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**A defect of the James & Brindley atomic scattering factors.** By W. COCHRAN, *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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James & Brindley (1931) have calculated atomic scattering factors based on Hartree's (1928*a*, *b*) calculations of the electron distributions in isolated atoms. Hartree's comparatively exact calculations applied to only a few atoms; James & Brindley used an interpolation method to extend them to many others. Their results have been found to be in fair agreement with experiment, and have been widely used in crystal-structure analyses. Recent experimental evidence (e.g. Bacon, 1952) has shown that the James & Brindley results for carbon deviate appreciably from experimental values in the range  $0 < \sin \theta/\lambda < 0.4$ . Another unsatisfactory feature of some of the James & Brindley curves is reported here. The atomic scattering factor for carbon should correspond to a (non-negative) distribution of 6.00 electrons, entirely contained in a sphere of radius not greater than, say, 2.5 Å. In investigations of the electron distribution in organic compounds using ( $F_o - F_c$ ) syntheses, one is particularly interested in the correctness of the  $f$ -curve (on which values of  $F_c$  depend) in the range  $0.1 < \sin \theta/\lambda < 0.7$ , this being the usual range of experimental measurement.

Suppose values of  $f$ , as given by theory, are 'sampled' at an interval  $q$  in  $\sin \theta/\lambda$ . A Fourier series with these values as coefficients then represents the electron density in the atom, projected on a line and repeated at intervals  $a = 1/2q$ .

The function

$$\rho'(x) = 2 \sum_{n=1}^{\infty} f(nq) \cos nx/a$$

should reach a constant value  $-Z$  in the region between atomic centres,  $Z$  being the number of electrons in the atom concerned. By first also multiplying the values of

$f$  by a temperature factor (taken as  $\exp[-4(\sin \theta/\lambda)^2]$  in what follows) a value for  $Z$  can be obtained which depends only on the shape of the  $f$ -curve in the range  $0.1 < \sin \theta/\lambda < 1.1$ . This has been done using the  $f$ -curves for carbon and nitrogen (James & Brindley), oxygen (Hartree), and carbon as given by McWeeny (1951). The values obtained for  $Z$  when  $q = 0.1$ ,  $a = 5.0$  Å, are shown in Column I of Table 1. The calculation was repeated with  $q = 0.065$ ,  $a = 7.7$  Å, and the results are given in Column II. In this case, the maximum distance from an atomic centre is 3.85 Å, and values of  $Z$  were taken as the average value of  $-\rho'$  in the range  $2.95 \text{ Å} < x < 3.85 \text{ Å}$ . The values of  $Z$  for carbon and for nitrogen (James & Brindley) were slightly higher than those from the first calculation, but were still significantly less than 6.00 and 7.00 respectively.

We may conclude that the James & Brindley curve for carbon, in the range  $0 < \sin \theta/\lambda < 1.1$ , corresponds to an electron distribution which does not fall to zero in a reasonable distance. The curve in the range  $0.1 < \sin \theta/\lambda < 1.1$  corresponds fairly closely to an acceptable distribution, which however contains only about 5.7 electrons. Similar conclusions apply to the James & Brindley curve for nitrogen, and it is possible that other curves obtained by the interpolation method are also defective.

This discrepancy is large enough to be serious in accurate work and was in fact first detected in the course of an investigation of the electron distribution in salicylic acid (Cochran, 1953), where use of the James & Brindley curve for carbon with the Hartree curve for oxygen produced ( $\rho_o - \rho_c$ ) maps which indicated an impossibly large transfer of electrons from oxygen to carbon atoms.

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Table 1

Atom	Value of $Z$	
	I	II
C (J.-B.)	5.5 <sub>5</sub>	5.7
N (J.-B.)	6.6	6.7
O (H.)	8.0	8.0 <sub>5</sub>
C (McW.)	5.9 <sub>5</sub>	5.9 <sub>5</sub>

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**The crystal structure of aluminum titanate.\*** By A. E. AUSTIN and C. M. SCHWARTZ, *Battelle Memorial Institute, Columbus, Ohio, U. S. A.*

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The crystal structure of aluminum titanate,  $\text{Al}_2\text{TiO}_5$ , has been determined. Small, single crystals were obtained

from a crushed friable briquette of a stoichiometric mixture of alumina and titania fired at 1800° C. Rotation and equi-inclination Weissenberg photographs were taken about the [100], [010] and [001] rotation axes, using

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filtered iron radiation. Extinctions observed were  $(hkl)$  with  $(h+k)$  odd and  $(h0l)$  with  $l$  odd. The Weissenberg photographs indicated an end-centered orthorhombic cell. These criteria led to possible space groups  $Cmcm$  or  $Cmc$ . Tests for pyroelectric effect were negative and therefore suggested the centrosymmetrical space group. The crystals (approximately 20 microns diameter) were too small for piezoelectric tests. An additional basis for trying the space group  $Cmcm$  was the possible isomorphism of aluminum titanate with pseudo-brookite,  $Fe_2TiO_5$  (Pauling, 1930).

The chosen point positions in space group  $Cmcm$  are  $4(c)$  for titanium,  $8(f)$  for aluminum,  $4(c)$  for one set of four oxygen atoms, and  $8(f)$  for two sets of eight oxygen atoms. Approximate atomic parameters were selected from atomic radii and coordination considerations. These were refined by comparison of calculated and observed structure factors. The final parameters are given in Table 1.

Table 1. Atomic parameters for  $Al_2TiO_5$

Atom	Position	X	Y*	Z*
Ti	4(c)	0	0.190	0.250
Al	8(f)	0	0.145	0.560
O <sub>1</sub>	4(c)	0	0.760	0.250
O <sub>2</sub>	8(f)	0	0.040	0.120
O <sub>3</sub>	8(f)	0	0.320	0.090

\*  $\pm 0.003$ .

An acceptable agreement between observed intensities and those computed from the structure was obtained. Atomic-scattering-factor data from the *Internationale Tabellen*, vol. 2, were used. The calculated intensities were corrected for absorption, Lorentz and polarization factors. Table 2 gives interatomic distances.

Powder X-ray diffraction patterns were obtained for

Table 2. Interatomic distances in  $Al_2TiO_5$

Atom	Neighbor	Number	Distance (Å)
Ti	O <sub>I</sub>	2	1.90
Ti	O <sub>II</sub>	2	1.90
Ti	O <sub>III</sub>	2	2.00
Al	O <sub>I</sub>	1	2.05
Al	O <sub>II</sub>	1	2.14
Al	O <sub>II</sub>	1	1.96
Al	O <sub>II</sub>	1	1.86
Al	O <sub>III</sub>	2	1.84
O <sub>I</sub>	O <sub>II</sub>	4	2.99
O <sub>I</sub>	O <sub>III</sub>	4	2.45
O <sub>II</sub>	O <sub>II</sub>	1	2.52
O <sub>II</sub>	O <sub>II</sub>	1	2.45
O <sub>II</sub>	O <sub>III</sub>	2	2.77
O <sub>II</sub>	O <sub>III</sub>	2	2.99
O <sub>II</sub>	O <sub>III</sub>	1	2.64
O <sub>III</sub>	O <sub>III</sub>	1	3.08
O <sub>III</sub>	O <sub>III</sub>	2	2.79

determination of the lattice constants. The values obtained were

$$a_0 = 3.557 \pm 0.002, \quad b_0 = 9.436 \pm 0.005, \quad \text{and} \\ c_0 = 9.648 \pm 0.005 \text{ \AA},$$

(Fe  $K\alpha_1$  radiation,  $\lambda = 1.93597 \text{ \AA}$ ). The measured density was  $3.67 \text{ g.cm.}^{-3}$ . The calculated density, assuming 4 molecules per unit cell, was  $3.71 \text{ g.cm.}^{-3}$ .

Aluminum titanate,  $Al_2TiO_5$ , is isomorphous with pseudo-brookite,  $Fe_2TiO_5$ . There is some shift of position parameters. Because of this shift, the aluminum atoms tend toward tetrahedral coordination more than do the iron atoms in pseudo-brookite, although both do maintain distorted octahedral coordination.

### Reference

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## A computational procedure for determining lattice parameters from powder photographs.

By G. D. ARCHARD,\* *The University, Reading, England*

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Cohen (1935) has given a method for computing lattice parameters of hexagonal crystals. Three summations are involved. In the expression for the parameters, these nearly cancel, so that a large number of significant figures must be carried throughout.

The same accuracy can be attained by the following method; this involves only one summation, and, after the plane spacings  $d_{hkl}$  have been deduced from the Bragg angles, three-figure working suffices. Consider

$$a = \left\{ \left( \frac{4}{3} \right) (h^2 + k^2 + hk) + l^2 / C^2 \right\}^{\frac{1}{2}} \cdot d_{hkl} = f(hkl) \cdot d_{hkl}. \quad (1)$$

Guess the axial ratio  $C (= c/a)$  and plot the values of

$a$  against  $x = \frac{1}{2} (\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$  (Nelson & Riley, 1945), obtaining a best straight line of slope  $m$ . Then the 'residuals' of the plot are given by

$$\Delta = a' - mx',$$

where

$$\left. \begin{aligned} a' &= a - \Sigma a/n, \\ x' &= x - \Sigma x/n, \end{aligned} \right\} \quad (2)$$

$n =$  number of reflexions  $hkl$ .

If the guessed value of  $C$  is varied, it is reasonable to accept as optimum that value which makes the variance  $\Sigma \Delta^2$  of the best straight line a minimum. This is easily shown to be

$$C_{\text{opt.}} = C_{\text{guessed}} - \Sigma \Delta a_m / a \Sigma A_m^2, \quad (3)$$

\* Now at Associated Electrical Industries Ltd, Aldermaston, Berkshire, England.