87
$\bar{1}$ 31 ^a	1.173	.35	.6	2.21	2.21	2.21
...
$\bar{1}$ 34	0.848	.38	1.0	2.46	2.80	3.14
$\bar{1}$ 54	.687	.37	0.1	0.16	0.43	0.70
16 $\bar{1}$.642	.38	1.0	2.43	2.77	3.11
34 $\bar{3}$.631	.36	0.5	0.94	1.38	1.82
037	.614	.37	1.6	3.70	4.18	4.66
071	.599	.36	0.4	1.88	2.15	2.42
524	.599	.42	.05	0.65	0.65	0.65
6 $\bar{1}$ $\bar{1}$.591	.37	.04	.70	0.26	0.18
6 $\bar{2}$ 1	.586	.38	.05	1.10	1.10	1.10
53 $\bar{3}$.572	.40	.1	1.99	1.99	1.99
3 $\bar{1}$ 7	.562	.35	.1	1.48	1.48	1.48
45 $\bar{3}$.541	.35	.4	1.85	2.19	2.53
239	.532	.45	.2	1.15	1.64	2.13
$\bar{1}$ 47	.532	.28	.04	0.87	1.35	1.83
6 $\bar{2}$ 5	.523	.39	.04	1.17	1.17	1.17
722	.518	.38	.08	1.86	1.86	1.86
3 $\bar{1}$ 8	.499	.30	.06	1.00	1.48	1.96
169	.486	.42	.3	1.88	2.09	2.30
518	.479	.37	.08	0.98	0.95	0.92
7 $\bar{3}$ 2	.475	.29	.06	2.38	2.72	3.06
1.3.10	.452	.30	.07	2.16	2.65	3.14
1.5.10	.450	.35	.06	1.75	1.96	2.17

^a These two planes are from Photograph No. 1; the remainder from No. 2.

The Atomic Arrangement.—The same transformation of axes as for hematite is found necessary in order to account for the Laue data for corundum; from the spectral data the smallest rhombohedral unit is found to have $a = 5.12 \pm 0.01$ Å., and $\alpha = 55^\circ 17'$, and to contain two Al_2O_3 . The density from these data is 3.96; the directly determined value is 3.99.

The Laue data for corundum (Table IV) are similar to those for hematite. By the arguments previously given the correct space group is seen to be D_{3d}^6 , and the possible arrangements are accordingly those listed

above. First-order reflections were observed from planes with $h + k + l$ odd, eliminating any arrangement with oxygen atoms at (d). The observation that $(\bar{1}31)$ reflected more strongly than $(02\bar{1})$ limits the oxygen parameter u in (e) to the region 0 to 0.20, or that of 0.28 to 0.40. We have found that the Laue data in Table IV eliminate the 0 to 0.20 region. The following comparisons from planes with $h + k + l$ odd, due to oxygen atoms alone, definitely limit u to between 0.296 and 0.310: $(53\bar{3}) > (5\bar{2}4)$, $\therefore 0.28 < u < 0.33$; $(7\bar{2}2) > (6\bar{2}5)$, $\therefore 0.28 < u < 0.310$; and $(3\bar{1}7) > (6\bar{2}1)$, $\therefore 0.296 < u$.

For this range of values of u the structure factor for $(\bar{1}54)$ is much greater than that for (037) , if aluminum atoms are at (a) and (b); the observation that the latter plane reflects much more strongly than the former despite its smaller interplanar distance accordingly eliminates this arrangement.

As shown in Table III, the second-order reflection from (110) is much stronger than the first-order reflection; this requires that the value of the aluminum parameter in (c) lie between about 0.075 and 0.20. The following comparisons restrict w to between 0.095 and 0.108: $(45\bar{3}) > (6\bar{1}1)$, $(34\bar{3}) > (\bar{1}54)$, and $(169) > (239)$. Moreover, a further limitation of the range of possible values of u and w can be made; the intensity relations $(3\bar{1}8) > (\bar{1}47)$, $(1.3.10) > (7\bar{3}2)$, and $(169) > (7\bar{2}2)$ require that u lie between 0.300 and 0.306, and that w lie between 0.1040 and 0.1060.

In calculating the values of S_1 given in Table IV, the relative reflecting powers of aluminum and oxygen atoms have been taken as proportional to the electron numbers of the ions, namely, 10 and 10; S_2 and S_3 have been calculated on the basis of an increase of 25% and 50%, respectively, in the reflecting power of aluminum. The comparisons used above in limiting u to 0.303 ± 0.003 and w to 0.1050 ± 0.0010 are not invalidated by assuming that the reflecting power of aluminum is as much as 50% greater than that of oxygen.

Discussion of the Structures

The arrangement of atoms in the units of structure of hematite and corundum is shown in Fig. 3. The values derived for the oxygen parameter u give for the smallest oxygen-oxygen distance the values 2.545 ± 0.060 Å. and 2.495 ± 0.025 Å., respectively. These relatively large distances show the effect of the mutual repulsion of similarly charged ions. It is noteworthy that these distances are larger than the oxygen-oxygen distances in calcite¹¹ (2.16 Å.) and in sodium nitrate¹² (2.19 Å.), in which the three oxygen atoms are grouped about an atom of carbon or nitrogen (at O).

¹¹ Wyckoff, *Am. J. Sci.*, **50**, 317 (1920).

¹² Wyckoff, *Phys. Rev.*, **16**, 149 (1920).

The distance between the oxygen atom A and the point O is 1.470 ± 0.035 Å. for hematite, and 1.385 ± 0.020 Å. for corundum. From these the oxygen-iron distances are found to be 2.060 ± 0.035 Å. (A to B or C) and 1.985 ± 0.025 Å. (A to D or E); and the oxygen-aluminum distances to be 1.990 ± 0.020 Å. and 1.845 ± 0.015 Å.

Each metal atom is surrounded by six oxygen atoms, which are not at the corners of a regular octahedron. Three of these oxygen atoms are a few per cent. nearer the metal atom than the other three, indicating that the location of the electrons in the outer shells of an ion causes it to have different effective radii in different directions. The difference between the two oxygen-metal distances is 0.075 ± 0.060 Å. for hematite, and 0.145 ± 0.035 Å. for corundum; this is in agreement with the conception that an iron ion, with 23 electrons within a volume only slightly greater than that of an aluminum ion with 10 electrons, would approximate a sphere much more closely than the aluminum ion.

Each oxygen atom is surrounded by four metal atoms, two of which are nearer than the other two. These atoms are not at the corners of a regular tetrahedron; the angle between the line connecting atoms B and C and that connecting D and E is about 60° , instead of 90° as in a regular tetrahedron.

The structures determined for hematite and corundum show that these crystals consist of a compact arrangement of approximately, but not exactly, spherical ions of oxygen and of iron or aluminum, held together by inter-ionic forces which are probably electrostatic in nature. No evidence of molecular grouping is observed.

The value 2.73 Å. for the distance between aluminum atoms B and C in ruby deduced³ with the aid of empirical quantitative laws from the spectrometrically measured relative intensities of different orders of reflection from (111) is in agreement with the value 2.74 ± 0.03 Å. determined by us. However, we have found that the hypothesis of a constant aluminum-oxygen distance is incorrect, and the value 1.33 Å. for the A to O distance

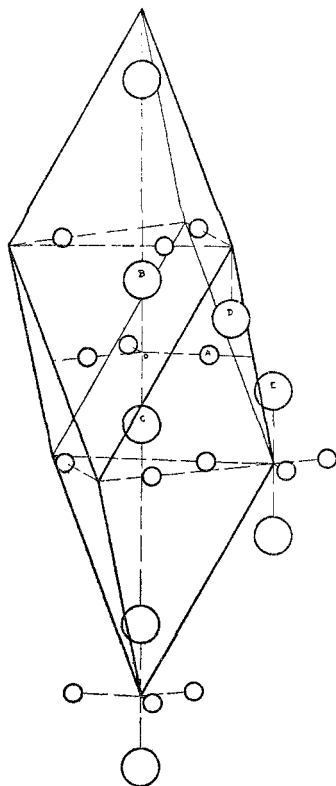


Fig. 3.—The arrangement of atoms in the units of structure of hematite and corundum; small circles represent atoms of oxygen, large circles atoms of iron or aluminum.

(Fig. 3) obtained³ through the use of this hypothesis is also wrong. The distance $1.440 \pm 0.015 \text{ \AA}$. determined by us is not completely outside of the range 1.45 to 1.58 \AA . for A to O, which has been calculated to be necessary in order to account for the observed birefringence of ruby.⁴

Summary

The crystal structures of hematite and corundum have been determined through the use of Laue and spectral photographs, interpreted with the aid of the theory of space groups. The unit of structure is a rhombohedron with $\alpha = 55^\circ 17'$ and $a = 5.420 \pm 0.010 \text{ \AA}$. for hematite, and with $\alpha = 55^\circ 17'$ and $a = 5.120 \pm 0.010 \text{ \AA}$. for corundum. The space group underlying the atomic arrangement is D_{3d}^6 .

The data require that atoms of iron or aluminum be located at www , $\bar{w}\bar{w}\bar{w}$, $\frac{1}{2}-w \frac{1}{2}-w \frac{1}{2}-w$, $w + \frac{1}{2}w + \frac{1}{2}w + \frac{1}{2}$, and atoms of oxygen at $u\bar{u}0$, $\bar{u}0u$, $0u\bar{u}$, $\frac{1}{2}-u \ u + \frac{1}{2} \ \frac{1}{2}$, $u + \frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}-u$, $\frac{1}{2} \ \frac{1}{2}-u \ u + \frac{1}{2}$, with $u = 0.292 \pm 0.007$ and $w = 0.1050 \pm 0.0010$ for hematite and $u = 0.303 \pm 0.003$ and $w = 0.1050 \pm 0.0010$ for corundum. These structures show that crystals of hematite and corundum consist of a compact arrangement of approximately but not exactly spherical ions, as shown in Fig. 3. The derived inter-atomic distances in Ångström units are as follows.

	Hematite	Corundum
Smallest oxygen-oxygen distance.....	2.545 ± 0.060	2.495 ± 0.025
Metal-oxygen distance (B or C to A).....	$2.060 \pm .035$	$1.990 \pm .020$
Metal-oxygen distance (D or E to A).....	$1.985 \pm .025$	$1.845 \pm .015$

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GERMANIUM. X. THE DETERMINATION OF GERMANIUM

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Since the time of its discovery by Winkler, germanium has been determined by precipitating it as the disulfide, oxidizing the disulfide to the dioxide by means of nitric acid and weighing the dioxide.

Winkler¹ used this method, but he published no experimental results from which its accuracy might be judged. Indeed, he employed the method only once in the direct determination of germanium in argyrodite,² and he says that the result was obtained "unter Anwendung einer allerdings noch mangelhaften Methode."

Dennis and Papish, who give³ the latest details for its application, also state that no great accuracy is claimed for the method.

It is evident that if the procedure is to give accurate results, the precipitation of the germanium as sulfide must be quantitative, and the oxidation of the sulfide to the dioxide must be complete and must be conducted in such manner as will avoid loss.

¹ Winkler, *J. prakt. Chem.*, **142**, 228 (1886).

² *Ibid.*, **142**, 188 (1886).

³ Dennis and Papish, *THIS JOURNAL*, **43**, 2131 (1921).