CRYSTAL STRUCTURE DETERMINATIONS

Thesis

by

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I N D E X

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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 made[2] 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 devised[3] 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 The dimensions of units of structure of aluminum, ferric, and chromic oxides which are said to agree with unpublished powder photographic data have been reported.[7]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 ± 0.010 Å. for d/n. If n is one, this corresponds to a unit of structure with $a = 3.70$ Å., and $\alpha = 85° 42'$. 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° 54′	3.693 Å.	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 MoKγ, $\lambda = 0.6197$ Å.; β, MoKβ, $\lambda = 0.6311$; α_1, MoKα_1, $\lambda = 0.7078$; α_2, MoKα_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
$\bar{3}1\bar{5}$	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
$\bar{5}.\bar{1}.\bar{10}$	.469	.33	.04	3.14	3.63	4.12
$\bar{4}.\bar{3}.\bar{11}$	.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 $\{5\bar{3}1\}'$, $\{\bar{7}31\}'$ and $\{91\bar{1}\}'$, 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 $d_{00\cdot1}$, is also eliminated by these data. However, the hexagonal unit with twice this value for $d_{00\cdot1}$ 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 $\alpha = 55° 17'$ 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, $\overline{\text{www}}$, $\frac{1}{2}-\text{w}\ \frac{1}{2}-\text{w}\ \frac{1}{2}-\text{w}$, $\text{w}+\frac{1}{2}\ \text{w}+\frac{1}{2}\ \text{w}+\frac{1}{2}$,
with O at (d) $\frac{1}{4}\frac{2}{4}\frac{3}{4}$, $\frac{3}{4}\frac{3}{4}\frac{1}{4}$, $\frac{3}{4}\frac{1}{4}\frac{2}{4}$, $\frac{1}{4}\frac{3}{4}\frac{1}{4}$, $\frac{2}{4}\frac{1}{4}\frac{1}{4}$, $\frac{1}{4}\frac{1}{4}\frac{2}{4}$,
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 $S = 2\overline{O}[\sin 2\pi(h-k)u + \sin 2\pi(k-l)u + \sin 2\pi(l-h)u]$. 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 (0.53) 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,

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

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

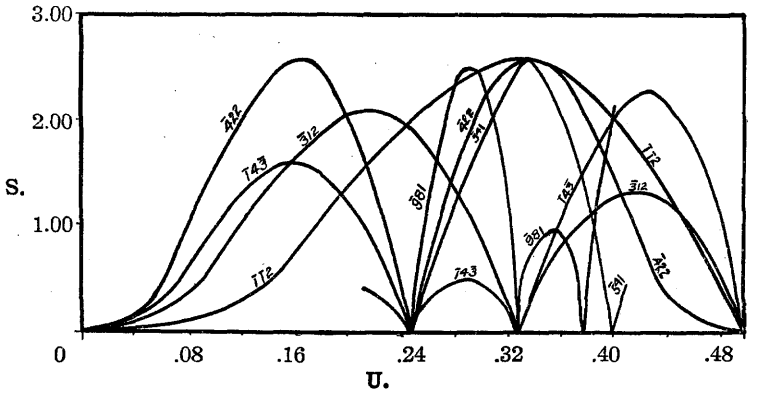

Fig. 1.—Curves showing values of the structure factor S for planes with $h + k + l$ odd; the numbers on each curve signify values of $h-k$, $k-l$ and $l - h$; for example, $\bar{4}22$ gives values of S for all planes with $h + k + l$ odd and with $h - k = -4$, $k - l = 2$, and $l - h = 2$.

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

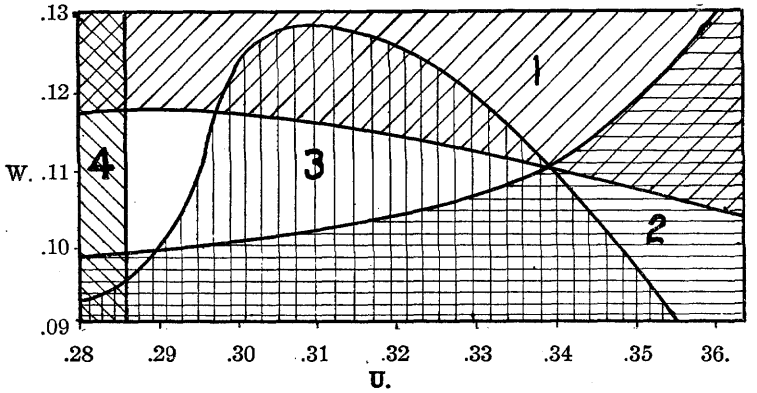

Fig. 2.—The shaded areas represent values of the parameters u and w for hematite excluded by the following comparisons: 1, (154) > (053); 2, (194) > ($\bar{4}3\bar{5}$); 3, ($\bar{4}1\bar{7}$) > ($\bar{4}3\bar{5}$); 4, comparisons from planes with $h+k+l$ odd.

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	$\frac{d_{111}}{n}$	Estimated intensity
		DATA FROM (111), CEYLON CORUNDUM		
			Å.	
γ	n	8° 13′	2.170	vvw
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		
			$\frac{d_{110}}{n}$	
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 ± 0.007, and for the iron parameter w the value 0.1050 ± 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
$52\bar{4}$	.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
$7\bar{2}2$	.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
$5\bar{1}8$	.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 $\alpha = 55° 17'$, 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^6_{3d}, 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: $(45\bar{3}) > (6\bar{1}\bar{1})$, $(34\bar{3}) > (\bar{1}54)$, 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 calcite[11] (2.16 Å.) and in sodium nitrate[12] (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.

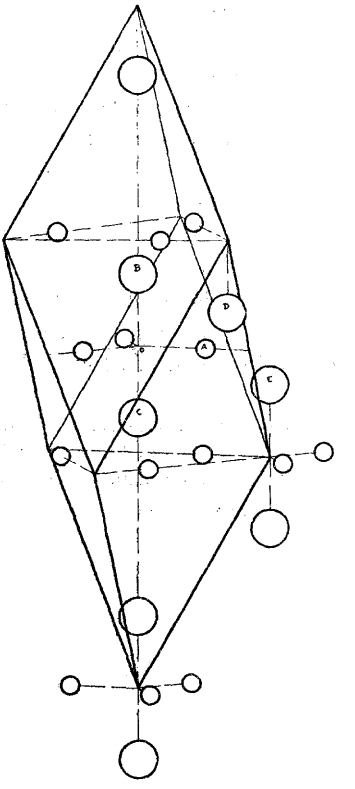

Fig. 3.—The arrangement of atoms in the units of structure of hematite and corundum; small circles represent atoms of oxygen, large circles atoms of iron or aluminum.

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 deduced[3] 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) obtained[3] through the use of this hypothesis is also wrong. The distance 1.440 ± 0.015 Å. determined by us is not completely outside of the range 1.45 to 1.58 Å. 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 $\alpha = 55° 17'$ and $a = 5.420 \pm 0.010$ Å. for hematite, and with $\alpha = 55° 17'$ and $a = 5.120 \pm 0.010$ Å. 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± .035	1.990± .020
Metal-oxygen distance (D or E to A).....	1.985± .025	1.845± .015

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 82]

CONFIRMATION OF THE PRESENCE OF A NON-TETRAHEDRAL CARBON ATOM IN CRYSTALS OF PENTA-ERYTHRITOL

BY MAURICE L. HUGGINS[1] AND STERLING B. HENDRICKS

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The crystal structure of penta-erythritol, $C(CH_2OH)_4$, has recently been investigated by Mark and Weissenberg,[2] using the rotating crystal method. Their conclusions may be summarized as follows. The structure possesses ditetragonal pyramidal symmetry, the space group being C_{4v}^9. The lattice is body centered. The unit cell, containing two molecules, has the dimensions $a_0 = 6.16$ Å. and $c_0 = 8.76$ Å. The symmetry of the position occupied by the central carbon atom of each molecule is that of the point group C_{4v}; the four surrounding carbon atoms must therefore be structurally equivalent and all in the same plane, at the corners of a square, although not necessarily in the same plane as the central atom. Similarly, all four oxygen atoms of each molecule are equivalent and coplanar.

It seemed to us that these results, indicating that the carbon atom in aliphatic organic compounds is not always tetrahedral in shape, are of such importance as to deserve verification, especially in view of the fact that similar methods had yielded[3] a structure of tin tetra-iodide which have been shown by Laue photographic data obtained in this Laboratory[4] to be incorrect. We have therefore investigated the structure of penta-

[1] National Research Fellow in Chemistry.

[2] Mark and Weissenberg, *Z. Physik*, **17**, 301 (1923).

[3] Mark and Weissenberg, *ibid.*, **16**, 1 (1923).

[4] Dickinson, THIS JOURNAL, **45**, 958 (1923).

erythritol, using not only spectral data obtained in a manner similar to those of Mark and Weissenberg, but also Laue photographic data. Our results completely verify the conclusions reached by these investigators.

The spectral data obtained by us give the same values of d/n for (001) and (100) as obtained by Mark and Weissenberg. The Laue data, summarized in Table I, further show that a unit with $a_0 = 6.16$ Å. and $c_0 = 8.76$ Å. satisfactorily accounts for the observed reflections, since the values of $n\lambda$'s calculated on the basis of this unit show the absence of wave lengths shorter than 0.24 Å., the minimum value present in the incident radiation. A Coolidge tube with a tungsten anticathode, operated at a peak voltage of 52 kv., was used throughout this investigation.

TABLE I

LAUE PHOTOGRAPHIC DATA FROM PENTA-ERYTHRITOL

Incident beam of X-rays about 3° from normal to (001)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity[a]	*hkl*	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity[a]
$1\bar{4}1$	1.48	0.46	0.6	532	1.03	0.47	1.5
411	1.48	.46	1.6	$\bar{5}11$	1.02	.39	*a*
331	1.43	.48	*a*	$\bar{7}12$	0.854	.29	0.1
421	1.36	.42	*a*	$\bar{1}72$	.854	.39	.5
$\bar{4}31$	1.22	.42	0.6	563	.825	.45	.45
$\bar{4}\bar{3}1$	1.22	.33	.8	$6\bar{5}3$	.825	.34	.05
$\bar{5}01$	1.22	.38	.3	$7\bar{2}3$	.813	.39	.08
061	1.20	.31	*a*	743	.740	.37	.10
$\bar{5}\bar{2}1$	1.12	.37	.4	$8\bar{3}5$	.710	.46	1.0
521	1.12	.31	.5	1257	.443	.33	v. f.
161	1.04	.30	.25				

[a] *a* signifies absent.

The absence of reflection in the first order from planes with two odd and one even indices, and with one odd and two even indices [such as (331), (421), (061) and ($\bar{5}$11)], although they were in a position to reflect the incident beam of X-rays, requires the underlying lattice to be the body-centered tetragonal one. The only space groups based on this lattice and possessing the observed crystal symmetry are C^9_{4v}, C^{10}_{4v}, C^{11}_{4v}, and C^{12}_{4v}.[5] The space groups C^{10}_{4v}, C^{11}_{4v} and C^{12}_{4v} do not admit of an arrangement of 10 carbon atoms in the unit.

In an arrangement arising from C^9_{4v} two carbon atoms must be equivalent and possess the symmetry of the point group C_{4v}, thus necessitating the presence of a four-fold axis about these atoms, and consequently a non-tetrahedral arrangement. If the logical assumption is made that the two $C(CH_2OH)_4$ in the unit act as structural entities, that is, as molecules, the analysis given below leads to a possible atomic arrangement.

If we place the origin (000) of our system of coördinates at the center

[5] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Inst. Pub.*, No. **318**, 1922, p. 85.

of one of the two central carbon atoms in a unit, the other must be[5] at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The eight equivalent carbon atoms within the unit may be in either of the positions designated (*c*) and (*d*) by Wyckoff:

(*c*) uuv; $u\bar{u}v$; u+½, ½−u, v+½; u+½, u+½, v+½;
$\bar{u}\bar{u}v$; $\bar{u}uv$; ½−u, u+½, v+½; ½−u, ½−u, v+½;
(*d*) uOv; Ouv; ½, u+½, v+½; u+½, ½, v+½;
$\bar{u}$Ov; O$\bar{u}$v; ½, ½−u, v+½; ½−u, ½, v+½.

Similarly, the eight equivalent oxygen atoms may be either in (*c*) or in (*d*). The position of the 24 hydrogen atoms need not necessarily conform to the space-group criteria,[6] but presumably eight atoms are in positions (*c*) or (*d*), and 16 in the general positions

(*e*) xyz; $\bar{y}$xz; $\bar{x}\bar{y}$z; y$\bar{x}$z;
yxz; x$\bar{y}$z; $\bar{y}$$\bar{x}$z; $\bar{x}$yz;
x+½, y+½, z+½; ½−y, x+½, z+½; ½−x, ½−y, z+½; y+½, ½−x, z+½;
y+½, x+½, z+½; x+½, ½−y, z+½; ½−y, ½−x, z+½; ½−x, y+½, z+½.

In order to maintain CH_2OH groups it is necessary that the eight equivalent carbon atoms, the eight equivalent oxygen atoms and the eight

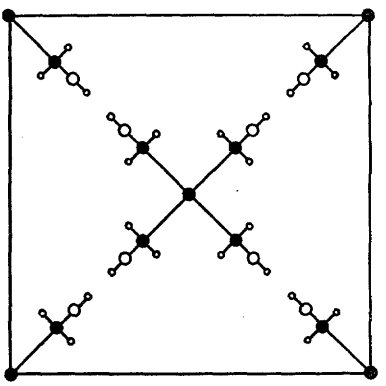

Fig. 1.—Illustrating, in plan, the type of arrangement of atomic centers within the unit of $C(CH_2OH)_4$, if the 8 equivalent atoms of C, of O and of H are all in positions (*c*) of C_{4v}^9. Large dots represent C, large circles O, and small circles H atoms.

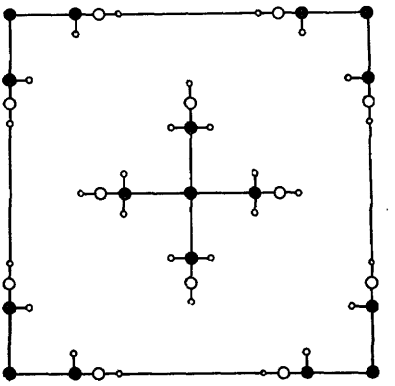

Fig. 2.—The same as in Fig. 1, assuming the 8 equivalent atoms of C, of O and of H to be all in positions (*d*) of C_{4v}^9.

equivalent hydrogen atoms all occupy positions (*c*) (with different values of the parameters) or positions (*d*). The data obtained were not sufficient to decide between these two molecular orientations (shown in Figs. 1 and 2), nor to determine any of the parameter values.

It should be noted that it is only the central atom of each molecule which cannot be tetrahedral. However, the tetrahedral arrangement may

[6] Wyckoff, *Z. Kryst.*, **57**, 595 (1923). Also, *Am. J. Sci.*, **5**, 209 (1923).

perhaps be the stable one in solution or in the liquid state; for the intermolecular forces operating during the process of crystallization may be sufficient to turn all the CH_2OH groups in the same direction and so transform the tetrahedral arrangement into the one actually found. It is of interest, however, that recent investigations[7] on thin films of the tetrapalmitate of penta-erythritol also indicate a square arrangement rather than a tetrahedral one of the CH_2OR groups around the central carbon atom of each molecule.

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Summary

Additional data confirming the crystal structure of penta-erythritol, $C(CH_2OH)_4$, as previously reported by Mark and Weissenberg, have been obtained. These data verify the non-tetrahedral arrangement of atoms about the central carbon atom of the molecule.

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[7] Adams and Dyer, *Proc. Roy. Soc.* (*London*), **106A**, 706 (1924).

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THE PREDICTION OF THE RELATIVE STABILITIES OF ISOSTERIC ISOMERIC IONS AND MOLECULES

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When in the future we acquire a complete knowledge of atomic and molecular structure we shall be able to predict the stability of any suggested ionic or molecular configuration, provided that insuperable mathematical difficulties do not present themselves. In this paper it will be shown that in certain simple cases it is already possible, using the present conceptions regarding atomic structure and chemical combination and making plausible assumptions, to calculate qualitatively the relative stabilities of similar atomic aggregations.

Many cases are known of molecules or ions that contain the same numbers of atomic nuclei and the same numbers of electrons, but differ in the positive charges on the nuclei. Very often such compounds have pronouncedly similar physical properties. In the development of the modern theories of molecular structure these atomic groups have been supposed to have the same nuclear and electronic arrangement; for example, Lewis[2] assigns to the nitrogen molecule, the carbon monoxide molecule, the cyanide ion, and the acetylide ion the following structures, in which the letters signify the kernels of the various atoms, that is, the nuclei and accompanying K-electrons:

:N:::N: :C:::O: (:C:::N:)$^-$ (:C:::C:)$^-$

Such molecules and ions are called *isosteric*.[3]

In some cases isosteric molecules or ions are also isomeric (composed of the same atoms), and differ only in the kernel arrangement; examples are the cyanate ion, $(NCO)^-$, and the fulminate ion, $(CNO)^-$. The relative stabilities of such isosteric isomers depend on their free energies, which like their energy contents are functions of their intramolecular energies. Since the two compounds contain the same atoms, their energy contents and free energies can be referred to the same reference substances. The identity in mass and similarity in physical properties of isosteric isomers would cause them to have the same or only very slightly different kinetic energies and entropies under the same conditions; hence, the free energy differences for these compounds would be nearly the same as the energy differences of their molecules.

[1] National Research Fellow in Chemistry.

[2] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, 1923, p. 127.

[3] Langmuir, THIS JOURNAL, 41, 1543 (1919). Our attention has been called to the fact that our principle may be considered as a definite statement of a special case included in Postulate 3 given by Langmuir, *Science*, 54- 59 (1921).

In order to determine qualitatively the relative stabilities of such atomic groups we shall use the following principle. The difference in the energies and free energies of isosteric isomeric molecules or ions has the same sign as the difference in the sums of the potential energies of their atom kernels with respect to one another, as calculated by Coulomb's law from the charges of the kernels and the distances between them. That is, the potential energy U of each molecule consisting of kernels with charges z_1e, z_2e, z_3e, ... at distances r_{21}, r_{31}, r_{32} ... from one another is given by the expression

$$U = e^2\left(\frac{z_2z_1}{r_{21}} + \frac{z_3z_1}{r_{31}} + \frac{z_3z_2}{r_{32}} + \ldots\right) + \text{electron energies} \qquad (1)$$

and the assumption is made that the energy terms due to the outer electrons (with respect to each other and to the nuclei) are, in considering the differences involved in isosteric isomeric molecules, not sufficiently large to cancel the effect due to the kernels. Furthermore, it is assumed that for the purpose of this calculation the interkernel distances can be taken as unchanged by a rearrangement of the kernels.

These assumptions seem to us to be not unreasonable. The fact that it is possible to interchange two atomic kernels without changing the arrangement of the external electrons indicates that the electronic arrangement about one of the two kernels is not greatly different from that about the other. For instance, it is possible that the cyanate ion has the structure $\cdot\ddot{\mathrm{N}}:\mathrm{C}:\ddot{\mathrm{O}}\cdot$; and in this case interchanging the nitrogen and carbon atoms would involve removal of a kernel with a charge of five units from two unshared and one shared electron pair and its addition to two unshared and two shared electron pairs, and the reverse operation on a kernel with a charge of four units. The accompanying energy effect due to the electrons would accordingly be small.

On the other hand, it is not true that the interkernel distances would remain constant when the kernel arrangement is changed. Upon interchanging the nitrogen and carbon kernels in the cyanate ion, $(NCO)^-$, to form a fulminate ion, $(CNO)^-$, the end kernels will be more strongly repelled by the central kernel than they previously were. As a result of this greater repulsion the interkernel distances will be somewhat increased, and the difference in kernel potential energies of the two structures will be somewhat reduced; but inasmuch as the increase in interkernel distance is the result of the greater kernel potential energy of the fulminate ion, it is evident that this increase, while sufficient to decrease the kernel energy to some extent, will not bring it to a value smaller than that of the cyanate ion. Hence, the sign of the energy difference of the two isosteric isomeric compounds can be found by the use of Equation 1; but the absolute value of this difference will be considerably smaller than that given by this equation.

We propose, for the sake of simplicity, to limit ourselves mainly to a

discussion of groups of atoms with small kernels, containing no electrons other than K-electrons. In calculating the kernel potential energy for a given configuration we have assumed that the K-electrons are sufficiently close to the nucleus so that the inverse square law can be used, with the effective kernel charge equal to the nuclear charge minus the charge of the K-electrons. We have taken the charge of the electron as unity, and used the Ångström as the unit of length. One energy unit in the table is then equal to 330,100 cal. per mole. It will be shown that the calculated differences in kernel potential energy for alternative configurations are of the order of one unit; it is evident that even though the effect of the electrons and of variations in the interkernel distance does neutralize the larger part of the calculated kernel effect, that remaining is still enough to account for great differences in stability. For example, it will be seen from the table that the calculated kernel energy difference of the fulminate ion and the cyanate ion has the extremely large value, 858,000 cal. per mole; without doubt the actual energy difference of the two ions is very much less than this, but still with the same sign.

The neglect of the effects due to external electrons allows us to apply the suggested principle without giving consideration to the actual distribution of these electrons, indeed, without even deciding whether to treat them as stationary, and distributed in pairs about the kernels, or as in motion in orbits about one or two nuclei. We shall, however, find it convenient to be more specific in discussing the chemical reactions considered; hence, we shall in these discussions assume definite electronic structures for the various compounds, and shall represent these structures by using double dots for electron pairs, as is done by Lewis. It is to be understood that we do not mean to imply that we consider the electrons to be stationary, for the symbol might be used to denote two electrons in orbits including either one or two nuclei; and it is to be strongly emphasized that the energy calculations and stability considerations made in this paper are independent of the assumption of any particular electronic configurations.

The Structure of Carbon Dioxide and its Isosteres.—There are a number of ions and molecules known containing three small kernels and sixteen external or valence electrons; namely, carbon dioxide, nitrous oxide, the trinitride ion, the acid fluoride ion, the cyanate ion, the fulminate ion, the metaborate ion and the beryllate ion. Of these the first five have been studied with X-rays, and in each case shown to have a structure in which the three atoms are collinear.[4] This result is verified by the infra-red oscillation-rotation absorption spectra of carbon dioxide.[5] It accordingly seems probable that all of these compounds are

[4] For references and further discussion see Hendricks and Pauling, THIS JOURNAL, 47, 2904 (1925).

[5] Barker, *Astrophys. J.*, 55, 391 (1922).

isosteres, and possess the same stable arrangement of their external electrons; the acid fluoride ion may, because of the small charge on the proton as compared with the other kernels, possess a unique electronic arrangement.

It is generally believed that in the acid fluoride ion the proton is sharing only two electron pairs with other nuclei. The structure of this ion may then be represented thus: $:\ddot{F}:H:\ddot{F}:$. Possibly the same electronic arrangement is to be assigned to the other similar groups; however, it seems improbable that in a group such as the trinitride ion, NNN^-, the central kernel, with a charge of five units, should be surrounded by only four shared electrons. Of the alternative structures $:\dot{N}::N::\dot{N}:$ and $:\dot{N}:\ddot{N}:\dot{N}:$ we shall use the latter, having in mind the evidence recently adduced by Lewis[6] concerning the instability of the double bond, and the tendency of small kernels in some cases to surround themselves by six instead of eight electrons.[7] In this structure the four electron pairs are not arranged tetrahedrally about the central kernel, but are co-planar.

In every case the distance between adjacent atoms for these compounds as found by X-ray methods is 1.15 Å., within the rather wide limits of experimental error. In giving calculations in illustration of our arguments we shall adopt this distance throughout; similar results would be obtained with any other distance.

Carbon Dioxide and Nitrous Oxide.—Two atomic arrangements are possible for carbon dioxide, one in which the central atom is the carbon atom, with a kernel charge of four, and one in which it is the oxygen atom, with a kernel charge of six. It is evident that the potential energy of the first configuration is the smaller; numerical results are given in Table I. This structure, which is of course the actual one, would then be predicted on the basis of our principle.

The predicted stable structure for nitrous oxide is NNO, with the oxygen atom at one end. This structure, rather than NON, was advanced by Langmuir,[8] who has given arguments in its favor. The formation of sodium trinitride from sodium amide and nitrous oxide, according to the reaction $NaNH_2 + ONN \longrightarrow NaNNN + H_2O$, further indicates that NNO is the true structure. Indeed, the pronounced oxygen-like chemical character of the gas strongly suggests that the oxygen atom is not in the inaccessible position between two nitrogen atoms.

The molecules of nitrous oxide would then be expected to have a permanent electric moment. The available data on the dielectric constant of the substance are, however, not accurate enough to permit verification of this prediction.

[6] Lewis, THIS JOURNAL, **46**, 1027 (1924).

[7] As in the nitrate ion, for example.

[8] Langmuir, THIS JOURNAL, **41**, 1543 (1919).

TABLE I

THE MUTUAL POTENTIAL ENERGY OF ATOMIC KERNELS FOR CERTAIN CONFIGURATIONS

Substance	Configuration	Kernel potential energy[a]	Substance	Configuration	Kernel potential energy[a]
Carbon dioxide	OCO	57.40	Cyanic acid	HCNO	61.30
	COO	62.61		HONC	62.47
Nitrous oxide	NON	63.05	Nitriles	RCN	40.00
	NNO	60.88	Isocyanides	RNC	41.74
Cyanate ion	NCO^-	51.32	Hydrocyanic acid	HCN	23.05
Fulminate ion	CNO^-	53.92		HNC	23.48
.....	CON^-	55.67	Cyanogen	NCCN	73.36
Isocyanates	RNCO	82.61		NCNC	75.80
Cyanates	ROCN	84.96		CNNC	78.59
Fulminates (nitrile oxides)	RCNO	83.48	Cyanogen fluoride	NCF	56.97
.....	RONC	88.12		CNF	60.00
.....	RCON	85.81			
.....	RNOC	88.12			

[a] It is to be borne in mind that only the relative, and not the absolute, values of the kernel potential energy are of significance.

The Cyanate and Fulminate Ions.—Three isosteric univalent negative ions of carbon, nitrogen and oxygen are possible, NCO^-, CNO^- and CON^-. Evidently the ion with the smallest charge on the central kernel will have the least potential energy and, hence, free energy, and that with the largest charge the greatest. The three ions are accordingly here arranged in the order of predicted greatest stability.

This prediction is in complete harmony with the available data. The structure NCO^- has been assigned by chemical reasoning to the stable cyanate ion, and the structure CNO^- to the fulminate ion, the compounds of which are explosive. Compounds containing the third ion CON^- have not yet been prepared, due no doubt to their great instability.

It is, moreover, possible to predict roughly the energy differences to be expected. From thermochemical experiments the following equations may be written.

$$CO\ (g) + \tfrac{1}{2}O_2\ (g) = CO_2\ (g) + 67{,}500\ \text{cal.} \qquad (2)$$

$$N_2\ (g) + \tfrac{1}{2}O_2\ (g) = N_2O\ (g) - 17{,}740\ \text{cal.} \qquad (3)$$

Subtracting (3) from (2) we obtain

$$CO - N_2 = CO_2 - N_2O + 85{,}240\ \text{cal.} \qquad (4)$$

Since carbon monoxide and nitrogen are isosteres, we may calculate their kernel potential energies in the usual way, obtaining the values 20.86 and 21.73 energy units, respectively. Using these and the values for carbon dioxide and nitrous oxide given in the table we may write

$$CO - N_2 = CO_2 - N_2O + 862{,}000\ \text{cal.} \qquad (5)$$

It is evident that the kernel energy calculation leads to a result approximately ten times too large. If we accept this factor of ten as applicable in other cases, then the energy and free-energy differences of the cyanate and fulminate ions should be about 86,000 cal. per mole.

Cyanates, Isocyanates, Fulminates, and Nitrile Oxides.—There are six possible isosteric compounds of an organic radical and a carbon-nitrogen-oxygen group, namely, RNCO, ROCN, RCNO, RONC, RCON and RNOC. The more stable compound of each pair differing only in the end attached to the radical, such as RNCO and ROCN, is, of course, the one in which the radical is near the kernel with the smaller charge. The relative stabilities of the six arrangements are roughly indicated by the calculations in the table; in these calculations the radical R is given the kernel charge of a carbon atom, and arbitrarily placed 1.15 Å. from the adjacent kernel.

Chemical data indicate that the isocyanates have the structure RNCO, and the normal cyanates ROCN; the relative stabilities are then the predicted ones, for the isocyanates are stable, while normal esters of cyanic acid have never been isolated, apparently because of the ease with which they condense to cyanurates.[9] It is worthy of mention that both the closely similar normal thiocyanates, RSCN, and isothiocyanates, RNCS, are known, and that the normal thiocyanates are the less stable, and are converted into the isothiocyanates on being heated.

Fulminic acid, through the work of Nef,[10] has been assigned the formula HONC, and its salts MONC, and these formulas have usually been accepted, although it is recognized that the evidence in their favor is not conclusive.[11] Our calculations show that compounds with these structures would have greater free energy than those with the structures HCNO and MCNO. Accordingly, we believe that the latter structures are the correct ones.

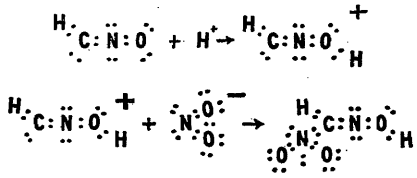
A consideration of the reactions on which the previous decision as to the structures of fulminates was based shows that they can be satisfactorily explained with the structures suggested by our potential calculations. One such reaction is the formation by fulminic acid of addition compounds with other acids; for example, with nitrous acid it forms methylnitrolic acid, the reaction being usually written $HO.N{=}C + HNO_2 \longrightarrow HO.N{=}C\begin{matrix}H\\NO_2\end{matrix}$. We should, however, write this as a reaction first with the hydrogen ion, and then with the nitrite ion, eliminating the necessity of attaching the two ions to the same atom.[11a]

[9] Sidgwick, "Organic Chemistry of Nitrogen," Oxford, 1910, p. 217.

[10] Nef, *Ann.*, 280, 303 (1894).

[11] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Veit, Leipzig, 1913, vol. 1, p. 1303.

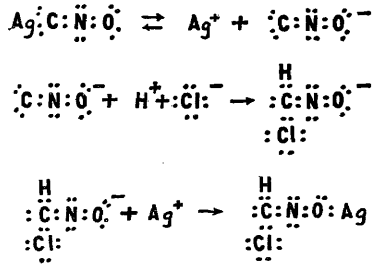
[11a] The argument does not depend on any particular choice of electronic structure for the nitrite ion. In the equations we have represented a structure which may not be the correct one.



Other arguments are based on the assumption that rearrangements through ionization and recombination cannot occur with salts of fulminic acid. But such rearrangements might occur; for the salts of fulminic acid are ionized to a certain extent, the conductivity of an aqueous solution even of mercuric fulminate being slightly greater than that of water. In the formation of this salt from sodium nitromethane and mercuric chloride it has been assumed that mercury isonitromethane is first produced, which then by intramolecular oxidation forms the fulminate, according to the reaction

$$CH_2{=}N\begin{matrix}O\\ \diagup\\ \diagdown\\ Ohg\end{matrix} \longrightarrow hgONC + H_2O \quad (hg = \tfrac{1}{2}Hg)$$

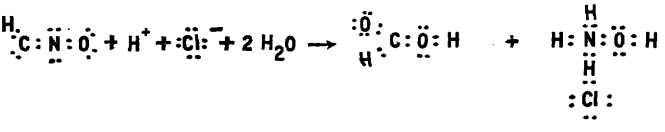
Even if we accept this as the course of the reaction up to this point, it is still possible that the structure hgONC is not that of mercuric fulminate; for we believe that if the compound hgONC, which would be more highly ionized than the stable form, were produced, it would by ionization and recombination be converted into the stable form hgCNO. We similarly explain the formation of the silver salt of formyl chloride oxime, $AgONC\begin{matrix}H\\ Cl\end{matrix}$, from silver fulminate and hydrochloric acid by assuming that the silver fulminate molecule, AgCNO, is ionized to a certain extent, and that the hydrochloric acid adds to the fulminate ion to form the oxime ion, which then combines with the silver ion.



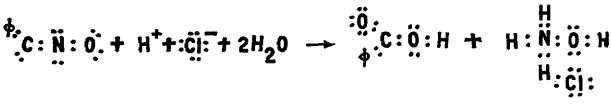
The structure usually assigned to the nitrile oxides is $R{-}C\begin{matrix}\diagup\\ \diagdown\\ O\end{matrix}{=}N$. It seems highly improbable to us that these three atoms should in this case form a ring, since in all other cases known three kernels with sixteen

external electrons form a chain. Accordingly, we have been led to believe that the nitrile oxides are the esters of fulminic acid, and have the structure RCNO. This structure is, of course, the alternative structure previously proposed;[12] but since fulminic acid has been written HONC the nitrile-oxides have not before been designated fulminates.

The properties of the nitrile oxides indicate that they are indeed esters of fulminic acid. Oxalic ester nitrile oxide is formed from nitro-acetic ester by loss of water: $C_2H_5O.CO.CH_2NO_2 \longrightarrow C_2H_5O.CO.CNO + H_2O$; and other nitrile oxides are formed by similar reactions, all of which are compatible with the suggested structure. Most of the reactions of the nitrile oxides are just those which would be expected of the esters of fulminic acid, and these have up to this time required the explanation[13] that they are accompanied by a preliminary isomeric change into these esters. For example, fulminic acid[14] with hydrochloric acid hydrolyzes to hydroxylamine hydrochloride and formic acid, which partially decomposes to carbon monoxide and water.

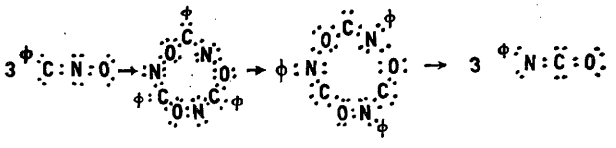


Completely analogous is the action of benzonitrile oxide and hydrochloric acid in forming benzoic acid and hydroxylamine hydrochloride.[15]



Evidently such reactions provide strong support for our view that the nitrile oxides are the esters of fulminic acid.

The remaining reactions of the nitrile oxides involve a change into the isocyanates; thus the triple polymer of benzonitrile oxide is converted into phenylisocyanate by heating with toluene. The migration postulated by us in explanation of this,



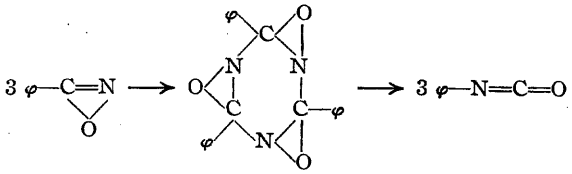
is at most no more violent than the migration and rearrangement previously accepted.

[12] Ley and Kissel, *Ber.*, **32**, 1365 (1899).

[13] Ref. 9, p. 230.

[14] Ref. 10, p. 1299.

[15] Wieland, *Ber.*, **40**, 1667 (1907).



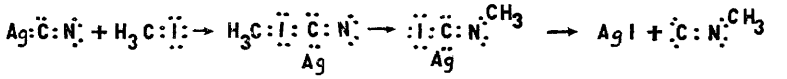
All of the chemical properties of the nitrile oxides are, then, in agreement with our suggestion that these substances are fulminates.

Compounds representing the three structures RONC, RCON and RNOC, which we have calculated to be the least stable, are unknown.

Cyanides, Nitriles and Isocyanides.—The structures of hydrocyanic acid and its salts and esters have been the subject of much discussion. Nef[16] has upheld the formula HNC for the acid, and MNC for its salts, while Wade[17] has argued for the formula HCN, retaining that of MNC. Of the esters the nitriles are generally conceded to have the structure RCN, and the isocyanides RNC.

The application of the principle suggested in this paper leads to the conclusion that the nitriles should be more stable than the isocyanides. This is in accordance with experiment; indeed, isocyanides reorganize to nitriles on being heated to about 250°.

The alkali cyanides are highly ionized,[18] so that no distinction can be made between cyanides and isocyanides. In the case of the cyanides of the heavy metals, however, the CN group is attached rigidly to the metal atom. The application of our principle leads to the inference that the carbon atom is adjacent to the metal atom; thus silver cyanide would have the formula AgCN or, if it is really the silver salt of the complex acid $HAg(CN)_2$, the formula $(Ag^+)(NCAgCN^-)$. These conceptions enable us to understand why an alkyl halide with an alkali cyanide forms the nitrile, and with a heavy metal cyanide, the isocyanide. In the first case reaction occurs between the cyanide ion and the halide; for example, $H_3CI + CN^- \longrightarrow H_3CCN + I^-$; and, inasmuch as the cyanide ion is free to attach itself by either end, the more stable compound, the nitrile, is formed. In the second case, however, the reaction is between molecules, and may occur in steps in the following way: the metal cyanide attaches itself to the alkyl halide, forming a double compound, from which the metal and halide atoms split off. The reaction between methyl iodide and silver cyanide would then be represented by the following steps.

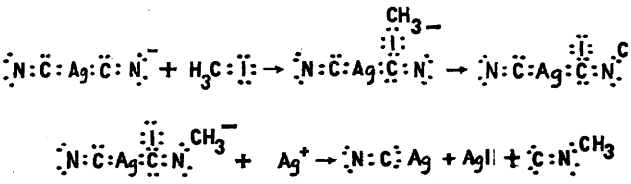


[16] Nef, *Ann.*, **270**, 328 (1892).

[17] Wade, *J. Chem. Soc.*, **81**, 1596 (1902).

[18] Complete ionization of potassium cyanide in the solid state is indicated by its crystal structure. Bozorth, THIS JOURNAL, **44**, 317 (1922).

or, in case the formula $(Ag^+)(NCAgCN^-)$ is used,



It is evident that the cyanide group is prevented from presenting its carbon end to the alkyl carbon, and that the isocyanide is accordingly formed. The increasing formation of nitrile as the alkyl group becomes larger, and with aryl halides, is to be attributed to an increasing ease of rearrangement to the more stable form.

From potential considerations we also conclude that a proton would attach itself more easily to the carbon than the nitrogen end of the cyanide ion, and accordingly we assign to hydrogen cyanide the structure HCN.

Cyanogen.—There are three possible collinear isosteric formulas for cyanogen; NCCN, CNCN and CNNC. It is shown to have the first of these by its chemical properties, which lead to the conclusion that the two carbon atoms are linked together.[19] This structure is the one which would also be predicted to be the most stable on the basis of our principle.

Cyanogen Halides.—The compound cyanogen fluoride would be expected from our calculations to have the structure NCF, rather than the less stable one CNF. This compound is not known, but the chloride, bromide and iodide are known; the predicted formulas are, however, not those generally accepted. The evidence[20] upon which these substances are assigned formulas such as CNCl is the similarity in the reactions of the halogen in this substance and in others in which it is attached to nitrogen, such as the halogen-substituted amines and amides; but such evidence is not trustworthy, and other reactions point strongly to the formula NCCl. For example, cyanogen chloride with ammonia forms cyanamide: $NCCl + NH_3 \longrightarrow NCNH_2 + HCl$. Moreover, by the Friedel and Crafts reaction cyanogen chloride forms benzonitrile: $NCCl + C_6H_6 \longrightarrow HCl + C_6H_5CN$; this reaction cannot be explained with the use of the formula CNCl, but definitely requires NCCl; so in this case also chemical evidence verifies the predicted structures.

Summary

In order to calculate the relative stabilities of certain compounds, the principle is suggested that the differences in the free energies of isosteric compounds arise principally in the terms involving the mutual potential

[19] Ref. 9, p. 196.

[20] Chattaway and Wadmore, *J. Chem. Soc.*, **81**, 191 (1902).

energy of the positive kernels. This principle is applied in a number of cases, with the following results.

It is shown, in agreement with chemical evidence, that the structures of carbon dioxide and nitrous oxide are OCO and NNO rather than COO and NON.

The greater stability of the cyanate ion, NCO^-, as compared with the fulminate ion, CNO^-, is explained.

It is shown that theoretically the isocyanates, RNCO, should be more stable than the cyanates, ROCN. Furthermore, the postulate leads to the conclusion that fulminic acid and the inorganic fulminates have the formulas HCNO and MCNO, rather than the accepted ones HONC and MONC. Moreover, the nitrile oxides are considered to be esters of fulminic acid, and to have the formula RCNO, rather than R.C(=N)O.

All of the suggested structures are shown to be compatible with the experimental evidence.

The principle explains the observation that the nitriles, RCN, are more stable than the isocyanides, RNC. The structures HCN for hydrocyanic acid, $(M^+)(CN^-)$ for the cyanides of the alkali metals, and MCN for those of the heavy metals are shown to be in agreement with their chemical properties.

The accepted formula NCCN for cyanogen is shown to be the predicted one. The accepted formula CNX for the cyanogen halides is, however, rejected in favor of the predicted formula NCX.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 76]

THE CRYSTAL STRUCTURES OF SODIUM AND POTASSIUM TRINITRIDES AND POTASSIUM CYANATE AND THE NATURE OF THE TRINITRIDE GROUP

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Introduction

The investigation with X-rays of the structures of crystals makes possible in many cases the elucidation of points of chemical interest, especially in regard to atoms connected by non-polar bonds. The tetrahedral arrangement of atoms about a carbon atom has been verified in hexamethylenetetramine,[2] $C_6H_{12}N_4$, but found not to prevail in penta-erythritol,[3] $C(CH_2OH)_4$. The nitrate and carbonate ions are formed of three atoms located about a central atom in positions such that the ions possess a 3-fold symmetry axis. Such information is of use in testing proposed theories of valence and molecular structure. The investigation reported in this paper involved the determination of the structures of three crystals containing triatomic ions which had not previously been studied in this way, namely, the trinitride and cyanate ions.

Sodium trinitride, NaN_3, is described[4] as forming hexagonal plates with prismatic cleavage. Potassium trinitride, KN_3, rubidium trinitride, RbN_3, and thallous trinitride, TlN_3, form apparently isomorphous tetragonal crystals[4] with only slightly different axial ratios, that of potassium trinitrides being given as $a:c = 1:0.5798$. Potassium cyanate, KNCO, is also reported[5] to form tetragonal crystals with $a:c = 1:0.5766$. We have determined the structures of crystals of sodium and potassium trinitride and potassium cyanate by using data obtained from Laue and spectral photographs interpreted with the aid of the theory of space groups.[6] Small basal plates of the two trinitride crystals were prepared by slow crystallization from aqueous solution,[7] and of the cyanate by crystallization from methyl alcohol. Photographs were made of the K-radiation of molybdenum reflected from the basal plane and prism planes of the

[1] National Research Fellow.

[2] Dickinson and Raymond, THIS JOURNAL, 45, 22 (1923).

[3] Mark and Weissenberg, *Z. Physik*, 17, 301 (1923); also an unpublished investigation by Huggins and Hendricks in this Laboratory.

[4] Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1908, vol. 1, p. 204.

[5] Ref. 4, vol. 2, p. 2.

[6] For a detailed description of the experimental methods see R. W. G. Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., New York, 1924, pp. 109–116 and 161–164.

[7] We wish to thank Mr. Richard Pomeroy for the preparation and crystallization of these compounds.

crystals. Symmetrical and unsymmetrical Laue photographs were made with thin basal plates, using the X-radiation from a tube with a tungsten anticathode operated at a peak voltage of 52 kilovolts. Indices were assigned to the Laue spots with the help of gnomonic projections.

The densities of the sodium and potassium trinitrides, which have not been reported previously, were determined by the suspension method of Retgers to be 1.853 and 2.038 g./cc., respectively.

The investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington. We further wish to thank Professor Noyes for suggesting the study of the trinitrides, and Dr. M. L. Huggins of this Laboratory for assistance in the preparation of the portion of this paper dealing with the nature of the trinitride group.

The Structure of Sodium Trinitride

The Unit of Structure.—Spectral data for sodium trinitride are given in Table I. The possible axial ratios determined from the positions of

TABLE I

SPECTRAL DATA FROM SODIUM TRINITRIDE

hkl	Line[a]	Order	Angle of reflection	*d*/*n*	Intensity of reflection[b]
111	β	n	3° 33.7′	5.081 Å.	w
	α	n	4° 0.2′	5.086	m
	β	$2n$	7° 9.5′	5.069	w
	α_1	$2n$	8° 0.7′	5.068	m
	α_2	$2n$	8° 4.0′	5.074	w
	γ	$3n$	10° 35.5′	5.059	vvw
	β	$3n$	10° 47.0′	5.077	mw-w
	α_1	$3n$	12° 5.7′	5.065	ms
	α_2	$3n$	12° 10.5′	5.065	m
	γ	$4n$	14° 9.7′	5.067	vw
	β	$4n$	14° 26.5′	5.061	mw
	α_1	$4n$	16° 14.0′	5.065	s
	α_2	$4n$	16° 20.5′	5.061	ms
$1\bar{1}0$	γ	n	9° 48′	1.819	vw
	β	n	9° 59.5′	1.819	w
	α	n	11° 15′	1.819	m

[a] In tables of spectral data γ indicates MoKγ, $\lambda = 0.6197$ Å.; β, MoKβ, $\lambda = 0.6311$; α_1, MoKα_1, $\lambda = 0.7078$; α_2, MoKα_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.

spots on Laue photographs are in agreement with these data. The smallest hexagonal unit compatible with these data has $a = 2.100$ Å. and $c = 5.067$ Å. Upon calculating values of $n\lambda$ on the basis of this unit for the X-rays producing the Laue spots for which data are tabulated in Table II, many of these values were much less than 0.24 Å., the short wave-length limit of X-rays present in the incident beam. This def-

initely eliminates this unit. Moreover, it can be shown that every possible hexagonal unit with $c = 5.067$ Å. and every one with $c = 10.134$ Å. are definitely eliminated by these data. The smallest hexagonal unit not eliminated by the observed reflections has $a = 3.638$ Å. and $c = 15.201$ Å., and contains 3 NaN_3.

TABLE II

LAUE PHOTOGRAPHIC DATA FROM SODIUM TRINITRIDE

Incident beam normal to (111)

hkl	d_{hkl}, Å.	$n\lambda$, Å.	Est. intensity	S for u = 0.423	Class
$1\bar{1}0$	1.832	0.46	10.0	36.00	1
$11\bar{1}$	1.578	.40	0.5	4.37	2
$2\bar{1}0$	1.195	.38	.05	4.37	2
$\bar{1}20$	1.195	.45	.05	4.37	2
310	1.145	.37	1.0	17.45	1
$21\bar{1}$	1.117	.28	1.0	29.95	1
320	1.117	.48	1.5	18.50	2
$22\bar{1}$	1.042	.46	0.15	6.30	2
$3\bar{1}0$	0.875	.38	.6	29.95	1
$32\bar{1}$	.862	.35	.12	17.45	1
$23\bar{1}$	.862	.48	.4	17.45	1
410	.846	.47	.3	18.50	2
430	.816	.41	.05	21.62	2
521	.802	.46	.1	11.50	1
541	.762	.46	.2	22.75	1
032[a]	1.117	.34	.2	18.50	2
$\bar{1}12$[a]	1.088	.41	1.3	36.00	1
241[a]	1.058	.39	0.4	21.62	2

[a] Data from another Laue photograph of NaN_3.

The rhombohedral units corresponding to the eliminated hexagonal units are, of course, also eliminated by the Laue data. The rhombohedral unit corresponding to the smallest possible hexagonal unit is, however, in complete agreement with all the observed reflections. This unit has $a = 5.481$ Å. and $\alpha = 38°43'$, and contains $1NaN_3$, corresponding to a calculated density of 1.838 g./cc., in good agreement with the directly determined value 1.853 g./cc.

It would be very difficult with any atomic arrangement based on the hexagonal unit to account for the observed absences in the first and second orders of all planes for which $-H + K + L$, $2H + K + L$, and $-H - 2K + L$ are not divisible by three. Accordingly, the rhombohedral unit described is accepted as the correct unit of structure. All indices used in this paper for sodium trinitride are referred to the axes of this unit.

The Space Group.—The observation that a Laue photograph taken with the incident beam normal to (111) shows a trigonal axis and three planes of symmetry requires that the structure be isomorphous with one of the point-groups C_{3v}, D_3, D_{3d}. The only space groups satisfying

this requirement and based on a rhombohedral lattice are[8] C_{3v}^5, C_{3v}^6, D_3^7, D_{3d}^5 and D_{3d}^6. Of these C_{3v}^6 and D_{3d}^6 do not provide any arrangement for one sodium and three nitrogen atoms in the unit.

The Atomic Arrangement.—Possible arrangements with the three nitrogen atoms in crystallographically equivalent positions are the following.

C_{3v}^5: Na at uuu; 3N at vvw, vwv, wvv;

D_3^7: Na at 000 or $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 3N at $u\bar{u}0$, $\bar{u}0u$, $0u\bar{u}$, or $u\bar{u}\frac{1}{2}$, $\bar{u}\frac{1}{2}u$, $\frac{1}{2}u\bar{u}$;

D_{3d}^5: Na at 000 or $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 3N at $00\frac{1}{2}$, $0\frac{1}{2}0$, $\frac{1}{2}00$, or $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$.

All of these arrangements are eliminated by the observed relative intensities of reflection in different orders from (111), given in Table I; namely, $4 > 3 > 2 > 1$. However, inasmuch as the intensity of reflection at small angles of X-rays from crystal faces is dependent to some extent on the nature of the reflecting surface,[9] some care must be taken in the use of these intensities. Indeed, we found that the intensity of reflection from (111) in the first order was somewhat increased if the crystal face were previously ground with fine emery and oil. Accordingly, we proceeded upon the assumption that the true intensity of the first-order reflection might be greater than that of the second, and attempted to determine the correct arrangement with the use of Laue photographic data, given in Table II. The use made of Laue data throughout our work is independent of quantitative assumptions concerning dependence of intensity of reflection on interplanar distance, and is based on the following principle: if a plane reflects X-rays of a given wave length more strongly than a second plane with a larger value of d/n, the structure factor for the first plane must be greater than that for the second. In this way it was found possible again to eliminate definitely all of the atomic arrangements listed above, without making any assumptions regarding the relative reflecting powers of the different atoms present other than the very safe one that a sodium atom reflects more strongly than a nitrogen atom. Since these arrangements are the only ones placing the three nitrogen atoms in a ring, such a structure cannot be assigned to the trinitride ion.

The only other possible arrangement is the following, derived from space-group D_3^7 or D_{3d}^5: Na at 000; N at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 2N at uuu, $\bar{u}\bar{u}\bar{u}$.

The structure factor S for any plane (hkl) has the following value.

Class 1; $n(h + k + l)$ even; $S = \overline{Na} + \overline{N} + 2\overline{N} \cos 2\pi n(h + k + l)\, u$;

Class 2; $n(h + k + l)$ odd; $S = \overline{Na} - \overline{N} + 2\overline{N} \cos 2\pi n(h + k + l)\, u$.

As is seen from Fig. 1 the observed intensities of reflection from (111) restrict u to the regions 0.083 to 0.105, 0.228 to 0.250 and 0.417 to 0.438. Further restrictions may be made by the use of Laue data. The intensity

[8] R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Publ.*, No. 318 (1922).

[9] W. L. Bragg, James and Bosanquet, *Phil. Mag.*, 41, 309 (1921). Dickinson and Goodhue, THIS JOURNAL, 43, 2045 (1921).

inequality (310) > (2$\bar{1}$0) eliminates the first of these regions, and that of (541) > (521) the second; moreover, the inequality (541) ≧ (430) requires that u be less than 0.425, as is seen from Fig. 2. The parameter is accordingly limited to the region 0.417 to 0.425; the approximate equality of intensities of reflection from (321) and (410) indicates that u is not far from 0.425, and we have taken as the most probable value 0.423.

It is interesting to observe that the comparison (22$\bar{1}$) > (2$\bar{1}$0) is satisfied for the above range of values of u only if the relative reflecting power of sodium ion is increased by more than 50% above its electron number

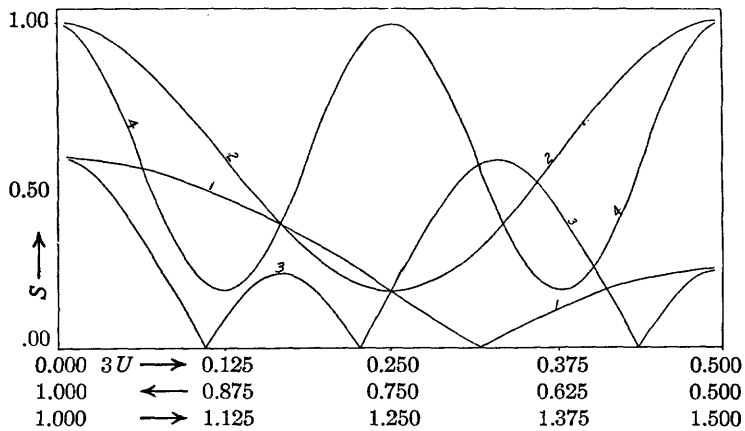


Fig. 1.—Structure-factor curves for the first four orders of reflection from (111) of sodium trinitride. The curves represent three sets of values of the abscissa $3U$; namely, 0 to 0.500, extending from left to right; 0.500 to 1.000, from right to left; and 1.000 to 1.500, from left to right. The numbers on the curves are the orders of reflection.

(Fig. 2). Values of the structure factor S in Table II are calculated for this 50% increase.

The Structure of Potassium Trinitride

The Unit of Structure.—Spectral photographic data for potassium trinitride are given in Table III. The possible axial ratios determined by the positions of the spots on Laue photographs are in agreement with these data. The smallest unit of structure compatible with them has d_{100} = 4.308 Å. and d_{001} = 1.764 Å. On calculating values of $n\lambda$ for the Laue spots for which data are given in Table IV on the basis of this unit, some of these values were found to be less than 0.24 Å., the short wave-length limit of X-rays present in the incident beam. This definitely eliminates this unit. In the same way the Laue data eliminate every unit with d_{001} = 1.764 Å., 3.528 Å. or 5.292 Å. The unit with d_{100} = 4.308 Å. and d_{001} = 7.056 Å. is similarly eliminated, but the unit obtained from it by rotation through 45° is in complete agreement with the Laue data; in

default of any evidence requiring a still larger unit of structure, this is accepted as the true one. It has $d_{100} = 6.094$ Å. and $d_{001} = 7.056$ Å., and contains 4 KN_3; the density calculated from this information is 2.045 g. per cc., in good agreement with the directly determined value 2.038. All indices used in this paper for potassium trinitride are referred to the axes of this unit.

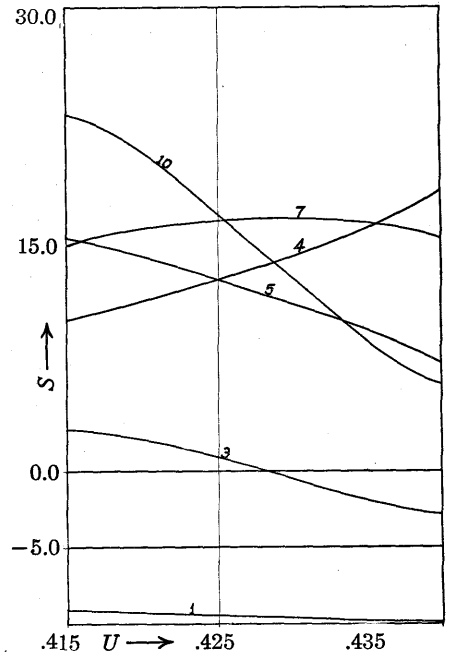


Fig. 2.—Structure-factor curves for first-order reflections from sodium trinitride; the attached numbers are the values of $h + k + l$ for the planes to which the curves correspond.

The Space Lattice and the Space Group.—The observation that a Laue photograph taken with the incident beam normal to (001) of this tetragonal crystal showed a 4-fold axis and four planes of symmetry requires that the structure be isomorphous with one of the point groups V_d, D_{4v}, D_4 and D_{4h}. In the absence of any evidence to the contrary, we have proceeded upon the assumption that the crystals are holohedral, and have considered only structures isomorphous with D_{4h}. This assumption is necessitated by the difficulty which would be introduced if consideration were afforded all of the possible arrangements with lower symmetry, some of which involve more than one parameter, and is justified to a considerable extent by the fact that an atomic arrangement completely explaining all the observed X-ray data was derived by means of it.

The absence of any first-order reflections from planes with $h + k + l$ odd makes it very probable that the structure is based on the body-centered tetragonal lattice Γ'_t. The space groups satisfying this requirement and isomorphous with D_{4h} are D_{4h}^{17}, D_{4h}^{18}, D_{4h}^{19} and D_{4h}^{20}. A choice may be made among these through use of the following criteria.[10]

Reflection in odd orders will not occur from these planes:

D_{4h}^{17}:

D_{4h}^{18}; $h = 0$;

D_{4h}^{19}; $h = k$, with $(2h + l)/4$ not integral; or $l = 0$;

D_{4h}^{20}; $h = = k$, with $(2h + l)/4$ not integral; or $h = 0$; or $l = 0$.

[10] These are taken from a complete tabulation of criteria for all tetragonal space-groups prepared by Dr. Huggins.

TABLE III

SPECTRAL PHOTOGRAPHIC DATA FROM POTASSIUM TRINITRIDE

hkl	Line	Order	Angle of reflection	Interplanar distance, Å.	Intensity of reflection
001	α	2	5° 45′	7.098	vvw
	γ	4	10° 6′	7.060	w
	β	4	10° 19′	7.046	m
	α_1	4	11° 35′	7.048	m
	α_2	4	11° 37′	7.064	ms
010	γ	2	5° 51′	6.082	w
	β	2	5° 57′	6.088	ms
	α	2	6° 38′	6.094	vs
	β	4	11° 57′	6.094	w
	α	4	13° 28′	6.096	m
110[a]	β	1	4° 12′	4.31	vw
	α	1	4° 42′	4.33	m
	β	2	8° 21′	4.33	w
	α	2	9° 26′	4.32	ms
	α	3	14° 26′	4.28	vw
	β	4	17° 10′	4.29	w
	α	4	19° 22′	4.29	m
	α	5	25° 10′	4.28	vw
	α_1	6	30° 14′	4.25	w
	α_2	6	30° 3′	4.28	w

[a] The data for this plane are less accurate than those for (001) and (010).

TABLE IV

LAUE PHOTOGRAPHIC DATA FROM POTASSIUM TRINITRIDE

Incident beam 30° from normal to (001)

hkl	$\frac{d_{hkl}}{n}$, Å.	λ, Å.	Estimated intensity	S for u = 0.135[a]	Class
132	1.69	0.33	5.0	12.00	2
051	1.20	.46	0	0	1
$\bar{5}21$	1.12	.32	0.25	7.06	1
053	1.10	.24	0	0	1
$\bar{5}32$	1.00	.41	5.0	19.22	2
$\bar{1}61$	0.97	.37	0.12	5.58	1
161	.97	.46	.20	5.58	1
$\bar{1}65$	.82	.43	.08	5.58	1
$7\bar{3}2$	.79	.33	.15	9.77	2
$5\bar{6}1$	.77	.41	.10	6.57	1
$\bar{5}54$	.76	.41	.25	6.23	3
$7\bar{5}2$	.70	.37	.17	12.60	2
$\bar{1}76$	.69	.38	1.0	21.19	2
091	.67	.37	0	0	1
376	.66	.38	.12	9.77	2
$\bar{9}12$	.66	.37	.17	17.40	2
556	.65	.34	.16	17.65	2
$7\bar{7}2$	.60	.36	.17	23.08	2

[a] The structure factor is materially affected by assumptions concerning the relative reflecting powers.

The observed first-order reflection from (110) (Table IV) definitely eliminates D_{4h}^{19} and D_{4h}^{20}. No first-order reflections from planes with $h = 0$ were observed on any Laue photograph, though several such planes were in positions favorable to reflection, as is seen from Tables III and IV. It would be difficult to explain these absences with an arrangement derived from D_{4h}^{17}; accordingly D_{4h}^{18}, which is in complete agreement with the above observations, is accepted as the correct space group.

The Atomic Arrangement.—The following atomic arrangements are provided[11] by D_{4h}^{18}.

4 K or 4 N at (a) $000, 00\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$;
(b) $0\frac{1}{2}0, \frac{1}{2}00, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}$;
(c) $00\frac{1}{4}, 00\frac{3}{4}, \frac{1}{2}\frac{1}{2}\frac{3}{4}, \frac{1}{2}\frac{1}{2}\frac{1}{4}$;
(d) $0\frac{1}{2}\frac{1}{4}, \frac{1}{2}0\frac{1}{4}, \frac{1}{2}0\frac{3}{4}, 0\frac{1}{2}\frac{3}{4}$;

8 N at (e) $\frac{1}{4}\frac{1}{4}0, \frac{3}{4}\frac{1}{4}0, \frac{3}{4}\frac{3}{4}0, \frac{1}{4}\frac{3}{4}0$;
$\frac{3}{4}\frac{3}{4}\frac{1}{2}, \frac{1}{4}\frac{3}{4}\frac{1}{2}, \frac{1}{4}\frac{1}{4}\frac{1}{2}, \frac{3}{4}\frac{1}{4}\frac{1}{2}$;
(f) $00u, \frac{1}{2}\frac{1}{2}u, \frac{1}{2}\frac{1}{2}\frac{1}{2}+u, 00\frac{1}{2}+u$,
$00\bar{u}, \frac{1}{2}\frac{1}{2}\bar{u}, \frac{1}{2}\frac{1}{2}\frac{1}{2}-u, 00\frac{1}{2}-u$;
(g) $0\frac{1}{2}u, \frac{1}{2}0u, \frac{1}{2}0\frac{1}{2}+u, 0\frac{1}{2}\frac{1}{2}+u$,
$0\frac{1}{2}\bar{u}, \frac{1}{2}0\bar{u}, \frac{1}{2}0\frac{1}{2}-u, 0\frac{1}{2}\frac{1}{2}-u$;
(h) $u\ \frac{1}{2}+u\ \frac{1}{4}, \frac{1}{2}-u\ u\frac{1}{4}, \bar{u}\ \frac{1}{2}-u\ \frac{1}{4}, \frac{1}{2}+u\ \bar{u}\frac{1}{4}$,
$\frac{1}{2}+u, u\frac{3}{4}, u\ \frac{1}{2}-u\ \frac{3}{4}, \frac{1}{2}-u, \bar{u}\frac{3}{4}, \bar{u}\ \frac{1}{2}+u\ \frac{3}{4}$.

No arrangement with atoms in Position e, f or g is able to give a larger structure-factor to the fifth order from (110) than to the third order; accordingly the observation on a spectral photograph that the fifth order of (110) actually reflects as strongly as the third order eliminates all such arrangements. Arrangements with the 4 potassium and 12 nitrogen atoms in Positions a, b, c and d are similarly eliminated. Of the arrangements with 8 nitrogen atoms at (h), those with 4 nitrogen atoms at (c) or (d) and 4 potassium atoms at (d) or (c) are ruled out by the fact that the fourth-order reflection from (001) is stronger than the second-order one, for the corresponding structure factors are the same. The structure factor for the second order of (001) is $4\overline{K} + 4\overline{N}$ for potassium atoms at (c) or (d) and nitrogen atoms at (a) or (b), and is $4\overline{K} - 4\overline{N}$ for potassium atoms at (a) and nitrogen atoms at (b). Inasmuch as the reflecting powers of potassium and nitrogen atoms are at least approximately proportional to their atomic numbers, 19 and 7, respectively, and previous experimental results indicate that the deviation from strict proportionality is in such directions as to increase the reflecting power of the heavier atom, all of these arrangements are removed from further consideration by their inability to explain the extremely weak observed second-order reflection from (001). The minimum value of the structure factor for the third order of (110) with potassium atoms at (b) and nitrogen at (c) or potassium at (b) and nitrogen at (d) is $4\overline{K} - 4\overline{N}$; with potassium atoms at (a) and

[11] Ref. 5, p. 100.

nitrogen at (c) it is $4\bar{K}$. These arrangements, also, are accordingly removed from further consideration, for they are incapable of accounting for the observed very weak third-order reflection from (110).

The only remaining arrangement is that with potassium atoms at (a) and nitrogen atoms at (d) as well as at (h). Changing the origin of coordinates to $00\frac{1}{4}$ for convenience, the arrangement becomes the following.

4K at $00\frac{1}{4}$, $00\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{3}{4}$;
4N at $0\frac{1}{2}0$, $\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$;
8N at u $\frac{1}{2}$+u 0, $\frac{1}{2}$−u u 0, ū $\frac{1}{2}$−u 0, $\frac{1}{2}$+u ū 0,
$\frac{1}{2}$+u u $\frac{1}{2}$, u $\frac{1}{2}$−u $\frac{1}{2}$, $\frac{1}{2}$−u ū $\frac{1}{2}$, ū $\frac{1}{2}$+u $\frac{1}{2}$.

With this arrangement the structure factor for the second-order reflection from (001) is $4\bar{K} - 12\bar{N}$; the extremely weak reflection obtained experimentally shows that the reflecting power of K^+ is almost exactly equal to that of N_3^-. With this information we can easily evaluate the parameter u. All distinct arrangements are provided by giving u values between 0 and 0.25. The only regions explaining the observation that the fifth-order reflection from (110) is as strong as the third order are 0 to 0.063 and 0.125 to 0.187.

All planes may be divided into three classes, which have the following structure factors.

Class 1, l odd, n odd; $S = 4\bar{N}\ [\cos 2\pi n(h+k)\,u - \cos 2\pi n(h-k)u]$;

Class 2, $\frac{nl}{2}$ odd, n odd; or $nl/2$ even, n even; $S = 4\bar{K} + 4\bar{N} + 4\bar{N}\ [\cos 2\pi n(h+k)u + \cos 2\pi n(h-k)u]$;

Class 3, $nl/2$ even, n odd; or $nl/2$ odd, n even; $S = 4\bar{K} - 4\bar{N} - 4\bar{N}\ [\cos 2\pi n(h+k)u + \cos 2\pi n(h-k)u]$.

Comparisons may be made between planes of the same class with only qualitative assumptions concerning relative reflecting powers. The observation that on a Laue photograph (912) reflects more strongly than (752) accordingly eliminates the first of the above regions and further restricts the second to 0.125 to 0.145. The data did not permit further rigorous restriction of the parameter; however, the observed intensities seem to be in best agreement with the structure factors for u = 0.135, which is accepted as the most probable value.

The Structure of Potassium Cyanate

The Unit of Structure.—Spectral photographic data for potassium cyanate are given in Table V, and Laue data in Table VI. The smallest unit of structure completely accounting for these data has d_{100} = 6.070 Å. and d_{001} = 7.030 Å., and contains 4 KNCO. The density calculated from these data is 2.065 g. per cc., in good agreement with the directly determined value[5] 2.056 g. per cc. All indices used in this paper for potassium cyanate are referred to the axes of this unit. The elimination of other units of structure was made in the same way as for potassium trinitride.

TABLE V

SPECTRAL PHOTOGRAPHIC DATA FROM POTASSIUM CYANATE

hkl	Line	Order	Angle of reflection	Interplanar distance	Intensity of reflection
001	α	2	5° 51′	6.97 Å.	vvw
	γ	4	10 10.5	7.020	w
	β	4	10 21	7.020	m
	α_1	4	11 36	7.034	vs
	α_2	4	11 41	7.030	s
010	γ	2	5 51	6.075	vvw
	β	2	5 59	6.060	w
	α	2	6 43.3	6.070	m
110[a]	α	1	4 47	4.26	m
	β	2	8 34	4.26	w
	α	2	9 29	4.31	m
	α	3	14 27.5	4.28	vvw
	α	4	19 19	4.26	mw
	α_1	5	24 21	4.30	vw
	α_2	5	25 0.5	4.22	w

[a] These measurements are less accurate than those from (001) and (010).

TABLE VI

LAUE PHOTOGRAPHIC DATA FROM POTASSIUM CYANATE

Incident beam 22.5° from normal to (001)

hkl	$\frac{d_{hkl}}{n}$, Å.	λ, Å.	Estimated intensity	Structure factor for u = 0.135	Class
$3\bar{3}2$	1.32	0.24	0.6	21.21	2
$4\bar{1}3$	1.25	.42	.2	1.60	1
$3\bar{5}0$	1.04	.43	1.0	4.84	3
$5\bar{1}4$	0.99	.46	1.5	10.61	3
$2\bar{3}0$, $n=2$	.84	.37	0.6	14.92	2
$7\bar{1}2$	.83	.26	.1	20.78	2
$\bar{1}\bar{7}2$	.83	.46	3.0	20.78	2
$6\bar{1}5$	.81	.36	0.05	5.58	1
$2\bar{3}2$, $n=2$	.76	.31	.15	14.92	2
$7\bar{5}0$	.71	.45	.3	11.36	3
$7\bar{1}6$	.69	.32	.3	21.19	2
$\bar{2}4\bar{1}$, $n=2$	.67	.46	.3	14.69	3
$7\bar{2}7$	.64	.39	.05	2.64	1
$\bar{3}\bar{9}2$	.63	.36	.15	14.24	2
$1\bar{9}4$	.63	.36	.05	6.64	3
$4\bar{3}0$, $n=2$	.61	.38	.15	18.49	2
$2\bar{4}3$, $n=2$	.59	.37	.07	14.69	3

The Space Lattice and the Space Group.—A Laue photograph taken with the incident beam of X-rays in the plane containing the *a* and *c* axes showed a plane of symmetry, requiring that the crystal be isomorphous with one of the point groups V_d, C_{4v}, D_4 and D_{4h}. As with potassium trinitride, we have preliminarily assumed that the crystals are isomorphous with D_{4h}, in the absence of evidence to the contrary. No first-order reflections were observed from any planes with $h + k + l$ odd, indicating

that the structure is based on the lattice Γ_i'. Of the space groups D_{4h}^{17}, D_{4h}^{18}, D_{4h}^{19} and D_{4h}^{20} satisfying these requirements the last two are eliminated by the observed odd-order reflections from (110) (Table V), and the first is made improbable by the absence of any odd-order reflections from planes with $h = 0$. D_{4h}^{18} is, accordingly, temporarily accepted as the correct space group.

The Atomic Arrangement.—The atomic arrangements provided by D_{4h}^{18} are listed in the discussion of potassium trinitride. The only arrangements of 4 potassium, 4 nitrogen, 4 carbon and 4 oxygen atoms are (a), (b), (c) and (d). These arrangements do not permit the structure factor for the fifth-order reflection from (110) to be greater than that for the third-order reflection; the experimental observation that this is true accordingly eliminates these arrangements.

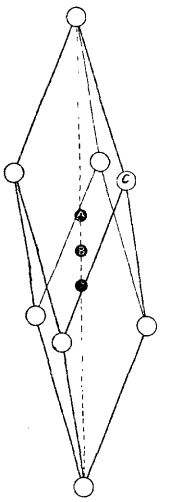


Fig. 3.—The unit of structure of sodium trinitride; the rings denote sodium atoms, the solid black circles nitrogen atoms.

If, however, it is assumed that atoms of two different elements, say oxygen and nitrogen, may be considered to be, as far as the diffraction of X-rays is concerned, in crystallographically equivalent positions, the remaining arrangements discussed for potassium trinitride must be given consideration. Reference to Table V shows that the relative intensities of the spectral reflections in different orders from (001) and (110) are the same as for potassium trinitride; the atomic arrangement is accordingly restricted to that determined for this crystal, the parameter u lying between 0 and 0.063 or 0.125 and 0.187. The observation that $(7\bar{1}6)$ reflects more strongly than $(2\bar{3}2)$, $n = 2$, eliminates the region 0 to 0.063, and the further comparison $(4\bar{3}0)$, $n = 2$, greater than $(\bar{3}9\bar{2})$ requires that u be less than 0.146. However, throughout the remaining region 0.125 to 0.146 the structure factor for $(7\bar{2}7)$ is less than that for $(6\bar{1}5)$, whereas the observation that $(7\bar{2}7)$ reflects more strongly than $(6\bar{1}5)$ requires the reverse relation to be true. Accordingly, the structure of potassium cyanate is not that of potassium trinitride; the fact that most of the experimental data are satisfied by the same arrangement, with a value of u of about 0.13 shows, however, that the true structure is closely similar to this one.

The experimental data are not sufficiently numerous to permit the deduction of the true structure; indeed, this deduction would be difficult because of the similarity to the structure discussed above, for very small variations in intensities of Laue spots would be of importance. The problem could be more easily solved by a study of the tetragonal crystal thallous thiocyanate, TlNCS, which has the very closely similar axial ratio $a:c = 1:0.5593$.[12]

[12] Ref. 5, p. 3.

Discussion and Conclusions

Description of the Structures.—The arrangement of atoms in the unit of structure of sodium trinitride is shown in Fig. 3. No NaN_3 molecules can be distinguished in the crystal; however, the nitrogen atoms are seen to be arranged in groups of three, evidently constituting the trinitride ion. Each such ion is surrounded by 6 sodium ions, and each sodium ion by 6 trinitride ions. The determined interatomic distances for this salt are given in Table VII.

TABLE VII

INTERATOMIC DISTANCES FOR THE THREE SUBSTANCES

Substance	N—N (or N—C, C—O) distance, Å.	Metal-metal distance, Å.	Metal-N (or O) distance, Å.
NaN_3	1.17	3.632	2.48
KN_3	1.16	3.528	2.96
KNCO	1.16	3.515	2.95

The similarity of this structure to others is seen by a consideration of Figs. 4, 5 and 6. In Fig. 5 is represented the unit of structure of the cubic crystal sodium chloride, containing $4NaCl$, with the zone axis [111] vertical, in Fig. 4 a portion of a crystal of sodium trinitride, the face-centered rhombohedron containing $4NaN_3$, and in Fig. 6 a cleavage rhombohedron of sodium nitrate, containing $4NaNO_3$. It will be observed

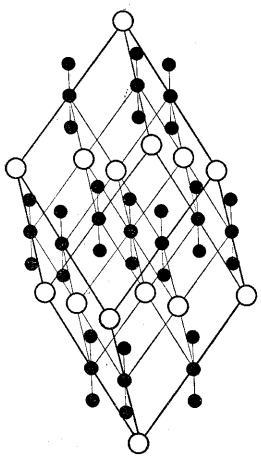


Fig. 4.—The face-centered rhombohedron of sodium trinitride; the rings denote sodium atoms and the solid black circles nitrogen atoms.

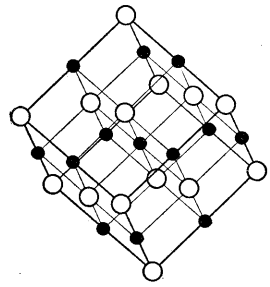


Fig. 5.—The unit of structure of sodium chloride; the rings denote sodium atoms and the solid black circles chlorine atoms.

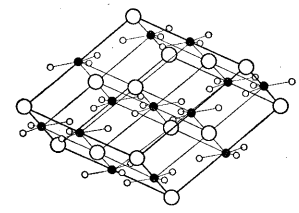


Fig. 6.—The cleavage rhombohedron of sodium nitrate; the large rings denote sodium atoms, the solid black circles nitrogen atoms and the small rings oxygen atoms.

that in all three crystals the ions are similarly located. By substituting trinitride for chloride ions the atomic arrangement is extended vertically and compressed horizontally; the substitution of nitrate ions has the reverse effect. The shortest distance between sodium ions in a plane parallel to (111) is 3.63 Å. for the trinitride, 3.98 Å. for the chloride, and 4.92 Å. for

the nitrate; the distances apart of these planes containing sodium ions are 5.07, 3.25 and 2.77 Å., respectively.

The unit of structure of potassium trinitride is shown in Fig. 7. Here also, no molecules of KN_3 can be distinguished, and the nitrogen atoms are in groups of three, forming trinitride ions. Each trinitride ion is equidistant from 8 potassium ions, and each potassium ion equidistant from 8 trinitride ions. The arrangement is closely similar to that of the cubic crystal cesium chloride, the structure of which is represented in Fig. 8. The approximately spherical chloride ions in cesium chloride are replaced by trinitride ions, whose infinite symmetry axes coincide with 2-fold symmetry axes of the crystal. In this figure the *h*- and *k*-axes are rotated 45° from the usual directions. This replacement expands the structure in directions normal to the *l*-axis; the axial ratio c/a becomes 1.158, as compared with the corresponding value 1.414 for crystals with the cesium chloride arrangement.

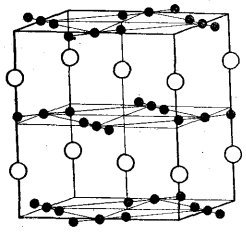


Fig. 7.—The unit of structure of potassium trinitride; the rings denote potassium atoms and the solid black circles nitrogen atoms.

Fig. 7 also represents approximately the structure of potassium cyanate, the trinitride ions being replaced by cyanate ions, NCO^-. Interatomic distances for potassium trinitride and potassium cyanate are included in Table VII. The space group symmetry of potassium cyanate crystals is not that of D_{4h}^{18}, as for potassium trinitride, but something else, presumably of a space group of lower symmetry than point group D_{4h}. The atomic arrangement is closely similar to that assigned potassium trinitride.

Langmuir[13] has stated that, since the trinitride ion and the cyanate ion are isosteric, similar compounds of these ions should be isomorphous, and has quoted morphological data for their potassium salts in support of this contention. While our work has shown that the crystals do not have completely identical structures, and so are not completely isomorphous, the great similarity found makes it probable that solid solutions of every composition could be formed. Any given solid solution could be assigned either the trinitride or the cyanate structure; if less than a certain fraction of cyanate were present, the crystal would be one of potassium trinitride with a number of the trinitride ions replaced by cyanate ions, introduced at random, and with no directional preference shown the nitrogen or carbon end of the group. With a greater fraction of cyanate the influence of the lack of a center of symmetry in the cyanate ions would be felt; the crystal

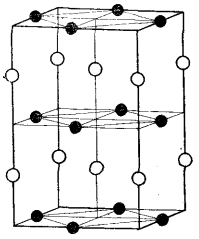


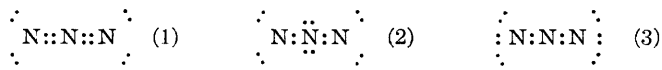
Fig. 8.—The arrangement of atoms in cesium chloride; the rings denote cesium atoms and the solid black circles chlorine atoms.

[13] Langmuir, THIS JOURNAL, **41**, 1543 (1919).

would be one of potassium cyanate, with some of the cyanate ions replaced at random by trinitride ions, and with lower point-group symmetry than potassium trinitride.

The Nature of the Trinitride Group.—The present research has shown that the crystals investigated contain trinitride ions composed of three collinear nitrogen atoms. Moreover, the trinitride ions in both sodium and potassium trinitrides are located in positions requiring that they possess centers of symmetry. These facts require that some suggested structures for these ions be discarded; for example, a structure in which the central nitrogen is connected with one end nitrogen by a triple bond and with the other by a double bond is no longer tenable. It is worthy of especial emphasis that this investigation has definitely shown that the trinitride ion does not possess a ring structure.

The trinitride ion consists of 3 nuclei and 22 electrons or, assigning 2 K-electrons to each nucleus, of 3 kernels and 16 outer electrons. We shall represent these kernels by the symbol N, and the electrons, which we shall assume to be paired, by dots. Possible electronic structures of the trinitride ion involving electron sharing and in agreement with our results are these



It is probable that all trinitride ions in crystals possess one of these arrangements. It is to be understood that the electrons are not necessarily static, but may be in orbits, possibly including, in the case of shared electrons, two nuclei. If, as has been suggested, the double bond does not involve the sharing of four electrons, choice remains to be made between Structures 2 and 3.

We cannot decide between these structures on symmetry considerations. Structure 2 possesses a 2-fold symmetry axis and 3 a 3-fold axis. In the potassium salt the trinitride ion is located on a 2-fold axis, and in the sodium salt on a 3-fold axis; evidently neither of the structures conforms completely with the symmetry of both crystals. It is possible, but very improbable, that the ion has one structure in one crystal and another in the other; the alternative and to us preferable explanation is that the electron arrangement of the group need not conform to the symmetry requirements of the crystals; that is, the group acts as though it had an infinite symmetry axis. That this is a plausible explanation is strikingly shown by the fact that it has been found that even the hydrogen nuclei in ammonia groups and ammonium ions do not conform to the symmetry of the entire crystal.[14] We are accordingly unable to decide between Structures 2 and 3.

The addition of an organic radical to the trinitride group can hardly

[14] Ref. 6, p. 398.

produce a large change in its structure; we accordingly believe that the azide group has the same collinear structure as the trinitride ion. The original statement of Fischer[15] that the azide group had a ring structure has been criticized also by Thiele,[16] Turrentine,[17] Langmuir[18] and others, but has been included in at least one modern text.[19] A careful investigation of the literature on the reactions of the azide group has led us to the conclusion that these reactions can be satisfactorily explained by the structures given above. It is probable that the aliphatic diazo-amino compounds, $RHCN_2$, have a closely similar structure.[18,19,20]

The Structures of the Acid Fluorides.—The acid fluoride ion, HF_2^-, consists of 3 atomic kernels and 16 outer electrons, and might be expected to have the structure of the trinitride ion, in which case its salts would probably have the crystal structures described in this paper. Crystals of both potassium and sodium acid fluorides have been previously investigated with X-rays.

The tetragonal crystals formed by potassium acid fluoride have an axial ratio only 4% greater than the trinitride. The X-ray data obtained are closely similar to those for the trinitride, and from them the same structure was assigned to the crystal.[21] The data were not as complete as for the trinitride, and assumptions not usually permitted were made in their treatment;[22] however, the agreement of the data with those from potassium trinitride makes it extremely probable that the structure assigned is correct. The hydrogen-fluoride distance was found to be 1.12 Å., with an estimated maximum error of 0.08 Å. The unit of structure has a = 5.67 Å. and c = 6.81 Å.

X-ray powder photographs[23] have been taken of the rhombohedral crystal sodium acid fluoride, $NaHF_2$. With the assumption that the structure of this crystal is similar to that of cesium dichloro-iodide; that is, of sodium trinitride with the center nitrogen replaced by hydrogen and the end nitrogens by fluorine, the variable parameter was evaluated. The structure assigned was in agreement with the data obtained, and is probably correct; the probable hydrogen-fluorine distance is said to be 1.18 Å., with a possible error of about 0.07 Å. The unit of structure has $\alpha = 39°44'$ and a = 5.17 Å.

[15] Fischer, *Ann.*, **190**, 67 (1878).

[16] Thiele, *Ber.*, **44**, 2522 (1911).

[17] Turrentine, THIS JOURNAL, **36**, 23 (1914).

[18] Langmuir, *ibid.*, **42**, 274 (1920).

[19] Henrich-Johnson and Hahn, "Theories of Organic Chemistry," J. Wiley and Sons, New York, **1922**, p. 149.

[20] See also Staudinger, *Z. angew. Chem.*, **27**, I, 334 (1914); *Helv. chim. Acta*, **5**, 87 (1922); **4**, 228 (1921).

[21] Bozorth, THIS JOURNAL, **45**, 2128 (1923).

[22] See Ref. 6, p. 332, for a criticism of the investigation.

[23] Rinne, Hentschel and Leonhardt, *Z. Krist. Mineralog.*, **58**, 629 (1923).

It seems improbable that a single proton, with unit positive charge, should be able to share more than 4 electrons with other kernels. Structure 3 is, then, to be assigned the acid fluoride ion; representing the proton by H, this is

$$:\ddot{F}:H:\ddot{F}:$$

Other Groups of Similar Electronic Configuration.—Carbon dioxide, CO_2 and nitrous oxide, N_2O, consist of 3 nuclei and 22 electrons, and might be expected to have the structure of the trinitride ion. X-ray measurements verify this, for crystals of these substances are found to consist of molecules made of three collinear atoms. The previous researches are not in complete agreement, for while one[24] gives the carbon-oxygen distance in a molecule of carbon dioxide as 1.15 Å., the other[25] gives the value 1.59 Å. Moreover, the structure of nitrous oxide[24] with the nitrogen-oxygen distance 1.05 Å., cannot be accepted, for the assumption was made that the molecule has the formula NON, whereas the formula NNO is indicated by a number of facts. These substances are now being investigated in this Laboratory.

Other groups with 3 nuclei and 22 electrons, and probably with the trinitride structure, are the metaborate ion, BO_2^-, the beryllate ion, $BeO_2^=$, the fulminate ion, CNO^-, and the positive nitrogen dioxide ion, NO_2^+.

The distances between adjacent atoms so far determined are listed in Table VIII.

TABLE VIII

DISTANCES BETWEEN ADJACENT ATOMS

Substance	Range, Å.	Prob. distance, Å.
N_3^- in KN_3	1.08 to 1.25	1.16
N_3^- in NaN_3	1.14 to 1.26	1.17
NCO^- in KNCO		1.16
HF_2^- in KHF_2	1.04 to 1.20	1.12
HF_2^- in $NaHF_2$	1.11 to 1.25	1.18
CO_2		1.15
CO_2		(1.59)
N_2O		(1.05)

Summary

The crystal structures of sodium trinitride, potassium trinitride and potassium cyanate have been determined. The rhombohedral unit of structure of sodium trinitride has $\alpha = 38°43'$ and $a = 5.481$ Å., and contains 1 NaN_3. The sodium atom is at 000, the nitrogen atoms at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, uuu, $\bar{u}\bar{u}\bar{u}$, with u equal to 0.423. The tetragonal unit of potassium trinitride has $a = 6.094$ Å. and $c = 7.056$ Å., and contains $4KN_3$. The potassium atoms are at $00\frac{1}{4}$, $00\frac{3}{4}$, $\frac{1}{2}\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}\frac{1}{2}\frac{3}{4}$, and the nitrogen atoms at $0\frac{1}{2}0$,

[24] Smedt and Keesom, *Proc. Amsterdam Akad.*, **37**, 13 (1924).

[25] Mark and Pohland, *Z. Krist. Mineralog.*, **61**, 293 (1925).

$\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$; $u\ \frac{1}{2}+u\ 0$, $\frac{1}{2}-u\ u\ 0$, $\bar{u}\ \frac{1}{2}-u\ 0$, $\frac{1}{2}+u\ \bar{u}\ 0$, $\frac{1}{2}+u\ u\ \frac{1}{2}$, $u\ \frac{1}{2}-u\ \frac{1}{2}$, $\frac{1}{2}-u\ \bar{u}\ \frac{1}{2}$, $\bar{u}\ \frac{1}{2}+u\ \frac{1}{2}$, with u equal to 0.135. The structure of potassium cyanate is shown to be closely similar to that of the trinitride; the unit of structure has $a = 6.070$ Å., and $c = 7.030$ Å.

Neither sodium nor potassium trinitride shows molecular segregation; the trinitride ion is, however, easily distinguished. This ion is shown to possess not a ring structure, but a linear arrangement of the three nitrogen atoms. Possible electronic configurations are discussed in light of these results.

A consideration of the previously studied structures of sodium and potassium acid fluoride is shown to indicate that the acid fluoride ion is similar in structure to the trinitride ion and the cyanate ion.

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