I. The Crystal Structures of Iodic Acid and of Potassium Oxyfluoiodate, and the Redetermination of the Parameters in Potassium Bifluoride and Ammonium Bifluoride

II. The Internuclear Distance in the Fluorine Molecule and The Electron Diffraction Investigation of Tellurium Dibromide.

III. The Determination of the Magnetic Anisotropy of Crystals.

Thesis

by

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The Crystal Structure of Iodic Acid

BY MAX T. ROGERS AND LINDSAY HELMHOLZ

Introduction

Although reports have been published on the crystal structures of all the alkali iodates, no completely satisfactory structure determination of any iodate has been made. The isomorphous crystals cesium iodate, rubidium iodate, potassium iodate, and ammonium iodate are pseudocubic and are said to give no powder lines indicating any deviation from the ideal perovskite structure assigned to them.[1,2,3] This places a regular octahedron of six oxygen atoms around each iodine atom with the distance I–O = 2.23 Å. and gives the alkali atom a coördination number of twelve. Sodium iodate, which is orthorhombic, has been assigned a deformed anti-perovskite structure the alkali atom having a coördination number of six and the iodine atom twelve. Lithium iodate is hexagonal with a reported structure based on hexagonal closest packing,[4] in which octahedra of oxygen atoms surround both lithium and iodine atoms, the IO_6 octahedra sharing corners and the LiO_6 octahedra sharing faces.

Potassium iodate and the isomorphous rubidium, cesium and ammonium compounds are known to be monoclinic hemihedral from crystallographic and piezoelectric measurements and the assignment of a simple cubic structure to them on the basis of powder pictures is unsatisfactory since the intensities of the lines are rather insensitive to the oxygen parameters and could be roughly accounted for by an essentially incorrect structure. The deviations from the ideal perovskite structure may also be appreciable for sodium iodate since the observed axial ratios 0.903:1:0.636 differ considerably from those of a cubic perovskite structure in that orientation, *viz.*, 1:1:0.707. The oxygen parameter in lithium iodate is not closely enough known to give the oxygen positions with any certainty. Hence none of the structure determintions can be accepted as showing what the configuration of the iodate group is.

One might expect on chemical grounds and from the correlation of Raman spectra in crystals and solution[5] that discrete iodate groups or simple polymers would exist in the crystal rather than regular IO_6 octahedra with shared corners. The observed I–O distance (2.23 to 2.33 Å.) in these crystals seems rather large in view of the value 1.93 Å. observed in KIO_2F_2 and $(NH_4)_2H_3IO_6$,[6]

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[1] V. M. Goldschmidt, "Geochem. Vert. Gesetze der Elemente," VII and VIII.

[2] W. H. Zachariasen, *Skrifter Norske Videnskapsakad. Oslo I, Mat. Natur. Klasse*, 1928, No. 4.

[3] J. Garrido, *Anales soc. españ. fis. quim.*, **30**, 811 (1932).

[4] W. H. Zachariasen and F. A. Barta, *Phys. Rev.*, **37**, 1628 (1931).

[5] James Hibben, "The Raman Effect and Its Chemical Applications," A. C. S. Monograph, 1939, p. 378.

[6] L. Helmholz and M. T. Rogers, THIS JOURNAL, **62**, 1537 (1940).

and the sum of the covalent single bond radii, 2.02 Å., obtained using the octahedra iodine radius, 1.35 Å., found for $KICl_4$[7] in which iodine has a formal charge of -1 as in the iodates. The distances I–O = 2.87 Å., 2.95 Å., 3.18 Å. reported for sodium iodate[2] seem especially unlikely.

In this paper we report the results of a thorough investigation of the structure of the α-modification of crystalline iodic acid. The only previous work on this compound reported is a determination of unit cell and probable space group.[2]

The presence of discrete pyramidal IO_3^- groups in the crystal has been shown, with the observed I–O distances 1.80 Å., 1.81 Å., and the O–I–O angles 96°, 98°, and 101°. Three oxygen atoms in positions approximately opposed to the three bonded IO_3 oxygens and at distances 2.45, 2.70, 2.95 Å. complete a distorted IO_6 octahedron with three strong bonds and three weaker ones. The hydroxyl oxygen atom of each iodate group has two nearest oxygen neighbors at 2.78 Å. There are thus two hydrogen bonds for each iodate group forming a moderately strong bifurcated bond of the type observed in glycine.[8] The oxygen atoms are in a somewhat distorted closest packed arrangement. The structure resembles somewhat that of perovskite with the oxygen atoms moved from a central position between iodine atoms to form iodate groups. The formation of hydrogen bonds has displaced the oxygen atoms slightly from the line joining the iodine atoms and the iodine atoms are no longer in the perovskite arrangement although each has six nearest iodine neighbors. Crystalline iodic acid is an aggregate of HIO_3 molecules held together by hydrogen bonds, and secondary I–O bonds of the type observed for arsenic and oxygen in arsenolite.[9]

Procedure

Iodic acid was prepared by oxidizing iodine with concd. nitric acid. The solution was evaporated at 150° to a thick sirup which was allowed to crystallize. Goniometric measurements agreed with those given by Groth[10] for the α-modification of iodic acid.

Laue photographs were taken with X-rays normal to each axis using continuous radiation from a tungsten target. Oscillation photographs of 12° and 24° angular range were obtained with each axis vertical using MoKα radiation and a zirconium filter. The crystals were dissolved down to an approximately cylindrical shape and such a size that the influence of absorption was negligible for pictures taken with the "a" and "c" axes vertical. The radius of the cylindrical crystal with b vertical was such that an absorption correction was necessary. The correction was taken from tables for powder rod absorption with $\mu r = 3.0$.[11] The intensities of all equatorial and of 75 hkl reflections were estimated visually using a calibrated scale. The estimation of intensities was facilitated by using two films with a sheet of 0.0015″ copper between so that the intensity of the reflections on the second film was about one-fifth of that on the first.

In order to obtain correct estimates of the relative intensities of strong reflections a powder picture was taken using CuKα radiation of a film of powder held by a thin coating of vaseline to a small diameter glass fiber.

Space Group and Unit Cell.—Laue photographs showed the Laue symmetry to be D_{2h}-mm. The regular absences $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; and $00l \neq 2n$, were observed on Laue and oscillation photographs. The space group is thus D_2^4-$P2_12_12_1$. This is in agreement with the crystallographic evidence that α-iodic acid is rhombic bisphenoidal, and the absence of a center of symmetry has been confirmed by a positive piezoelectric experiment.[12] The dimensions of the unit cell are $a_0 = 5.525 \pm 0.010$ Å., $b_0 = 5.855 \pm 0.010$ Å., and $c_0 = 7.715 \pm 0.010$ Å. This gives the axial ratios 0.944:1:1.317 from X-ray data to be compared with the crystallographic values 0.9388:1:1.3181 given by Groth.[8] Using the observed density, 4.63 g./cc. the number of molecules in the orthorhombic unit cell is found to be four. Long exposure Laue photographs gave no reflections requiring a larger unit.

This is in essential agreement with the values $a_0 = 5.53 \pm 0.05$ Å., $b_0 = 5.92 \pm 0.05$ Å., $c_0 = 7.75 \pm 0.05$ Å. and $Z = 4$ with possible space groups $V^1 - V^4$ found by Zachariasen[2] from measurements of powder pictures.

Determination of Structure.—The space group D_2^4 has only the fourfold positions

$$4{:}(a)\ x,y,z;\ {}^1/_2-x,\bar{y},{}^1/_2+z;\ {}^1/_2+x,{}^1/_2-y,\bar{z};\ \bar{x},{}^1/_2+y,{}^1/_2-z$$

There are thus three parameters each to be determined for iodine and for the three oxygen atoms. The hydrogen parameters cannot be found directly.

The iodine parameters were obtained from Patterson projections made with $(0kl)$ and $(hk0)$ data. The Patterson projection on the xy plane

$$P(X, Y) = \Sigma h \Sigma k \mid F_{hk0} \mid^2 \cos 2\pi(hX + kY)$$

was made using observed intensities for 58 reflec-

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[7] R. C. L. Mooney, *Z. Krist.*, **98**, 377 (1938).

[8] Albrecht and Corey, THIS JOURNAL, **61**, 1087 (1939).

[9] R. M. Bozorth, *ibid.*, **45**, 1621 (1923).

[10] P. Groth, "Chemische Kristallographie," Teil II, Leipzig, 1908, p. 74.

[11] "Int. Tab. zur Bestimmung von Kristallstrukturen II," Ch. XI.

[12] A. Hettich and H. Steinmetz, *Z. Physik*, **76**, 700 (1932).

tions (*hk*0). From this the iodine parameters $x = 0.204$, $y = -0.088$ were obtained. The intensities of 70 reflections (0*kl*) were used to make a Patterson projection on (100) from which the iodine parameter $z = 0.156$ was obtained and the value $y = -0.088$ confirmed. These projections were not used to obtain the oxygen parameters.

The oscillation photographs with the *b*-axis vertical gave 200 equatorial reflections (*h*0*l*) going out to $\sin \theta/\lambda = 1.38$. The signs of the *F*'s of about 175 of these were determined at once from the sign of the iodine contribution using the above parameters in the structure factor. A preliminary Fourier projection of relative electron density on the *x*-*z* plane

$$p(x, y) = \Sigma h \Sigma l \; F_{(h0l)} \cos 2\pi(hx + lz)$$

was then made. This gave the approximate positions of the oxygen atoms so that the signs of most of the remaining reflections could be calculated and these added to the Fourier plot. The intensities of the strong reflections, which are observed relatively too weak due to extinction, were corrected using the method of Darwin.[11] The corrected intensity I_0 was obtained from the observed I using the formula $I = I_0/1 + gI_0$ with $g = 0.005$. The final Fourier plot, shown in Fig. 1, gave resolved peaks for the oxygen atoms from which their *x* and *z* parameters were obtained by reading maximum values of contour lines. The parameter values obtained from this projection are

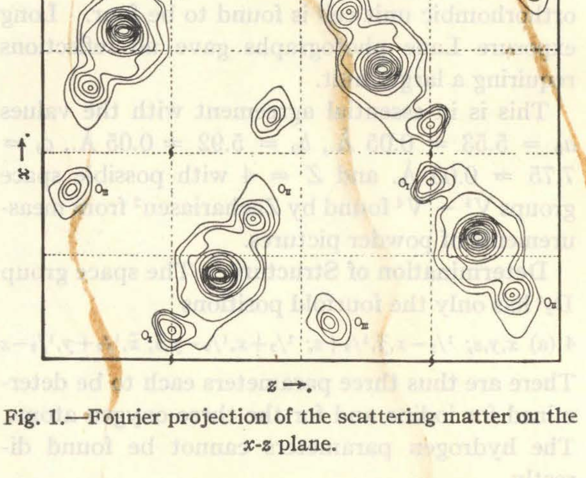

Fig. 1.—Fourier projection of the scattering matter on the *x*-*z* plane.

O_I: $x = 0.069$, $z = 0.250$; O_{II}: $x = 0.341$, $z = 0.090$
O_{III}: $x = 0.407$, $z = 0.447$

The *y*-parameters of the oxygen atoms were obtained from a Fourier projection of scattering matter on the *x*-*y* plane. The signs of the *F*'s for most of the reflections were determined by the iodine contribution alone and a preliminary projection made with these. This was then refined by adding the remaining reflections, a correction for extinction being applied as before. The projection is shown in Fig. 2. The peaks are not as well resolved as in the projection on (010) since O_{II}, O_{III}, and iodine fall close to one another. It was possible to correlate the two Fourier projections in the manner shown and so to derive the structure. The *y*-parameters for the three oxygen atoms and a check on the *x*-parameters are thus obtained. The values found are:

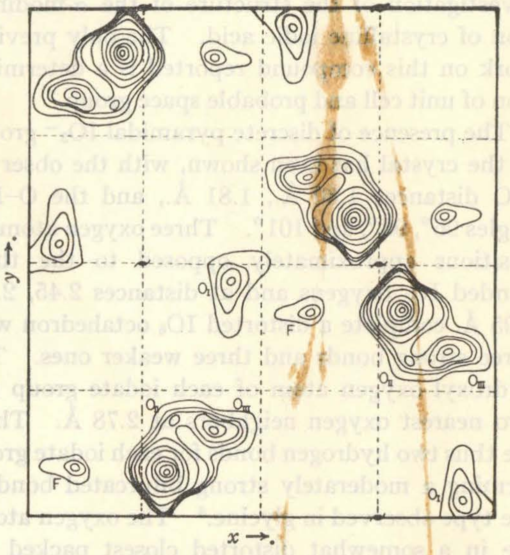

Fig. 2.—Fourier projection of the scattering matter on the *x*-*y* plane.

O_I: $x = 0.063$, $y = 0.534$; O_{II}: $x = 0.315$, $y = 0.193$
O_{III}: $x = 0.407$, $y = 0.173$

The peak marked *F* (Fig. 2) is believed to be false since any structure which could be derived interpreting it as due to an oxygen atom, and taking the *x* and *z* parameters from the Fourier projection on (010), was ruled out on spatial grounds. It also introduces serious discrepancies in the comparison of relative calculated intensities with observed values. This peak may arise from the incompleteness of the data for (*hk*0).

A confirmation of these parameter assignments and a more accurate value of the *y*-parameter for O_{II}, which was difficult to obtain from the projection on (001), was obtained by making a Fourier projection on (100). About 70 reflections (0*kl*) were used. The parameters obtained from this projection are

O_I: $y = 0.533$, $z = 0.242$; O_{II}: $y = 0.187$, $z = 0.086$
O_{III}: $y = 0.160$, $z = 0.458$

We thus have two independent estimates of each parameter agreeing with but one exception, to 0.01 Å. or better. Slight changes in some parameters were then made to give the best agreement with observed intensities. The final parameter values are shown in Table I.

TABLE I

	x	y	z
I	0.204 ± 0.002	−0.088 ± 0.002	0.156 ± 0.002
O_I	.068 ± 0.005	.534 ± 0.005	.250 ± 0.005
O_{II}	.340 ± 0.005	.195 ± 0.005	.090 ± 0.005
O_{III}	.407 ± 0.005	.170 ± 0.005	.447 ± 0.005

The values of F_{hkl} were calculated for all equatorial and for 75 *hkl* reflections using the Pauling–Sherman tables of *F*-values and a Debye–Waller temperature factor with $B = 1.0$.[11] Tables III and IV give observed and calculated *F*'s for approximately one-third of the experimental data used in the determination. The strongest reflections are usually observed somewhat weaker than they are calculated. That this is due to extinction was verified by estimating the intensities of some lines on the powder photograph. The observed amplitudes, shown in Table V, give the same relative values for strong and weak reflections as calculated. The empirical correction for extinction applied to the stronger amplitudes used in the final Fourier projections is therefore justified.

Discussion

The structure of iodic acid is shown in Fig. 3 and its projection on the *y-z* plane in Fig. 4.

The iodate group is pyramidal with the distances I–O_I = 1.81 Å., I–O_{II} = 1.89 Å., I–O_{III} = 1.80 Å., and O_I–O_{III} = 2.78 Å. O_{II}–O_{III} = 2.78 Å., O_I–O_{II} = 2.75 Å., giving the angles O–I–O the values 95°40′, 98°10′, 101°25′. The distances are probably not in error by more than

TABLE II[a]

VALUES OF F_{hkl}

(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.
(002)	50	70	(180)	28	18	(01, 12)	abs.	6	(102)	100	190
(004)	76	112	(1, 10, 0)	16	12	(021)	77	112	(104)	72	112
(006)	64	88	(210)	78	98	(023)	abs.	7	(106)	45	49
(008)	13	22	(230)	75	71	(025)	100	118	(108)	63	74
(00, 10)	57	66	(250)	17	17	(027)	57	52	(10, 10)	40	36
(00, 12)	42	45	(270)	abs.	10	(029)	37	28	(10, 12)	31	29
(00, 14)	abs.	8	(290)	25	22	(02, 11)	43	49	(10, 14)	39	43
(00, 16)	30	27	(220)	41	42	(022)	63	75	(10, 16)	abs.	4
(00, 18)	12	8	(240)	52	58	(024)	39	26	(10, 18)	23	16
(00, 20)	14	11	(260)	68	65	(026)	59	48	(10, 20)	18	11
(200)	77	134	(280)	16	14	(028)	24	10	(201)	46	59
(400)	35	35	(310)	64	90	(031)	75	100	(203)	63	66
(600)	10	10	(330)	15	18	(033)	91	146	(205)	36	29
(800)	43	34	(350)	47	50	(035)	35	19	(207)	43	45
(10, 00)	30	23	(370)	30	28	(037)	70	71	(209)	41	38
(12, 00)	17	24	(320)	102	105	(039)	68	60	(20, 11)	12	14
(020)	70	75	(340)	58	54	(03, 11)	abs.	5	(20, 13)	26	20
(040)	74	67	(360)	abs.	1	(032)	17	14	(20, 15)	16	9
(060)	84	67	(380)	25	31	(034)	abs.	11	(20, 17)	6	4
(080)	22	25	(011)	50	65	(036)	abs.	13	(20, 19)	15	10
(0, 10, 0)	30	26	(013)	71	110	(038)	abs.	5	(202)	50	45
(0, 12, 0)	17	18	(015)	45	31	(101)	49	66	(204)	77	120
(110)	91	180	(017)	58	46	(103)	40	50	(206)	73	93
(130)	36	41	(019)	53	42	(105)	44	39	(208)	11	7
(150)	90	77	(01, 11)	18	14	(107)	12	7	(20, 10)	44	43
(170)	57	49	(012)	80	155	(109)	22	19	(20, 12)	31	33
(1, 11, 0)	30	25	(014)	82	105	(10, 11)	20	20	(20, 14)	15	13
(120)	63	65	(016)	57	42	(10, 13)	7	9	(20, 16)	29	26
(140)	abs.	1	(018)	79	71	(10, 15)	6	6	(20, 18)	10	7
(160)	abs.	5	(01, 10)	22	26	(10, 17)	abs.	2	(20, 20)	10	6

[a] The X-ray photographs from which the (*hk*0) and (0*k*1) data were obtained were considerably less intense than the (*h*0*l*) pictures; hence the fact that some reflections (*hk*0) and (0*kl*) are not observed, in spite of the fact that the calculated *F*'s are larger than for reflections (*h*0*l*) which are observed, does not indicate a discrepancy between calculated intensities and experimental data.

TABLE III

VALUES OF F_{hkl}

(hkl)	Obsd.	Calcd.	(hkl)	Obsd.	Calcd.
(111)	71	75	(223)	51	50
(112)	50	46	(224)	69	58
(121)	92	106	(331)	68	76
(122)	56	52	(332)	78	79
(123)	103	125	(333)	14	12
(131)	103	135	(411)	81	93
(132)	41	35	(412)	47	46
(133)	39	35	(413)	30	31
(231)	71	72	(431)	24	24
(232)	42	41	(432)	33	31
(233)	100	106	(433)	38	41
(241)	81	83	(441)	36	37
(242)	57	54	(442)	32	47
(221)	85	100	(443)	32	47
(222)	69	71			

TABLE IV

VALUES OF F_{hkl} FROM A POWDER PHOTOGRAPH

(hkl)	Calcd.	Obsd.
(020)	73	72
(200)	134	142
(011)	65	55
(110)	179	150
(101)	66	59
(102)	190	172
(012)	155	146
(021)	112	100
(111)	75	78
(013)	110	99
(031)	100	115
(022)	75	70
(204)	120	122

±0.04 Å. or the angles by more than ±5°. Each iodine atom has, in addition to these three closest oxygen neighbors, three more at distances considerably less than the sum of the van der Waals radii, 3.55 Å. These are I–O′$_{\text{I}}$ = 2.45 Å., I–O′$_{\text{III}}$ = 2.70 Å., I–O″$_{\text{III}}$ = 2.90 Å. (the prime and double prime refer to the oxygen atoms of second and third iodate groups) (the next iodine–oxygen contacts are at 3.30 Å. and 3.45 Å.). These six nearest oxygen atoms form a distorted octahedron about the iodine atom; the angles between the four atoms approximately in a plane are 66°, 84°, 100° and 110°, while these make angles of 79°, 90°, 97° and 101° with O$_{\text{I}}$ at one apex. The longer I–O distances are intermediate between bonded and non-bonded values and so correspond to secondary bonds of the type formed in arsenolite and senarmontite.[9] The angles I–O–I = 114°, 131° and 138° for these weak bonds differ considerably from the tetrahedral value expected for two covalent bonds with oxygen but are not far from the tetrahedral single bond-double bond value—indeed they are close to the angles Sb–O–Sb = 116° and 132° observed in valentinite[13] where the Sb–O bond has less double bond character than the I–O$_{\text{I}}$, I–O$_{\text{III}}$ bonds here. Each iodine atom has six nearest neighbors, two at each of the

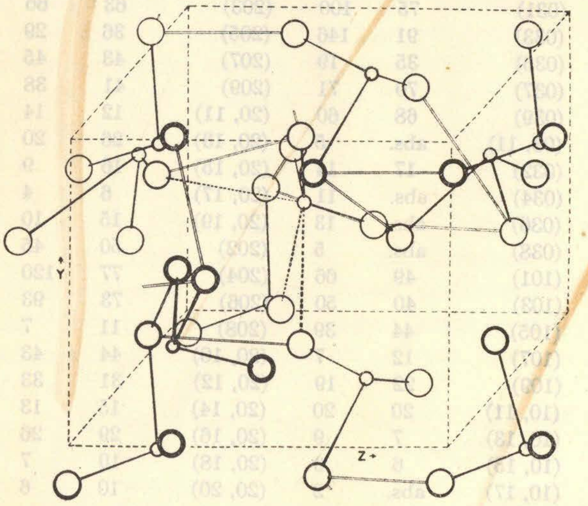

Fig. 3.—Crystal structure of the α-modification of iodic acid showing I–O bonds with solid lines and secondary (weak) I–O bonds with dotted lines. Hydrogen bonds between oxygen atoms are represented by double lines.

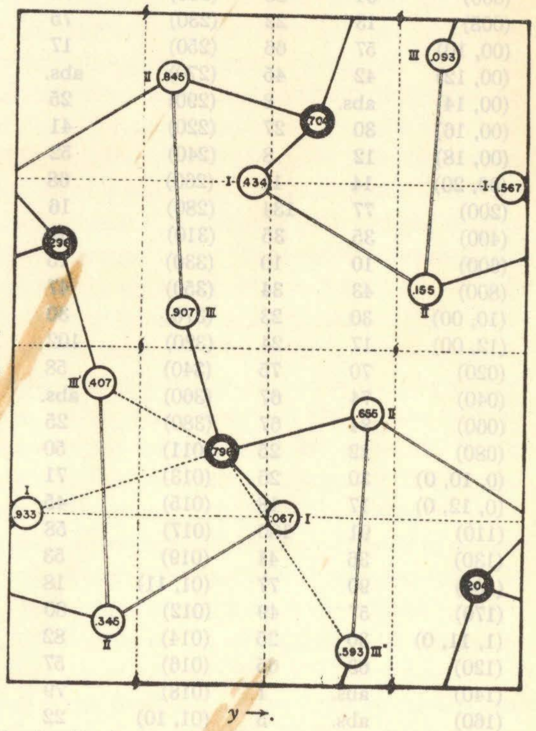

Fig. 4.—Projection of iodic acid structure on y-z plane. Bonds are designated as in Fig. 3. The numbers within the circles give the x-parameters.

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(13) M. J. Buerger and S. B. Hendricks, *Z. Krist.*, **98**, 1 (1937).

three distances 3.79 Å., 4.03 Å., and 4.13 Å. There is an oxygen atom of the distorted octahedron between each of the six iodine nearest neighbors and the central iodine atom but these are displaced both from the position central between the iodine atoms and from the line joining them. This is not a true distorted perovskite structure although it bears certain analogies to such an arrangement.

The observed closest I–I contacts are 0.20 Å. to 0.33 Å. less than the sum of the van der Waals radii, 4.30 Å. (the I–I contacts reported for KIO_2F_2 are 4.40 Å. and for the alkali iodates 4.45 to 4.65 Å.). This shortening is to be expected since the direction of the I–I contact makes only a small angle with either one or two covalent I–O bonds and the electron pairs which give the atom size in that direction are pulled in to form the bond, thus reducing the effective van der Waals radius. The oxygen–oxygen distances of 2.78 Å. between oxygen atoms of the same group are not abnormal for this reason. The partial double-bond character of the I–O bonds indicating the use of a second electron pair from the oxygen atom in the bond will further tend to reduce the oxygen radius in directions near that of the bond.

Each of the three types of oxygen atoms has a different set of iodine contacts which correspond to no simple arrangement. O_{II} has four nearest neighbors at 3.40 Å., 3.44 Å., 3.60 Å., 3.85 Å., O_{III} four at 2.70, 2.90, 3.70, and 4.30 Å. and O_I three at 2.45, 3.70, 4.00 Å. exclusive of the iodine atom of the group to which each belongs. The oxygen atoms form a nearly closest packed structure. There are twelve nearest neighbors for O_I, three at 2.78 ± 0.02 Å. and nine at 2.90, 3.00, 3.00, 3.07, 3.12, 3.20, 3.25, 3.32, 3.60 Å.; for O_{II} four at 2.78 ± 0.02 Å. and eight at 3.10, 3.13, 3.16, 3.16, 3.20, 3.35, 3.58, 4.12 Å.; for O_{III} three at 2.78 ± 0.02 Å. and nine at 2.90, 3.00, 3.00, 3.11, 3.14, 3.22, 3.37, 3.38, 4.30 Å. The formation of iodate groups and hydrogen bonds has considerably distorted the true hexagonal closest packed arrangement. The volume per oxygen atom is 2.1 cu. Å.

In addition to two oxygen contacts of 2.78 and 2.76 Å. within the group O_{II} has two neighbors O'_I and O''_{III}, one from each of two other groups, at 2.76 and 2.78 Å. Since the distance $I–O_{II} = 1.89$ Å., O_{II} may be considered to be the hydroxyl oxygen. It forms the two hydrogen bonds $O_{II}–H–O'_I$ and $O_{II}–H–O''_{III}$ of equal strength. The oxygen–oxygen distances indicate that the bifurcated bond is strong (there are here two bonds per iodate group each of which is about the strength of the single hydrogen bond in water and ice). The hydrogen atom was now given parameters such that the distance $O_{II}–H = 1.01$ Å., the angle $I–O–H = 109°$, and the $O_{II}–H$ bond bisected the $O''_{III}–O_{II}–O'_I$ angle. The parameters so derived are $x = 0.340$, $y = 0.300$ and $z = 0.197$ making the angles $O–H–O \cong 121°$. The hydrogen bonds along with the weaker iodine–oxygen bonds link the iodate groups together forming a relatively hard crystal (hardness = 3). The observed complete cleavage (101) breaks two hydrogen bonds and one of the two weakest I–O bonds; the incomplete cleavage (011) must also break the stronger I–O bond corresponding to the distance $I–O'_I = 2.45$ Å. The O–I–O angles, with an average value of 98° ± 3°, indicate that the orbitals involved in bonding are between *p*-orbitals (three at right angles to one another) and sp^3 (tetrahedral) orbitals. The radius of iodine may thus be taken as intermediate between the tetrahedral and octahedral radii, 1.27 Å. and 1.35 Å., respectively. Using the value 1.29 Å. the I–O single bond distance would be 1.95 Å. and the double bond distance 1.75 Å. Although there is nominally a formal charge of −1 on the iodine atom no correction to the radius value has been made for this since resonance with structures in which unshared electron pairs from the oxygen atoms form additional covalent bonds will leave the iodine neutral or perhaps with a slight residual positive charge. The observed interatomic distances within the group I–O = 1.80, 1.81 and 1.89 Å. thus correspond to a slight amount of double bond character for the bond to the hydroxyl oxygen and a large amount for the remaining oxygen atoms. The formation of the three weaker iodine–oxygen bonds might be expected to decrease the double-bond character of the oxygen atoms of the group and make the distances correspondingly longer as for the As–O bonds in arsenolite[9]; however, the sharing of oxygen atoms by SiO_4 tetrahedra in silica and the silicates and of PO_4 tetrahedra in the pyrophosphates causes no lengthening of the Si–O or P–O distances.[14] In KIO_2F_2[6] the distance I–O = 1.93 ± 0.05 Å. and the angles O–I–O = 100 ± 7° were observed.

The influence of the various factors in deter-

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(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 226.

mining the structure may now be seen clearly. The HIO_3 molecule contains essentially covalent bonds, the pyramidal shape of the IO_3 group being determined by the type of iodine orbitals used for the single bonds (*p*-orbitals with some *s* character). The hydrogen atom of the hyroxyl group might form either one strong hydrogen bond to one of the two remaining oxygen atoms (of another iodate group) or two weaker bonds, one to each of them; it actually forms the bifurcated bond. The iodine atom has less stable orbitals available to form additional octahedral bonds which it now can do partially by forming weak bonds with three oxygen atoms of other iodate groups. Since the hydroxyl oxygen (O_{II}) is not available for these bonds the iodine atom must form the three weak bonds with the remaining two oxygen atoms and it does this by forming one weak bond with one of them (O'_I) and two weaker bonds with the other (O'_{III} and O''_{III}).

Considering the relation of the structure of HIO_3 to that reported for the iodates it seems likely that in those crystals the oxygen atoms are displaced from the symmetry positions of the perovskite structure in such a manner as to form iodate groups. An investigation of one of the pseudocubic iodates using the proper monoclinic hemihedral space group and unit cell would settle this question.

The authors are indebted to Professor Linus Pauling for detailed discussion of this work and many helpful suggestions.

Summary

The structure of the α-modification of crystalline iodic acid has been determined. Laue and oscillation photographs show that the orthorhombic unit cell with $a_0 = 5.520 \pm 0.005$, $b_0 = 5.855 \pm 0.005$, $c_0 = 7.715 \pm 0.005$ contains four molecules of HIO_3. The space group is $D_2^4 - P2_12_12_1$. Patterson and Fourier projections on the three axial planes calculated from visually observed intensity data gave the twelve parameters for the oxygen and iodine atoms (Table II). The structure is an aggregate of HIO_3 molecules held together by hydrogen bonds of the bifurcated type and weak iodine oxygen bonds. Iodine atoms are surrounded by distorted octahedra of oxygen atoms and the oxygen atoms are in a nearly closest packed arrangement. The influence of the different types of bond on the structure has been discussed and its relation to the perovskite structure shown.

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The Following Tables of Data are appended to 'The Crystal Structure of Iodic Acid'

Table II.

Values of F_{hkl}

(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd
(002)	50	70	(310)	64	90	(630)	65	66
(004)	76	112	(330)	15	18	(650)	26	22
)006(	64	88	(350)	47	50	(670)	abs.	21
(008)	13	22	(370)	30	28	(690)	abs.	17
(0010)	57	66	(510)	abs.	3	(011)	50	65
(0012)	42	45	(530)	abs.	3	(013)	71	110
(0014)	abs.	8	(550)	abs.	15	(015)	45	31
(0016)	30	27	(710)	abs.	14	(017)	58	46
(0018)	12	8	(910)	29	27	(019)	53	42
(0020)	14	11	(120)	63	65	(01,11)	18	14
(200)	77	134	(140)	abs.	1	(031)	75	100
(400)	35	35	(160)	abs.	5	(033)	91	146
(600)	10	10	(180)	28	18	(035)	35	19
(800)	43	34	(1,100)	16	12	(037)	70	71
(1000)	30	23	(320)	102	105	(039)	68	60
(1200)	17	24	(340)	58	54	(0311)	abs.	5
(020)	70	75	(360)	abs.	1	(0313)	39	43
(040)	74	67	(380)	25	31	(051)	21	16
(060)	84	67	(520)	86	72	(053)	59	45
(080)	22	25	(540)	67	61	(055)	abs.	8
(010.0)	30	26	(560)	37	65	(057)	32	27
(0120)	17	18	(580)	40	35	(059)	abs.	17
(220)	41	42	(720)	47	44	(071)	20	24

Table II--con.

(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd
(240)	52	58	(740)	37	33	(073)	42	49
(260)	68	65	(810)	abs.	17	(075)	abs.	6
(280)	16	14	'830)	25	32	(077)	57	30
(420)	20	31	(10,10)	abs.	2	(079)	28	22
(440)	20	19	(210)	78	98	(091)	24	27
(460)	22	28	(230)	75	71	(093)	42	49
(620)	abs.	2	(250)	17	17	(095)	abs.	13
(640)	abs.	3	(270)	abs.	10	(097)	50	35
(820)	18	15	(290)	25	22	(011,1)	26	10
(1020)	16	10	(410)	50	50	(011,3)	abs.	7
(110)	91	180	(430)	86	79	(011,5)	abs.	1
(130)	36	41	(450)	23	24	(022)	63	75
(150)	90	77	(470)	36	33	(024)	39	26
(170)	57	49	(490)	47	33	(026)	59	48
(1,11,0)	30	25	(610)	37	37	(028)	24	10
(0210)	40	33	(010,1)	30	30	(10,10)	40	36
(042)	17	18	(012)	80	155	(10,12)	31	29
(044)	50	53	(014)	82	105	(10,14)	39	43
(046)	58	60	(016)	57	42	(10,16)	abs.	4
(048)	abs.	8	(018)	79	71	(10,18)	23	16
(0410)	22	32	(01,10)	22	26	(10,20)	13	11
(062)	50	41	(01,12)	abs.	6	(201)	46	59
(064)	69	60	(032)	17	14	(203)	63	66
(066)	75	73	(034)	abs.	11	(205)	36	29
(068)	abs.	1	(036)	abs.	13	(207)	43	45

Table II--con.

(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd
(0610)	28	38	(038)	ab.	5	(209)	41	38
(082)	ab.	4	(052)	77	87	(20,11)	12	14
(084)	ab.	16	654	71	65	(20,13)	26	20
(086)	ab.	20	(056)	46	21	(20,15)	16	9
(088)	ab.	3	(058)	68	68	(20,17)	6	4
(010,2)	26	10	(0510)	ab.	19	(20,19)	15	10
(010,4)	24	25	(072)	57	58	(202)	50	45
(021)	77	112	(074)	39	33	(204)	77	120
(023)	ab.	7	(076)	ab.	16	(206)	73	93
(025)	100	118	(078)	29	37	(208)	11	7
(027)	57	52	(092)	ab.	13	(20,10)	44	43
(029)	37	28	(094)	ab.	10	(20,12)	31	33
(02,11)	43	49	(096)	ab.	0	(20,14)	15	13
(041)	80	92				(20,16)	29	26
(043)	48	50	(101)	49	66	(20,18)	10	7
(045)	79	76	(103)	40	50	(20,20)	10	6
(047)	49	44	(105)	44	39	(301)	60	80
(049)	ab.	20	(107)	12	7	(303)	12	4
(0411)	36	46	(109)	22	19	(305)	77	95
(061)	20	23	(10,11)	20	20	(307)	44	46
(063)	ab.	3	(10,13)	7	9	(309)	31	31
(065)	ab.	1	(10,15)	6	6	(30,11)	42	40
(067)	ab.	4	(10,17)	ab.	2	(30,13	13	5
(069)	ab.	1	(10,19)	ab.	0	(30,15)	24	18

Table II--con.

(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd
(081)	79	56	(102)	100	190	(30,17)	20	14
(083)	ab.	5	(104)	72	112	(30,19)	ab.	2
(085)	32	45	(106)	45	49	(302)	73	98
(087)	ab.	27	(108)	63	74	(304)	50	49
(306)	23	15	(502)	10	4	(702)	40	35
(308)	50	56	(504)	23	14	(704)	20	15
(30,10)	25	18	(506)	ab.	2	(706)	ab	6
(30,12)	25	24	(508)	11	13	(708)	23	22
(30,14)	21	19	(50,10)	ab.	0	(70,10)	12	10
(30,16)	ab.	3	(50,12)	ab.	6	(70,12)	15	10
(30,18)	14	10	(50,14)	ab.	2	(70,14)	13	9
(30,20)	10	5	(50,16)	ab.	0	(70,16)	ab.	1
(402)	37	30	(50,18)	ab	1	(70,18)	6	6
(404)	34	30	(602)	ab.	2	(802)	22	23
(406)	47	42	(604)	23	19	(804)	28	26
(408)	ab.	2	(606)	15	10	(806)	32	30
(40,10)	20	23	(608)	ab.	2	(808)	ab.	5
(40,12)	17	14	(60,10)	ab.	4	(80,10)	29	29
(40,14)	ab.	4	(60,12)	8	7	(80,12)	21	17
(40,16)	12	10	(60,14)	ab.	4	(80,14)	ab.	2
(40,18)	ab.	2	(60,16)	ab.	6	(80,16)	13	9
(401)	55	49	(60,18)	ab.	0	(801)	41	32
(403)	80	106	(601)	54	45	(803)	52	37
(405)	29	29	(603)	79	71	(805)	7	4
(407)	60	66	(605)	22	15	(807)	34	20

Table II.--con.

(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd
(409)	49	49	(607)	47	51	(809)	26	24
(40,11)	abs.	7	(609)	40	41	(80,11)	abs.	3
(40,13)	37	35	(60,11)	abs.	3	(80,13)	23	14
(40,15)	20	14	(60,13)	33	29	(80,15)	13	8
(40,17)	12	12	(60,15)	20	11	(80,17)	12	4
(40,19)	18	11	(60,17)	10	8	(901)	34	20
(501)	73	84				(903)	5	9
(503)	33	26	(701)	66	61	(905)	30	27
(505)	70	87	(703)	10	5	(907)	18	10
(507)	50	50	(705)	54	50	(909)	abs.	8
(509)	34	31	(707)	27	23	(90,11)	17	10
(50,11)	45	46	(709)	26	28	(90,13)	6	4
)50,13)	11	5	(70,11)	34	35	(90,15)	9	9
(50,15)	23	21	(70,13)	12	11	(902)	51	37
(50,17)	25	17	(70,15)	18	13	(904)	40	31
(50,19)	abs.	0	(70,17)	18	9	(906)	15	14
						(908)	34	30
(90,10)	13	10	(12,01)	abs	7			
(90,12)	20	12	(12,03)	11	7			
(90,14)	23	12	(12,05	abs.	1			
(10.02)	18	13	(12,07)	8	4			
(10,04)	35	25	(12,09)	8	5			
(10,06)	54	34	(12,0,11)	abs.	1			
(10,08)	abs.	3	(13,01)	14	9			
(10,0,10)	29	22	(13.03)	5	4			
(10,0,12)	18	10	(13,05)	18	6			

Table II.--con.

(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd
(10,0,14)	6	4	(13,07)	8	5
(10,01)	ab.	7	(13,02)	20	13
(10,03)	12	10	(13,04)	16	9
(10,05)	ab.	0	(13,06)	ab.	2
(10,07)	ab.	5	(13,08)	16	11
(10,09)	7	4	(13,010)	5	3
(10,0,11)	ab.	0	(14,02)	7	3
(10,0,13)	6	4	(14,04)	7	4
(11,01)	8	0	(14,06)	11	5
(11,03)	ab.	0	(14,08)	ab.	0
(11,05)	ab.	2	(14,01)	8	6
(11,07)	ab.	2	(14,03)	14	10
(11,09)	ab.	1	(14,05)	ab.	0
(11,0,11)	ab.	0	(14,07)	8	6
(11,0,13)	ab.	0			
(11,02)	36	25			
(11,04)	30	25			
(11,06)	14	14			
(11,08)	34	22			
(11,0,10)	13	6			
(11,0,12)	15	9			
(11,0,14)	15	9			
(12,02)	12	10			
(12,04)	19	15			
(12,06)	26	19			
(12,08)	ab.	0			
(12,0,10)	15	11			
(12,0,12)	13	7			

Table III.

Values of F_{hkl}

(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd
(111)	71	75	(243)	39	37
(112)	50	46	(244)	48	51
(113)	42	35	(245)	62	61
(121)	92	106	(251)	62	63
(122)	56	52	(252)	67	69
(123)	103	125	253	30	34
(125)	32	24	221	85	100
131	103	135	222	69	71
132	41	35	223	51	50
133	39	35	224	69	58
134	35	28	331	68	76
135	80	104	332	78	79
142	66	66	333	14	12
143	93	98	334	67	61
144	53	48	335	71	59
145	29	20	336	34	29
146	37	34			
151	51	43	542	19	23
152	42	46			
153	33	30	544	28	38
154	52	55	513	65	59
155	30	29	523	13	17
156	60	65	411	81	93
161	26	22	412	47	46
162	77	74	413	30	31

Table III.--con.

(hkl)	Obs'd	Calc'd	(hkl)	Obs'd	Calc'd
163	abs.	16	414	46	50
164	47	56	415	51	63
261	22	22	416	34	36
262	35	29	431	24	24
263	43	46	432	33	31
264	37	46	433	38	41
231	71	72	434	57	59
232	42	41	435	abs.	11
233	100	106	436	60	72
234	45	38	441	36	37
235	18	15	442	63	67
241	81	83	443	32	47
242	57	54	444	44	38

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The Crystal Structure of Potassium Fluoroiodate, KIO_2F_2

BY LINDSAY HELMHOLZ AND M. T. ROGERS

Introduction

A complete knowledge of the crystal structure of potassium fluoroiodate should afford considerable evidence concerning the steric effect of unshared electron pairs in molecules and ions and concerning the influence of relative electronegativity on the interatomic distances. The structure determination has been carried out to investigate these questions. Unfortunately it has turned out that the number of parameters to be determined is so great that, although the general characteristics of the structure are certain, the accuracy of the determination permits us to make only qualitative remarks about the effects mentioned above.

It has been found that the $IO_2F_2^-$ group approximates an octahedral group with two of the positions unoccupied. A tetrahedral configuration for the ion, which might have been anticipated from the similarity of the unit dimensions of this crystal and those of KIO_4, is clearly impossible.

A distinction between oxygen and fluorine atoms or ions in the structure is suggested by the intensities and the interatomic distances, but it is impossible for us to insist on our assignment and so to give any detailed discussion of the influence of electronegativity on bond distance.

The observation that potassium iodate, formed by the hydrolysis of the compound in moist air, is oriented to a considerable extent on the surface of the fluoroiodate suggests (as is borne out by the structure) that the crystal resembles KIO_3 much more than KIO_4.

Procedure.—Potassium fluoroiodate was prepared by dissolving potassium iodate in concentrated hydrofluoric acid and allowing the resulting solution to stand until, after a few days, tabular crystals were precipitated. Some smaller crystals were formed for which the principal direction of growth was normal to the plate. Goniometric measurements showed the crystals to be identical with those described by Groth.[1] In order to prevent reaction of the crystals with atmospheric moisture they were coated with a layer of lacquer. Oscillation photographs were taken with CuK_α and MoK_α radiations and Laue photographs with continuous radiation ($\lambda_{\text{min.}} = 0.24$ Å.) from a tungsten target. Intensities were estimated visually using a calibrated scale and photographs of different exposure times. For the CuK_α pictures the influence of absorption was considered; for the Mo pictures the crystals were small enough so that the absorption correction was shown to be negligibly small.

Space Group and Unit Cell.—Laue photographs taken with the X-ray beam normal to the plates showed the Laue symmetry D_{2h}. The regular absences $h0l$, $h \neq 2n$ and $0kl$, $l \neq 2n$ were observed giving C_{2v}^5 and D_{2h}^{11} as possible space groups. A pyroelectric experiment which gave a positive result eliminated D_{2h} and established $C_{2v}^5 - Pca$ as the correct space group for the crystal.

The dimensions of the unit cell were found, from oscillation photographs, to be $a_0 = 8.38 \pm 0.02$ Å.; $b_0 = 5.97 \pm 0.02$ Å.; $c_0 = 8.41 \pm 0.02$ Å. The data from which these values were obtained are listed in Table I. The X-ray data give the axial ratios $a:b:c = 0.996:0.7098:1$ to be compared with the crystallographic axial ratios $a:b:c = 0.9925:2 \times 0.7074:1$ given by Groth.[1]

Assuming the density of the fluoroiodate to have a value close to the densities of potassium iodate (3.89 g./cm.^{3}) and periodate (3.61 g./cm.^{3}) the number of molecules in the orthorhombic unit was found to be four. The density calculated for four molecules per unit cell is 3.71 g./cm.^{3} Numerous Laue photographs of long exposure time showed no reflections requiring a large unit.

Determination of the Structure.—For the space group $C_{2v}^5 - Pca$ there exists only one set of positions, the general four-fold positions 4a):[2]

$x, y, z;\ \bar{x}, \bar{y}, \frac{1}{2} + z;\ \frac{1}{2} - x, y, \frac{1}{2} + z;\ \frac{1}{2} + x, \bar{y}, z.$

There are then three parameters to be determined for iodine and three for potassium. The eight fluorine atoms in the unit are to be placed in two sets of positions 4a, and the eight oxygen atoms also in two sets of the four-fold positions.

The first step in the structure analysis was the determination of the iodine parameters. For this

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[1] Groth, "Chemische Krystallographie," Teil II, Leipzig, 1908, p. 94.

[2] "Int. Tab. z. Bestimmung v. Kriststrukturen."

TABLE I

	a_0			b_0			c_0	
(h00)	a_0 (obsd.)	a_0 (calcd.)	0k0	b_0 (obsd.)	b_0 (calcd.)	00l	c_0 (obsd.)	c_0 (calcd.)
(200)	8.346	8.38	010	5.963	5.97	(002)	8.30	8.41
(400)	8.376		020	5.974		(004)	8.37	
(600)	8.382		030	5.990		(006)	8.47	
(800)	8.368		050	5.960		(008)	8.408	
(10,00)α_1	8.381		060	5.984		(00,10)α_1	8.412	
α_2	8.378		070α_1	5.978		α_2	8.409	
			α_2	5.974				

purpose a Patterson projection on the x–z plane was made using $h0l$ data. This projection (Fig. 1) shows strong peaks, corresponding to iodine–iodine interactions, at $x = \frac{1}{2}$, $z = 0$; $x = 0$, $z = \frac{1}{2}$; and $x = z = \frac{1}{2}$. This distribution can be accounted for only if the iodine parameters $x_1 = z_1 = 0$, or an arrangement equivalent to this. This assignment of parameters may be checked by a qualitative consideration of the intensities. The intensities of reflection from planes (hkl), with $h + l \neq 2n$ were observed to be very much weaker than the reflections with $h + l = 2n$ even for large values of h, k and l. For the iodine parameters $x_1 = z_1 = 0$ the iodine contribution to the intensities of the type of planes first mentioned is zero.

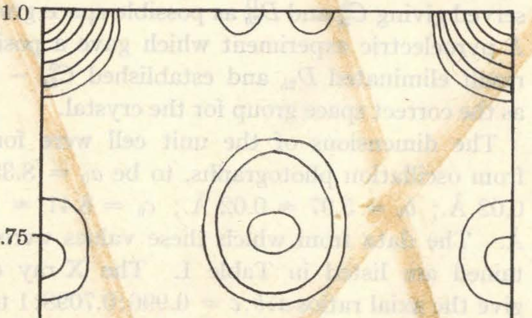

Fig. 1.—Patterson projection, $P(x,z)$, on x–z plane.

A Harker projection, $H(xy\frac{1}{2})$, making use of the two-fold screw axis parallel to z, was calculated as the next step in the determination. This gave a value for the y-parameter for iodine, $2y = 0.135$. Complete data were not used in preparing this projection but the final structure indicates that the 200 important reflections which were used gave a very reliable value for the parameter. No other use was made of the projection.

Since the projection of the scattering matter in the cell on the x–y plane contains a center of symmetry it was profitable next to make a Fourier projection on this plane using the ($hk0$) data. The signs of the F's for all strong reflections are unambiguously determined by the iodine contribution, so that, starting with these reflections, a complete Fourier projection could be made by a process of successive approximations. From the first of these the potassium ions were found to have $x \approx 0.25$, $y \approx 0.50$.

As long as only reflections to which iodine contributes were used, a plane of symmetry, not present in the crystal, persists along a line $x = 0$. The strongest F to which iodine does not contribute, F_{310}, was next introduced arbitrarily with positive sign. The introduction of this single F_{310} destroys the plane of symmetry and permits the assignment of approximate x and y parameters for potassium ions, fluorine and oxygen atoms. The final projection, shown in Fig. 2, was obtained by including all the $F_{(hko)}$'s in the Fourier series. The letters refer to the atoms with parameter z, the primed letters to equivalent atoms at $z + \frac{1}{2}$. The c-glide planes are indicated by dotted lines, the a-glide plane by the dashed line. Contour lines have been drawn at 20, 30, 40, 50, 100, 150, 250, and 350 on an arbitrary scale.

Figure 2 shows clearly the iodine atoms at I and

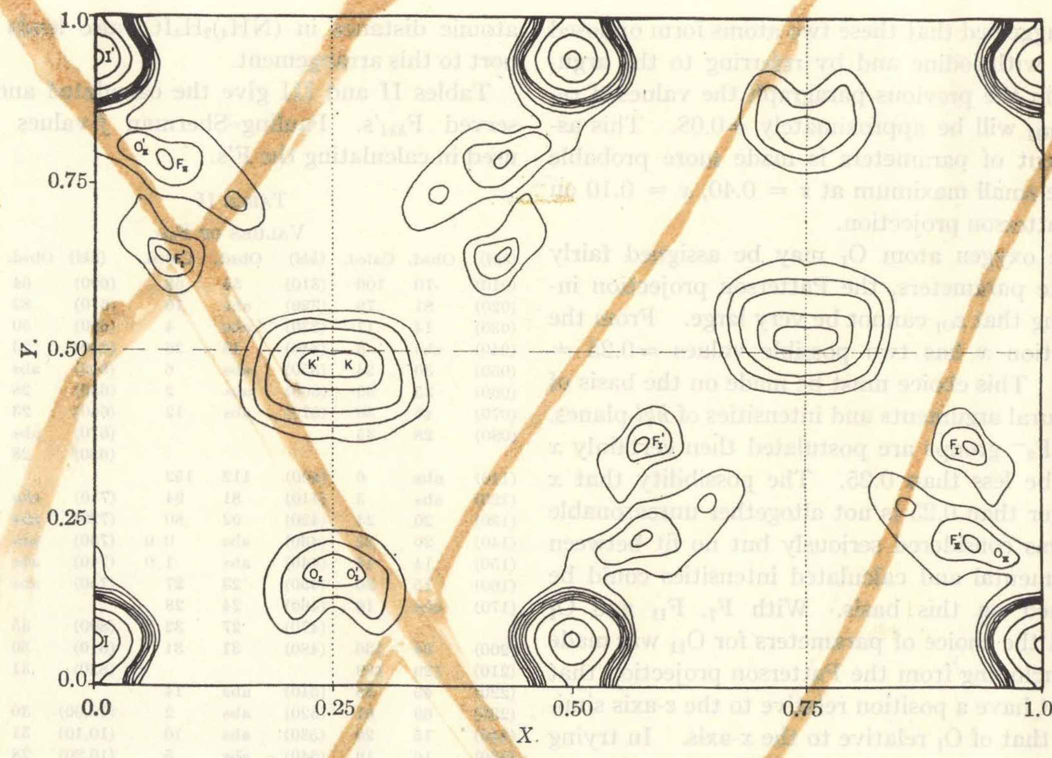

Fig. 2.—Fourier projection of scattering matter on (001) face.

I′. The peak K (and K′) is unresolved and due to equivalent potassium ions at *xyz* and $\frac{1}{2} - x, y, z + \frac{1}{2}$. The differentiation of oxygen and fluorine atoms cannot be made on the basis of the projection, and evidence for the distinction finally made is not entirely conclusive but the discussion will be continued on the basis of the final assignment and it will be borne in mind that an exchange of oxygen atoms for fluorine in the structure is possible within the limits of error of the X-ray data. The unresolved peak at O_I (O_I') is due to oxygen atoms and the clearly defined maximum at F_I can be identified as a fluorine atom. The remaining somewhat diffuse maximum in the neighborhood of F_{II} and O_{II} is believed to be due to the superposition of two maxima.

The atoms were given *x*- and *y*-parameters as indicated by the lettering of the maxima and as seem reasonably definite from the size of the maxima for all cases except that of O_{II}. Two possible positions for this atom are compatible with the projection; (1) the maximum corresponding to O_{II} lies so close to I that it is not observed, or (2) the maximum for O_{II} is part of the O_{II}–F_{II} maximum which is unresolved. A decision in favor of the second alternative was made with reasonable certainty on the basis of the intensities of reflection which are independent of the iodine atoms.

The evaluation of the *z* parameter was carried out by making use of the general characteristics of the X-ray spectra, the Patterson projection, and structural arguments as outlined below. It is seen (most clearly on Laue photographs) that, for all pairs of reflections (*hkl*) and (*lkh*) having the same type of structure factor, the intensities are very nearly equal for all values of *h* and *l*. This fact together with the evidence of the Patterson projection indicates that a projection of the scattering matter on the *x*–*z* plane has approximately tetragonal symmetry.

If F_I is associated with any iodine atom it must be bonded to I and not to I′ since the projection of the distance $I' - F_I$ on the *x*–*y* plane (see Fig. 2) is greater than could correspond to an iodine–oxygen bond. The projection places another fluorine atom at F_{II}, which might be bonded to I′ as far as the projection is concerned. If this were the case and if $I - F_I$ were equal to $I' - F_{II}$ then the projection of the interatomic distance on the *x*–*z* plane should show up on the Patterson projection where no maximum is observed. Since F_{II} is the same distance from I as F_I and lies on a straight line through I and F_I (in the projection) it is suggested that these two atoms form opposed bonds with iodine and by referring to the argument in the previous paragraph the values of x_{F_I} and $x_{F_{II}}$ will be approximately ±0.08. This assignment of parameters is made more probable by the small maximum at $z = 0.40$, $x = 0.10$ on the Patterson projection.

The oxygen atom O_I may be assigned fairly definite parameters, the Patterson projection indicating that z_{O_I} cannot be very large. From the projection x has two possible values $\approx 0.25 \pm 0.025$. This choice must be made on the basis of structural arguments and intensities of *hkl* planes. If $IO_2F_2^-$ groups are postulated then certainly x must be less than 0.25. The possibility that x is larger than 0.25 is not altogether unreasonable and was considered seriously but no fit between experimental and calculated intensities could be obtained on this basis. With F_I, F_{II} and O_I placed the choice of parameters for O_{II} was made by concluding from the Patterson projection that it must have a position relative to the z-axis similar to that of O_I relative to the x-axis. In trying to find the proper parameters the iodine to fluorine distances were considered to be equal, as were the iodine to oxygen distances.

The potassium parameters were determined roughly from the projections and then refined by comparison of observed and calculated intensities. The parameters were varied subject to the condition that distances from potassium to oxygen and fluorine be larger than 2.60 Å.

The atomic positions fixed by the means described in the previous paragraphs were finally varied by small amounts (0.005 to 0.01) to obtain the best fit between experimental and observed intensities. The resulting parameters are given below:

	x	y	z
I	0.00	0.067 ±0.001	0.00
K	.215 ±0.005	.465 ± .005	.29 ±0.005
F_I	− .08 ± .01	.355 ± .01	.09 ± .01
F_{II}	.08 ± .01	− .22 ± .01	− .09 ± .01
O_I	.215 ± .01	.175 ± .01	.035 ± .01
O_{II}	− .02 ± .01	.19 ± .01	.210 ± .01

The atoms occupying the positions F_I and F_{II} it was felt must be the same, either oxygen or fluorine. The position of these atoms is fairly well fixed and it is found that the agreement is considerably better for some of the weak reflections if fluorine atoms are placed in positions F_I and F_{II}. The fact that the I–O distance for this assignment is so closely equal to the same interatomic distance in $(NH_4)_2H_3IO_6$ also lends support to this arrangement.

Tables II and III give the calculated and observed F_{hkl}'s. Pauling–Sherman *f*-values were used in calculating the F's.

TABLE II

VALUES OF F_{hkl}

(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.
(010)	70	100	(310)	54	68	(600)	64	56
(020)	81	79	(320)	abs	10	(610)	82	89
(030)	14	17	(330)	abs	4	(620)	50	52
(040)	abs	6	(340)	18	26	(630)	23	19
(050)	30	24	(350)	abs	6	(640)	abs	7
(060)	35	30	(360)	abs	2	(650)	28	24
(070)	46	50	(370)	abs	12	(660)	23	30
(080)	28	35				(670)	abs	25
						(680)	28	30
(110)	abs	6	(400)	112	152			
(120)	abs	3	(410)	81	94	(710)	abs	1
(130)	20	24	(420)	92	80	(720)	abs	5
(140)	26	28	(430)	abs	0.0	(730)	abs	1
(150)	14	15	(440)	abs	1.0	(740)	abs	4
(160)	15	20	(450)	23	27	(750)	abs	1
(170)	abs	16	(460)	24	28			
			(470)	27	32	(800)	35	42
(200)	94	136	(480)	31	31	(810)	50	54
(210)	129	169				(820)	31	32
(220)	45	35	(510)	abs	14			
(230)	69	61	(520)	abs	2	(10,00)	36	50
(240)	15	20	(530)	abs	10	(10,10)	31	28
(250)	16	19	(540)	abs	5	(10,20)	28	27
(260)	38	43	(550)	abs	8			
(270)	37	43				(12,00)	abs	22
(280)	33	27				(12,10)	23	34

TABLE III

VALUES OF F_{hkl}

(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.	(*hkl*)	Obsd.	Calcd.
002	87	145	(801)	abs	9	(211)	30	30
004	98	148	(802)	63	55	(212)	85	94
006	68	70				(213)	23	24
008	56	49				(214)	100	126
00,10	29	61	(111)	71	78	(215)	abs	3
			(112)	abs	10	(216)	69	80
(201)	10	8	(113)	55	76	(217)	abs	14
(202)	130	172	(114)	abs	29	(218)	50	50
(203)	53	65	(115)	52	57			
(204)	88	89	(116)	abs	12	(221)	25	33
(205)	abs	14				(222)	102	134
(206)	73	68	(121)	83	98	(223)	abs	13
			(122)	37	46	(224)	49	64
(208)	50	62	(123)	70	89	(226)	49	64
			(124)	abs	5	(228)	38	45
(401)	33	47	(125)	78	96			
(402)	84	91	(126)	abs	16	(231)	23	25
(403)	abs	31	(127)	39	50	(232)	32	33
(404)	119	128	(128)	abs				
(405)	25	22						
(406)	74	80	(131)	98	131			
			(132)	12	28			
			(133)	106	105			
(601)	22	33						
(602)	80	73						
(603)	27	32	(141)	125	103			
(604)	65	83	(142)	abs	9			
(605)	abs	22	(143)	101	83			
(606)	65	68						
(608)	45	45						

As an additional check on the parameters the ratio of intensities I_{hkl}/I_{lkh} were compared with the calculated intensity ratio. Since the interplanar distances d_{hkl} and d_{lkh} are so nearly equal quantitative use could be made of the Laue intensities for such pairs of reflections. Reflections with $n\lambda$ in the neighborhood of the critical absorption limit for iodine were not used in these comparisons. The intensities were estimated visually with the use of a calibrated scale. Table IV gives the results.

TABLE IV

hkl	I_{hkl}/I_{lkh} obsd.	I_{hkl}/I_{lkh} calcd.
1 (415)	15.0	13.10
2 (611)	5.5	4.22
3 (613)	2.4	2.02
4 (614)	1.0	0.98
5 (615)	7.5	6.30
6 (617)	7.5	10.8
7 (811)	4.5	4.5
8 (813)	3.5	4.9
9 837	2.0	30.0[a]
10 429	8.0	6.2

[a] The calculated F's for both reflections are so small for this case 5.7 and 1.0 that a very small error in parameters makes a very large error in the calculated intensities.

Discussion of the Structure.—The crystal structure derived from the above parameters is shown in Fig. 3. The fluoroiodate ion, as shown in the figure, consists of a central iodine atom forming bonds to two fluorine and two oxygen atoms. The fluorine atoms lie on a straight line through the iodine atom and may be thought of as forming opposed bonds. The oxygen atoms lie in a plane perpendicular to the I–F bonds and form bonds with the iodine atom at about 100°. This arrangement gives the group as a whole the appearance of an octahedron with two of the corners removed. It may perhaps better be thought of as a trigonal bipyramid in which one of the three equivalent orbitals is occupied by an unshared pair and the angle between the remaining two decreased from 120 to approximately 100°. The interatomic distances are: $I–O_I = 1.93 \pm 0.05$ Å.; $I–O_{II} = 1.92 \pm 0.05$ Å.; $I–F_I = 2.00 \pm 0.05$ Å.; $I–F_{II} = 1.99 \pm 0.05$ Å.; $O_I–O_{II} = 2.85 \pm 0.10$ Å.; and the angle $O_I–I–O_{II} = 100 \pm 7°$. The fluorine–oxygen contacts are the same within the limits of error and equal to 2.75 ± 0.10 Å.

This configuration of the $IO_2F_2^-$ group is the same, within the limits of error, as that reported by Stevenson and Schomaker[3] for $TeCl_4$ in which the unshared pair of electrons has apparently the same steric effect as in the $IO_2F_2^-$ ion.

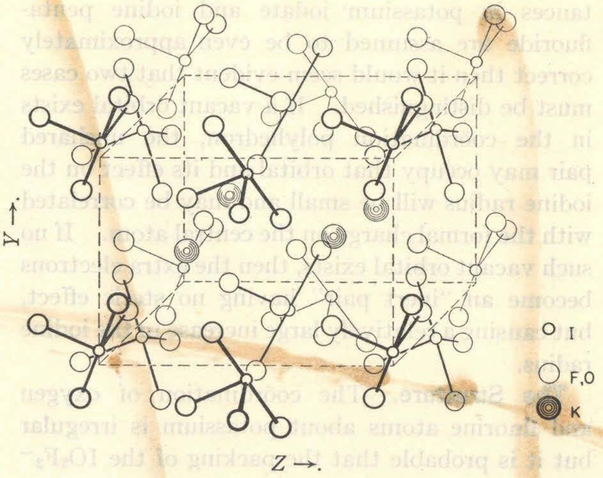

Fig. 3.—Structure of potassium fluoroiodate.

The effect of the unshared pair of electrons on the bond distances may be discussed by comparing the effective iodine radius in this compound with the iodine radii in other related compounds. The data for a number of these compounds are shown in Table V. The table shows that a considerable decrease in the effective iodine radius can be correlated with an increase in formal charge. Since the unshared pair in $IO_2F_2^-$ contributes the same number to the formal charge of iodine as the two additional electron pair bonds in IO_6^{5-} the I–O distances in the two ions might be expected to be nearly the same. The iodine radii for the cases of the iodates and of IF_5 seem to be much too large to be accounted for on the assumption that the radius is a simple function of the formal charge. It is true, however, that the determinations of these two distances are not completely reliable, and satisfactory answer has not yet been given to the question of the existence of discrete IO_3^- ions in iodate crystals.

TABLE V

Compd.	I − X, Å.	Configuration	Formal charge	I-radius
KIO_4[a]	2.23	Octahedral	+3	1.18
$(NH_4)_2H_3IO_6$[b]	1.93	Octahedral	+1	1.27
KIO_2F_2	1.93 (O)	Octahedral or	+1	1.27
	2.00 (F)	trig. bipyr.	+1	1.36
IF_5[c]	2.56	Trig. bipyr.	0	1.90
$KICl_4$[d]	2.34	Octahedral	−1	1.35
KIO_3[e]	2.23	Octahedral	−1	1.58

[a] E. A. Hazelwood, *Z. Krist.*, **98**, 439 (1938).
[b] L. Helmholz, THIS JOURNAL, **59**, 2036 (1937).
[c] Braune and Pinnow, *Z. physik. Chem.*, **35**, 239 (1937).
[d] R. C. L. Mooney, *Z. Krist.*, **98**, 377 (1938).
[e] Zachariasen, *Phys. Rev.*, **37**, 1626 (1931).

If the iodine–oxygen and iodine–fluorine dis-

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(3) D. P. Stevenson and Verner Schomaker, THIS JOURNAL, **62**, 1267 (1940).

tances in potassium iodate and iodine pentafluoride are assumed to be even approximately correct then it would seem evident that two cases must be distinguished. If a vacant orbital exists in the coördination polyhedron, the unshared pair may occupy that orbital and its effect on the iodine radius will be small and may be correlated with the formal charge on the central atom. If no such vacant orbital exists, then the extra electrons become an "inert pair" having no steric effect, but causing a relatively large increase in the iodine radius.

The Structure.—The coördination of oxygen and fluorine atoms about potassium is irregular but it is probable that the packing of the $IO_2F_2^-$ groups is the determining factor in the structure. The K–O and K–F contacts are: $O_I - K = 2.75$, 2.76 Å.; $O_{II} - K = 2.63$, 3.03 Å.; $F_I - K = 2.64$, 3.06 Å.; $F_{II} - K = 2.74$, 3.04 Å.

The interatomic distances which are less than 3.50 Å. between oxygen and fluorine atoms of different anion groups are: $F_I - F_{II} = 2.77$, 3.23 Å.; $F_I - O_{II} = 3.40$ Å.; $F_{II} - O_I = 3.24$ Å.

There are, in addition, two distances between iodine atoms and oxygen atoms in different $IO_2F_2^-$ groups that are shorter than three Ångströms: $I\text{–}O_I = 2.82$ Å.; $I\text{–}O_{II} = 2.88$ Å.

The similarity between this structure and that reported for potassium iodate may be seen if one considers an altered KIO_2F_2 in which the I–O contacts just mentioned are made real bonds so that each oxygen atom is shared between two iodine atoms. If, then, the iodine atoms and bonds to oxygen atoms are placed in the x–z plane, then this plane will be identical with a plane $z = 0$ for the potassium iodate structure. In this altered structure the I–F bonds will be in a vertical position along the lines $x = z = 0$, etc. If now one atom of oxygen is substituted for two atoms of fluorine and this atom shared between two iodine atoms the structure would become the cubic structure attributed to potassium iodate. It is suggested that the similarity, although not very great, is sufficient to cause the orientation effects observed on photographs of KIO_2F_2 in which some of the salt had hydrolyzed. The powder lines had quite definite maxima at positions corresponding to the equator and layer lines for potassium iodate oriented with the cube edges parallel to the orthorhombic axes of KIO_2F_2.

Summary

From a determination of the crystal structure of KIO_2F_2 it has been found that the $IO_2F_2^-$ group is composed of an iodine atom forming bonds at approximately 100° with two oxygen atoms, and perpendicular to the plane of these three atoms, two opposed bonds at 180° to fluorine. The configuration may perhaps best be thought of as that of a trigonal bipyramid in which one of the three equivalent orbitals is occupied by an unshared electron pair. The interatomic distances in the ion were found to be: $I - O = 1.93 \pm 0.05$ Å.; $I - F = 2.00$ Å. ± 0.05 Å. The O–I–O bond angle $= 100 \pm 10°$. The influence of the unshared pair on the bond distance is discussed.

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[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 762]

A Redetermination of the Parameters in Ammonium Bifluoride

By M. T. Rogers and L. Helmholz

Introduction

The structure of ammonium bifluoride has been determined by Pauling,[1] who gave approximate values of the parameters obtained with the use of the data of Hassel and Luzanski.[2] He found a hydrogen-bonded structure with each nitrogen atom surrounded by four fluorine atoms at tetrahedral corners, the mean N–F distance being 2.76 ± 0.06 Å. and the F–F distance 2.37 ± 0.10 Å. The value we have found[3] for the F–F distance in KHF_2, 2.26 ± 0.01 Å., is equal to Pauling's value of the distance in NH_4HF_2 to within its limits of error, so it is not possible to say whether or not the distance has been increased by the formation of two additional hydrogen bonds in NH_4HF_2. For this reason a more accurate determination of this distance has been made. The unit translations found by Hassel and Luzanski[2] and the parameters given by Pauling[1] have been revised and the limits of error reduced. From these new values the F–F and N–F distances have been calculated to be F–F = 2.32 ± 0.03 Å. and N–F = 2.82 ± 0.03 Å. The weakening of the F–F bond in the formation of two hydrogen bonds in passing from KHF_2 to NH_4HF_2 is thus shown to exist; the increase in bond length amounts to 0.06 ± 0.04 Å. The space group D_{2h}^7 used by Pauling has been confirmed by the absence of reflections of the type (*h0l*), *h* odd, observed by Hassel and Luzanski.

Experimental Method and Results

Oscillation photographs about the *c* and *a* axes were taken of crystals of orthorhombic NH_4HF_2 prepared by evaporation of solutions of NH_4HF_2 in glacial acetic acid.

The space group was shown to be D_{2h}^7 by the

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(1) L. Pauling, *Z. Krist.*, **(A) 85**, 380 (1933).

(2) O. Hassel and N. Luzanski, *Z. Krist.*, **83**, 448 (1932).

(3) L. Helmholz and M. T. Rogers, This Journal, **61**, 2590 (1939).

absence of reflections of type ($h0l$), h odd, and ($hk0$), h and k odd. The reflection (102) reported by Hassel and Luzanski, which would eliminate this group, was sought but not observed on any photographs. This justifies the choice made by Pauling. The unit cell contains four molecules and the dimensions of the unit were found to be

$$a_0 = 8.426 \pm 0.020 \text{ Å.};\ b_0 = 8.180 \pm 0.020 \text{ Å.};\ c_0 = 3.69 \pm 0.05 \text{ Å.}$$

The first two are from oscillation photographs, the third from layer line measurements. Data giving a_0 and b_0 are shown in Table I. These correspond to axial ratios $1:0.971:0.438 = a_0:b_0:c_0$ compared by goniometric values $1:0.977:0.444 = a_0:b_0:c_0$ (Groth).

TABLE I

EQUATORIAL MEASUREMENTS

(hkl)	d_{obsd}. Å.	a_0 obsd. Å.
400	2.105	8.421
600	1.405	8.434
800	1.053	8.424
1000	0.0842	8.423
	Average a_0	8.426
020	4.097	8.195
040	2.045	8.180
060	1.362	8.172
080	1.022	8.177
	Average b_0	8.180

The relative intensities of all observed reflections were estimated visually using a calibrated scale.

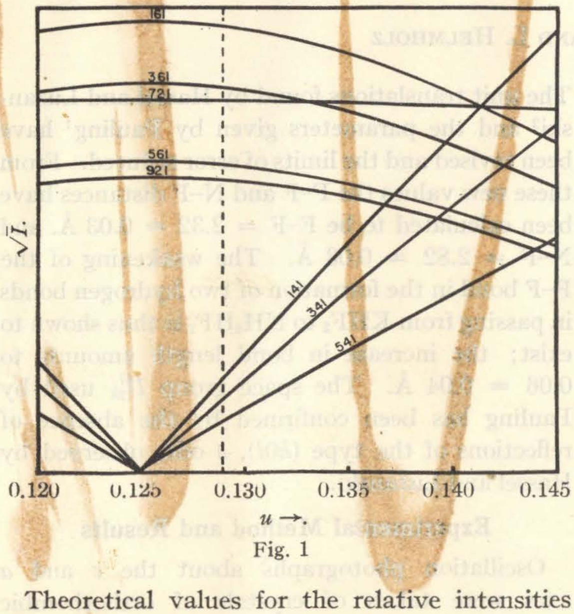

Fig. 1

Theoretical values for the relative intensities were calculated using the formula

$$I = C \frac{1 + \cos^2 2\theta}{\sin 2\theta} F^2 \exp -3.0 \left(\frac{\sin \theta}{\lambda}\right)^2$$

where F is the structure factor and $\exp -3.0 \left(\frac{\lambda}{\sin \theta}\right)^2$ the temperature factor. The structure factors for the four classes of planes are

I $F = 4f_F \sin 2\pi ku \sin 2\pi lv$ for h odd, k even

II $F = 4f_{NH_4} \cos 2\pi \left(\frac{h+k}{4} + lz\right) - 4f_F \sin 2\pi ku \sin 2\pi lv$ for h even, k odd

III $F = 4f_F(\cos 2\pi hw - \cos 2\pi ku \cos 2\pi lv)$ for h odd, k odd

IV $F = 4f_{NH_4} \cos 2\pi \left(\frac{h+k}{4} + lz\right) + 4f_F(\cos 2\pi kw + \cos 2\pi ku \cos 2\pi lv)$ for h even, k even

The f values used were those of Pauling and Sherman.[4] The intensities of reflections ($h00$) depend only on parameter w, and of reflections ($0k0$) only on parameter u, and a rough determination of these parameters might have been made using the observed ($h00$) and ($0k0$) intensities. The intensities of these reflections, however, are so sensitive to the choice of f values for F^- and NH_4^+ that little confidence was felt in the determination carried out from this starting point, and, indeed, the parameters thus obtained led to marked discrepancies between calculated and observed intensities for planes of different types.

To overcome this difficulty the determination was carried out in the following manner. The parameter u was determined first using observed intensities for planes of class I with $l = 1$. The factor $\sin v$ is known closely enough from Pauling's determination of $v = 0.135 \pm 0.01$ since it enters only as a common factor. The calculated intensities are plotted as functions of u in Fig. 1. The value $u = 0.131 \pm 0.002$ is found.

Accepting this value of u it is now possible to choose the f values for NH_4^+ which will account for the observed intensities of ($0k0$) planes. The appropriate f_{NH_4} values were found to be close to the values used by Pauling.[1] Experimental values of f_{NH_4} have been obtained by Wyckoff and Armstrong[5]; a comparison of these values with those we have used is shown in Table II.

TABLE II

Sin Θ/λ	0.1	0.2	0.3	0.4	0.5	0.6	0.7
f_{NH_4} (Pauling)	8.11	6.01	3.96	2.65	1.99	1.68	1.55
f_{NH_4} (Hartree)	6.7	4.4	3.1	2.50	2.0	1.65	1.65
f_{NH_4} (used)	7.7	5.64	3.70	2.43	2.00	1.68	1.55
f_{NH_4} (Wyckoff)	8.8	5.5	3.1	1.8	1.2		

We next obtained an approximate value of w, 0.137 ± 0.004, from reflections ($h00$). The value of v was obtained by comparing intensities of

(4) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(5) Wyckoff and Armstrong, *ibid.*, **72**, 319 (1930).

planes of Class I with varying values of l, using the value found for u. The calculated intensities plotted as functions of v are shown in Fig. 2. Planes with $k = 2, 6, 10$ were used since these vary negligibly with u in the allowed range for that parameter.

The value $v = 0.131 \pm 0.003$ was obtained in this way. A more accurate value of w was then found using intensities of reflections of type III with $l = 0$, which depend only on u and w. Plots were made of the calculated intensities as functions of both u and w for these planes and values of these parameters giving the best agreement with observed intensities were taken. To account for the observed intensity ratios of 910:930:350:530 it was found necessary to use the lower limit for u ($u = 0.129$). The value of w chosen was $w = 0.137 \pm 0.002$. This choice was confirmed by plotting calculated intensities for reflections of type III with $l = 1$ as functions of w using previously obtained values of u and v.

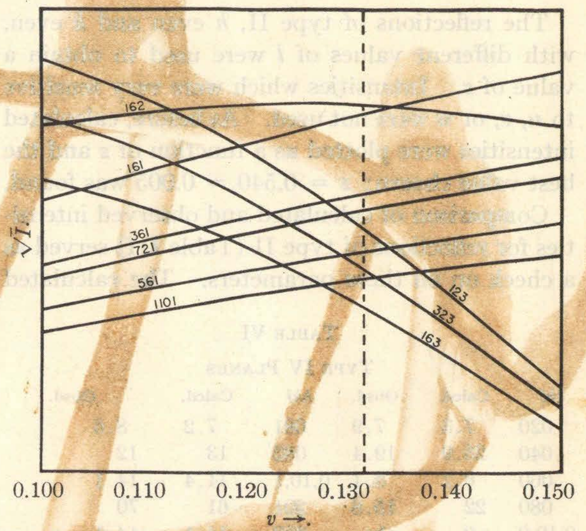

Fig. 2

TABLE III

TYPE I PLANES

hkl	Calcd.	Obsd.	*hkl*	Calcd.	Obsd.
121	32	33	921	5.4	4.5
141	1.9	2.3	122	20.5	14
161	8.4	7.4	142	1.4	1.2
181	1.2	abs.	162	8.5	6.7
1,10,1	5.0	4.1	322	12.5	14
321	20.5	20	342	1.1	abs.
341	1.4	1.8	362	7.8	4.0
361	6.8	6.6	123	7.0	5.4
521	11.2	14	143	0.8	1.0
541	1.0	abs.	163	4.7	4.1
561	5.6	4.5	323	5.6	4.4
721	6.4	5.7	343	0.5	abs.
741	0.6	abs.	363	4.6	2.5
761	5.3	4.0			

TABLE IV

TYPE II PLANES

hkl	Calcd.	Obsd.	*hkl*	Calcd.	Obsd.
011	20.4	18.7	012	27.7	30
031	22	26.5	032	7.9	7.9
051	12.6	10	052	4.6	4.2
071	2.2	abs.	072	7.5	8.2
211	31	36	092	9.2	10
231	9	11	212	7.8	6.1
251	5.7	7.1	232	15.6	17.8
271	5.2	6.3	252	11.7	11.6
291	6.1	4.4	272	1.4	abs.
411	8.9	7.1	013	0.2	abs.
431	11.3	14.1	033	8.5	10
451	8.1	9.2	053	7.9	8.5
471	1.8	2.0	073	1.1	5
611	8.5	10.0	213	9.7	11
631	3.3	3.1	233	0	abs.
651	3.2	3.1	253	0.8	abs.
671	4.6	3.6	273	6.6	7.1
811	2.8	1.1	014	4.1	7.5
831	5.2	5.1	034	5.2	4.1
851	6.2	3.4	054	5.5	5.4
10,1,1	5.3	5.0	214	4.4	1.4
			234	4.1	5.2

TABLE V

TYPE III PLANES

hkl	Calcd.	Obsd.	*hkl*	Calcd.	Obsd.
110	3.7	4.2	931	4.6	4.9
310	67	61	151	17.7	23
510	22.5	30	351	5.6	7.7
710	2.6	3.3	551	0.2	abs.
910	4.4	3.3	751	10.5	8.6
130	63	61	171	0.2	abs.
330	2.6	4.0	371	12.4	11
530	5.5	5.8	571	8.3	8.1
730	15.2	17	771	2.0	abs.
930	6.6	7.3	191	1.6	3.6
150	25	37	391	9.6	7.4
350	3.6	4.3	112	16.8	16.7
550	2.0	abs.	312	13.9	14
750	11.7	11.5	132	10.6	14
950	5.2	5.0	332	11.0	7.5
170	1.6	abs.	152	6.7	5.8
370	14.5	15.3	352	6.7	5.8
570	9.4	10.2	172	5.4	2.5
770	0.3	abs.	372	5.7	5.8
190	0.9	abs.	113	12.8	13
390	10.3	8.4	313	2.8	4
590	w+	6.0	133	0.6	2.5
111	10.4	14.0	333	11.7	7
311	42.5	45	153	1.5	abs.
511	12.6	14	173	9.5	3.5
711	4.6	5.9	114	10.2	5.8
911	3.4	2.5	314	1.2	2
131	37	43	134	0,6	abs.
331	7.3	7	334	10.5	6
531	1.5	abs.	552	3.4	vvw
731	12.3	15	553	6.5	vvw

The reflections of type II, h even and k even, with different values of l were used to obtain a value of z. Intensities which were very sensitive to u, v, or w were not used. As before, calculated intensities were plotted as a function of z and the best value chosen; $z = 0.540 \pm 0.005$ was found.

Comparison of calculated and observed intensities for reflections of type II (Table III) served as a check on all these parameters. The calculated and observed intensities for all reflections observed are listed in Tables III to VI. Intensities of reflections observed by Hassel and Luzanski[2] and not by us are designated by letters rather than numbers.

Table VI

Type IV Planes

hkl	Calcd.	Obsd.	*hkl*	Calcd.	Obsd.
020	7.3	7.9	081	7.2	8.6
040	25.9	19.4	082	13	12
060	6.7	8.1	0,10,1	11.4	14.1
080	22	15.8	201	61	70
0,10,0	0	abs.	202	14.1	14.1
200	0	abs.	203	4.1	abs.
220	35.8	40	204	12.5	w
240	27.0	43	221	30	44
260	9.1	8.6	222	13.5	10.6
280	1.0	abs.	223	6.0	6.1
400	27	27	224	2.5	3.3
420	42	31.5	241	4.4	4.5
440	20.2	19	242	10.5	12.3
460	14.6	13	243	7.9	7.2
480	5.5	3.4	261	7.4	5.9
600	10.8	13	262	4.0	8
620	16	14	263	5.9	4.4
640	12.8	12	281	9.7	8.2
660	9.6	7.7	282	5.5	5
680	4.4	2.6	401	21.2	28
800	20.8	20	421	6.8	10.5
820	1.4	2.2	441	12.4	19.4
840	4.7	5.3	461	1.4	3.6
860	1.9	2.0	481	7.6	5.2
10,0,0	3.3	2.5	601	22.4	20
003	0	abs.	621	2.7	3.8
004	3.0	vvw	641	3.4	5.5
021	78	75	661	1.1	abs.
022	9.7	9.3	801	7.0	8.3
023	15.7	14.7	821	11.8	10
024	5	3.3	841	4.9	3.3
041	7.1	10.5	404	11.5	w
042	21.7	21	402	6.3	vw
043	10.4	8.3	403	18.9	m
044	17.8	10	802	10.7	m
061	21.3	16.4	442	2.7	vw(w)
062	3.3	5.6	443	5.5	vw(m$^-$) (m$^+$)
063	10.8	10.5	662	8.1	m^{++}

Conclusions.—The values of the F–F distance calculated using these parameters are

$$F_1\text{–}F_1 = 2.31 \pm 0.035 \text{ Å.}$$
$$F_2\text{–}F_2 = 2.320 \begin{array}{l} +0.03 \\ -0.02 \end{array} \text{ Å.}$$

The lower limit is less in the latter case since the value chosen for u was the lower limit (0.129) given it in the determination above; probably u cannot be less than 0.129.

Comparing these values with the value F–F 2.26 ± 0.01 Å. for KHF_2 it is seen that there is a slight increase in the distance in NH_4HF_2, amounting to between 0.03 and 0.08 Å., due to the weakening of the bond by the two extra hydrogen bonds formed in NH_4HF_2.

The N–F distances found are $N\text{–}F_1 = 2.80 \pm 0.02$ Å., and $N\text{–}F_2 = 2.80 \pm 0.03$ Å. This value is larger than the average found by Pauling (2.76 Å.) and is 8% larger than the value N–F = 2.63 Å. for NH_4F. We thus confirm the observation of Pauling that the hydrogen bond in NH_4HF_2 is weaker than that in NH_4F. The longer ammonium ion to fluorine contacts are: $N\text{–}F_I = 3.02$ Å. and $N\text{–}F_{II} = 3.40$ Å.

Summary

The unit translations for the orthorhombic crystal NH_4HF_2 have been revised to $a_0 = 8.426$ Å., $b_0 = 8.180$ Å., $c_0 = 3.69$ Å. The space group and structure given by Pauling have been confirmed and the parameters redetermined:

$$z = 0.540 \pm 0.005 \text{ Å.} \qquad u = 0.129 \begin{array}{l} +0.003 \text{ Å.} \\ -0.001 \text{ Å.} \end{array}$$
$$w = 0.137 \pm 0.002 \text{ Å.} \qquad v = 0.131 \pm 0.003 \text{ Å.}$$

The four smallest N–F distances are all equal to 2.80 ± 0.025 Å. and the F–F distances in the two non-equivalent HF_2^- ions are found to be 2.32 ± 0.03 Å.

Pasadena, California Received March 13, 1940

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[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 715]

A Redetermination of the Fluorine–Fluorine Distance in Potassium Bifluoride

By L. Helmholz and M. T. Rogers

Introduction

In an electron diffraction investigation of gaseous hydrogen fluoride, Bauer, Beach and Simons[1] obtained the value 2.55 ± 0.03 Å. for the F–H–F distance and confirmed the existence of polymers $(HF)_n$. The reported values for the F–H–F distance in crystals are:

NH_4HF_2 = 2.37 ± 0.1 Å.[2]
$NaHF_2$ = 2.50 ± 0.2 Å.[3]
KHF_2 = 2.25 ± 0.2 Å.[4]

The assumption that the mean value 2.25 Å. reported for potassium bifluoride is correct leads to the conclusion that the F–H–F bond is weakened and the distance correspondingly increased when additional hydrogen bonds are formed as in $(HF)_n$. Also the distance is not accurately enough known to judge whether the two additional hydrogen bonds from fluorine to nitrogen in ammonium bifluoride cause a lengthening of the F–H–F distance over that in alkali bifluorides. In view of the large limits of error ascribed to the F–H–F distance, a redetermination of the parameter in potassium bifluoride has been carried out in order to test this conclusion.

In this work the value 2.26 ± 0.01 Å. has been found for the F–H–F distance in close agreement with the mean value reported by Bozorth.[4]

Experimental

Potassium hydrogen fluoride crystallizes in the tetragonal system forming plates with {001} developed and sides parallel to {110}. The structure was determined by Bozorth,[4] who gives it the space group D_{4h}^{18}, four molecules in the unit cell, with the atoms in the following positions

4H in $0\frac{1}{2}0$; $\frac{1}{2}00$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$
4K in $00\frac{1}{4}$; $00\frac{3}{4}$; $\frac{1}{2}\frac{1}{2}\frac{1}{4}$; $\frac{1}{2}\frac{1}{2}\frac{3}{4}$
8F in $u,\frac{1}{2}+u,0$; $\bar{u},\frac{1}{2}-u,0$; $\frac{1}{2}-u,u,0$; $\frac{1}{2}+u,\bar{u},0$; $\frac{1}{2}+u,u,\frac{1}{2}$; $\frac{1}{2}-u,\bar{u},\frac{1}{2}$; $u,\frac{1}{2}-u,\frac{1}{2}$; $\bar{u},\frac{1}{2}+u,\frac{1}{2}$
a = 5.67 Å. c = 6.81 Å. u = 0.14 + 0.01 F–H–F = 2.25 ± 0.02 Å.

Symmetric and asymmetric Laue photographs were taken with the beam normal to (001). The parameter was narrowed down to a small range by the use of qualitative Laue data.

Theoretical curves for the dependence of intensity on the parameter u were calculated from the equation

$$I = C\left|S\right|^2 e^{-3.0(\sin\theta/\lambda)^2}$$

using f values from the Pauling–Sherman tables.

Comparing observed intensity ratios with the theoretical curves of Fig. 1, the upper and lower limits shown in Table I were placed on the value

Table I

Parameter Determination for Potassium Bifluoride Using Intensities of Laue Reflections

Reflecting planes	$\frac{\sin\theta}{\lambda}$	λ	Observed intensity ratio	Parameter
(802)	0.720	0.349	(802) < (732)	$u > 0.1393$
(732)	.687	.350		
$(6\bar{6}2)$	.762	.333	$(7\bar{5}2) > (6\bar{6}2)$	$u < .1413$
$(7\bar{5}2)$	.773	.328		
(914)	.851	.361	$(\bar{1}94) > (7\bar{3}2)$	$u > .1390$
(732)	.687	.367		
$(8\bar{6}4)$	.924	.406	$(8\bar{6}4) > (934)$	$u > .1381$
(934)	.884	.408		

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(1) S. H. Bauer, J. Y. Beach and J. H. Simons, This Journal, **61**, 19 (1939).
(2) L. Pauling, *Z. Krist.*, **85**, 380 (1933).
(3) C. Anderson and O. Hassel, *Z. physik. Chem.*, **123**, 151 (1926).
(4) R. M. Bozorth, This Journal, **45**, 2128 (1923).

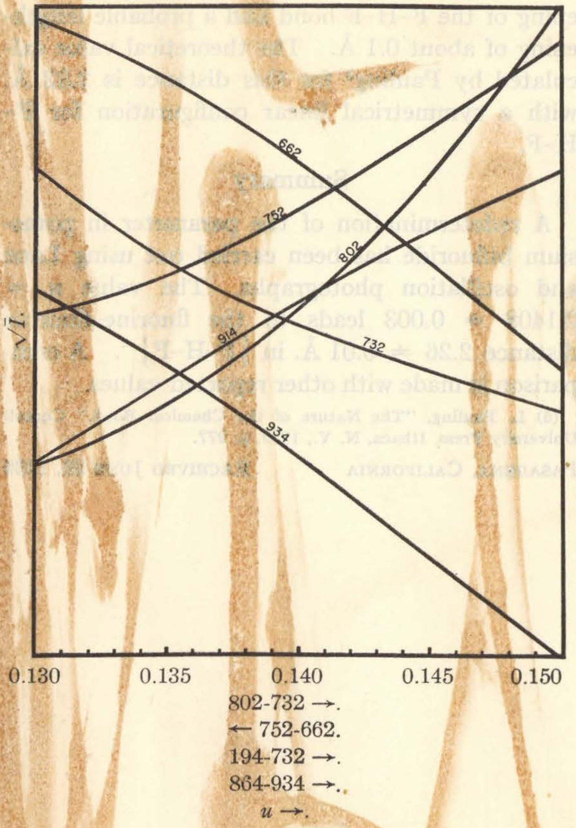

Fig. 1.

of u. This gives $0.1394 \leqq u \leqq 0.1413$ and $2.235 \leqq$ F–H–F distance $\leqq 2.265$ Å.

A more exact value of the parameter was then found by visually comparing intensities of reflections on oscillation photographs. Theoretical curves for the dependence of intensity on parameter were drawn (Fig. 2) using

$$I = \text{Const.}\ \frac{1 + \cos^2 2\,\theta}{\sin^2 2\,\theta}\left|\, S\, \right|^2 e^{-3.0(\sin\theta/\lambda)^2}$$

From a visual estimate of the ratio of the intensities of two reflections, estimates of the parameter value probably good to ±5% were made using the theoretical curves. Comparisons were made between reflections in the same layer line and not too widely separated values of sin θ. The mean value for the twenty-seven independent estimates made was weighted by multiplying each value by the angle between the intensity curves for the planes involved. The weighted mean for the parameter u is 0.1408, the average deviation is 0.0015 and the most probable deviation is $0.0015/27^{1/2}$ or 0.0003. The value $u = 0.1408 \pm 0.0003$ corresponds to the distance F–H–F = 2.258 ± 0.005 Å. This is in good agreement with the

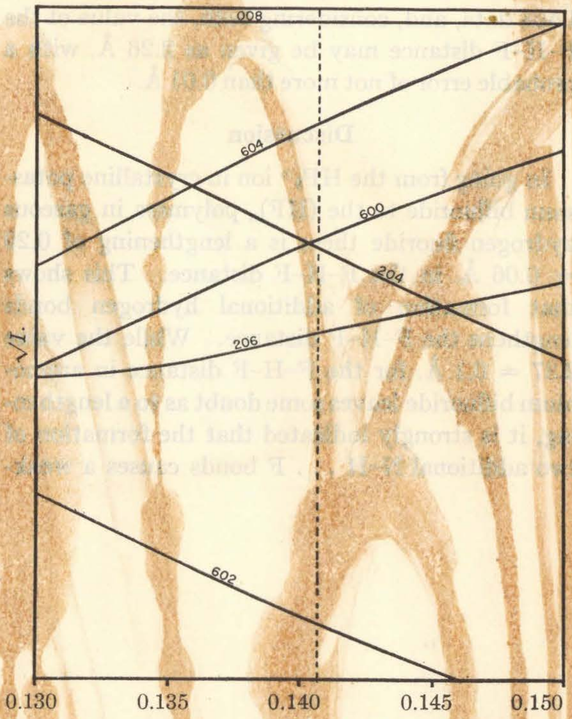

Fig. 2.

TABLE II

PARAMETER DETERMINATION FOR POTASSIUM BIFLUORIDE USING INTENSITIES OF OSCILLATION REFLECTIONS

No.	(*hkl*)	Angle between F curves	Intensity ratio	Parameter
1	(400) (006)	22.5	0.5	0.1432
2	(600) (204)	55	1.10	.1417
3	(204) (206)	35	1.25	.1408
4	(008) (604)	20	1.20	.1423
5	(602) (604)	6	0.20	.1409
6	(026) (024)	24	0.91	.1410
7	(026) (422)	20	1.3	.1400
8	(321) (125)	27	1.1	.1420
9	(224) (024)	20	1.25	.1408
10	(323) (523)	20.5	0.83	.1417
11	(600) (206)	15	1.25	.1408
12	(512) (215)	16	1.33	.1416
13	(420) (024)	30	1.1	.1368
14	(424) (024)	24.5	0.91	.1420
15	(521) (323)	23	.74	.1411
16	(321) (226)	22	.57	.1423
17	(321) (422)	13	.67	.1396
18	(125) (323)	19	1.75	.1390
19	(424) (321)	31	2.3	.1419
20	(026) (321)	31	2	.1400
21	(611) (411)	37	1.75	.1370
22	(611) (413)	32	2	.1402
23	(316) (411)	31	3.3	.1389
24	(510) (514)	34	0.91	.1418
25	(512) (514)	24	0.74	.1442
26	(510) ($\bar{2}$15)	20	2	.1445
27	(413) (316)	23	0.22	.1422

Laue data, and, considering both, the value of the F–H–F distance may be given as 2.26 Å. with a probable error of not more than 0.01 Å.

Discussion

In going from the HF_2^- ion in crystalline potassium bifluoride to the $(HF)_n$ polymers in gaseous hydrogen fluoride there is a lengthening of 0.29 ± 0.06 Å. in the F–H–F distance. This shows that formation of additional hydrogen bonds lengthens the F–H–F distance. While the value 2.37 ± 0.1 Å. for the F–H–F distance in ammonium bifluoride leaves some doubt as to a lengthening, it is strongly indicated that the formation of two additional N–H . . . F bonds causes a weakening of the F–H–F bond and a probable lengthening of about 0.1 Å. The theoretical value calculated by Pauling[5] for this distance is 2.32 Å. with a symmetrical linear configuration for F–H–F.

Summary

A redetermination of the parameter in potassium bifluoride has been carried out using Laue and oscillation photographs. The value $u = 0.1408 \pm 0.003$ leads to the fluorine–fluorine distance 2.26 ± 0.01 Å. in $\{F\text{–}H\text{–}F\}^-$. A comparison is made with other reported values.

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[5] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 277.

PASADENA, CALIFORNIA RECEIVED JUNE 26, 1939

The Unit Cell and Space Group of Silver Iodate
(with Lindsay Helmholz)

Introduction

A satisfactory crystal structure determination had not been made on any iodate although several had been studied (see above, 'The Crystal Structure of Iodic Acid', Introduction), and it seemed desirable to make a complete study of one. The pseudo-cubic crystals KIO_3, and the Cs, Rb, and NH_4, isomorphous compounds are probably monoclinic and hemihedral (see appended note on KIO_3), and good, untwinned, single crystals have not been prepared. The X-ray work done on these was on the powder (Goldschmidt(1)).

It was thought that orthorhombic Ag IO_3, which is readily obtainable in good single crystals, might be a suitable substance for a structure determination. No X-ray work had been done on this compound.

Experimental

Crystals of $AgIO_3$ were grown from aqueous ammonia solution by slow evaporation. The crystals are thin plates, c(001), with q(011) and r(101) developed. The crystallography agreed with Groth(2), who quotes the axial ratios

$$a:b:c = 0.4416 : 1 : 1.3072$$

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(1) V. M. Goldschmidt, "Geochem. Vert-Gesetze der Elemente," VII and VIII.

(2) P. Groth, "Chemische Kristallographie", Teil II, Leipzig, 1908, p. 90.

Experimental

The cleavage parallel to c(001) is complete, and the plane of the optic axes is c(001). The crystals were observed to show a positive pyroelectric effect.

Laue photographs of long exposure showed the Laue symmetry to be D_{2h}- mmm. Marignac (see Groth(2)) considered the crystals monoclinic.

Oscillation photographs were taken with each axis vertical, yielding the following preliminary unit translations:

$a_o = 7.24 \text{Å}$,

$b_o = 5.80 \text{ Å}$,

$c_o = 15.14 \text{ Å}$.

The density was determined by pycnometer to be $\rho_{25°} = 5.76$, giving $z = 4$ molecules in the unit cell.

A long exposure Laue picture taken with the a-axis vertical was indexed. Reflections were observed with $n\lambda < 0.23 \text{Å}$ which required doubling the length of the b axis.

The final values of the unit translations required to account for all observed data are, then,

$a_o = 7.24 \text{ Å}$,

$b_o = 11.60 \text{ Å}$,

$c_o = 15.14 \text{ Å}$,

and $z = 8$,

The first order Laue reflections and oscillation photographs indexed showed the characteristic extinctions:

$(h\,0\,l)$ - $h \neq 2n$,

$(0\,k\,l)$ - $l \neq 2n$,

$(h\,k\,0)$ - all orders observed.

Experimental

These data correspond to the space group Pca, Pmc or Pma are not definitely eliminated,however.

A needle elongated along a was obtained which was nearly 0.05 x 0.05 mm. in dimensions.It was mounted with a vertical and twelve oscillation photographs taken using Mo K_α radiation. About fifty four reflections (Okl) were indexed and the intensities estimated.Values of $|F|^2$ were calculated using the formula:

$$I = C \frac{1 + \cos^2 2\theta}{\sin 2\theta} A \cdot |F|^2 \ \text{exp.} \ -3.0 \frac{\sin^2 \theta}{\lambda^2} ,$$

where A is the absorption correction coefficient calculated from the powder rod absorption formulae [3] . The observed values of $|F|^2$ were used to make a Patterson projection

$$P(y,z) = \sum_k \sum_l |F_{okl}|^2 \cos 2\pi(ky + lz).$$

This projection gave sharp peaks which correspond to Ag-I, I-I,and Ag-Ag distances,enabling rough parameters for these atoms to be estimated.

The investigation was dropped at this point since the Ag and I atoms must be placed in two sets of four-fold positions and the oxygen atoms in six sets. This would require the determination of 30 parameters - made especially difficult by the absence of centers of symmetry in all but one projection, so that only one Fourier projection could be made.readily. The low scattering power of oxygen compared to Ag and I also is unfavorable.

(3) "International Tabellen zur Bestimmung von Kristallstrukturen 11", Ch.XI.

Summary

$AgIO_3$ has been shown by Laue and oscillation data to be orthorhombic hemihedral with Laue symmetry mmm ,and unit translations $a_o = 7.24$ Å , $b_o = 11.60$ Å, $c_o = 15.14$ Å , $Z = 8$ molecules in the unit cell. The space group is C_{2v}^{5}-Pca or , less probably, C_{2v}^{4} -Pma or C_{2v}^{2} -Pmc. The crystal is not suitable for a complete structure investigation by X-ray diffraction.

Note on the Crystal Structure of Potassium Iodate

Introduction

An X-ray diffraction investigation of KIO_3 was made by Goldschmidt,(1) on the crystal powder. He used a cubic unit with $a_0 = 4.46$ Å and assigned the perowskite structure to this substance, reporting that no powder lines showing any deviation from the ideal perowskite structure were observed. In view of the structure obtained for HIO_3 (see above) it seemed unlikely that this would be correct, and Laue photographs were taken to obtain some qualitative information on this point.

Experimental

Crystals of KIO_3 were prepared by slow evaporation over conc. H_2SO_4 of a solution of KIO_3 in dilute H_2SO_4. Large crystals were obtained twinned always on m(110), four individuals twinning to form a cube but revealed by etch figures. The crystals are reported by Groth(2) to be monoclinic prismatic with

$$a : b : c = 1.0089 : 1 : 1.4394 , \quad \beta = 90^\circ 45' .$$

They are colorless and strongly double refracting, showing a negative birefringence, $2V = 45^\circ$.

V. M. Goldschmidt, "Geochem. Vert. der Elemente", VII and VII

P. Groth, "Chemische Kristallographie" Teil II, Leipzig, 1908, p. 93.

Experimental

An individual was cleaved from one of the groups of four crystals forming a pseudo-cube, and long exposure Laue photographs taken with $\overline{s}_0$ along the $\overline{c}$ axis((110) vertical) and along $(\bar{1}10)$. A mirror plane normal to $\overline{b}$ was observed, making the Laue class C_{2h}. The crystals show a positive pyro-electric effect and so belong to either class C_2 or C_s. The intensities of the strongest reflections correspond to cubic symmetry, but rather large variations in the intensities of the weaker reflections are observed indicating that the potassium and iodine atoms are in positions of cubic symmetry, while the oxygen atoms are displaced from such positions. The strong birefringence and the deviations of intensities from cubic symmetry indicate that the oxygen atoms are considerably moved from the positions of the ideal perowskite structure. This is in agreement with the behavior expected by analogy with iodic acid, i.e., we would expect that discrete iodate groups (IO_3) would be present, probably formed by the iodine atom drawing three oxygens of an IO_6 octahedron about it somewhat closer than the other three, forming distorted octa-hedra, IO_6.

Summary

Crystals of potassium iodate have been prepared and the symmetry shown by Laue photographs to be monoclinic. From a qualitative observation of the intensities it is concluded that the structure, while based on that of perowskite, deviates considerably from it for the positions of the oxygen atoms.

Miscellaneous X-Ray Data

The following data are presented without comment.

Sodium nitroprusside $Na_2Fe(CN)_5NO.2H_2O$

Deep red crystals were obtained from aqueous solution. They are orthorhombic bipyramidal with axial ratios:

a:b:c = 0.765: 1 : 0.4155 , (Groth I, 432).

They show positive birefringence with (100) the axial plane, $\bar{c}$ the bisectrix, 2E = 61° ; and diamagnetic anisotropy, with $\bar{b}$ the axis of greatest susceptibility.

Oscillation photographs about each axis were taken and the following unit translations calculated from layer line spacings:

a_o = 11.80 Å,

b_o = 15.40 Å,

c_o = 6.18 Å.

The density ρ_{25° = 1.71, hence Z = 4. The axial ratios from the X-ray data are a : b : c = 0.766 : 1 : 0.400.

Laue photographs with γ_o along $\bar{a}$ and $\bar{b}$ show it to have Laue symmetry D_{2h}-mmm.

Creatinine (1-methyl glycocyamidine)

This substance crystallizes from cold aqueous solution in monoclinic prisms containing $2H_2O$ per molecule, and efflorescing in air.

Groth (III,567) gives:

a : b : c = 1.1571 : 1 : ? ,

β = 110° 36'.

Cleavage is complete parallel to a(100).

Creatinine-

Oscillation photographs about each axis were taken and the unit translations obtained from layer line spacings are:

$a_0 = 13.63$ Å,

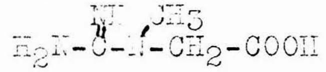
$b_0 = 5.90$ Å,

$c_0 = 14.60$ Å,

The X-ray axial ratios are $a:b:c = 2.31 : 1 : 2.48$, and the density $\rho < 1.5 > 1.2$, hence $Z = 8$.

The dimensions of the unit cell and the cleavage suggest that the planes of the molecules are nearly parallel to b and perpendicular to c . The reflection (004) is the strongest reflection observed, in agreement with the suggested orientation.

Laue photographs with $\gamma_0 \parallel b$, and $\gamma_0 \perp b$, show a two-fold axis and mirror plane, respectively, showing the Laue symmetry to C_{2h} - 2/m. Good Laue photographs are obtained, and oscillation pictures go out to the limit of Cu K_α radiation.

Creatine ((methyl guanido) acetic acid) 
$H_2N-\overset{\overset{NH}{\|}}{C}-\overset{CH_3}{N}-CH_2-COOH$

Crystals from aqueous solution contain one molecule of water of crystallization per molecule. They are monoclinic:

$a:b:c = 2.404 : 1 : 2.479$,

$\beta = 71° 8'$ (Groth, 111, 575).

There is a perfect basal cleavage parallel to (001). The birefringence is low and negative. The axial plane is (010) and through c(001) an axial figure can be observed.

The unit translations were obtained from layer line measurements on oscillation photographs.

Creatine

$a_0 = 12.05$ Å,
$b_0 = 12.55$ Å,
$c_0 = 5.12$ Å,
$\beta = 109^\circ$ (crystallography),
$a : b : c = 2.35 : 1 : 2.45.$

The density was found by experiment to be less than 1.446 and greater than 1.34, hence $Z = 4$ molecules in the above unit cell.

The molecules must lie with their planes nearly perpendicular to c(001), but tilted somewhat since the birefringence is negative. The basal cleavage agrees with this orientation.

The substances creatine and creatinine are in equilibrium in aqueous solution the composition depending on pH. In acid solution creatinine is formed since it is the stronger base. Because of the ease of interconversion and the similarity in axial ratios and monoclinic angles it has been suggested that the two crystals are isomorphous. The X-ray data show this is not so. It is probable that the configuration of creatine is close to that of the creatinine ring, however.

Part II

Electron Diffraction Investigations

The Internuclear Distance in the Fluorine Molecule

by

Max T. Rogers, Verner Schomaker and D. P. Stevenson

Introduction:

There exists no spectroscopic value for the equilibrium internuclear distance in the ground state of the fluorine molecule. Gale and Monk[1] photographed the band spectrum obtained in a discharge tube through which fluorine gas was flowed. They analysed two bands at $\nu_0 = 16,378.8$ and $\nu_0 = 17,439.5$, and reported the values $r'_0 = 1.48$ Å, $r''_0 = 1.28$ Å for the initial and final states of a transition $^1\Sigma \rightarrow {}^1\Pi$. Since these bands do not occur in absorption, and the absorption maximum of fluorine is not in this region, the transition does not involve the ground state of the fluorine molecule. It has further been shown by Mulliken[2] that it is unlikely that the ground state is other than $^1\Sigma$, so that we may assume that the spectroscopic values $r''_0 = 1.28$ Å and $\omega_e = 1130$ cm^{-1}. refer to an excited state. The only value reported for the ground state is, then, the result of an electron diffraction investigation of flourine vapor[3] which gave F-F = 1.45 ± 0.05 Å. Attempts to observe ω_e directly by Raman spectroscopy have failed but a value $\omega_e = 836$ cm^{-1} has been estimated using Badger's rule[4].

(1) Gale and Monk, Astrophys. J., 69 , 77 (1929).

(2) R. S. Mulliken, Phys. Rev., 36 , 699 (1930).

(3) L. O. Brockway, J. A. C. S., 60 , 1348 (1938).

(4) C. S. Garner and D. M. Yost, J. A. C. S., 59, 2738 (1937).

In the discussion of his work, Brockway pointed out that the determination was based on somewhat unsatisfactory photographs showing five rings. The values for the internuclear distance obtained from the various rings show rather wider variations, and the quoted limit of error is much larger, than is usual for electron diffraction determinations, so that the reported value, 1.45 ± 0.05 Å, was regarded as only provisional.

In building up a table of covalent radii Pauling and Huggins [7] used the value 0.64 Å for fluorine. This led to deviations from the sums of the covalent radii for bonds between fluorine and very electronegative elements e.g., (F_2 (observed 1.45 ± 0.05 Å, sum of radii, 1.30 Å); F_2O (observed 1.41 ± 0.05 Å, sum of radii, 1.30 Å); $FONO_2$ (observed 1.42 ± 0.05 Å, sum of radii, 1.30 Å). It has recently been shown [4] that a table of radii in which fluorine is given a covalent radius of about 0.72 Å is much more satisfactory. An accurate value of the internuclear distance in fluorine is therefore of interest.

It has been shown [5] that the electron diffraction method will give accurate values of distances in light molecules, agreeing, for diatomic molecules, to better than 1% with spectroscopic values.

We report in this paper the results of an electron diffraction investigation of fluorine vapor in which we have obtained a value of the internuclear distance with this degree of precision

(4) C.S.Garner and D.M.Yost, J.A.C.S., 59, 2738(1937).

(5) Verner Schomaker and D.P.Stevenson, J.A.C.S., 63, 37(1941).

(7) Linus Pauling and M.L.Huggins, Z.Krist., 87, 205(1934).

Experimental:

Fluorine was prepared by the high temperature method. A mixture of KHF_2 and HF in a monel can was electrolyzed at 200° with a graphite anode. The gas produced was passed over KF to remove HF and through a copper trap immersed in dry ice to remove easily condensable impurities. Several volumes of fluorine were allowed to pass through a brass container fitted with an all-metal sylphon valve which was then closed off and attached by brass tapered joints to the nozzle of the electron diffraction machine. The system in which the fluorine was handled was entirely metal and care was taken to eliminate all grease and organic matter which, if present, reacts very rapidly with the fluorine. The chief impurities are small amounts of CF_4 resulting from the decomposition of the graphite anode, and O_2 from the electrolysis of H_2O not completely removed from the electrolyte. The rate at which the anode is attacked indicates that the gas probably contains less than 3% CF_4, and the amount of O_2 is probably much smaller since the samples were collected after 20-30 hours electrolysis which should remove all H_2O. Samples of fluorine were also collected by condensing the gas to a liquid in a pyrex trap and distilling into an evacuated metal container. Only very slight differences in the appearance of pictures taken with different fluorine samples could be observed. The electron diffraction apparatus has been described[6] and a discussion of the present technique given[5]. Cut film was used and a small correction applied for errors

(6) L. O. Brockway, Rev. Mod. Phys., 8, 231 (1936)

arising from this source.

Four different samples of fluorine gave twenty-five pictures of good diatomic appearance showing six clearly resolved maxima and six minima. In general there were only very slight deviations if any, from normal diatomic appearance. The heavier pictures were taken using high pressures (up to 1000 mm.) of gas and only one or two one-tenth second exposures with a strong, but small, electron beam. In this way pictures with rings extending to s = 30 were obtained without the background of incoherent scattering building up too much. The lack of sharpness of the diffraction pattern observed by Brockway was not observed. This was attributed by him to the slow removal of fluorine from the apparatus which results, not only in an unsteadiness in the operation of the tube due to the resulting rise in pressure and high voltage discharge, but also a scattering of electrons along the beam. This investigation, along with those of other light molecules [4], has shown that, although the gas is not condensed out and so spreads through the apparatus causing a high voltage discharge, the pictures are as good, and the results as reliable, as for rapidly condensable substances. The photograph is taken before the spreading of the gas has caused the discharge and while the voltage is still reasonably constant. The quality of the pictures shows that incoherent scattering is not appreciably larger than for condensable substances.

Results:

Each of us has made two or more sets of measurements of the ring diameters. From these measurements values of $S_0 = 4\pi(\sin \theta/2)/\lambda$, $(\pi/\lambda L = 4.723)$, were calculated and compared with the maxima and minima of the theoretical curve for a diatomic molecule (the function $\frac{\sin ls}{ls}$ with $l = 1$ was used). Values of the internuclear distance $(\frac{s}{s_0})$ so obtained were averaged for each set of measurements and these averages, along with their average deviations for eight sets of measurements, are shown in Table I.

Table I

Ovserver	No. of features included in average	No. of meas. on each feature	Features included in average	Average r	Average Deviation
V.S.	7	5	2nd max.-5th max.	1.428 Å	0.008 Å
V.S.	7	5	"	1.430	0.004
M.T.R.	6	10	2nd max.-5th min.	1.437	0.004
V.S.	8	5	2nd min.-5th max.	1.431	0.004
V.S.	7	10	2nd max-5th max.	1.432	0.005
D.P.S.	7	10	"	1.441	0.005
D.P.S.	6	5	4th min.-6th max.	1.430	0.004
M.T.R.	9	8	2nd max.-6th max.	1.435	0.008
			Final Average	1.434 Å	0.005 Å

The precision of these measurements is 1/3 of 1%. The accuracy of the electron diffraction method applied to other diatomic molecules, where comparison with spectroscopic values is possible[4], is in all cases better than 1%, hence it is improbable that this result is in error by more than

± 0.01 Å. From this value we may calculate, using Badger's rule[7], a value of ω_e for F_2. The values $\omega_e = 1060$ cm^{-1} and $\omega_e = 892$ cm^{-1} are obtained using the constants c_{nm}, d_{ij}, for columns and for rows of the periodic table respectively.

Summary

The internuclear distance in the fluorine molecule has been found by the electron diffraction method to be F-F = 1.43$_5$ ± 0.01 Å.

The Electron Diffraction Investigation
of
Tellurium Dibromide

Introduction:

An electron diffraction investigation of tellurium dihalides was made by Grether (1) who reported the values Te-Cl = 2.36Å, Te-Br = 2.49Å, and ∠Br-Te-Br and ∠Cl-Te-Cl ≥ 150°. The vapors of these compounds show extensive band systems in absorption and various investigators have studied these spectra. Wehrli (2) reported that $TeCl_2$ is nearly linear in both the ground and first excited state, from an investigation of isotope effect in the spectrum. Larionov (3), on the other hand, considered that the angles were closer to 90°. The interpretation of the spectra is, however, very difficult and, in the absence of a complete analysis of any of these spectra, the conclusions of the above authors carry little weight.

One would expect that the bonds in these compounds would be p bonds with some s character giving an angle between 90° and 109°28¹ as is the case for SCl_2 (∠Cl-S-Cl = 103°) and for Se and Te in the crystal (∠Te-Te-Te = 102°). In view of the above results tending to establish a nearly linear configuration for the tellurium dihalides a more careful investigation of one of these compounds by the electron diffraction method was considered desirable. Tellurium dibromide is the most suitable of these because it is stable in the vapor state and has a more favorable ratio of structure factors than $TeCl_2$. The angles should be similar for $SeCl_2$, $SeBr_2$, $TeCl_2$ and $TeBr_2$, hence a value for the latter will establish the others to within a few degrees.

Experimental:

Powered c. p. tellurium metal was placed in a tube and c. p. bromine added in slight excess. The mixture was heated until the reaction was over and the product then distilled in vacuo to remove halides of heavy metals, Br_2, and $TeBr_4$. The product was sublimed in vacuo and placed in the high-temperature nozzle of the electron diffraction machine, avoiding contact with moist air.

A series of photographs obtained using temperatures up to the boiling point showed maxima out to S=28.

Tellurium dibromide was studied by Yost and Hatcher (4) who report that the vapor is not appreciably dissociated until 750°. Selenium dibromide and dichloride decompose in the vapor state, and may not be studied by the electron diffraction method.

The results of the radial distribution treatment (5,6) are shown in Table I and in curve R of the figure. The prominent peak at 2.52 Å. and the smaller one at 3.80 Å. may be taken as representing the Te-Br and Br-Br distances respectively; the Br-Te-Br angle is then 98°. The asymmetrical peak at about 5 Å. is without significance--in the curve containing only negative coefficients a deep minimum appears in this region. If these coefficients were multiplied through by the proper factor, the total curve would be nearly smooth beyond the peak at 3.80 Å. False peaks at abcissae nearly twice those of prominent features are common in radial distribution curves.

The theoretical curves were calculated with the use of the formula

$$I \propto \frac{2}{2.51} \frac{(Z-f)_{Te}}{(Z-f)_{Br}} \sin\left(\frac{2.51\pi}{10} q\right) + \frac{1}{r} \sin\left(\frac{r\pi q}{10}\right)$$

where Z is the atomic number, f the atom form factor, r the Br-Br distance, and $q = \frac{40}{\lambda} \sin\frac{\theta}{2}$. Though account was taken of the variation of the scattering coefficients with θ , it was found that curves drawn with atomic numbers as coefficients were also satisfactory. The Te-Br distance was taken as 2.51 Å. in all cases. The models are A, r = 3.70 Å., ∡ Br-Te-Br = 95°; B, 3.77 Å., 97.5°; C, 3.85 Å., 100°; D, 3.98 Å., 105°; E, 4.90 Å., 155°.

B and C both reproduce nearly sufficiently well the appearance of the photographs. One observes that the third, fifth, and seventh minima are shallow, but decreasingly shallow in the order named. The fifth, sixth, seventh, and eighth maxima decrease nearly regularly in intensity, with the sixth a little more prominent than the rest. Our conclusions are that the photographs would be best represented by a curve intermediate between B and C, and we have chosen as most probable the angle 98° ± 3° given by the radial distribution curve. Comparison with B and C (Table II), gives Te-Br = 2.51 Å. This angle is reasonable in the light of the value 101° which has been reported(7) for sulfur dichloride, and the known tendency for bond angles of elements in a column of the periodic table to decrease with increasing atomic number. The Te-Br distance is the sum of the covalent radii[8].

Curve E, with ∡ Br-Te-Br = 155°, has been included because it has been reported(1) that the bond angle in TeBr$_2$ is greater than 150°. This curve bears no relation to the appearance of our photographs. A wider angle is also not possible: curves for such models show regularly spaced strong maxima falling off somewhat more gradually on the outside; these do not correspond to the photographs.

Summary:

The structure of TeBr$_2$ has been redetermined by the electron diffraction method. Te-Br = 2.51 Å. ± .02 Å., $\measuredangle$ Br-Te-Br = 98° ± 3°, Br-Br = 3.80Å ± .08 Å.

Figure for Tellurium Dibromide.

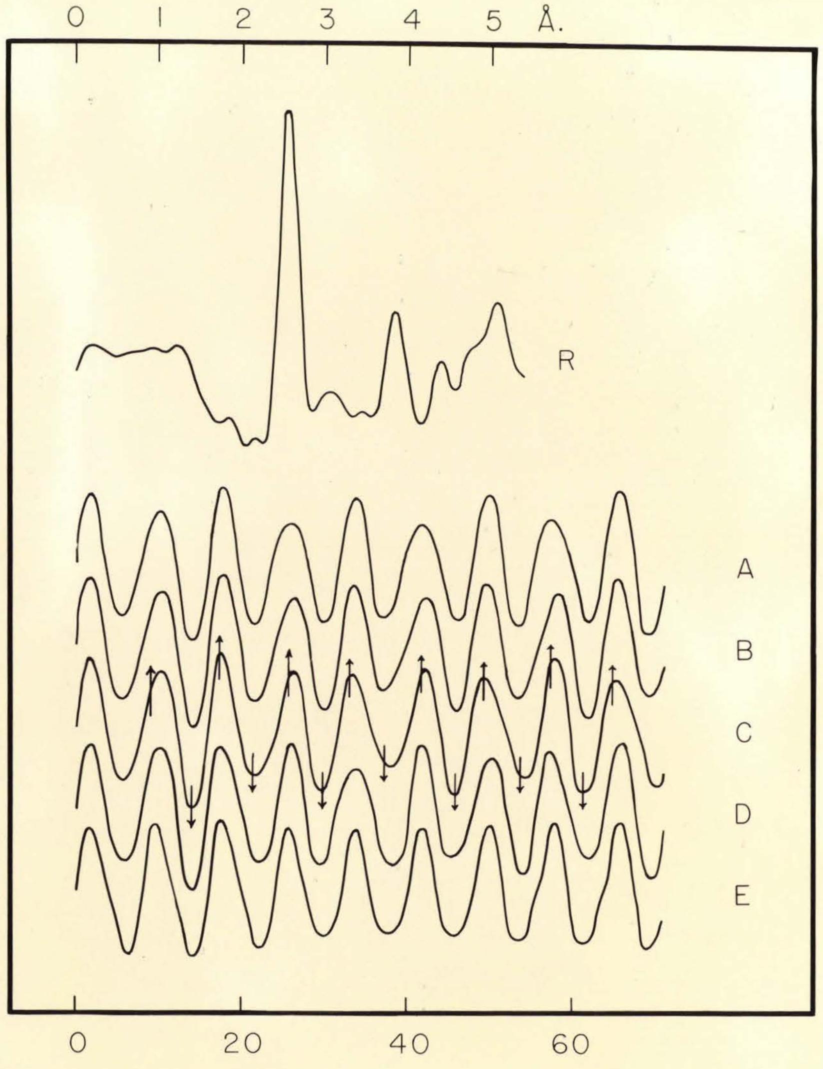


Table I

Min.	Max.	q_{obs}	I	C_k
	1	9.23	10	9.5
2		13.94	-10	-9.0
	2	17.54	10	8.5
3		21.52	-5	-3.9
	3	25.87	8	5.6
4		30.08	-10	-6.2
	4	33.33	12	6.6
5		37.62	-6	-2.8
	5	42.04	8	3.1
6		46.39	-10	-3.3
	6	49.92	10	2.8
7		54.14	-7	-1.5
	7	57.92	8	1.3
8		62.02	-10	-1.3
	8	65.62	10	1.0

Table II

Min. Max.	$q_{obs.}$	$q_{calc.}$(B)	q_o/q_c (B)	$q_{calc.}$(C)	q_o/q_c (C)
1	9.23	10.4	(1.127)	10.3	(1.116)
2	13.94	14.2	1.019	14.0	1.004
2	17.54	17.7	1.009	17.5	.998
3	21.52	21.5	.999	21.6	1.004
3	25.87	26.5	.986	26.2	1.013
4	30.08	30.0	.997	29.9	.994
4	33.33	33.5	1.005	33.3	.999
5	37.62	37.1	.986	38.0	1.010
5	42.04	42.3	1.006	42.0	1.000
6	46.39	46.0	.991	45.7	.985
6	49.92	49.6	.993	49.4	.990
7	54.14	53.5	.988	54.3	1.003
7	57.92	58.2	1.005	58.0	1.001
8	62.02	62.0	1.000	61.3	.988
8	65.62	65.5	.998	64.9	.990
Average			.999		.999
Average deviation			.007		.007
Final Te-Br			2.51 Å.		2.51 Å.

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6. The coefficients were chosen according to the recommendations of Schomaker: Verner Schomaker, American Chemical Society Meeting, Baltimore, April, 1939.

7. K. J. Palmer, J. A. C. S., 60, 2360 (1938)

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The work on tellurium dibromide was done in collaboration with Mr. Robert A. Spurr.

Part III

Determination of Magnetic Anisotropy

The Determination of the Magnetic Anisotropy of Crystals

I. Introduction

It was discovered by Faraday that the induction in a crystal is not in the same direction as the applied field but depends, in general, upon direction, the magnetic constants in different directions defining a triaxial ellipsoid. Qualitative measurements of the susceptibilities of crystals were made by Tyndall,(15) Plücker,(16) Grailich and Lang,(17) and Rowland and Jacques,(18) and later, quantitative measurements on a few diamagnetic crystals by Stenger,(4) König,(5) and Voigt and Kinoshita,(2) and on paramagnetic crystals by Fincke,(19) Jackson,(20) and Rabi.(3) The relation of the magnetic constants of a crystal to those of the individual molecules building it up was first shown by Krishnan.(1) He showed that diamagnetic crystals of aromatic substances showed relatively large anisotropies and that if the magnetic constants of a single molecule could be estimated those of the crystal might indicate the orientation of the molecules in the crystal.

A value of the principal susceptibilities of a molecule can be obtained from a knowledge of the Cotton-Mouton constant for the liquid and the depolarisation factor for light if we can assume an axis of symmetry for the molecule. Then the principal susceptibilities of the crystal must be obtained by the tensor addition, for all the molecules in a unit cell of the crystal, of the constants for the individual molecules. Since the induced moments are very small we may neglect the interactions between molecules and their orientation only is significant.

I.Introduction

Thus we may,with certain limitations discussed later, deduce the orientations of the molecules in the crystal from the magnetic data if the anisotropies are not too small. For aliphatic molecules and most inorganic substances the electron distributions are nearly isotropic,and the information obtained is much less. The metals bismuth and tellurium show a relatively large anisotropy which is of theoretical interest.The anisotropy of paramagnetic crystals is more difficult of interpretation, but gives information as to the symmetry of the crystalline field acting on the paramagnetic ion. When more data are available for crystals of known structure it may be possible to obtain structural information from the data. The results of measurementsof magnetic anisotropy of crystals thus provides,in favorable cases,information of value in a complete structure determination by X-ray diffraction.

The measurement of the magnetic constants of some crystals has been undertaken with the purpose of providing information of aid in crystal structure research.

II. General Theory

A crystal placed in a magnetic field experiences a magnetization $\widetilde{M}$ proportional to the applied field:

$$\widetilde{M} = X\widetilde{H}$$

where X is the magnetic susceptibility per unit volume. For diamagnetic substances X is of the order of -10^{-6} cgs (e. m. u.) in a direction opposing the field, and its magnitude depends chiefly on the distribution of electron density in the constituent molecules or atoms. For paramagnetic substances X is about 10^{-3} cgs (e. m. u.) and depends on temperature. The paramagnetism arises largely from the presence of unpaired electrons in constituent molecules or ions. X is independent of $\widetilde{H}$ for both these cases but not for ferro magnetic materials.

$\widetilde{M}$ does not have the same direction as $\widetilde{H}$, in general, but the components of $\widetilde{M}$ along any three orthogonal directions are linear functions of the field components:

$$M^{i} = X_{ki} H_{k} .$$

Since $\widetilde{M}$ is a contravariant tensor and $\widetilde{H}(= -\nabla \Phi_{m})$ a covariant tensor of rank one, the coefficients X_{ki} transform as a doubly contravariant tensor of second rank,

$$X_{ik} = C_{il} C_{km} X_{e}^{lm} \text{ (for cartesian axes)},$$

and depend on the orientation of the crystal axes to the coordinate axes.

$X_{ki} = X_{ik}$ by conservation of energy, and the tensor is symmetrical.

II. General Theory

The susceptibility in any direction is obtained by a transformation of axes from OX, OY, OZ to OX^1, OY^1, OZ^1; when X is desired in the OZ^1 direction, then $X^1_{3} = C^2_{13} X_{11} + C^2_{23}X_{22} + C^2_{33}X_{33} + 2C_{13}C_{23} X_{12} + 2C_{13}C_{33}X_{13} + 2C_{23}C_{33}X_{23}$ (1), where the C_{ik} are the direction cosines of the unprimed axes with respect to the primed ones.

This is the equation of a triaxial ellipsoid so we may choose the coordinates appropriately and obtain

$$X^1_{33} = C^2_{13} X_1 + C^2_{23} X_2 + C^2_{33} X_3 ,$$

where X_1, X_2, X_3 are the principal susceptibilities along the three orthogonal directions of principal magnetization.

Then X in any direction is the length of the radius vector to the surface of the ellipsoid from the center.

The number of coefficients of susceptibility is limited by the crystal symmetry. Magnetism is a centro-symmetric property so only the 11 Laue point groups need be considered. These reduce to 5 groups here since all non-cubic groups with an axis of order higher than 2, (the order of the tensor), have the same restrictions.

The transformations of these five symmetry groups applied to the X_{ik}'s give the non-zero components.

Group	Matrix of non-zero components
$\bar{1}$	$\begin{pmatrix} X_{11} & X_{12} & X_{13} \\ X_{21} & X_{22} & X_{23} \\ X_{31} & X_{32} & X_{33} \end{pmatrix}$
$\frac{2}{m}$	$\begin{pmatrix} X_{11} & X_{12} & 0 \\ X_{12} & X_{22} & 0 \\ 0 & 0 & X_{33} \end{pmatrix}$
mmm	$\begin{pmatrix} X_{11} & 0 & 0 \\ 0 & X_{22} & 0 \\ 0 & 0 & X_{33} \end{pmatrix}$
$\bar{3}$m, 4/m m m, 6/m m m $\bar{3}$, 4/m, 6/m	$\begin{pmatrix} X_{11} & 0 & 0 \\ 0 & X_{11} & 0 \\ 0 & 0 & X_{33} \end{pmatrix}$
m 3, m 3 m	$\begin{pmatrix} X_{11} & 0 & 0 \\ 0 & X_{11} & 0 \\ 0 & 0 & X_{11} \end{pmatrix}$

These limitations on the X's applied to equation (2) give the possible orientations of the ellipsoid of induction with respect to the crystal axes.

II. General Theory

Thus in the triclinic system the orientation is arbitrary. In the monoclinic system one axis of the ellipsoid must coincide with the twofold axis of the crystal, the other two are in the (010) plane with ψ The angle from X_1 to C. In the orthorhombic system, and higher, the axes of crystal and ellipsoid are coincident. In uniaxial systems the ellipsoid is one of revolution and, in the cubic system, a sphere.

There is a relation among the principal magnetic constants of the crystal, viz., $X_1 + X_2 + X_3 = 3\overline{X}$, where $\overline{X}$ is the mean value found from a measurement on the crystal powder. Thus a measurement of two values of ΔX with the crystal in known orientation (combined with a measurement of ψ in the monoclinic system or ψ_1, ψ_2, ψ_3 in the triclinic system) will give the absolute values of X_1, X_2, X_3, if the value of $\overline{X}$ is known.

Methods of Measurement.

The orientation of the magnetic axes with respect to the crystal axes for monoclinic crystals may be measured directly by observation of the orientation of the crystal in the magnetic field. It may also be obtained by measurement of ΔX about three crystal directions from which ψ and the anisotropies can be found by equation(1).

The anisotropy may be measured by directly determining X along the principal axes (Voigt and Kinoshita(2), Rabi(3)). This method is more difficult and gives a less accurate value than the method of Stenger (4) in which a sphere of the material is suspended from a quartz fiber with a known axis vertical in a homogenous magnetic field and the couple acting on the crystal measured. This is done by measuring the angle ϕ through which the crystal moves when the torsion fiber is rotated through a measured angle, α radians.

If, for convenience, we say X_3 is vertical and perpendicular to $\tilde{H}$, and X_1 the axis of greatest susceptibility in the plane perpendicular to X_3, then

$$X_h = X_1 \cos^2\phi + X_2 \sin^2\phi$$ is the value of X in any direction in the X_1 X_2 plane where ϕ is the angle between X_1 and $\overline{H}$. The couple acting on the crystal is:

$$\frac{dE}{d\phi} = \frac{d}{d\phi}\left(-\tfrac{1}{2} X_h H^2 V\right),$$ Where E = potential energy of crystal in field,

$$= \tfrac{1}{2} V (X_1 - X_2) \sin 2\phi \, H^2 .$$

If the torsion constant of the fiber is k, and X molal is used instead of X per unit volume,

$$K\alpha = \tfrac{1}{2}\frac{m}{M} H^2 \sin 2\phi \, (X_1 - X_2) \qquad (3)$$

The value of $X_1 - X_2$ may be obtained from α and ϕ, or, more easily, by measuring α_c, the value of α when the couple is a maximum ($\phi = 45°$), then

$$k\,(\alpha_c - \pi/4) = \frac{m}{M} H^2 (X_1 - X_2) .$$

This is observed directly as the point beyond which a small increase in α causes the crystal to move through a large angle.

II. General Theory

Methods of Measurement

The couple acting on the crystal may also be determined from its period of oscillation in and out of the field. An anisotropic crystal is subject to a varying force when oscillating in a homogeneous field and the equation of motion, obtained by equating the accelerating torque to the angular acceleration for simple vibratory motion plus a term representing the instantaneous magnetic force on the body, is

$$I \frac{d^2\phi}{dt^2} = \frac{-\pi^2 I}{T^2}\phi + V H^2 (X_1 - X_2) \sin\phi \cos\phi ,$$

where ϕ is defined as above and I is the moment of inertia of the crystal aboutits axis of suspension.

This reduces to $t = \sqrt{I} \int \frac{d\phi}{\sqrt{\frac{\pi^2 I}{T^2}\phi^2 - VH^2(X_1 - X_2)\cos 2\phi + \text{const.}}}$

and so can only be integrated for the case of infinitely small vibrations.

Then $X_1 - X_2 = \frac{M}{m} \frac{4\pi^2 I}{H^2} \left(\frac{1}{T_1^2} - \frac{1}{T_0^2}\right)$,

or $= \frac{T_1^2 - T^2}{T_1^2} \frac{k}{H^2} \frac{M}{m}$, if I is not known but k is.

The values of T_1 must be reduced to infinitely small amplitudes of oscillation.

If the anisotropy of the crystal is large and the field sensibly homogeneous then the crystal may be used in its natural form rather than a sphere. These methods have been applied by Krisnan et al.(6) to a large series of crystals and the method has been discussed (see Lonsdale(7)).

III Experimental

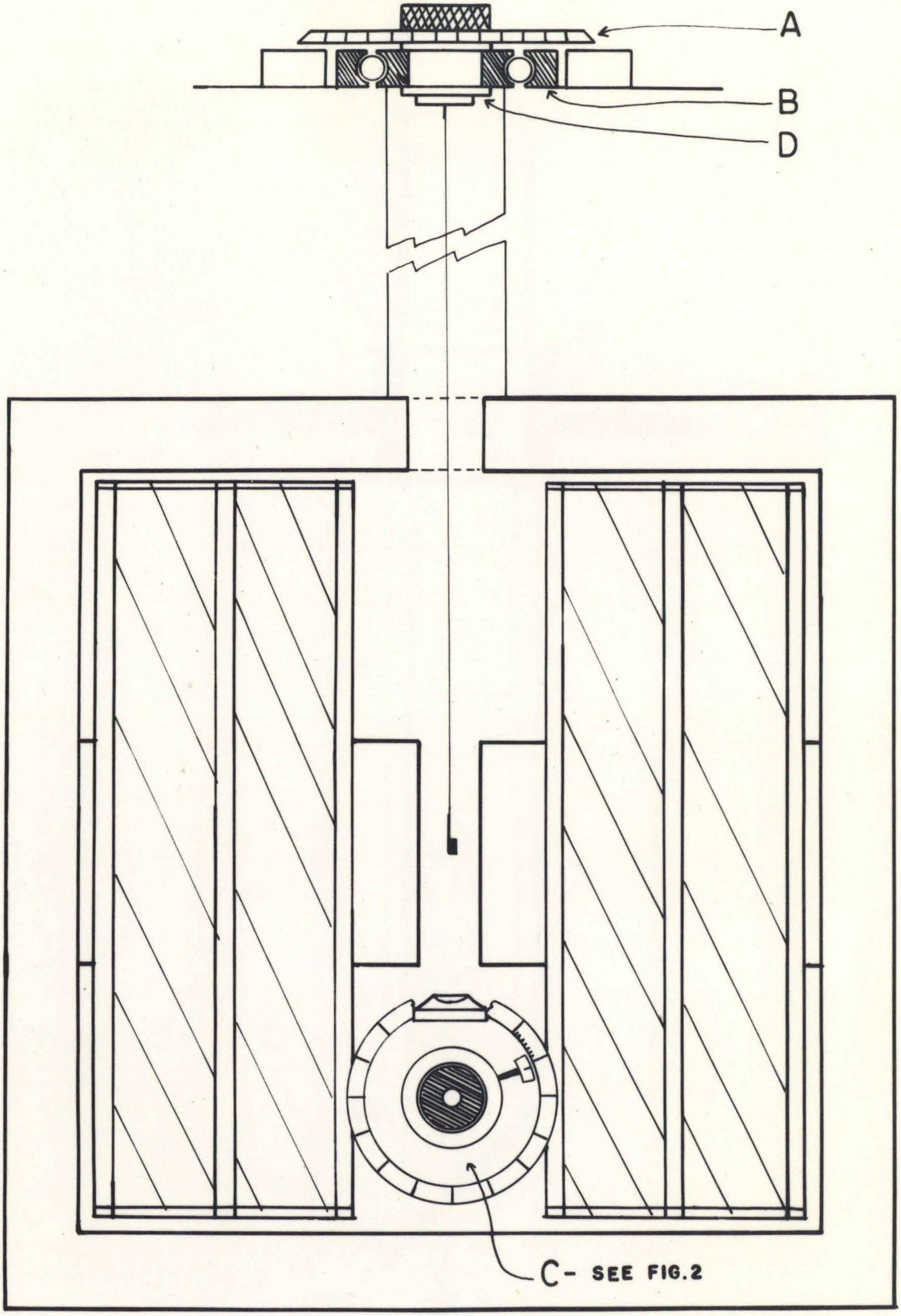
(a) Apparatus

The apparatus used for the measurement of crystal anisotropy is illustrated diagrammatically in Figs. 1 and 2. The magnet has a square yoke with the pole pieces centrally placed. 3" diameter plane parallel pole pieces of mild steel, separated by a gap of 2 cm., were used. The winding is in four parts, of 300 turns S.C.C. enameled copper wire each, separated by pancake cooling coils of 3/8" copper tubing through which cool water is circulated. A field of 8375 gauss was obtained at 12 amp. and could be maintained without heating. A reversing switch and variable resistance was provided for demagnetizing the iron.

The torsion head was mounted on a shelf about 60 cm. above the magnet and consisted of a 3" ball bearing to the bottom of which was attached a lucite disc and to the top a protractor and knob for turning.

The torsion head pin was fixed in a second lucite disc which was attached to the first by contact—a film of oil held the discs together but enabled the lower one to be moved to center the suspension. One end of the quartz fiber was attached to the pin, the other had a short, stiff, glass fiber 2 cm. long permanently attached to it. This was suspended centrally between the polepieces and the whole shielded from air currents by glass tube and box (not shown).

Fig.1 - Apparatus for the Determination of Magnetic Anisotropy.

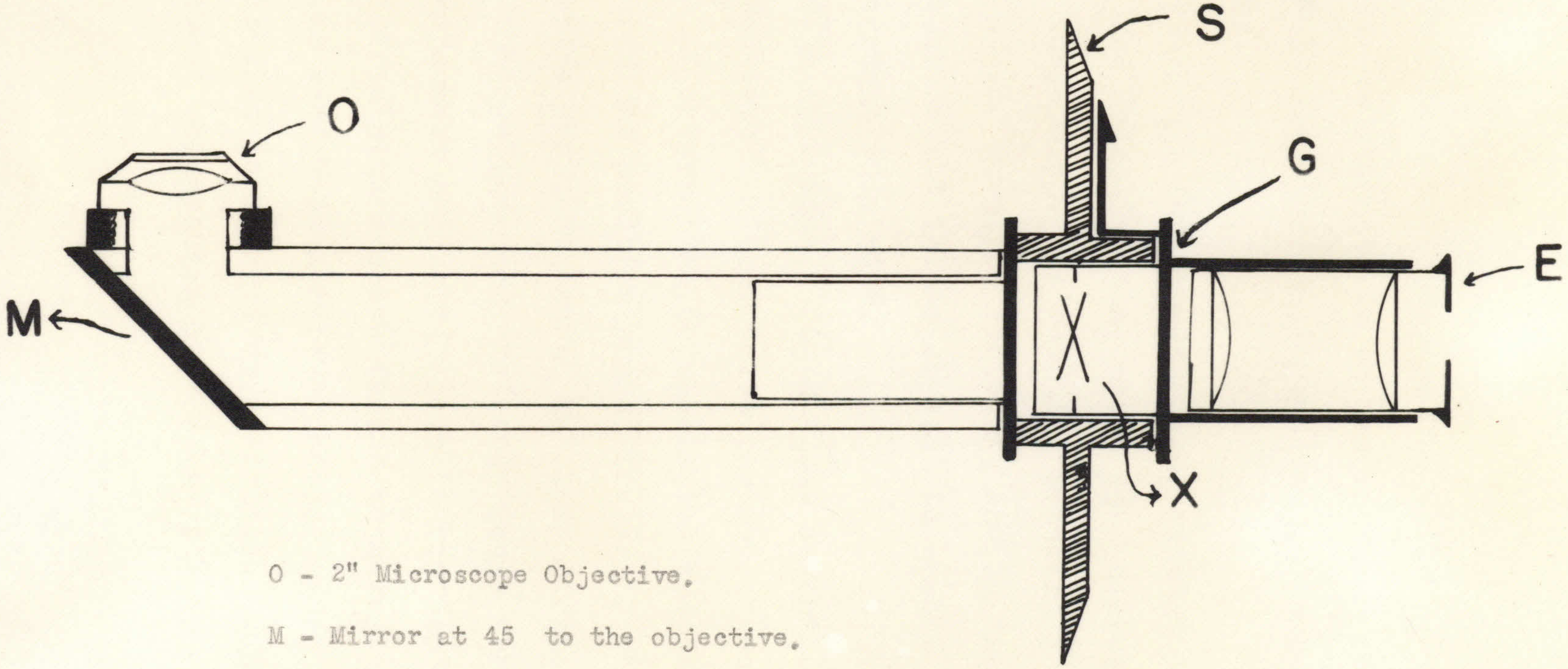


A - 6" Protractor divided to 0.5 .

B - 3" Ball bearing mounting.

C - Viewing system.

Fig. 2 - System for Viewing the Crystal.



O - 2" Microscope Objective.

M - Mirror at 45 to the objective.

S - 360 scale graduated to 1 .

G - Mounting carrying the eyepiece, crosshair, and pointer.

E - Eyepiece.

X - Crosshair.

III. Experimental

(a) Apparatus

The quartz fibers were prepared by allowing fibers of 50-100 μ diameter to elongate in an oxygen flame (Strong[3]). They were 3-7 μ in diameter and 75 cm. long, of apparently uniform diameter.

Below the crystal the apparatus for viewing the crystal was mounted so the objective came about 1½" directly below the end of the suspension. The mounting provided motion of the microscope up and down, for focusing, and in two perpendicular directions normal to the crystal to enable the crystal to be brought into view.

The viewing apparatus (fig.2) was essentially a microscope fitted with a mirror below the objective, and at 45° to the line of observation, to enable the eyepiece to be placed in a convenient position perpendicular to the suspension. The objective was a 2" Bausch and Lomb microscope objective, and the eyepiece and graduated scale were from a Schmidt polarimeter. The graduated scale is graduated in degrees, and is fixed with respect to the mounting. Rotating with the eyepiece and crosshair is a pointer which enables the angle of rotation to be read on a scale. A telescope was provided for direct observation of the crystal from above.

III. Experimental

(b) Method

The magnetic field strength was measured for a range of current values from 3-15 ampères by measuring the charge when a search coil was removed from the field, using a ballistic galvanometer. The galvanometer was calibrated against a standard mutual inductance with secondary placed in series with the search coil.

The inhomogeneity of the field was estimated by suspending a crystal of KI of known anisotropic shape and mass in the field and measuring the torque on it. The results are expressed in terms of the crystal anisotropy equivalent to this torque, $\frac{\Delta X}{X}$ (see below). It was reduced by a trial and error shimming of the magnet, and by moving the windings, but could not be eliminated. Narrowing the gap failed to reduce it so the 2cm. gap was retained as most convenient.

Crystals were mounted with a known axis vertical in the following manner. A thin glass fiber was set vertical on a goniometer head in a two circle goniometer. The crystal was mounted on this fiber in the field of the goniometer with the desired axis approximately vertical using shellac dissolved in a suitable solvent (one in which the crystal is insoluble). The crystal was then moved until it was correctly oriented, as determined by observation in the goniometer, and was kept in this position until the shellac became firm. Some time was allowed to make certain the crystal did not move. This glass fibre was now attached to the suspension by a small amount of glyptal or shellac so that the fiber was parallel to the suspension.

The orientation of the crystal in the field could now be observed by determining the orientation of a developed face or edge with respect to the cross hair of the viewing system. If no face was developed a very fine quartz fiber was attached to the crystal in known orientation, using the goniometer, so that the orientation in the field could now be measured by measuring the orientation of the fiber.

The angle ψ of a monoclinic crystal was now observed directly by recording the angle of a face or the cross fiber in the eyepiece, the angle corresponding to the field direction was then found by suspending a needle of benzil (or other suitable crystal) in the field and noting the direction of its edge in the eyepiece-this is the field direction. Since this measurement of ψ is by direct comparison, and is made without any adjustment of the viewing system mounting, it is not affected by the accuracy of the construction of the mounting.

The anisotropy of the crystal was then measured by setting the crystal torsionless in the field. This was done by rotating the torsion head until, when observed in the viewing system, the crystal did not rotate when the field was excited. The torsion head wasnow slowly rotated until it was at 45° to the field, when it suddenly turns through a large angle. The reading of the torsion head for this position is recorded (α_c). This is repeated, rotating the torsion head in the reverse direction, and values recorded.

About 6-10 measurements were made at each field strength and, in general, measurements were made at two field strengths, 8375 gauss and 6000 gauss.

Measurements were also made on two or three different crystal specimens in the same orientation, where possible, and three values of ΔX obtained for each crystal (the three orientations used depended somewhat on the developed faces of the specimen).

The mass of the crystal was determined by weighing on a micro, or semi-micro, balance.

The torsion constant of the fiber was measured by suspending bodies of known moment of inertia from the fiber and measuring the period of oscillation. A piece of aluminum rod of known mass and length was suspended from its center of gravity, and caused to execute small oscillations which were timed with a stop watch.

$$k = \frac{4\pi^2 I}{T_0^2}$$

I = moment of inertia of body
T_0 = period of oscillation
k = torsion constant

For fibers of very small torsion constant the period becomes long for bodies with a moment of inertia which is accurately measurable (i.e., errors in measurement of length and mass are less than 1-2%). Since the oscillations damp out rapidly the period is very difficult to measure in this way for thin fibers, and it is more practical to measure the torque on a crystal of known anisotropy and calculate k from this.

For the fiber used in most of these experiments:

Aluminum rod $m = 0.02670$ gram, $T_0 = 30.0$ sec.,

$l = 0.754$ cm.,

$$I = \frac{ml^2}{12} = 0.001265 \text{ gmcm}^2,$$

$$k = 5.73 \times 10^{-5} \text{ gmcm}^2 \text{ sec}^{-2}.$$

IV. Discussion of Method

In a perfectly homogeneous field the only torque on a spherical mass of crystal is that due to its magnetic anisotropy. If the shape deviates from cylindrical symmetry about the axis of suspension, there will be a couple due to this shape anisotropy tending to rotate the crystal so that its long axis is along the field. The force on a diamagnetic substance is toward weaker fields, and the field $H^1 = H - DM$ inside the body is least along the long axis since the demagnetizing factor D is least then. For a prolate ellipsoid of revolution of semi-major axis m, semi-minor axis n, and permeability μ, suspended from its minor axis, where α is the angle between the major axis and the field,

$$T = 1/6\ (\mu-1)\ m^2 n\ H\ (H-H^1) \sin 2\alpha\ , \qquad *)$$

Since $H-H^1 \approx (\mu-1)H$ and $\mu-1 \approx 10^{-6}$ for diamagnetic substances,

$$T \approx 10^{-7} \text{ gmcm}^2 \text{ sec}^{-2}, \text{ for } m = 20n\ .$$

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* Smythe - 'Static and Dynamic Electricity' - McGraw-Hill, 1939, p97.

This causes a rotation of about 0.01 radian when $k = 5.7 \times 10^{-5}$ for the torsion constant of the fiber, hence it may be neglected.

In an inhomogeneous field there is no torque on a sphere of isotropic material, but there is on a body whose shape deviates from cylindrical symmetry about the axis of suspension. This tends to rotate it so its length is in the position of minimum demagnetizing force. This torque is equivalent to a magnetic anisotropy in the body of $\frac{\Delta X}{X}$, and gives rise to an error in the result, since this torque acts independently of that due to magnetic anisotropy, and cannot be separated from it. The value of $\frac{\Delta X}{X}$ was measured using a plate of a cubic crystal (see above), and amounts to $\frac{\Delta X}{X} \approx 0.01$ to 0.02 for the field used here and a body with $m = 10n$. Hence for crystals of regular shape and large magnetic anisotropy the error is small (about 1% for a crystal with $m = 5n$ and $\Delta X = 50$), but for a large difference in dimensions and a small anisotropy the error is large and it is not possible to obtain reliable values of ΔX. In such cases it is possible to surround the crystal by a bath of the same volume susceptibility and so eliminate largely the torque due to shape anisotropy which depends on (X crystal —X medium). (Krishnan (6)).

The inhomogeneous component of the field causes an additional torque on an anisotropic crystal. A sphere of anisotropic crystal will tend to be rotated so that its axis of greatest susceptibility is the position of minimum demagnetizing force. Since the long axis of the crystal and the X_1 axis are not related it is not possible, in general, to calculate the effect in a given case and attempts to correct for these effects have not been found practical. A third effect which enters is a translational force on the crystal due to the inhomogeneous component of the field tending to move the crystal to the weakest part of the field. This is very small, but the bending moment of a long quartz fiber is so small that the effect is in some case observed. Since the field is constant to 1% in the space within which the crystal can move, the error introduced in this way is small.

The torque due to crystal anisotropy is independent of the distance of the center of gravity from the axis of suspension (since the magnitude of a couple is the same for all axis that are parallel), and the couple produces no translation, so the change in rotation is about an axis through the center of mass. However, the torque in an inhomogeneous field may increase with this distance, hence it is desirable to have the crystal suspended as nearly from the center of mass as possible.

The anisotropy of a crystal may thus be measured with some accuracy by suspending the crystal in its natural shape with a known axis vertical, and measuring the torque on it in a homogeneous field.

The alternative method of measuring torque, i.e., by measuring the period of oscillation of the crystal in and out of the field, was not used since it is subject to the same errors as the above and is less convenient. In order to obtain accuracy in the result using equation (5)(above), the period must be measured for small amplitudes of oscillation which makes the experiment rather difficult.

The value of ΔX (and mass) varies widely with available crystals and as a result periods very inconvenient to measure are encountered unless different fibers are used for each crystal. If a method of counting small amplitude oscillations of a wide range of periods were available this would be a useful method. A photoelectric relay and counter using a beam of light reflected from a crystal face might be used.

The precision of the measurements may be estimated—

$$\frac{\delta\Delta X}{X} = \frac{\delta m}{m} + 2\frac{\delta H}{H} + \frac{\delta\alpha}{\alpha} + \frac{\delta k}{k}$$

The mass was measured on a micro, or semi-micro, balance and was accurate to better than 1%. The field strength is measurable to 0.5% but may not be constant or reproducible to that, so 1% is a more reasonable probable error.

The angle α_c is measurable to 0.01% or better but is not reproducible to that accuracy. Fluctuations in temperature, air currents, and fluctuations in $\tilde{H}$, may cause an error in the measurement of α_c due to irreproducibility of, say, 1%.

The measurement of the torsion constant of the fiber, k, involves the measurement of mass and length of a small object and of time of oscillation (here 30.0 sec.). We may estimate an error of 1% in this value.

Then $\frac{\delta \Delta X}{X} = 0.05$, or $\Delta X_{obs} = \Delta X \pm 5\%$. While absolute values have this probable error, relative values of ΔX obtained on the same crystal have only the error in α_c contributing.

Measurements of ΔX are, in general, reproducible to within 5% although individual deviations from the mean may be higher. The value of the angle ψ can be read to $\pm 0.2^\circ$ but is reproducible to only about $\pm 0.5^\circ$. In agreement with these general considerations of the accuracy of the method results of different authors usually agree to within about 5% although there are many cases of greater deviations. Certain errors are possible which are difficult to estimate. The desired axis may not be quite vertical—up to 2° this should cause no appreciable error and the eye can detect deviations from vertical of this order. This error could be eliminated entirely by mounting an autocollimating goniometer perpendicular to the axis of suspension. Imperfections in the crystal or deformations such as often occur in organic crystals cause variation in results from specimen to specimen. Large crystals which are as perfect as possible are therefore used.

The properties of quartz fibers are unique and make them especially suited to this purpose. The coefficients of thermal expansion and hysteresis are both small. The Young's modulus $Y = 11 \times 10^{-11}$, the modulus of rigidity $Z = 6.6 \times 10^{-11}$, the value of $\frac{\Delta l}{l}$ for failure ≈ 0.06, and the value of $\frac{r\phi}{l}$ for failure ≈ 0.05. The strength thus compares with the strongest materials and a fiber 5μ in diameter can be twisted through

20 revolutions per cm. before it fails.

The elastic limits for normal and tangential stresses coincide with point of failure, hence, even in cases where α_c was 200 revolutions, the elastic limit was not approached. The fibers used here should show a fairly constant value of the torsion constant for the variations in room temperature of 2° C, and K should remain constant for the small variations in load and for variations in angle of rotation (temperature coefficients of Y and Z are $\approx 10^{-4}$ per degree).

The internal viscosity is very low, $\eta = 1 \times 10^{-12}$ poises, hence for periods of the order of 1—100 seconds the vibrations should damp out very slowly. Actually the damping is inconveniently rapid and it might be best to work in a vacuum when determining the torsion constant of the suspension (or the torque by the measurement of period).

Using the finest fibers ($k = 5 \times 10$ gm cm^2 sec^{-2}) it is possible to measure very small torques so that with proper refinement of technique an anisotropy of the order of $\Delta X \approx 10$ in a crystal weighing 0.01mg would still correspond to a value $\alpha_c \approx 100^\circ$, and so be easily measurable to the desired accuracy. For crystals weighing about 1 mg. it would be possible to use the field of Helmholtz coils which is the most uniform available.

V. Results (a)

A check on the measurement of field strength and torsion constant was provided by measuring ΔX for naphthalene. Large crystals of naphthalene weighing up to 2.5 mg., and of regular shape, were grown from amyl alcohol solution. Crystals were suspended from the monoclinic b-axis and ΔX determined as described above for several crystals.

Crystal #1. $m = 0.00232$gm., $M = 128.06$, $k = 5.73 \times 10^{-5}$ gm cm^2 sec^{-2},

$$X_1 - X_2 = \frac{2 \times 5.73 \times 10^{-5} \times 128.06}{0.00232 \times 36 \times 10^{-6}} (\alpha_c - \pi/4) \quad \text{for } H = 6000 \text{ gauss}$$

and $\alpha_c = 515.5$ radians (average),

$\pi/4 = 0.786$ radians.

Hence $X_1 - X_2 = 90.6 \times 10^{-6}$ cgsemu.. (6000 gauss)

and $\alpha_c = 980$ radians (av.),

$X_1 - X_2 = 88.3 \times 10^{-6}$ cgsemu.. (8375 gauss)

Crystal #2 $m = 0.00118$ gm.,

$\alpha_c = 268.8$ radians, and $X_1 - X_2 = 91.0$.

Note:

[Values of ΔX are in cgsemu. per mole and the factor 10^{-6}, where omitted, is understood.]

The average value $X_1 - X_2 = 90.7 \pm 3.0 \times 10^{-6}$ was obtained.

This is in agreement with the value given by Lonsdale & Krishnan (9), $X_1 - X_2 = 90.6$, and confirms their statement that the original value, $X_1 - X_2 = 122$, given by Krishnan (6) in an earlier paper, was in error.

(b) Measurements of ΔX and ψ were made on the substances listed below chiefly because crystals of them were obtainable with regular shape and appreciable mass (about 1 mg. or more).

V. Results

Naphthazarin*

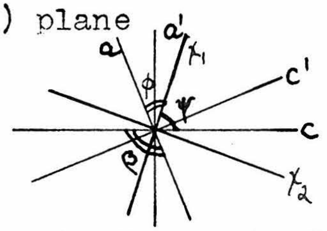
Dark red prisms of a form of naphthazarin not previously reported were obtained by evaporation of a benzol solution. The crystals are monoclinic prismatic with

$$\begin{aligned} a_0 &= 5.41, \\ b_0 &= 6.40, \\ c_0 &= 12.81, \\ \beta &= 91^\circ 32', \\ Z &= 2 . \end{aligned}$$

The anisotropies observed were

$$\begin{aligned} X_1 - X_2 &= 63.0, \\ \Delta X &= 10.4, \ (\ (100) \text{ horizontal}), \\ \Delta X &= 12.9, \ (\ (100) \text{ vertical}), \\ \psi &= 41^\circ 40^1, \\ \phi &= 50^\circ . \end{aligned}$$

The notation adopted is that of Krishnan and Lonsdale. The susceptibility along the monoclinic b-axis is X_3. In the (010) plane



X_1 is the axis of greatest susceptibility and X_2 is at right angles to it.

The angle from $\underset{\sim}{c}$ to X_1 in obtuse β is ψ, and from $\underset{\sim}{a}$ to X_1 in obtuse β is ϕ.

We may then transform from a set of axes $\underset{\sim}{a}$, $\underset{\sim}{b}$, and $\underset{\sim}{c}^1$, which is perpendicular to the ab plane, to the magnetic axes, to obtain the expressions for ΔX in terms of X_1, X_2, X_3.

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* The X-ray study was made by Mr. W. Shand to whom I am indebted for the crystals used here.

V. Results

Naphthazarin

The direction cosines for the transformation are (for Naphthazarin)

	a	b	c^1
X_1	$\cos\phi$	0	$\sin\phi$
X_2	$\sin\phi$	0	$\cos\phi$
X_3	0	1	0

.

Hence if the crystal is suspended from the c^1 axis (((001) horizontal) we have $X_{aa} = X_1 \cos^2\phi + X_2 \sin^2\phi$, along the $\underset{\sim}{a}$-axis, and the observed $\Delta X = \pm X_3 \mp (X_1 \cos^2\phi + X_2 \sin^2\phi)$, the upper signs holding if the twofold axis is along the field direction. The case is similar for (100) vertical and horizontal except that we transform to axes a^1, b, c, and $\phi^1 = 42.2^\circ$

$$\text{Hence } \Delta X = X_3 - (0.546\, X_1 + 0.454\, X_2) = 12.9$$

$$\Delta X = X_3 - (0.454\, X + 0.546 \chi_2) = 10.4$$

From these and $\frac{X_1 + X_2 + X_3}{3} =$ X mean $= -84.7$ (Banerjee(11))

we obtain

$X_1 = -57.3$,
$X_2 = -120.3$,
$X_3 = -77.1$.

The crystal was now suspended from the three principal magnetic axes, in turn, and the anisotropies determined directly.

From these the values were found, in agreement with the above,

$X_1 = -58.2$,
$X_2 = -119.2$,
$X_3 = -77.2$.

providing a check on the results.

V. Results

Coronene $C_{24}H_{12}$

Long yellow--brown needles of coronene were obtained from Melvin S. Newman. They are monoclinic prismatic with $\underset{\sim}{b}$ the needle axis, and have a fibrous cleavage parallel to $\underset{\sim}{b}$. The largest crystals available weighed only 0.25 mg.

The unit cell is:*

$a_0 = 10.13$ Å, $\beta = 110^\circ\ 49^1$,
$b_0 = 4.82$ Å.
$c_0 = 16.17$ Å, $Z = 2$.

The anisotropy was determined about each magnetic axis:

$$X_1 - X_2 = 180 ,$$
$$X_2 - X_3 = 40 ,$$
$$X_1 - X_3 = 220 ,$$
$$\psi = 90.8^\circ ,$$
$$\phi = 20.0^\circ .$$

An estimate of X mean = -213 was made from Pascal's law adapted to condensed ring hydrocarbons. The empirical relation for these hydrocarbons that $\overline{X}_m = -M. \times 0.718$ gives the value -215. Using the average of these

$$X_{mean} = \frac{X_1 + X_2 + X_3}{3} = -214 .$$

Then,
$X_1 = -83$,
$X_2 = -263$,
$X_3 = -302$.

Because the crystals are highly anisotropic in shape and of small mass the error introduced by inhomogeneity in the field may be rather large so there values have a large possible error.

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* Dr. J. H. Sturdivant

V. Results

Potassium nickelocyanide $K_2Ni(CN)_4 \cdot H_2O$

Orange yellow crystals weighing up to 20 mg. were obtained by evaporation of an aqueous solution of $Ni(CN)_2$ in KCN. They are monoclinic prismatic with:

$a_0 = 13.7$ Å,
$b_0 = 15.4$A, $\beta = 107° 16'$,
$c_0 = 18.6$A.
$Z = 16$.

The measurements of anisotropy gave:

$$X_1 - X_2 = 20.3,$$

$$(001) \text{ vertical } \Delta X = (X_1 \operatorname{Cos}^2 17.1 + X_2 \operatorname{Sin}^2 17.1) - X_3 = 15.5,$$

$$(001) \text{ horizontal } \Delta X = (X_1 \operatorname{Sin}^2 17.1 + X_2 \operatorname{Cos}^2 17.1) - X_2 = 2.9,$$

$$\psi = 0°,$$

$$\phi = 17.1°.$$

The mean susceptibility has been measured by Biltz(10) who reported

$$X \text{ mean} = -140 \times 10^{-6} \text{ per mole},$$
$$= 3(X_1 + X_2 + X_3).$$

Hence the principal susceptibilities are:

$$X_1 = -127.8 \times 10^{-6},$$
$$X_2 = -148.0 \times 10^{-6},$$
$$X_3 = -144.2 \times 10^{-6}.$$

V. Results

Copper Imidazole Complex $Cu\,(C_3H_4N_2)_4.2H_2O$

Crystals of this compound obtained deep blue from an aqueous solution of imidazole and Cu^{++} weighed about 1.5 mg.*1 They are orthorhombic with the following dimensions for the unit cell:

a_1 = 9.1 Å,

b_1 = 13.8 Å,

c_1 = 12.5 Å,

Z = 4 molecules of $Cu\,(C_3H_4N_2)_4 \cdot 2H_2O$.

The values of ΔX were measured suspending crystals from each crystallographic axis:

$X_1 - X_3 = 228$,

$X_2 - X_3 = 293$,

$X_2 - X_1 = 65$.

If we choose a mean value $\mu_B = 1.83$ for Cu^{++} in complex salts and add to this the diamagnetism of imidazole and water we may estimate:

$X_{mean} = 1234 \times 10^{-6}$ per mole.

Then $X_1 = 1288$, $X_2 = 1353$, $X_3 = 1060$

are the individual susceptibilities.

Copper phenylpropiolate $Cu\,(C_6H_5C \equiv C\text{-}COOH)_2.4H_2O$

A crystal of this compound weighing 3.88 mg. was obtained from aqueous solution.*2

*1 These crystals were obtained from Mr. P.A. Shaffer who has done the preliminary X-ray work quoted.

*2 These crystals were prepared by Mr. R. W. Spitzer and the dimensions of the unit cell are from his X-ray investigation.

V. Results

Copper phenylpropiolate

The crystals are a deep green color and show a complete cleavage parallel to a(110). The size of the orthorhombic unit cell is:

$a_0 = 6.5$ Å,
$b_0 = 30.1$ Å,
$c_0 = 9.0$ Å,

The values of ΔX obtained are:

$X_1 - X_2 = 630$,
$X_1 - X_3 = 10.4$,
$X_2 - X_3 = 620$.

An estimate of $X_{mean} = 1164 \times 10^{-6}$ gives the approximate values:

$X_1 = 1377$,
$X_2 = 747$,
$X_3 = 1367$.

The crystals are nearly uniaxial magnetically with the b-axis the unique axis.

VI. Discussion of Results

The observed values of X may be interpreted in terms of the molecular anisotropies K_1, K_2, K_3 and the orientations of the molecules in the crystal by making certain assumptions. This problem has been treated by Lonsdale and Krishnan(9)

To relate the observed susceptibility for the crystal to the principal susceptibilities K_1, K_2, K_3 of an individual molecule we add up the tensor components for each molecule in the crystal with proper regard to symmetry.

In the monoclinic system the coordinates of equivalent points related by reflexion and inversion are:

$$\pm \mid xyz \; ; \; x\bar{y}z \mid$$

(considering only the holohedry since magnetism is a centrosymmetric property). A molecule at (xyz) and its inversion will now be related to a set of orthogonal axes (a,b,c^1) by a set of direction cosines,

	a	b	c^1
K_1	α_1	β_1	γ_1
K_2	α_2	β_2	γ_2
K_3	α_3	β_3	γ_3

,

the orientation of the reflected molecule and its inversion are then given by:

	a	b	c'
K_1	α_1	$-\beta_1$	γ_1
K_2	α_2	$-\beta_2$	γ_2
K_3	α_3	$-\beta_3$	γ_3

.

These are added and the resultant components along (a,b,c^1) are:

$$K_{aa} = K_1\alpha_1^2+K_2\alpha_2^2+K_3\alpha_3^2 \, ,$$
$$K_{bb} = K_1\beta_1^2+K_2\beta_2^2+K_3\beta_3^2 \, ,$$
$$K_{cc} = K_1\gamma_1^2+K_2\gamma_2^2+K_3\gamma_3^2 \, ,$$
$$K_{ca} = K_{ac^1} = K_1\alpha_1\gamma_1+K_2\alpha_2\gamma_2+K_3\alpha_3\gamma_3 \, ,$$
$$K_{bc} = K_{cb} = K_{ab} = K_{ba} = 0 \, ,$$

where the K's are per gram molecule.

VI. Discussion of Results

Thus one of the principal axes of the crystal lies along $\underset{\sim}{b}$,

$$X_3 = K_{bb} = K_1\beta_1{}^2 + K_2\beta_2{}^2 + K_3\beta_3{}^2,$$

and the other two lie in the (010) plane (X_1 and X_2 as defined above).

We may now transform the K_{xy}'s in the (010) plane to the magnetic axes. If (as before) the angle between $\underset{\sim}{a}$ and X_1 is ϕ, then the cosines for the transformation are:

	a	b	c¹
X_1	Cosϕ	0	Sinϕ
X_2	Sinϕ	0	Cosϕ
X_3	0	1	0

,

and $K_{x_i x_j} = C_{i\ell} \quad C_{km} \quad K_{(abc')\ell m}$;

or $K_{\chi_1\chi_1} = K_{aa}\,\text{Cos}^2\phi + K_{c'c'}\,\text{Sin}^2\phi + 2K_{ac'}\,\text{Cos}\phi\,\text{Sin}\phi = X_1$;

$K_{\chi_2\chi_2} = K_{aa}\,\text{Sin}^2\phi + K_{c'c'}\,\text{Cos}^2\phi - 2K_{ac'}\,\text{Cos}\phi\,\text{Sin}\phi = X_2$;

$K_{x3\chi3} = X_3$; $K_{x2x3} = K_{x3x2} = K_{x1x3} = K_{x3x1} = 0$;

$K_{x1x2} = K_{x2x1} = -K_{aa}\text{Sin}\phi\,\text{Cos}\phi + K_{c'c'}\text{Cos}\phi\,\text{Sin}\phi + K_{ac'}\,(-\text{Sin}^2\phi + \text{Cos}^2\phi) = 0.$

This gives the values of $X_1\ X_2\ X_3$ in terms of the $K_{(a,b,c')}$.

The last relation gives a relation for **Tan ϕ**:

$$\text{Tan}\,\phi = \frac{K_{c'c'} - K_{aa} \pm \sqrt{(K_{c'c'} - K_{aa})^2 + 4K_{ac^1}{}^2}}{2\,K_{ac^1}}.$$

This enables us to simplify the values for X_i to:

$$X_1 = K_{aa} + K_{ac'} \quad \text{Tan}\,\phi = \tfrac{1}{2}(K_{aa} + K_{c'c'} \pm \sqrt{(K_{aa} - K_{c'c'})^2 + 4K_{ac'}{}^2} \; ;$$

$$X_2 = K_{c'c'} - K_{ac'} \quad \text{Tan}\,\phi = \tfrac{1}{2}(K_{aa} + K_{c'c'} \mp \sqrt{(K_{aa} - K_{c'c'})^2 \quad 4K_{ac'}{}^2} \; ;$$

the latter relations

$$\text{since} \quad \text{Tan}\,\phi = \frac{X_1 - K_{aa}}{K_{ac'}} = \frac{K_{c'c'} - X_2}{K_{ac'}} \quad ;$$

and, further, $X_1 + X_2 + X_3 = K_1 + K_2 + K_3 = K_{aa} + K_{bb} + K_{c'c'}$.

VI. Discussion of Results

Hence, expanding,

$$X_1 = \tfrac{1}{2}(aK_1 + bK_2 + cK_3 + \sqrt{(dK_1 + eK_2 + fK_3)^2 + lK_1 + mK_2 + nK_3)^2}\ );$$

$$X_2 = \tfrac{1}{2}(aK_1 + bK_2 + cK_3 - \sqrt{(dK_1 + eK_2 + fK_3)^2 + (lK_1 + mK_2 + nK_3)^2}\ );$$

$$\text{Tan}\,\phi = \text{Tan}\,(\phi - \psi) = \frac{X_1 - K_1\alpha_1^2 - K_2\alpha_2^2 - K_3\alpha_3^2}{K_1\alpha_1\gamma_1 + K_2\alpha_2\gamma_2 \quad K_3\alpha_3\gamma_3}.$$

Hence we conclude that:

(1) If X_1, X_2, X_3 and 3 independent direction cosines of the molecule are known we can calculate K_1, K_2, K_3 and Tan ϕ. The measured value of Tan ϕ is then a check on the calculation.

(2) If X_1, X_2, X_3 and Tan ϕ are known, and if $K_1 \approx K_2$, we can obtain approximate values of K_i and the direction cosines of K_3 with respect to the axes (a, b, c′). Thus supplying $K_1 \approx K_2$ in the above equations we obtain:

$$X_1 \approx K_1 ,$$

$$X_2 \simeq K_3 - (K_3 - K_1)\beta_3^2 ,$$

$$X_3 \simeq K_1 + (K_3 - K_1)\beta_3^2 , \qquad \text{Tan}\,\phi \approx -\frac{\alpha_3}{\gamma_3} .$$

X_1 is thus the line in which the plane of the molecule cuts (010) if $K_1 = K_2$, and X_2 is the projection of K_3 (the normal to the molecular plane and, for aromatic molecules, where $K_3 \gg K_1 \approx K_2$, a unique axis).

If we cannot assume $K_1 \approx K_2$ then the above does not hold. However, in two special cases the angle ψ turns out to be the angle between $\underset{\sim}{c}$ and the projection of K_1 (the long axis of the molecule) on (010). Those cases are:

(a) Molecule is plane and normal to (010) so $X_2 = K_3$;

(b) K_1 of molecule lies in (010) plane so $X_1 = K_1$.

VI. Discussion of Results

In either of these cases, and only then, can we determine the orientation of the molecule in the plane of K_1 K_2 from measurements of X_1, X_2, X_3 and $\tan\phi$, even though K_1, K_2, K_3 are known.

If a structure approximates to one of these cases the orientation of the molecules may be completely obtained if the K's can be estimated. Otherwise it is necessary to assume $K_1 \approx K_2$ and only the direction of the normal to the plane is fixed.

Orthorhombic System

A similar treatment may be applied to the eight equivalent points of D_{2h} -mmm, $\pm|(xyz;\bar{x}yz;x\bar{y}z;xy\bar{z})|$.

The result gives

$$X_a = K_1 \alpha_1^2 + K_2 \alpha_2^2 + K_3 \alpha_3^2 ,$$

$$X_b = K_1 \beta_1^2 + K_2 \beta_2^2 + K_3 \beta_3^2 ,$$

$$X_c = K_1 \gamma_1^2 + \quad + K_2 \gamma_2^2 + K_3 \gamma_3^2 .$$

Then if three independent cosines are known the X's give the K's directly. If the X's are known and $K_1 \approx K_2$, then we can, as before, obtain the direction cosines of the normal to the molecular plane:

$$X_a = K_1 + (K_3 - K_1)\alpha_3^2 ,$$

$$X_b = K_1 + (K_3 - K_1)\beta_3^2 .$$

Uniaxial systems

A knowledge of X_a, X_c and three independent cosines will give the values of K_1, K_3, if $K_1 \approx K_2$.

VI. Discussion of Results

If the X's are known, and $K_1 \approx K_2$, an estimate of K_1 and K_3 will give the orientation of K_3 to c, but not its azimuth.

Note- If molecules are in two or more independent sets of positions in a space group there will be more than three independent direction cosines and the orientations cannot be deduced unless there is a relation known among the sets.

Naphthazarin

There are no values for K_1, K_2, K_3, hence we can only assume $K_1 \approx K_2$ for the plane of the ring. Then

$$K_1 \approx X_1 = -57.3, \qquad \Delta K = 82.3, \quad K_3 = -140.1;$$

$$\text{and } \beta_3 = \sqrt{\frac{X_3 - K_1}{K_3 - K_1}} = 0.489, \qquad \cos^{-1}\beta_3 = 60^\circ\ 43' = \theta_1;$$

$$\text{Tan } \phi = \tan 50^\circ = 1.192 = \frac{-\alpha_3}{\gamma_3}, \qquad \cos^{-1}\gamma_3 = 55^\circ\ 52' = \theta_2;$$

$$\text{hence, } \gamma_3 = \sqrt{\frac{1 - \beta_3^2}{1 + 1.42}} = -0.561; \qquad \cos^{-1}\alpha_3 = 48^\circ\ 05' = \theta_3;$$

where $\theta_1, \theta_2, \theta_3$ are the values of the angles of the normal to the plane of the molecule, K_3, with axes (a,b,c'), respectively, and the planes of the molecules cut the (010) plane in the line X_1.

A similar interpretation of the data for another crystalline variety of naphthazarin investigated by Banerjee[11] gives the values $K_1 = -60.7$, $K_3 = -132.8$, $\Delta K = 72.1$ for naphthazarin. Values of ΔK would be expected to be between the probable value $\Delta K \approx 104.8$ for naphthaquinone and twice the value observed for benzoquinone, i.e., $\Delta K = 80$. The assumption that $K_1 \approx K_2$ is probably nearly true since it is for benzene, naphthalene, and benzoquinone (for benzoquinone $K_1 - K_2 = 3.7$).

VI. Discussion of Results

Coronene

For coronene the assumption that $K_1 \approx K_2$ should be very good since it has symmetry D_{6h}. We then obtain:

$$K_1 \simeq X_1 = -83,$$

$$K_3 \cong X_2 + X_3 - K_1 = -482,$$

$$\text{and } \Delta K = 399.$$

Then $\beta_3 = \dfrac{X_3 - K_1}{K} = 0.741$, and $\theta_2 = \text{Cos}^{-1}\beta_3 = 42^\circ\, 10'$,

And $\text{Tan}\,\phi = \text{Tan}\, 20^\circ = 0.364 = -\dfrac{\alpha_3}{\gamma_3}$;

$$\text{and } \alpha_3 = 0.231, \qquad \theta_1 = \text{Cos}^{-1}\alpha_3 = 76^\circ\, 40^1;$$

$$\gamma_3 = 0.634, \qquad \theta_3 = \text{Cos}^{-1}\gamma_3 = 50^\circ\, 40^1;$$

where θ_1, θ_2, θ_3 are the angles between K_3 and the (a,b,c') axes. Relative to the (X_1 X_2 X_3) axes $\theta_1' = 90^\circ$, $\theta_2' = 47^\circ 48'$, $\theta_3' = 42^\circ 10'$, give the position of K_3.

The value of $K_1 = K_2$ seems too low for coronene in view of the values observed for somewhat similar condensed ring hydrocarbons (-88 in chrysene, -80.6 in pyrene, -81 in perylene, -93 in naphthacene, -100 in benzpyrene—all of these in some doubt due to assumptions made in arriving at the values; vide Krishnan(12), Banerjee(11)). Hence the value of $K_3 = -482$ and of $\dfrac{K_3}{K_1} = 5.8$ are probably upper limits.

The value of θ_2 the angle of tilt of the normal to the ring to the b-axis, calculated from the thickness of the ring (3.70Å estimated) and the unit translation along b, is $39^\circ 45'$.

VI. Results

Coronene

The anisotropy of condensed ring aromatic hydrocarbons has been calculated theoretically by Pauling*, and by London**. Pauling considered the $2p_z$ electrons of the aromatic ring free to move under the influence of the magnetic field and, for benzene, calculated $\Delta K = -49.2 \times 10^{-6}$, assuming that the value of χ is given by the Pauli expression:

$$\chi = \frac{-N e^2}{4 m c^2} (\rho^2)_{av.},$$

where $(\rho^2)_{av.}$ is the mean square of the distance of the electron from an axis through the nucleus and parallel to the field $\tilde{H}$, for the impressed field parallel to the plane of the molecule; and ρ is measured from the hexagonal axis of the molecule to the carbon atoms, for $\tilde{H}$ perpendicular to the plane of the molecule. For higher condensed aromatic ring compounds solution of the equivalent problem of the magnetic effect of currents induced in a conducting network gave the expression:

$$\Delta K = - 38.0 \times 10^{-6}\, k \sigma f \ ,$$

where k is the ratio of the strength of magnetic dipoles for the hydrocarbon network and the benzene network, σ is the electron density per C-C bond, and f is a correction factor to take into account the tendency of the electrons to move in circular arcs rather than rectilinear paths.

For coronene, $C_{24}H_{12}$, Pauling calculates:

$$K_2 = K_1 = - 132 \times 10^{-6},$$

$$K_3 = - 704 \times 10^{-6},$$

$$\Delta K = - 572 \times 10^{-6};$$

using the empirical relation

$$K_1 = K_2 = -(2.0\, n_H + 6.0\, n_{Cal.} + 4.5\, n_{Car.}) \times 10^{-6},$$

VI. Results

Coronene

For Coronene this is equivalent to $\overline{K} = 323$. If the experimental results are combined with this value of $\overline{K}$ we obtain:

$\chi_1 = -189 \times 10^{-6}$, $K_1 = K_2 = -189 \times 10^{-6}$,

$\chi_2 = -369 \times 10^{-6}$, $K_3 = -590 \times 10^{-6}$,

$\chi_3 = -409 \times 10^{-6}$, $\Delta K = -401 \times 10^{-6}$.

It is thus probable that the Pauling theory gives somewhat too high values for the anisotropy of the higher molecular weight aromatic condensed ring hydrocarbons. London calculates ΔK quantum mechanically and obtains values which are, in general, smaller than those given by the Pauling theory. The calculation for coronene has not been made on the basis of the London theory, however.

* L.Pauling, J.Chem.Phys., 4, 673 (1936).

** F.London, J.Phys.Radium, 8, 397 (1937).

Discussion of Results

Copper Imidazole

The interpretation of paramagnetic anisotropies is, as yet, somewhat obscure because the values depend on the environment of the ions, which varies with the different crystals containing a given ion, and depends on the coordination of the ion. The magnetic anisotropy of $CuSO_4.5H_2O$ has been determined and correlated with the structure (Krishnan et al.[13]). They found that the Cu^{++} ion, surrounded in the crystal by four oxygen ions in a plane at closer distance, and two somewhat farther away completing an octahedron, showed approximately tetragonal symmetry magnetically: $K_{\parallel} = 1787 \times 10^{-6}$ (unique axis), and $K_1 \cong K_2 = K_{\perp} = 1237 \times 10^{-6}$, so that the anisotropy of the Cu^{++} ion is about $K_{\parallel} - K_{\perp} = 550 \times 10^{-6}$. It might be expected that in copper imidazole a similar situation would exist with four imidazole groups held in a plane about Cu^{++} and the two oxygen atoms of the water molecules at larger distances completing the octahedron. If this were the case, and the value $K_{\parallel} - K_{\perp}$ for $CuSO_4.5H_2O$ assumed, we could calculate the orientation of the planes containing the groups $Cu(imidazole)_4$.

Copper phenylpropiolate

This is likewise paramagnetic and the interpretation is complicated by a considerable contribution to the anisotropy by the benzene rings. The large anisotropy observed would be expected if Cu^{++} were surrounded by $4H_2O$ (large distance) and 2 $C_6H_5-C \equiv C-COOH$ (closer).

VI. Discussion of Results

Potassium Nickelocyanide

It is interesting that this compound shows a magnetic anisotropy large compared to inorganic compounds in general. This suggests that there is considerable anisotropy associated with the square covalent group $Ni(CN)_4$. This might be expected to be similar in magnitude to that observed for $CO_3^=$ and NO_3^-, about 4 or 5 x 10^{-8} cgs. per group, since there is possibility of resonance to structures having double bonds from nickel to carbon (Pauling*). A knowledge of the structure of a crystal containing square covalent complexes combined with a knowledge of the anisotropy of the crystal would give an estimate of the value of ΔK for the group and so enable the orientation of the complexes to be discussed in other crystals.

The presence of 16 molecules $K_2Ni(CN)_4$ in this crystal makes quantitative interpretation impossible until the crystal structure is known. The magnetic data are in qualitative agreement with the optical data—the crystals are strongly birefrigent with $\alpha = 1.44$, $\beta = 1.594$, $\gamma = 1.598$, $2V = 15°24'$ (Mellor[14]). Groth gives (010) as the plane of the optic axes and Mellor (100), however.

*L. Pauling, "The Nature of the Chemical Bond", 2nd Ed., Cornell University Press, Ithaca, N.Y., 1939, p. 256.

VII. Summary

An apparatus for measuring the magnetic anisotropy of crystals has been constructed. The magnetic anisotropies and orientations of magnetic axes have been measured for several crystals. The results have been interpreted, where possible, in terms of the orientations of molecules in the crystal.

The experimental method, and the interpretation of the results of measurements, have been discussed.

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Summary of Thesis

(a) The crystal structure of iodic acid has been determined and shown to contain IO_3^- groups held together by hydrogen bonds. The structures of other iodates have been discussed in the light of this knowledge.

(b) The crystal structure of potassium oxyfluoiodate has been determined. It has been shown to contain $IO_2F_2^-$ groups with the unshared pair of electrons on the iodine atom sterically active.

(c) A redetermination of the parameters in ammonium and potassium bifluorides has given accurate values of the distances F-F of the HF_2^- groups. It is shown that the two extra hydrogen bonds formed in ammonium bifluoride weaken the F-H-F bond of the bifluoride ion.

(d) The internuclear distance in the fluorine molecule has been precisely determined and thus the covalent radius of fluorine established.

(e) The molecular structure of tellurium dibromide has been determined and the results of other authors shown to be in error.

(f) The magnetic anisotropy of several crystals has been measured and, in the case of two aromatic diamagnetic compounds, the approximate orientation of the molecules in the unit cell has been calculated.

Propositions.

I. The point group symmetry mmm determined for m-dinitrobenzene by Hendricks[1], and Hertel and Bergh[2], and assumed by Banerjee[3] in interpreting his Patterson (hk0) projection of that substance, is wrong. If we assume the crystal hemihedral, the space group becomes Pna, and the difficulty of accounting for intensities, which led Hendricks to postulate an improbable structure, is overcome.

II. A structure may be derived for cinnabar which has normal S-Hg-S and Hg-S-Hg angles and distances. The parameters suggested by De Jong and Willems[4] correspond to this structure.

III. A study of the reactions of interhalogen compounds with one another should yield interhalogens containing three different halogens. The reaction of I_2 with ClF in the vapor phase probably gives rise to such a compound.

IV. If it is correct to assume that the splitting of the peak at 2.67μ, observed by Buswell, Maycock and Rodebush[5] for crystalline KHF_2, is due to a double minimum in the potential function of the ion, then the potential barrier is greater than 32 K.Cal. per mole. It is thus unlikely that the observed splitting is due to a double minimum.

V. Tellurium hexafluoride is a suitable substance for use in an ionization chamber when high stopping power is desired.

VI. There is a torque on an anisotropic crystalline sphere in an inhomogeneous magnetic field. This torque is only appreciable if the axis of suspension is not through the center of gravity of the crystal, and is not completely eliminated by immersing the crystal in a medium of the same mean susceptibility. This has been neglected in discussions of related phenomena[6].

VII. The discussion of the effect of formal charge on the iodine radius given by Helmholz and Rogers (above p. 20) reflects a general tendency to overestimate this effect. A revised table of interatomic distances largely removes this difficulty.

The discussion of iodine radius given by Braune and Pinnow[8] is not harmless as shown by a remark of Skinner and Sutton[7] about "the shortening observed in IF_5 with I-F = 2.57 Å".

IX. An E.M.F. will exist between two electrodes placed at the top and bottom of a tube containing the solution of a paramagnetic salt if one end of the tube is in a magnetic field and the other outside the field. It is thus possible to have electric polarization in a medium due to magnetization.

X. The crystal mesityloxide oxalic acid methyl ester dimer described by Sommerfeldt[10] is monoclinic, C_s-m. It provides the only example of an optically active crystal containing a symmetry element of the second kind as predicted by the Born theory[13]. This provides proof that the criteria given by Dana[11] or Tutton[12] for the classes in which optical activity is possible are not correct. If a crystal is optically active we may only say with certainty that it lacks a center of symmetry.

XI. 'An Elementary Formulation of Statistical Mechanics' by Eyring and Walter[14] achieves little by way of simplification for a sacrifice of logic and rigor in presentation.

XII. The magnetic and peculiar optical properties of $MgPt(CN)_4 \cdot 7H_2O$ are qualitatively accounted for by the presence of square covalent $Pt(CN)_4$ groups in the crystal (Bozorth and Pauling[9]).

VIII. The Br-F distance in BrF_3 is Br-F = 1.81 ± 0.02 Å. The molecule is probably pyramidal with ∠F-Br-F = 35° ± 5°. The I-F distance in IF_5 is 1.95 ± 0.05 Å rather than the value 2.54 Å reported by Braune and Pinnow[10].

Their value suggests that it might be due to I_2 from the decomposition of IF_5, which they handled in the presence of stopcock grease. Their other investigations on fluorides are suspect for this reason, since these fluorides react very rapidly with apiezon.

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