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## Anisotropic Temperature Vibrations in Crystals. II. The Effect of Changes in Atomic Scattering Factors and Temperature Parameters on the Accuracy of the Determination of the Structure of Urea

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The effects of changes in atomic scattering factors and temperature parameters on the atomic co-ordinates and  $R$ -factors obtained for urea are demonstrated.

Re-calculation of the structure factors to be expected from Vaughan & Donohue's parameters shows that the value of  $R = \Sigma\{|F_o| - |F_c|\} \div \Sigma|F_o|$  is reduced from 0.099 to 0.061 when proper allowance is made for the anisotropic thermal vibrations deduced by them. The method used in making the calculations is described. Attention is drawn to the importance of separating thermal anisotropy from the bonding anisotropy implicit in directed scattering factors. New values of the temperature parameters and co-ordinates necessitated by the use of McWeeny's scattering factors are obtained from a least-squares refinement utilizing  $hk0$  and  $h0l$  data only. These values lead to  $R(hkl) = 0.071$ . They have been used by Gilbert & Lonsdale for comparison with values of temperature factors obtained directly from X-ray measurements on 12 reflexions at different temperatures, and are also compared with results obtained by neutron diffraction. The same co-ordinates give  $R(hkl) = 0.178$  when used with an isotropic temperature factor.

As a result of this work it is suggested that for accurate structure determination, anisotropic temperature factors should be introduced when  $R \sim 20\%$ , before any serious attempt is made to refine the atomic co-ordinates any further. Attention is drawn to the fact that two-dimensional refinement produced a value of  $\sigma(\Delta F)$  for the three-dimensional data which is comparable with the probable experimental error,  $\sigma(F_o)$ , thereby suggesting that further refinement might be unprofitable in this structure, and that three-dimensional refinement may be unprofitable in comparable structures unless extremely accurate intensities are obtained.

### 1. Introduction

In Part I of this paper Gilbert & Lonsdale (1956: hereafter GL) have made direct measurements of the Debye factors for 12 reflexions from urea and have compared these with the Debye factors deduced from Vaughan & Donohue's (1952: hereafter VD) temperature factors for the individual atoms. In the course of this work it became obvious that although the agreement obtained was apparently excellent, yet the previous results for urea not only needed amendment, but also afforded an excellent example upon which to demonstrate the difficulty of obtaining really reliable and unique atomic parameters, even for a simple substance, and the need for introducing temperature

corrections (either measured directly, or computed) at a much earlier stage of structure refinement than is usually supposed.

VD took considerable trouble to achieve an accurate structure determination of urea ( $P\bar{4}2_1m$ ,  $a = 5.661$ ,  $c = 4.712$  Å, 2 molecules of  $\text{CO}(\text{NH}_2)_2$  in the unit cell). They obtained intensities from cylindrical crystals, and measured the strongest intensities from powder photographs to minimize extinction. They refined their atomic parameters by iterative least-squares procedures, included the hydrogen atoms in their calculations, and applied anisotropic temperature factors to the C, O and N atoms individually. Their final  $R$  factor was given as 0.099. However, since recent structures with even more variable parameters than urea

(e.g. salicylic acid (Cochran, 1953)) have given  $R$  factors as low as 0.041 when similar painstaking methods were employed, and since structure factors had to be computed for the 12 reflexions considered by GL, it was decided to re-compute all the three-dimensional structure factors to try to discover where the remaining discrepancies might lie.

In addition, the structure of urea has recently been determined from  $h0l$  data by neutron diffraction (Peterson & Levy unpublished: hereafter PL) and appreciable differences in bond lengths and angles have been reported for this investigation. These two sets of parameters are given (with others referred to later) in Table 1. It should be noted, however, that these values of PL's co-ordinates have been obtained by triangulation from their inter- and intra-molecular distances communicated at the Paris Congress of the International Union of Crystallography (Levy, 1954), and may thus not do justice to their results. X-ray intensities to be expected for these parameters have

also been computed and compared with VD's observed X-ray data.

As VD used James & Brindley (1931: hereafter JB) scattering factors, while better curves, such as McWeeny's (1951: hereafter MW) values, are now in fairly general use, calculations have been made for both. Various changes in the atomic co-ordinates suggested by the introduction of MW curves have also been tried (see § 5(c)).

PL obtained somewhat different values of the temperature parameters for individual atoms. These values are shown in Table 2 together with VD's values, GL's 'average' value obtained from intensity measurements on 12 reflexions at different temperatures, and values appropriate to a transverse molecular vibration ( $M$ ) instead of a torsional one (see § 5(g)).

The values proposed in the present paper (Grenville-Wells: hereafter GW) from a two-dimensional least-squares refinement using VD's values of  $F_o(h0l)$  and  $F_o(hk0)$ , MW scattering factors, and a scaling

Table 1. Atomic co-ordinates in urea

	VD	PL	GW	$a$ [§ 5(c)]	$b$ [§ 5(c)]	$c$ [§ 5(f)]	$d$ [§ 6(b)]
$z_C$	0.3308	0.331	0.332	0.3308	0.3308	0.3308	0.331
$z_O$	0.5987	0.592	0.598	0.602	0.602	0.5987	0.602
$z_N$	0.1429	0.145	0.142	0.1429	0.1429	0.1443	0.142
$z_{H1}$	0.1848	0.180	0.186	0.188	0.1848	0.1848	0.186
$z_{H2}$	0.253*	0.259	VD	VD	VD	VD	VD
$z_{H1}$	0.287*	0.282					
$z_{H2}$	0.137*	0.141					
$z_{H2}$	0.972*	0.970					

\* Values kindly supplied by J. Donohue: private communication.

Table 2. Temperature factors used in calculating structure factors for urea

Values are of  $B$ , where  $F = F_o \exp [-B \sin^2 \theta / \lambda^2]$

Author	Vibrating unit	$B[110]$ ( $\text{\AA}^2$ )	$B[1\bar{1}0]$ ( $\text{\AA}^2$ )	$B[100]$ ( $\text{\AA}^2$ )	$B[001]$ ( $\text{\AA}^2$ )	Method
Vaughan & Donohue (VD)	(Molecule $P$ )					Fourier and least-squares refinement of X-ray $hkl$ data
	C, O	3.9	3.9	3.9	1.9	
	N	3.9	9.6	6.75	1.9	
	H	4.0	4.0	4.0	4.0	
Peterson & Levy (PL)	C	—	—	3.0	1.0	Neutron diffraction $h0l$ data reported at Paris (Levy, 1954)
	O	—	—	3.2	1.2	
	N	—	—	6.5	1.3	
	$H_1$	—	—	6.5	2.0	
	$H_2$	—	—	6.0	3.5	
This paper (GW)	C	3.3	3.3	3.3	1.5	Least-squares refinement starting from VD co-ordinates, PL $B$ -factors, MW scattering factors
	O	3.5	3.5	3.5	0.6	
	N	2.9	7.5	5.2	1.5	
	H	3.9	9.6	6.75	1.9	
This paper ( $M$ )	Molecule vibrating as a rigid unit	2.9	5.9	4.4	1.9	Calculated from $F_o(600)$ and $F_o(550)$
Gilbert & Lonsdale (GL)	'Average' for whole crystal ( $B^{293} - B^0$ )	4.25	4.25	4.25	0.5	Least-squares refinement involving 12 X-ray $hkl$ reflexions measured at 3 temperatures
This paper ( $S$ )	Isotropic value for whole crystal			3.0		Statistical method (Wilson, 1942)

factor based on zero-point energies given in Table 9 of GL's paper, are also given, together with the isotropic value ( $S$ ) obtained from the usual statistical examination of intensities (Wilson, 1942), in Table 2.

## 2. Method of calculating structure factors involving anisotropic thermal vibrations

It will be noted that while VD give their final  $R$ -factor as 0.099, it is here given as 0.061 (Table 4 below). Their value of 0.099 was due to an inadequate method of applying the anisotropic temperature factor to non-parallel molecules (J. Donohue, private communication). For molecules which are not parallel to each other—or at least parallel in the projection considered—the anisotropic temperature factor must be applied to each molecule *separately*, and not merely to the representative molecule embodied in the structure factor equations given in the *International Tables* (1952); these apply in general only to spherically symmetrical scattering centres, though lower symmetry may suffice in special cases, as here, where cylindrical symmetry about the  $c$  axis would be sufficient. Hence the calculation of structure factors is more readily performed by methods intended primarily for low-symmetry crystals (e.g. Radoslovitch & Megaw, 1955) than by methods using sine and cosine products.

The importance of this asymmetry is considerable in urea, where a very anisotropic vibration has to be assigned to the nitrogen. The maximum vibration direction is shown by the arrows in Fig. 1. (Fig. 1

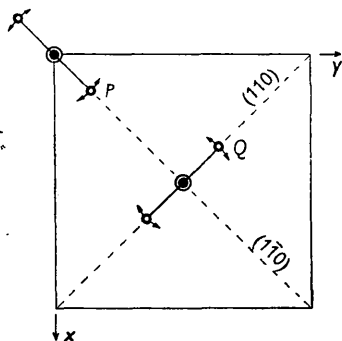


Fig. 1. [001] projection of urea, showing the orientations of the molecules  $P$  and  $Q$ , and the amplitude of the vibration assigned to the nitrogen by Vaughan & Donohue.

actually shows arcs appropriate to an oscillating molecule. The effect of replacing these arcs by a linear vibration is discussed in § 5( $f$ ).) The corresponding temperature factor is represented (VD) by the equation

$$B[h] = \exp \left[ -\sin^2 \theta / \lambda^2 (3.9 \sin^2 \varphi_h + 1.9 \cos^2 \varphi_h + 5.7 \sin^2 \varphi_h \sin^2 \psi_h) \right], \quad (1)$$

where  $\varphi_h$  and  $(\psi_h + 45^\circ)$  are the polar co-ordinates of the reciprocal-lattice vector  $h$  ( $= hkl$ ) relative to the  $z$

and  $x$  axes respectively. Thus  $B[110] = 3.9$ ,  $B[1\bar{1}0] = 9.6$ ,  $B[001] = 1.9$  and  $B[100] = 6.75 \text{ \AA}^2$ .

However, this expression for  $B[h]$  applies only to molecule  $P$  in Fig. 1, i.e. gives  $B_p$ . The  $B$ -factor for the molecule  $Q$  will be of the form

$$B_q = \exp \left[ -\sin^2 \theta / \lambda^2 (3.9 \sin^2 \varphi_h + 1.9 \cos^2 \varphi_h + 5.7 \sin^2 \varphi_h \cos^2 \psi_h) \right] \quad (2)$$

since  $\psi_h(Q) = \psi_h(P) \pm 90^\circ$ , i.e.  $B_q[110] = 9.6$ ,  $B_q[1\bar{1}0] = 3.9 \text{ \AA}^2$ . Since  $(1\bar{1}0)$  is a mirror plane in the  $B$ -function,  $B_p[hk0] = B_p[\bar{h}k0]$ , so that  $B_p[hkl]$  values are required only for  $h \leq k$ . Further, since  $\varphi_q(hk0) = \varphi_p(hk0) \pm 90^\circ$ ,

$$B_q[hk0] = B_p[\bar{h}k0]. \quad (3)$$

The anisotropic temperature factor for each reflexion  $hkl$  was obtained graphically by using a distorted reciprocal lattice for each atom, as suggested by Cochran (1954), a method which was found to be highly satisfactory and very fast for three-dimensional as well as two-dimensional work. If for an atom in molecule  $P$ ,  $B_p[110]$ ,  $B_p[1\bar{1}0]$  and  $B_p[001]$  are the values of the anisotropic temperature factor along the axes of the vibration ellipsoid, and the mean value  $B_m = \frac{1}{3}(B_p[110] + B_p[1\bar{1}0] + B_p[001])$ , the reciprocal-lattice spacings in the directions given must be distorted by the factors  $(B_p[110]/B_m)^{\frac{1}{2}}$ ,  $(B_p[1\bar{1}0]/B_m)^{\frac{1}{2}}$ , and  $(B_p[001]/B_m)^{\frac{1}{2}}$  respectively. From Table 2, this gives for the VD nitrogen parameters distortion factors of 0.87 and 1.37 in the  $\{hk0\}$  zone, so that in Fig. 2, the distance  $O-110_p = 0.87a^* \sqrt{2}$ , while  $O-110_q = 1.37a^* \sqrt{2}$ . From equation (3) it can be seen that the

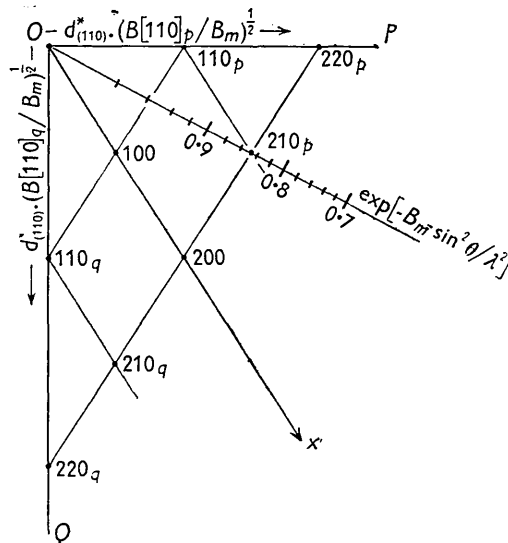


Fig. 2. The  $\{hk0\}$  reciprocal-lattice net for urea, distorted so that the values of  $\exp[-B \sin^2 \theta / \lambda^2]$  can be obtained for the nitrogen atoms in molecules  $P$  and  $Q$ , having the anisotropic thermal vibration deduced by Vaughan & Donohue. The appropriate exponential scale obtained from Fig. 3 for  $B = B_m = 5.13 \text{ \AA}^2$  is shown, giving the result that  $f^{2\theta}(210)_p = 0.848f^\theta(210)$ .

values of the temperature factor for each reflexion  $hkl$  for corresponding atoms in molecules  $P$  and  $Q$  will be found in the regions  $XOP$  and  $XOQ$  (Fig. 2) respectively.

The reciprocal lattices were plotted on a scale of 1.0 r.l.u. = 5.0 in., so that the atomic scattering factors for atoms at rest could be plotted on a scale where  $0.1 \sin \theta/\lambda = 1.0$  in., and the value of  $f_r(hkl)$  for the  $r$ th atom could be read for each reflexion from the *undistorted* reciprocal lattice. The temperature factor for the  $r$ th atom and the reflexion  $hkl$ ,  $\exp[-B_r(hkl)]$ , is then the value of  $\exp[-B_m \sin^2 \theta/\lambda^2]$ —obtained from a 'temperature scale' also plotted so that  $0.1 \sin \theta/\lambda = 1.0$  in.—read from the *distorted* reciprocal lattice. This 'temperature scale' is readily obtained from Fig. 3, as it is the horizontal line corresponding to  $B = B_m$ .

It will be realized from Fig. 2 that while  $B_x = B_y$  for  $h0l$  reflexions, the values of  $B_x$  and  $B_y$  diverge appreciably as  $h \rightarrow k$ , and exhibit a maximum variation for  $hhl$ , as would be expected from Fig. 1, since nitrogen  $P$  vibrates in the plane (110), while nitrogen  $Q$  vibrates perpendicular to it.

Calculations of this type have been discussed by Rollett & Davies (1955), who have expressed their results in terms of sine and cosine products suitable for least-squares refinements, with particular reference to the class  $2/m$ . If, however, the temperature factors are already known (e.g. from peak shapes in Fourier syntheses) and the structure factors are to be calculated by hand, computation of the geometrical structure factors by regarding as independent all atoms whose vibration ellipsoids are not parallel, irrespective of whether or not their centres are related by space-group symmetry, has been found very convenient. The structure-factor equations involving independent atoms are not then in such a suitable form for the further refinement of temperature factors for non-

parallel molecules, but the atomic co-ordinates can be further refined by the usual least-squares procedures.

### 3. Accuracy of the calculated values

The geometrical structure factors were computed to three decimal places from sine and cosine tables (Buerger, 1941), these values being interpolated where necessary because VD's co-ordinates are given to four decimal places.

Errors in constructing the scales and reciprocal lattices probably resulted in errors of up to 0.05 in the scattering factors, which were read to two decimal places, and up to 0.005 in the temperature scales, which were read to three decimal places. The necessary multiplications were done on a Facit desk calculator, and the structure factors for one molecule given to two decimal places: these values were then doubled to give the required values of  $F_c$ . Structure factors computed independently in different batches occasionally differed by as much as 2%, though almost always by less than 1%. It is doubtless too much to hope that the computations are free from random errors. General consistency between all the trials is the only check which has been applied.

### 4. Two-dimensional least-squares refinement of the temperature factors

The least-squares refinement of the  $B$ -factors (in the case of parallel molecules, i.e. in the  $h0l$  projection) was made as follows:

For the carbon atom alone,

$$F_c(h0l) = G_c f_c^0 \exp[-S(sB_{x(x)} - cB_{z(z)})]$$

where

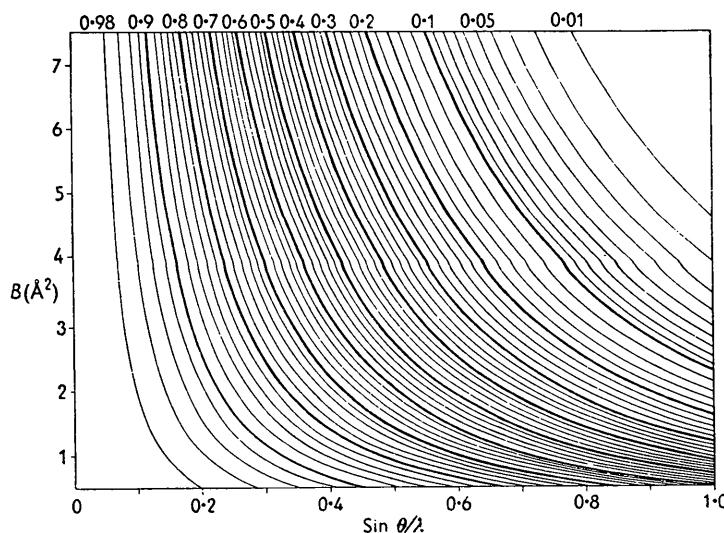


Fig. 3. Curves of constant  $\exp[-B \sin^2 \theta/\lambda^2]$ .

- $B_{x,z}$  = temperature factor in the [100], [001] direction,  
 $G$  = geometrical structure factor,  
 $f^0$  = atomic scattering factor for the atom at rest,  
 $s$  =  $\sin^2 \varphi_h$ ,  $c = \cos^2 \varphi_h$  ( $\varphi_h$  as in equation (1))  
 $S$  =  $\sin^2 \theta / \lambda^2$ .

Hence  $\partial F(h0l) / \partial B_{x(C)} = -SsF_C(h0l)$ , and  $\partial F(h0l) / \partial B_{z(C)} = -ScF_C(h0l)$ . Similar expressions are obtained for oxygen and nitrogen.

Structure factors  $F_c$  are obtained including hydrogen contributions, but no attempt has been made to refine the co-ordinates or  $B$ -factors for the hydrogen atoms by least-squares techniques. Hence

$$F_c - F_o = \Delta F = SsF_C(h0l)\Delta B_{x(C)} + \dots \\ + ScF_C(h0l)\Delta B_{z(C)} + \dots$$

If the equations are used in this form, the low-order reflexions are effectively given a very small weight, since (ignoring the off-diagonal terms)

$$\Delta B_{x(C)} = \Sigma[\Delta F S s F_C(h0l)] / \Sigma[S s F_C(h0l)]^2, \quad (4)$$

and  $S$  is very small for low-order reflexions.

If, however, the equations are all divided through by  $S$ , so that

$$\Delta F' = \Delta F / S = sF_C(h0l)\Delta B_{x(C)} + \dots$$

and

$$\Delta B_{x(C)} = \Sigma[\Delta F' s F_C(h0l)] / \Sigma[s F_C(h0l)]^2, \quad (5)$$

then low-order terms have much more effect on the answer, and errors due to extinction, or neglect of hydrogen contributions, or ionization of the atoms, become much more important. Values of  $\Delta B$  obtained from equation (5) were indeed unsatisfactory unless the three reflexions for which  $\sin \theta / \lambda < 0.2$  were arbitrarily excluded.

To form an idea of the accuracy of the results obtainable in this way, structure factors were calculated for one set of atomic co-ordinates (VD), firstly with PL temperature factors, giving  $F_1(h0l)$ , and secondly with VD temperature factors, giving  $F_2(h0l)$ . The  $R$ -factor between  $F_1(h0l)$  and  $F_2(h0l)$  was 0.101, which is the order of magnitude in which we are interested. The least-squares method was then used to adjust  $F_1$  to agree with  $F_2$ . The results obtained are shown in Table 3, for a single cycle of refinement.

Table 3. *Test of procedure for refining temperature factors*

	True value of $\Delta B$ from Table 2, i.e. $B(\text{VD}) - B(\text{PL})$	Values of $\Delta B$ from equation (4)
$\Delta B_{x(C)}$	+0.9	+1.39
$\Delta B_{x(O)}$	+0.7	+1.04
$\Delta B_{x(N)}$	+0.25	+0.42
$\Delta B_{z(C)}$	+0.9	+0.96
$\Delta B_{z(O)}$	+0.7	+0.62
$\Delta B_{z(N)}$	+0.6	+0.66

These results were considered good enough to justify the use of equation (4) for the final calculations.

The two-dimensional least-squares refinement of the temperature factors for the  $\{hk0\}$  zone, in which the molecular projections are not parallel, was less satisfactory. There are only 20 observed reflexions (as opposed to 33 in the  $\{h0l\}$  zone). Such a refinement did give slight  $\{hk0\}$  anisotropy for the C and O atoms, but this was not introduced, since the torsional oscillation about the  $c$  axis does not require it unless there is also a transverse vibration. The values of  $B[110]$  and  $B[1\bar{1}0]$  for the nitrogen, although combining to give the same value of  $B[100]$  as had been obtained from the  $\{h0l\}$  refinement, were manifestly less satisfactory than those obtained by combining the VD ratio of  $B[110]/B[1\bar{1}0]$  with the value of  $B[100]$  obtained from the  $\{h0l\}$  refinement. The latter values are those given as GW in Table 2. This  $B[110]/B[1\bar{1}0]$  ratio was here selected from several possibilities on the basis of the  $\{hk0\}$   $R$ -factor, to avoid having recourse to three-dimensional data, but nevertheless the small number of independent  $\{hk0\}$  reflexions available in urea is the most serious weakness in the argument for the sufficiency of two-dimensional data advanced in § 6(a) below.

## 5. Discussion of results

The reliability factors  $R$  for the 27 combinations of atomic co-ordinates, temperature factors and atomic scattering factors discussed in §§ 5 and 6 are collected in Table 4. These combinations are referred to hereafter by italic numbers in brackets, e.g. (22).

### (a) Scale factors

The first 20 trials were carried out allowing the scale factor  $S$  to take the value appropriate to the  $F_c$  values being considered—i.e.  $S(\Sigma|F_o| / \Sigma|F_c|)$  was equated to unity. Trials (21)–(27) were made assuming that the scale of  $F_o$  had been determined by GL's measurements of  $(B^T - B^0)hkl$  together with their assumptions about the magnitude of the zero-point energy. Reasonable variations in zero-point energy could change the scaling factor by about 5%. The value of  $S$  applied to the  $F_o$  values published by VD was 1.16. This large increase is mainly due to the use of MW scattering factors instead of JB, and to a lesser extent to the decrease in temperature factors (see Table 2) as compared with the VD values.

### (b) Hydrogen atoms

The agreement factor  $R(hkl)$  for VD's original data, re-calculated as described in § 2 above (I), is still superior to any of the other possibilities tried. Although the neutron-diffraction results (7) and (8) do not give such a good  $R$ -value, they do suggest that the hydrogen atoms have anisotropic  $B$ -factors similar to those applicable to the nitrogen—a result which could hardly be established by X-ray work, though it might be

Table 4. Reliability factors  $R = \Sigma ||F_o| - |F_c|| \div \Sigma |F_o|$  for models tried

No.	Atomic co-ordinates (Table 1)	Temperature parameters (Table 2)	Scattering factors	Scaling factor (§ 5(a))	$R(hkl)$	$R(h0l)$	$R(hk0)$
	Published by	VD	JB	1.00	0.099	0.092	0.106
(1)	VD	VD	JB	0.965	0.061	0.060	0.039
(2)	VD	VD	MW	1.00	0.100	0.116	0.087
(3)	VD	VD*	JB	0.962	0.061	0.058	0.041
(4)	VD	VD	MW	Layer scaling	0.082	0.092	0.062
(5)	a	VD†	MW				
(6)	b	VD‡	MW	1.08	—	0.091	0.062
(7)	PL	PL'§	JB	1.07	—	0.134	—
(8)	PL	PL'	MW	1.13	—	0.114	—
(9)	VD	PL'	JB	1.07	—	0.097	—
(10)	VD	PL'	MW	1.13	—	0.089	—
(11)	PL	VD	JB	0.965	—	—	0.054
(12)	PL	VD	MW	1.07	—	—	0.069
(13)	PL	VD'	JB	0.959	—	—	0.057
(14)	PL	VD'	MW	1.056	—	—	0.055
(15)	c	VD	JB	0.972	—	0.059	—
(16)	c	VD	MW	Layer scaling	—	0.092	—
(17)	VD	GL	JB				
(18)	VD	GL	MW	1.09	—	—	0.115
(19)	VD	M	JB	1.00	—	—	0.125
(20)	VD	M	MW	1.09	—	—	0.113
(21)	VD	GW	MW	1.16	0.071	0.058	0.056
(22)	GW	GW	MW	1.16	0.072	0.062	0.055
(23)	PL	GW	MW	1.16	—	0.092	—
(24)	GW	GL	MW	1.16	0.138	0.135	0.126
(25)	GW	S	MW	1.16	0.178	0.169	0.163
(26)	PL	S	MW	1.16	0.187	0.190	0.170
(27)	d	S	MW	1.16	—	0.174	—

\* VD' = VD with  $B_H = B_N$ .† Except  $B[001] = 1.0 \text{ \AA}^2$  for C and O.§ PL' = PL with  $B_H = B_N$ .‡ Except  $B[001] = 1.0 \text{ \AA}^2$  for O.

regarded as probable. Inclusion of the hydrogen atoms with the same  $B$ -factor as the nitrogen (3) does not, however, produce any overall improvement, although it changes a few  $F_c$  values slightly. In the final (GW) set of temperature factors the hydrogen atoms were given the  $B$ -factors assigned by VD to nitrogen, since these fulfil the reasonable conditions that hydrogen  $B$ -factors should be similar to, and larger than, those of the atom to which the hydrogen is attached.

#### (c) Bonding anisotropy and McWeeny's scattering factors

The computations involving MW scattering factors include allowance for the directional effect of the bonded oxygen atom, according to the formula  $f = f_{||} \cos^2 \varphi + f_{\perp} \sin^2 \varphi$  for  $hkl$ , where  $f_{||}$  and  $f_{\perp}$  are the scattering factors parallel and normal to the bond direction, and  $\varphi$  is the angle between the bond direction and the reciprocal-lattice vector  $[hkl]$ . This allowance was easily made in this case, since the C=O bond lies along the  $c$  axis, so that  $\varphi$  is the same as  $\varphi_h$  in equation (1). There is no correction of this type for nitrogen, nor for carbon, since the C atom is involved in three coplanar bonds, and corresponds to a 'valence state' (McWeeny, 1951). Substitution of the MW curves in the calculated  $F$ -values results in a substantial deterioration in the  $R$ -factor (2), which is partly due to the fact that out to about  $\sin \theta/\lambda = 0.5$ , i.e. for most of the observed reflexions, the steady

increase of  $f_{\perp}/f_{||}$  (in this case  $f_x/f_z$ ) is very similar to the effect which would be produced by thermal anisotropy with  $B_x < B_z$ . Since  $B_x$  and  $B_z$  have been treated as variables for which values were obtained by VD using JB scattering factors, introduction of anisotropy at this stage is uncalled for. If, however, the vibration amplitudes were to be obtained from the given values of  $B_x$  and  $B_z$  for oxygen, quite substantial errors would result from failure to separate bonding anisotropy from thermal anisotropy.

For the oxygen, VD found that  $B_x = 3.9$  and  $B_z = 1.9 \text{ \AA}^2$ . Hence at  $\sin \theta/\lambda = 0.5$  anisotropy in the scattering factor,  $f_z/f_x$ , is  $[f_0^z/f_0^x] \cdot \exp[-0.25(B_z - B_x)] = 1.65$ , since for the isotropic JB factor,  $f_0^z = f_0^x$ . If the MW bonded oxygen factor is introduced, then  $(f_{||}/f_{\perp})_{MW} = f_0^z/f_0^x = 0.80$ , so that if VD's experimental value of 1.65 for the total anisotropy is accepted, then  $\exp[-0.25(B_z - B_x)] = 1.65/0.80 = 2.06$ , whence  $(B_x - B_z) = 2.9 \text{ \AA}^2$ ; i.e. the thermal anisotropy must be larger than VD's value. In urea thermal and bonding anisotropies oppose one another.

GL's results suggest a relatively very small  $[001]$   $B$ -factor. Hence the increased anisotropy should probably be provided by a decrease in  $B[001]$  for oxygen rather than by an increase of  $B$  in the  $\{hk0\}$  zone, a conclusion also supported by the fact that  $R(hk0)$  is already better than  $R(h0l)$ . If we leave  $B[hk0] = 3.9 \text{ \AA}^2$ , then  $B[001]$  for oxygen should become  $1.0 \text{ \AA}^2$ . A decrease in  $B[001]$  would in any case

be necessitated by the use of MW factors, since  $R(hkl)$  (2) is noticeably improved (4) by scaling the  $F_c(hkn)$  layers separately to the  $F_c(hkn)$  values, the scaling factor  $S_n$  used for the  $n$ th layer decreasing regularly from  $S_0 = 1.079$  to  $S_5 = 0.912$ . Calculations show that the application of this reduction in  $B[001]$  to C and N as well as to O, with appropriate co-ordinate changes [ $a$  in Table 1] would be too drastic, but it has been applied to C and O (5), and to O alone (6). It will be seen from the GW temperature factors given in Table 2 that the drastic reduction of  $B[001]$  for oxygen expected from the above considerations does appear from the final least-squares refinement utilizing MW factors (22). Calculations of  $F(h0l)$  involving only a change in the oxygen co-ordinate [ $b$  in Table 1] to compensate for the change in the oxygen scattering factor almost removed the necessity for separate scaling factors for each layer, and, taking  $S_n = S_0 = 1.08$ , as in (4),  $R(h0l)$  was reduced to 0.091 (6).

(d) *Interdependence of atomic parameters and scattering factors*

It is interesting that for all the pairs of trials involving different scattering factors, it can be seen from Table 4 that MW curves give a lower  $R$ -factor in all cases except those involving VD temperature factors, which were derived from  $F_c$  values involving JB curves, and may thus be expected to have been adjusted to suit them. The new  $F_c$  values involving MW curves produce a different set of  $\Delta F = |F_c| - |F_o|$  values to be minimized, and thus lead to a slightly different set of atomic co-ordinates, which are shown in Table 2 (GW). No finality is claimed for these changes in the atomic parameters; in any case they do not alter the bond lengths by more than 0.01 Å. They are given merely to emphasize the fact that in all procedures which involve minimizing  $\Delta F = |F_c| - |F_o|$ , it is essential to recognize the dependence of the final co-ordinates on the scattering factors and temperature parameters used.

The straight substitution of MW factors in VD's equations gave the relatively poor  $R$ -value of 0.100 (2). With the same co-ordinates,  $R$  is reduced to 0.071 by the use of improved temperature factors more appropriate to MW factors (21). These co-ordinates may still be slightly superior to the GW co-ordinates (22), as judged by the  $R$ -factor, but the differences are insignificant.

(e) *Reliability of available theoretical atomic scattering factors*

The new refinement involving MW factors has only been carried out for the two-dimensional  $\{hk0\}$  [ $R = 0.055$ ] and  $\{h0l\}$  [ $R = 0.062$ ] data, and leads to a three-dimensional  $R(hkl) = 0.072$  after a single cycle of refinement (22). It has thus not yet produced a better  $R$ -factor than that obtained with JB curves (1), but it is felt that this would be possible, as it is already

the experience of several workers (e.g. Cochran, 1953; Rollett, 1955) that the JB curves for C, O and N are appreciably in error. The good internal agreement between recent theoretical  $f$ -curves (McWeeny, 1951; Hoerni & Ibers, 1954; Berghuis *et al.*, 1955) has here been taken to mean that adjustment of  $f$  curves, other than by the introduction of bonding or thermal anisotropy, to improve the agreement between  $F_c$  and  $F_o$ , on the grounds that  $f$  is not known accurately anyway, cannot now be justified.

The considerable difference between the experimental  $f$  curve for accurate work on aromatic hydrocarbons, e.g. naphthalene (Abrahams, Robertson & White, 1949) and MW's carbon curve appears at first sight to cast doubt upon this assumption. However, examination of the numerical data given for naphthalene shows that in order to obtain the carbon scattering factor, the published one-electron curve must be multiplied by 68 (the total number of electrons in  $C_{10}H_8$ ) and not by 60, to obtain  $F_c$  values for the 10 carbon atoms alone in one molecule. (This one-electron curve is a result of a computational method designed to allow for the presence of hydrogen without actually computing structure factors for it.) When the experimental one-electron curve is multiplied by 6.8, and rounded off to give 6.0 at  $\sin \theta/\lambda = 0$ , it corresponds very closely to the MW curve with a temperature factor of  $4.3 \sin^2 \theta/\lambda^2$ . Work on naphthalene thus provides experimental support for the newer atomic scattering factors, already authenticated for the single-bond C atom by work on diamond (Brill, 1950). In addition, the experimental curve for di-*m*-xylylene (Brown, 1953), which is a mixture of aliphatic and aromatic carbon, agrees very closely with the MW curve, and thus supports the contention that variations in  $f$  curves in individual organic structures are ordinarily quite negligible compared with other errors.

(f) *Errors in co-ordinates produced by torsional vibrations*

Permutations of the available parameters (i.e. X-ray co-ordinates with neutron temperature parameters (9) and (10), and vice versa (11) and (12), or with hydrogen having the nitrogen temperature factor (13) and (14), do not result in a lower  $R$ -factor than (1) or (3). The failure of (11), (12), (13) and (14) is interesting, because for the  $\{hk0\}$  zone the only variable atomic co-ordinate (apart from those for hydrogen) is  $x_N$ . The C-N bond length, calculated from assumptions about double-bond character (VD) is about 0.015 Å greater than the observed value of 1.335 Å. Use of PL's value of  $x_N$ , which involves an increase of about this magnitude, does improve  $R(hk0)$  slightly for MW factors, so perhaps such an increase is justified. However, Cox, Cruickshank & Smith (1955) have shown for benzene that for torsional oscillations of the type postulated here, the observed value of CN', the projection of C-N on (001), would be less than the

true value,  $CN''$ , by about  $0.015 \text{ \AA}$ . The value of  $CN''$  has not been calculated accurately as for benzene, but a correction of this order of magnitude would be obtained from the empirical formula

$$CN'' = [(CN')^2 + (\frac{1}{2}u)^2]^{\frac{1}{2}}, \quad (6)$$

where  $u^2 = B[1\bar{1}0]^2/8\pi^2$  for molecule  $P$ . For the VD nitrogen parameters,  $u=0.35 \text{ \AA}$ , and  $CN'=1.144 \text{ \AA}$ , so that  $CN'' = CN'+0.014 \text{ \AA}$ , and  $C-N = 1.346 \text{ \AA}$ , which is in good agreement with VD's calculated value of  $1.35 \text{ \AA}$ .

It is interesting that VD found a much larger discrepancy between their Fourier (0.1415) and least-squares (0.1443) values of  $x_N$  than for any other parameter. It is not immediately obvious why this torsional shortening should not falsify the least-squares results as well as the Fourier synthesis, but this point may be worth examining. Use of the least-squares  $x_N$  value (Table 1, c) shows no significant improvement (15) and (16), over (3) and (4) for the  $\{h0l\}$  zone.

(g) *Structure models for different types of thermal motion*

GL derived an 'average' temperature factor of the type  $A+B\cos^2\varphi$  for the whole crystal from their measurements on 12 reflexions at different temperatures. The factors given by this formula (Table 2) would be expected to be too small anyway, because the temperature factor actually derived is  $B^T - B^0$ , where  $B^0$  is the zero-point energy, and they thus lead to a slightly higher scaling factor than that used for the GW results (22). However, the relatively poor agreement (17) and (18) is to be expected, because this overall factor is not expected to be a very satisfactory type of approximation (see § 6(b)).

It is notable that the PL temperature factors, which are independent of both JB and MW, are considerably less than the VD values. The GW values (22) would agree closely with the PL values (see Table 2) if a slightly smaller value of zero-point energy had been chosen. As it is, the GW values are intermediate between the VD and the PL values. For further information on this part of the work on urea, GL's paper should be consulted.

An attempt was also made to see whether the results could distinguish between rather similar types of thermal vibration. Accordingly,  $F$  values were calculated for a transverse molecular vibration (i.e. one in which all the atoms had the same anisotropic  $B$ -factors, which were similar to those assigned to the nitrogen, but rather smaller). Approximate values were obtained from the observed values of  $F(600)$ —which gives  $\frac{1}{2}(B[110]+B[1\bar{1}0])$ —and  $F(550)$ , which gives a reasonable value of  $B[1\bar{1}0]$ , since the contribution from molecule  $P$  is very small. Although these values could be improved by more rigorous calculations, they are sufficiently near the values which would have to apply to show that such a vibration gives a much worse  $R$ -factor (19) and (20) than a torsional

oscillation. It thus appears as though it is possible in this case to discriminate quite significantly between different types of thermal motion. As an illustration of the interdependence of scale and temperature factors, it may be noted that  $S'$  would increase from 1.09 to 1.16 if these temperature factors ( $M$  in Table 2) were multiplied by 0.905.

The absolute scale having been fixed by other considerations, it is then possible to obtain the value of the isotropic temperature factor which would result from the usual (Wilson, 1942) consideration of the average intensity of  $F_o$  in successive ranges of  $\sin\theta/\lambda$ . It is found to be  $B = 3.0 \text{ \AA}^2$ , which is incidentally the mean value of the 'average' crystal factor ( $B^{293} - B^0$ ) found by GL. The  $R$ -factor corresponding to this isotropic  $B$ -factor is extremely poor (25).

## 6. Possible procedures for efficient structure determination

### (a) *The merits of three-dimensional data*

The most disquieting feature of these results is the large number of combinations of significantly different variables which produce  $R$ -factors of about 0.10. Although it is often claimed that the  $R$ -factor is a poor indicator of the accuracy obtained, it does measure the agreement with the observed data, which must after all be the final criterion, and  $R$ -factors of about 0.10 are still considered very good.

If the efficiency of a structure determination can be measured by the accuracy achieved relative to the work required, one may question the automatic desirability of three-dimensional work. For urea, which is non-centrosymmetric, three-dimensional work is relatively laborious. The two-dimensional refinement which gave the GW atomic co-ordinates and temperature parameters leads to  $F_o$  values giving the  $\Delta F$ 's shown in Table 5, and a three-dimensional  $R$ -factor of 0.072 (22).

$R$ -factors obtained separately for groups of  $F$ -values of different magnitudes for (22) are shown in Table 6.

Since there is no reason to suppose that small  $F$  values calculate less accurately than large ones, the average  $\Delta F$  values in Table 6 suggest that there is a constant, rather than a percentage, error in  $F_o$  (at any rate for  $F_o \leq 13$ ), a conclusion reached by Lipson & Cochran (1953), and favoured by Abrahams (1955) as a result of examining the consistency of bond lengths in sulphur as obtained from least-squares refinements involving different weighting systems.

This accounts for the fact that the 12 planes considered by GL always show an  $R$ -factor of about half the  $R(hkl)$  value for the complete set to which they belong, since the GL planes were chosen to have medium intensity (actually 5.86–12.82), which, as can be seen from Table 6, is, as expected, the most favourable range. The figures also suggest that, with the possible exception of the two strongest reflexions, the use of the powder method by VD to obtain good in-



Table 5. Observed structure factors for urea, and differences from them for four sets of calculated structure factors

The phase angles  $\alpha(22)$  for the combination No. (22) in Table 4 will correspond to  $\alpha(\text{VD}) + \tau$  when  $k = 2n + 1$ , where  $\alpha(\text{VD})$  are the phase angles published by Vaughan & Donohue, since their  $|F_c|$  values were obtained for an origin at  $\bar{4}$ . Their published co-ordinates are measured from an origin at  $mm2$ , which origin has been used throughout this paper.  $F'_0 = 0.965 \times F_0$  published by Vaughan & Donohue,  $F''_0 = 1.16 \times F_0$  published by Vaughan & Donohue.  $F(22)$ ,  $F(25)$ ,  $F(26)$  = structure factors calculated for the combinations (22), (25), (26) in Table 4. The twelve reflexions measured at different temperatures by Gilbert & Lonsdale are marked by an asterisk.

$hkl$	$\alpha(22)$	$F'_0$	$F(1) - F'_0$	$F(22) - F'_0$	$F(25) - F'_0$	$F(26) - F'_0$
200	0°	12.62	-0.08	+0.22	0	-0.69
4	0	2.55	+0.36	-0.19	-1.21	-0.96
6	0	3.97	-0.14	+0.09	+1.18	+1.44
110	0	35.00	-0.65	-3.10	-2.16	-2.56
2	180	13.69	-0.07	-0.69	+0.30	+0.35
3	0	5.15	+0.02	+0.15	-0.15	-0.17
4	0	1.33	-0.07	-0.03	+0.95	+1.36
5	0	4.47	+0.20	-0.09	-0.39	-0.10
6	0	1.02	+0.01	+0.20	+0.93	+0.79
7	0	2.29	-0.12	+0.09	+1.06	+1.03
*220	0	11.99	+0.84	+0.83	+3.35	+3.58
3	180	3.63	-0.50	-0.41	+0.72	+0.23
4	0	7.12	+0.29	+0.18	+0.21	+0.36
5	0	2.53	-0.10	+0.23	+1.55	+1.59
6	0	2.90	+0.01	0	-0.28	-0.39
*330	0	10.27	+0.66	+0.45	+2.54	+2.82
4	0	1.88	+0.10	+0.06	-0.91	-0.89
5	0	4.14	+0.03	+0.16	+0.25	-0.01
6	0	< 0.56	~	~	> 0.27	> 0.11
440	0	5.39	-0.05	+0.11	+1.77	+1.54
5	180	< 0.68	~	~	> 0.39	> 0.58
550	0	0.93	+0.05	+0.05	+1.32	+1.24
001	180	4.66	+0.40	+0.12	-0.09	-0.67
1	90	12.37	-0.23	-0.05	0	-0.06
2	180	12.62	+0.28	-0.02	-0.06	+0.51
*3	270	8.24	-0.05	+0.06	+1.20	+1.08
*4	180	7.24	+0.12	+0.08	+0.81	+1.01
5	270	< 0.70	~	> 0.04	> 0.38	~
6	180	1.50	+0.02	+0.08	-0.09	-0.24
7	90	1.13	-0.32	-0.17	+0.77	+0.78
111	231	13.62	+2.69	+2.22	+2.42	+2.59
*2	209	6.76	-0.13	-0.90	-0.86	-0.52
*3	195	10.17	-0.04	-0.03	+0.29	+0.49
4	348	2.33	-0.02	+0.37	+1.44	+1.10
5	147	3.36	-0.02	+0.16	+1.11	+1.11
6	61	1.43	-0.43	-0.43	-0.14	-0.01
7	170	0.87	+0.10	+0.09	+0.02	+0.03
*221	235	12.62	+0.04	+0.14	+0.60	+0.32
3	173	1.60	-0.27	-0.34	+0.34	+0.54
4	152	3.71	+0.15	+0.03	+0.43	+0.55
5	42	1.97	-0.38	-0.51	-0.36	-0.22
6	147	1.62	+0.07	+0.26	+1.12	+1.05
331	178	2.83	+0.15	-0.03	-0.18	-0.48
4	75	3.34	-0.48	-0.46	+0.09	+0.09
5	147	1.97	+0.04	+0.07	+1.03	+0.48
6	274	< 0.50	~	~	> 0.53	> 0.65
441	158	1.74	-0.01	-0.02	-0.31	-0.22
5	156	0.74	-0.50	-0.54	-0.02	-0.06
551	215	1.87	-0.19	-0.07	+0.25	+0.39
002	180	11.25	+0.36	+0.17	-0.35	-1.86
1	90	11.47	+0.20	-0.75	-1.71	-1.60
2	0	2.63	+0.13	-0.07	-0.11	+0.48
3	270	3.35	-0.99	-1.11	-0.53	+0.11
4	0	2.09	-0.04	+0.49	+0.93	+0.74
5	90	0.79	-0.38	-0.47	-0.67	-0.51
6	180	< 0.80	~	~	> 0.24	> 0.19
*112	241	6.68	-0.56	-0.80	-0.73	-0.60
2	19	5.49	-0.16	-0.17	-0.14	-0.67
3	324	3.61	-0.10	-0.15	-0.16	-0.15
4	202	1.19	-0.51	-0.45	+0.24	+0.38
5	92	1.26	-0.01	+0.12	+0.78	+1.07
6	127	0.80	+0.11	+0.42	+0.74	+0.72
222	272	6.15	+0.65	-0.75	-0.48	-0.21
3	57	2.23	+0.17	+0.41	+0.84	+0.79

Table 5 (cont.)

$hkl$	$\alpha(22)$	$F''$	$F(1)-F'_0$	$F(22)-F''_0$	$F(25)-F''_0$	$F(26)-F'_0$
422	118°	1.40	+0.05	+0.08	+0.04	+0.32
5	140	1.46	+0.22	+0.50	+0.72	+0.56
6	109	0.74	-0.10	+0.04	+0.53	+0.51
332	173	1.90	+0.12	+0.14	+0.87	+0.56
4	164	2.51	+0.16	+0.53	+0.53	+0.62
5	132	1.06	-0.12	-0.06	-0.13	-0.25
6	180	< 0.50	~	~	> 0.15	> 0.23
442	161	1.19	+0.01	+0.03	+0.61	+0.29
5	48	< 0.56	~	~	> 0.40	> 0.38
003	180	2.84	+0.32	-0.10	-0.37	+0.55
*1	270	8.64	+0.37	0	-1.61	-2.04
*2	0	6.09	+0.25	-0.23	-1.12	-1.28
3	270	2.51	-0.12	-0.53	-1.26	-0.64
4	0	5.71	+0.01	+0.09	+0.10	-0.16
5	270	1.51	+0.15	+0.21	-0.15	+0.08
6	0	0.92	-0.12	-0.32	-0.81	-0.68
113	45	3.70	-0.10	-0.26	-0.86	-1.55
*2	319	6.75	+0.18	-0.25	-1.06	-0.76
*3	6	6.48	+0.17	-0.16	-0.86	-1.10
4	248	2.24	-0.02	-0.16	-0.46	0
5	344	2.03	-0.05	-0.03	+0.19	-0.19
6	240	1.35	+0.12	+0.37	+0.45	+0.06
223	26	5.36	+0.18	-0.44	-1.53	-2.26
3	296	3.60	+0.15	+0.06	-0.17	-0.19
4	341	1.68	-0.10	-0.20	-0.21	-0.53
5	228	2.35	-0.02	+0.27	+0.31	+0.42
333	12	0.74	-0.16	-0.56	-0.06	+0.35
4	248	2.60	+0.22	+0.28	0	-0.19
5	336	0.93	-0.01	-0.09	+0.02	-0.01
443	323	< 0.64	~	~	~	~
004	180	4.84	+0.30	-0.44	-1.90	-1.46
1	90	1.51	-0.41	-0.89	-1.36	-0.93
2	180	4.20	-0.03	-0.24	-1.42	-1.88
2	90	7.35	+0.04	+0.03	-1.36	-1.08
4	180	2.11	+0.08	+0.27	-0.41	-0.96
5	90	2.55	-0.20	-0.01	-0.46	-0.52
114	140	5.78	+0.11	-0.26	-1.83	-1.71
2	89	5.44	+0.11	-0.32	-1.88	-1.52
3	151	3.42	+0.07	+0.10	-0.84	-1.36
4	90	3.76	+0.11	+0.40	-0.19	-0.14
5	217	2.13	-0.18	+0.09	-0.10	-0.18
224	127	5.15	+0.08	+0.25	-0.82	-1.03
3	90	3.05	-0.14	-0.29	-1.36	-1.26
4	207	2.37	+0.05	+0.13	-0.45	-0.44
5	93	1.22	-0.09	-0.04	+0.08	+0.27
334	184	2.51	-0.14	-0.16	-0.75	-0.62
005	0	5.96	+0.02	+0.18	-2.37	-2.75
1	270	1.69	+1.43	+1.47	+0.38	+0.91
2	0	1.06	-0.30	-0.04	-0.80	-0.89
3	270	< 0.53	~	~	~	~
115	18	3.42	-0.27	-0.04	-1.46	-1.51
2	210	2.71	+0.14	+0.27	-0.63	-0.75
3	110	0.79	-0.04	-0.25	-0.18	-0.18
225	51	1.69	-0.15	-0.03	-0.46	-0.19
3	236	1.95	-0.30	-0.29	-0.64	-0.49
006	0	2.63	+0.07	-0.65	-1.16	-1.03

tensities for the strong reflexions gave satisfactory results.

The powder method should, however, be used with caution, because preferred orientations may exist. If urea, for example, is powdered, a large number of needles occur in the powder. A specimen prepared by tamping the powder down in a tube should produce too many horizontal needles, with an enhancement of the  $\{001\}$  reflexions on the equatorial layer of a powder

photograph; conversely, specimens prepared by rolling should contain too many vertical needles, resulting in enhanced  $\{h k 0\}$  intensities on the equatorial layer. Both these types of preferred orientation were obtained on powder photographs of urea taken by us to see whether the 110 reflexion, which always calculates too weak, was likely to have been enhanced by preferred-orientation effects. It is quite easy to detect these effects if the powder photograph is recorded in

Table 6. *Dependence of the R-factor on the magnitude of  $F(hkl)$* 

Average $ \overline{\Delta F}  =  F_o  -  F_c $	$F$ range	Number of reflexions	$R$ -factor for (22), neglecting $F$ 's not observed
0.30	0-1.0	13	0.468
0.19	1.01-1.5	13	0.154
0.24	1.51-2.5	23	0.118
0.31	2.51-3.5	20	0.105
0.18	3.51-4.5	10	0.045
0.31	4.51-5.5	7	0.060
0.23	5.51-10	14	0.035
0.33	10.1-13	10	0.028
(2.6)	Above 13	2	(0.112)

a rotation camera, but, as the orientation is not very sharp, they might well be missed on the narrow strip recorded in the usual powder camera. Photographs free from preferred orientation were also obtained, but no new intensity measurements for urea were actually made in the course of this work.

Ignoring  $F(111)$  and  $F(110)$ , i.e. considering only  $F_o \leq 13$ , we find  $|\overline{\Delta F}| = 0.27$  (instead of 0.31, when  $F(111)$  and  $F(110)$  are included), and  $\sigma(F_o) = \{(\overline{\Delta F})^2\}^{\frac{1}{2}} = 0.37$ , assuming that the GW calculated values are exactly correct, and that all the remaining  $\Delta F$ 's are due to errors in  $F_o$ . For adenine hydrochloride, Cochran (1951), by comparing independent measurements made with a Geiger counter, found  $\sigma(F_o) > 0.3$ , and since  $|\overline{\Delta F}| = 0.44$ , concluded that  $\sigma(F_o)$  must be  $< 1.25|\overline{\Delta F}|$ , i.e.  $< 0.55$ ; 199 out of his 229 observed reflexions fall in the range  $F_o \leq 13$ , and for these  $|\overline{\Delta F}| = 0.36$ . It is unlikely that the photographic intensities for urea are more accurate than these Geiger counter intensities, and so it seems extremely doubtful whether much would have been gained by undertaking the considerable extra work involved in a three-dimensional refinement of urea when the two-dimensional refinement has already produced a three-dimensional  $|\overline{\Delta F}|$  which is comparable with the expected experimental error.

It is true that statistical considerations indicate that the errors remaining in the co-ordinates after refinement are inversely proportional to the square root of the number of reflexions employed, assuming that all observations have the same probable error. It may well be that intensities in the axial zones are in fact obtained with greater accuracy than the general reflexions (except under very favourable conditions involving the use of spherical crystals, etc.); in which case the advantage gained from the use of a greater number of reflexions would be largely offset by their relative inaccuracy. Assuming, however, that for urea all reflexions were equally valuable, and thus that VD's three-dimensional analysis must be intrinsically better than GW's two-dimensional one, the latter gives bond lengths differing by  $< 0.01 \text{ \AA}$  from VD's values, so that very little was in fact gained through three-dimensional work. In any case it does not seem reasonable to claim any significance at all for molecular distortions obtained, for example, from least-squares,

when  $F_c$  values obtained with other distortions of the same magnitude also produce  $\sigma(\Delta F) \sim \sigma(F_o)$ . Computations of least-squares shifts between two sets of calculated data show that exact answers never are obtained, and it seems doubtful whether the cautious reminders that significant distortions should be  $> 3\sigma$ , where  $\sigma$  is the estimated standard deviation for bond lengths or bond angles etc., do really convey an adequate impression of their dubious nature to non-crystallographers reading crystallographic papers, although much help may be obtained on this question of significance from Lipson & Cochran (1953) or Jeffrey & Cruickshank (1953).

(b) *The importance of temperature corrections for individual atoms*

Many least-squares analyses of considerable magnitude have been carried out using isotropic temperature factors, and have resulted in molecular distortions being regarded as established. In this analysis of urea it was found that for the  $h0l$  reflexions, starting from  $R = 0.089$  (10), the co-ordinate shifts obtained from least-squares calculations after the temperature parameters had been improved were all reversed in sign as compared with those obtained before this improvement. It seems particularly significant that co-ordinates which lead to  $R = 0.072$  with appropriate temperature factors (22) give  $R = 0.178$  with an isotropic temperature factor (25) obtained by the usual statistical method (Wilson, 1942). While this might suggest that all  $R$ -factors of this magnitude could be improved merely by the improvement of the  $B$ -factors, it is unfortunately true that various combinations of substantially different co-ordinates (e.g. the PL (26) and the GW (25) co-ordinates given here) lead to  $R$ -factors of about this magnitude, which can hardly be regarded as a final value for a simple structure.

Attention is drawn to the parallelism of the  $\Delta F$  values (see Table 5) obtained for GW (25) and PL (26) co-ordinates (which differ appreciably) when the same isotropic temperature factor is used: neither could really be confidently preferred, but application of the GW  $B$ -factors produced  $R(h0l) = 0.062$  (22) and 0.092 (23) respectively—a much more decisive difference. A specimen least-squares calculation of the co-ordinate shifts for C and O from the  $\Delta F(h0l)$  values obtained for the GW co-ordinates with an isotropic  $B$ -factor (25) changed the C=O bond length by 0.023 Å (co-ordinates  $d$  in Table 1), but actually increased the  $R$ -factor from 0.169 to 0.174 (27), so that it may be true that suitable least-squares procedures in the absence of anisotropic temperature factors can give correct atomic co-ordinates. However, the great importance for theoretical chemistry of small irregularities in bond lengths and angles makes it desirable to eliminate the risk, especially since refinements of the temperature factors actually involve less work than co-ordinate refinements.

As an alternative to the complete procedure of determining anisotropic temperature factors for individual atoms, a variable temperature factor,  $B''$ , is generally applied to each structure factor as a whole, so that  $F(hkl)_{293} = F(hkl)_{\text{rest}} \exp[-B'' \sin^2 \theta / \lambda^2]$ . In considering the validity of such temperature corrections one can distinguish four main cases:

(a) All individual atoms have isotropic vibrations of the same magnitude. The  $B''$  factor for each reflection can be accurately represented by a spherical temperature factor.

(b) Individual atoms have isotropic vibrations of unequal magnitudes. This will produce a different  $B''$  factor for each reflexion (since the geometrical structure factor for each atom will in general be different) which cannot be represented accurately by any sphere, but which can be approximated by a sphere.

(c) All individual atoms have anisotropic vibrations of the same magnitude and orientation. This will produce a  $B''$  factor for each reflexion which can be represented accurately by an expression of the form  $A + B \cos^2 \varphi + C \cos^2 \varphi \cos^2 \psi$ . This case can in general only apply in crystals in which all the molecules are parallel, or in projections in which all the molecules are parallel, such as (010) in  $P2_1/c$ , and does not necessarily apply even then.

(d) Individual atoms have anisotropic vibrations which are unequal in magnitude and/or orientation. This will produce a  $B''$  factor for each reflexion which cannot be represented accurately by any ellipsoid, but which may sometimes be approximated by a sphere and sometimes, especially for a uniaxial crystal, be approximated much better by an ellipsoid than by a sphere.

It will be seen that with the exception of (a), which is never likely to be encountered in practice, and of (c), which corresponds to the vibration of the molecule as a rigid unit without any oscillation, and is probably not common—it is excluded for urea (19) and (20)—the temperature corrections cannot be applied accurately by means of an ellipsoid for the crystal as a whole.

Urea belongs to case (d); a mean vibration ellipsoid parallel to the crystal axes has already been shown to be unsatisfactory (17) and (18) (see also Fig. 7(a) of GL) for the  $\{hk0\}$  zone (in which this mean ellipsoid must have a circular section, since the crystal is tetragonal), as would be expected from the above considerations. However, GL's values for such an ellipsoid, used in conjunction with MW scattering factors and GW's co-ordinates, do show a considerable improvement (24) over the isotropic value (25) in  $R(hkl)$ , principally because the crystal is uniaxial.

For crystals without a unique axis, especially in the orthorhombic system, highly anisotropic molecular vibration ellipsoids could more readily combine to produce a 'mean' ellipsoid with very little anisotropy

along the crystal axes. (This must happen in cubic crystals, but would be unlikely in triclinic crystals, where fewer different molecular orientations would generally be present.) This fact may be partly responsible for the failure of the trivial axial corrections derived for the atomic  $B$ -factors in orthorhombic sulphur (Abrahams, 1955), which probably belongs to case (d) above, to produce a significant improvement in the  $R(hkl)$ -factor, as compared with the great improvement produced for the (010) projection of melamine (Hughes, 1941), which must approximate to case (c) above.

Our calculations for urea seem to us to demonstrate the inadequacy of half-measures of the types discussed above in the application of temperature corrections in structure determination, and the importance of actually applying anisotropic temperature factors to the atoms individually, from which procedure a value of

$$B'' = (\lambda^2 / \sin^2 \theta) \log_e [F(hkl)_{\text{rest}} / F(hkl)_T],$$

different for every reflexion, will result. The large scatter of these values for urea can be seen in Figs. 7(a) and 7(b) of GL's paper. These values of  $B''$  may be checked by intensity measurements at different temperatures, as described by GL; the derivation of the anisotropic  $B$ -factors for the individual atoms from such measurements as those of GL is possible in principle, if sufficient data were available.

## 7. Conclusion

It is suggested, therefore, that as soon as an  $R$ -factor of about 0.20 is reached, anisotropic temperature factors for each atom should be obtained from structure factors calculated, including hydrogen, from an *undistorted* chemical molecule before any serious attempt is made to improve the atomic co-ordinates. (Undistorted, because distortions present at this stage may well be incorrect, and the correct distortions should appear more readily from a regular structure than from one already distorted in the opposite direction.)

We are of course aware of the unwisdom of assuming that a procedure which gave such satisfactory results in the case of urea, a structure with only four atomic parameters (excluding hydrogen) for which we already had a number of very accurate values from which to commence operations, will necessarily prove transferable to more complicated structures in their earlier stages. Nevertheless, the results seem to us to justify the attempt to apply them more widely. As a further test of these procedures, particularly of the sufficiency of two-dimensional refinements, a new refinement of naphthalene is now in progress, commencing from the best *regular* molecule which can be chosen from Abrahams, Robertson & White's (1949) co-ordinates, including hydrogen atoms at distances of 1.09 Å from the carbon atoms, and using MW scattering factors. Only the reflexions in the axial zones

are being utilized. Details of this work will be published separately.

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## The Morphology of Zircon and Potassium Dihydrogen Phosphate in Relation to the Crystal Structure

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The periodic bond chain theory of crystal morphology is applied to zircon. The lattice energy and the attachment energies of several faces are calculated, assuming an ionic structure with  $Zr^{4+}$  and  $SiO_4^{4-}$  ions. Corrections are made for the tetrahedral shape of the silicate ion. In general a higher attachment energy corresponds to lower  $P$ - and  $F$ -values (persistences) of the forms.

The most important zones are [001], [100] and [111]. An explanation is given of their development.

The electrostatic lattice energy and the attachment energies of (010) and (011) of  $KH_2PO_4$  are calculated.

A 'theoretical habit' is derived for zircon and for  $KH_2PO_4$ ; the agreement with the observed habit is good.

The growth fronts on (010) of  $KH_2PO_4$  parallel to [100] are explained in terms of growth controlled by surface migration.

### Introduction

Recently, a method was proposed of deriving the morphology of crystals from the crystal structure (Hartman & Perdok, 1955*a, b*). This method will be applied to the zircon type of crystal structure, which is found, for instance, in zircon,  $KH_2PO_4$ , scheelite, wulfenite,  $KReO_4$  and so on. The structures of these substances are closely related, as regards positions and coordination of atoms, although they belong to different space groups. First, the morphology of zircon

will be treated in detail, and then some remarks will be made on the morphology of  $KH_2PO_4$ .

### Morphology of zircon

The relative morphological importance of the forms is given by the *Kombinationspersistenz* ( $P$ -value) and the *Fundortspersistenz* ( $F$ -value) (cf. Niggli, 1923). These quantities were obtained from an inspection of 129 figures appearing in Goldschmidt's *Atlas der Krystallformen* (1923), which gave 43 different ob-