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Anisotropic Temperature Vibrations in Crystals. I. Direct Measurements of Debye Factors for Urea

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Debye factors have been measured for 12 reflexions of urea, from intensity measurements at 90, 293 and 370° K. The values of (B^T-B^0), where B^0 is due to zero-point energy, thus obtained are distributed *about* curves of the type $A+B\cos^2\varphi$, but this approximation is, as expected, rather poor. If B^{293} values for these 12 reflexions are calculated from Vaughan & Donohue's corrected data for urea, using their temperature factors for the individual atoms, the agreement is excellent. The Debye factors obtained by comparing the structure in thermal motion with the structure at rest at the same temperature ought not necessarily to be identical with the Debye factors which relate the thermally moving structure with one at rest at absolute zero. Reasons are given for believing that in the case of urea the atomic parameters change very little with temperature, but it is very desirable that structures should be determined accurately at more than one temperature, if possible. The importance of determining Debye factors at an early stage of structure refinement is emphasized.

Symbols used in this paper

θ_{hkl}: Bragg angle for the *hkl* reflexion.

φ: angle between normal to (*hkl*) and [001].

ψ: angle in the plane (001) between [110] and the projected normal to the plane (*hkl*).

$F^T_{hkl} = F^T$: structure factor at the temperature T° K.

F^0: structure factor at 0° K. obtained by direct extrapolation from observed F^T values.

F^0_1: structure factor at 0° K. obtained by extrapolation with artificial flattening factor applied.

$F^T_{R(hkl)} = F^T_R$ structure factor for a structure at rest at the temperature T° K.

$F^{0/R}_o$ ($F^{0/R}_c$): structure factor for a structure at rest at 0° K., derived from observed (calculated) data.

$F^T_{R\,\mathrm{II}}$: structure factor for a structure at rest at temperature T° K., for the atomic co-ordinates II given in Table 6.

$B^T_{hkl} = B^T$: Debye factor for the *hkl* reflexion at the temperature T° K.

B^0: correcting factor to the Debye factor, which is required to allow for zero-point energy.

B^T_{C} (B^T_{O}, B^T_{N}, B^T_{H}): Debye factor for the carbon atom (oxygen, nitrogen, hydrogen) at the temperature T° K.

B^{293}_1: Debye factor for a given reflexion at 293° K. calculated as in equation (6) [B^{293}_2...equation (7): B^{293}_{II}...equation (8)].

$B^{293}_{0/R}$: Debye factor obtained for a given reflexion, by comparing the structure factors for the structure *in motion at* 293° K. with those for the structure *at rest at* 0° K.

B_X: Debye factor for a given atom in respect of its thermal motion in one (X) direction only.

B: Debye factor for a given atom in respect of its thermal motion in all directions.

m: mass of an atom in atomic units.

M: mass of a vibrator (whether atom or molecule or some arbitrary form of matter) in atomic units.

Introduction

Anisotropic temperature factors are now frequently found to be necessary in structure analysis of crystals. These may be applied to the scattering factors of individual atoms: or to the scattering from sets of crystal planes. It is quite certain that in the last stages of crystal-structure refinement such factors are of more importance than co-ordinate changes, and that their omission may cause serious errors in interatomic distances and angles. Temperature factors are determined, as a rule, either by Wilson's statistical method, or by difference Fouriers, or from electron-density contours, or by trial and error, or by least-squares adjustment of calculated structure factors, or by a combination of these methods, using as many observed intensities as possible, but at one temperature only. In the earliest structure determinations, however, Debye factors were sometimes determined directly by careful measurements of Bragg intensities at more than one temperature, and the existence of zero-point energy was confirmed in this way (James, Waller & Hartree, 1928).

Now that satisfactory devices have been contrived for maintaining crystals at low or high temperatures over long periods, there is no reason why this direct method should not be more universally applied, in which case it may be used (*a*) to give experimental temperature factors for individual crystal reflexions at different temperatures;

(*b*) to determine the anisotropic temperature factors for the different atoms, or sets of crystal planes, or to check these factors as derived by other methods;

(*c*) to test the existence of certain types of molecular vibration or thermal distortion required, for example, to explain infra-red spectra;

(*d*) to determine zero-point energies, Debye characteristic temperatures, root-mean-square amplitudes of vibration and related physical properties;

(*e*) to determine coefficients of expansion for the crystal and for inter- and intra-molecular bonds.

In the experimental investigation described in this paper the experimental technique was deliberately kept as simple as possible, so that its value as a routine procedure in structure analysis could be tested. Pentaerythritol and urea were chosen as typically anisotropic (tetragonal) organic structures and hexamine as an isotropic (cubic) structure. Thermal expansions were also measured in various directions in all the crystals and the principal coefficients of expansion were determined for the approximate temperature range 90–370° K. Some observations were made of thermal diffuse scattering and a few measurements were made also on a monoclinic crystal (anthracene). In this paper only the results on urea will be described and correlated with measurements by other observers.

Experimental technique

Crystals of urea were grown from aqueous solution and sets of rotation photographs of a well formed prism were taken with the *a* and *c* axes as approximate rotation axes, in a semi-cylindrical camera of 5·73 cm. radius, at temperatures of 90, 293 and 370° K. The crystals were deliberately mis-set in order to avoid multiplicity and to render unimportant any slight change of orientation with change of temperature. Visual estimations of intensity were made, using for comparison an intensity scale made with the same crystal and experimental arrangement. In order to be able to eliminate possible fluctuations in tube output or variation in film processing, an internal standard was used in the form of a backstop incorporating a finely-powdered layer of NaCl (Ahmed, 1952), other methods having proved less satisfactory. The backstop was fastened rigidly to the film-holder and its temperature and position relative to the X-ray beam remained constant throughout the whole series of experiments. Intensity measurements of the strongest NaCl powder ring (made by eye estimation, using an intensity scale made from the backstop itself) enabled diffraction effects from the crystal at different temperatures to be brought to a common scale.

The low temperature (90° K.) was obtained by allowing liquid air to flow over the crystal, the latter being enclosed in a thin-walled collodion tube. In order to prevent freezing-up of the rotating spindle, this was kept warm by means of a small heating coil. Better methods of cooling to give intermediate temperatures would have been those described by Post, Schwartz & Fankuchen (1952) or by Kreuger (1955). Similar methods are now being used by us, but the work here described was carried out prior to the publication of these methods. The present method does get a low temperature with relatively simple apparatus.

A small furnace of 18 gauge nichrome wire with a window of strain-free cellulose acetate sheet could bring the crystal to any desired temperature below its melting point and above room temperatures, and yet allow all X-ray reflexions to be recorded on the semi-cylindrical film. The temperature was measured with a calibrated copper–constantan thermocouple placed in the position of the crystal relative to the furnace immediately after the taking of each photograph, the furnace being raised slightly for this purpose. The crystal was mounted on a glass fibre using a drop of collodion solution, the glass fibre being sealed with collodion into a fine brass tube which itself fitted into the collodion tube which covered the crystal. This gave the whole system rigidity against the effects of changes of temperature. The crystal was taken down to a low temperature before any photograph was taken, in order that maximum mosaicity should be attained. No hysteresis effects were observed on taking pentaerythritol and urea crystals through a complete cycle of temperatures.

The error in the determination of the Debye factor is proportional to d^2 and therefore low-order planes, having large *d* values, were not used in these experiments. This made it unnecessary to use a film pack; two films were usually sufficient to give a range of intensities covering all suitable reflexions.

Care had to be taken that the crystal was at the same position in the beam at all temperatures; any necessary adjustments were made using a graduated eyepiece scale.

Coefficients of expansion

The camera radius was determined by calibration with aluminium wire, but with the experimental arrangement adopted there was no automatic calibration of each film. Care was of course taken to process the films under standard conditions, but high accuracy is not claimed for the results. Nevertheless, their internal consistency is evidence that extreme care is not required for useful results to be obtained. The values of the interplanar spacings *d* of 19 planes whose normals make angles φ varying from 0° to 90° with [001] were plotted against temperature and were found to give an approximately linear graph for each plane over the temperature range taken. Mean coefficients of expansion α were then calculated for each plane over the ranges of temperature 90–293–370° K. Table 1 gives

Table 1. *Interplanar spacings at* 90, 293 *and* 370° K.

hkl	φ	*d* (90° K.)	*d* (293° K.)	*d* (370° K.)
002	0	2·342	2·353	2·355
103	15·5	1·507	1·513	1·515
102	22·6	2·157	2·172	2·179
203	29·0	1·365	1·373	1·378
112	30·5	2·015	2·029	2·035
213	31·8	1·326	1·334	1·338
122	43·8	1·709	1·724	—
111	49·6	3·020	3·048	3·061
201	59·0	2·398	2·425	2·435
211	61·8	2·195	2·223	2·232
221	67·0	1·818	1·840	1·850
301	68·2	1·730	1·750	1·759
311	69·2	1·649	1·671	1·681
401	73·3	1·338	1·357	1·366
420	90	1·250	1·268	1·276
330	90	1·316	1·335	1·343
310	90	1·764	1·790	—
220	90	1·969	2·001	2·014
210	90	2·492	2·530	2·544

the actual spacings found at the various temperatures, which lead to the following equation for the coefficient of expansion over the whole temperature range 90–370° K.:

$$\alpha = (2{\cdot}3+5{\cdot}2\sin^2\varphi)\times10^{-5}.$$

Hence $\alpha[100] = 7{\cdot}5\times10^{-5}$ (°C.)$^{-1}$ and $\alpha[001] = 2{\cdot}3\times10^{-5}$ (°C.)$^{-1}$ over the range 90–370° K., and we find the following values of the crystal axes:

$$a = 5{\cdot}576,\ c = 4{\cdot}690\ \text{Å at}\ \ 90°\ \text{K.},$$

given

$$a = 5{\cdot}661,\ c = 4{\cdot}712\ \text{Å at}\ 293°\ \text{K.}$$

(Vaughan & Donohue, 1952).

The change in shape of the unit cell with temperature may produce a change in parameter of the atoms. Since the C–C bonds, even in diamond and in the (001) planes of graphite, expand with rising temperature (in the latter case only at high temperatures, because of the competing effect of a Poisson contraction due to the very large expansion along [001]), we know that the intramolecular distances may also change with temperature in urea, although the expansions of the two kinds of hydrogen bond may be expected to be larger than those of intramolecular bonds.

The expansion of the crystal axes will also cause a variation of the Bragg angles with temperature and hence of all angle-dependent factors, including the atomic scattering factors. These changes are small, however, whereas those due to changes in atomic coordinates may not be small. The number of diffraction intensities measured at low and high temperatures was, however, insufficient for a complete structure determination.

Calculation of Debye factor differences from observed structure factors

The relative intensities of 14 reflexions were measured at three different temperatures The 00*l* reflexions, although most interesting, could not be included because it was difficult to get reliable measurements from 001 and 002 on account of liquid-air fogging, and 003 and 004 were both small. The 301, 031 spectra were measured on different layer lines (as were also 401, 041) and, being structurally equivalent, they should give equal structure and Debye factors, and could provide a check on the general accuracy or reproducibility of the data.

Table 2 gives the actual structure factors deduced from the observed intensities at different temperatures, and it shows also the Debye factor differences deduced directly from these observed structure factors, using the formula

$$\Delta B_{hkl} = (B^{T_2}-B^{T_1})_{hkl} = (\lambda^2/\sin^2\theta_{hkl})\log_e(F^{T_1}/F^{T_2});\quad(1)$$

φ is the angle between the plane normal and the [001] direction. It will be seen that although, in general, ΔB increases with φ, the increase is not a smooth one.

The $|F_o|$ values are not comparable from plane to plane, but since only ratios at different temperatures have been used this is not important. It would, however, have been desirable to have had measurements

Table 2. *Observed structure factors at different temperatures (not comparable from plane to plane) and Debye factor differences deduced from them*

hkl	φ (°)	$(\sin\theta)/\lambda$ (Å^{-1})	$\lambda^2/\sin^2\theta$ (Å^2)	F^{90}	F^{293}	F^{367}	F^{378}	$(B^{293}-B^{90})$	$(B^{367}-B^{293})$ or $(B^{378}-B^{293})$
013	15·5	$0{\cdot}3304\times10^8$	$9{\cdot}16\times10^{-16}$	5·00	5·00	—	4·57	$0{\cdot}00\times10^{-16}$	$0{\cdot}82\times10^{-16}$
023	29·0	0·3640	7·55	2·95	2·63	—	2·28	0·87	1·08
112	30·5	0·2462	16·5	4·87	4·47	—	4·06	1·41	1·59
123	31·8	0·3746	7·13	3·35	2·74	—	2·37	1·43	1·03
133	41·2	0·4235	5·58	3·16	2·50	—	2·07	1·31	1·05
121	61·8	0·2242	19·9	4·18	3·71	—	3·49	2·37	1·22
221	67·0	0·2714	13·6	6·16	5·06	4·60	—	2·67	1·23
301	68·2	0·2855	12·3	6·32	4·71	4·29	—	3·61	1·15
031	68·2	0·2855	12·3	4·88	3·71	—	3·09	3·37	2·25
131	69·2	0·2988	11·2	5·48	4·74	—	4·27	1·63	1·17
401	73·3	0·3689	7·34	5·48	3·79	3·07	—	2·71	1·55
041	73·3	0·3689	7·34	4·18	2·96	—	2·47	2·53	1·33
330	90	0·3748	7·12	5·63	3·49	2·97	—	3·41	1·15
220	90	0·2498	16·0	6·82	5·48	4·60	—	3·50	2·80

at more than three temperatures and, in particular, at much lower temperatures, because in order to obtain absolute Debye factors and zero-point energies it is necessary to extrapolate back to absolute zero. Although we may expect the F curves to flatten out near to 0° K., no attempt has been made to estimate the actual amount of flattening for lines of such different slopes (Fig. 1); they have in the first place simply been extended without change of slope. This extrapolation is certainly one of the principal sources of error in the method. On the other hand, it is possible to get some idea of the error involved, by imposing an artificial flattening dependent upon the slope (taken as $(F^{90}-F^{293})/6$) and to see how this affects the B values and the zero-point energy.

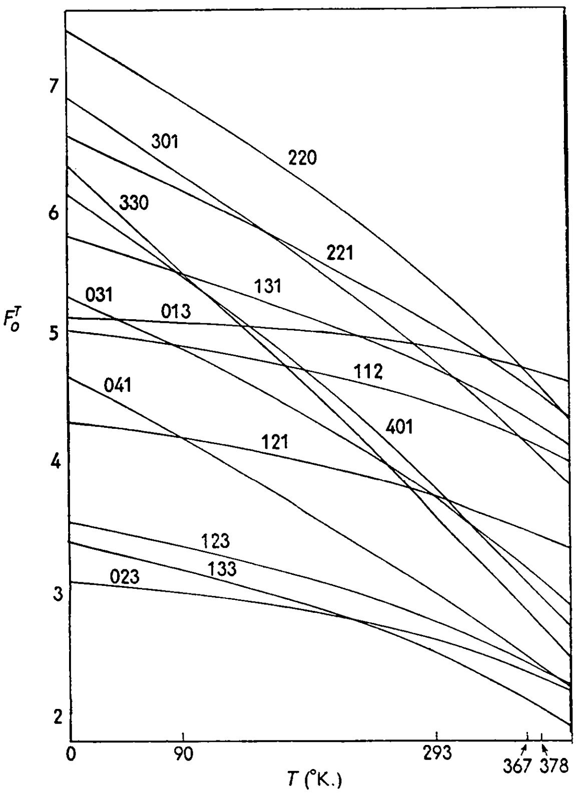


Fig. 1. Curves of F_0^T versus T, extrapolated to 0° K.

Table 3 shows the smoothed values of F^0, F^{90}, F^{293}, F^{370} as read off from the extrapolated curves, and also $F_1^0 = F^0-(F^{90}-F^{293})/6$.

Method of calculation of the Debye temperature factors for different reflexions, from the observed intensities

If the ideal structure of the crystal at rest (R) is known at any given temperatures (T), then the absolute structure factors $F^T_{R(hkl)}$ corresponding to the stationary, or mean, structure for the unit cell of dimensions and parameters appropriate to the temperature T can be calculated. A Debye factor at the given temperature T for each reflexion, B^T_{hkl}, may then be obtained by comparing these calculated values with the actual structure factors F^T_{hkl}, using the equations

Table 3. F^T *values from extrapolated curves*

hkl	F^0	F^{90}	F^{293}	F^{370}	F_1^0
013	5·14	5·08	4·90	4·73	5·11
023	3·08	2·98	2·60	2·34	3·02
112	5·03	4·90	4·44	4·13	4·95
123	3·54	3·35	2·74	2·41	3·44
133	3·40	3·16	2·50	2·11	3·29
121	4·30	4·18	3·72	3·48	4·22
221	6·58	6·16	5·06	4·58	6·40
301	6·90	6·32	4·79	4·09	6·65
031	5·30	4·88	3·71	3·16	5·10
131	5·78	5·48	4·74	4·32	5·66
401	6·12	5·48	3·79	3·04	5·84
041	4·66	4·18	2·98	2·48	4·46
330	6·35	5·55	3·59	2·82	6·02
220	7·44	6·88	5·42	4·66	7·20

$$F^T = F_R^T \exp\left(-B^T \sin^2\theta/\lambda^2\right)\,, \qquad (2)$$

$$B^T_{hkl} = (\lambda^2/\sin^2\theta)\,\log_e\left(F_R^T/F^T\right)\,. \qquad (3)$$

However, the F_R^T values differ from F_R^0, the structure factors for a stationary structure of dimensions and parameters appropriate to absolute zero, by those corrections which depend upon changes in size, shape and parameters of the unit cell. The extrapolated F^0 (or F_1^0) values given in Table 3 differ also from F_R^0, by including the effect of an unknown zero-point energy, as well as errors of extrapolation.

Using the data given in Table 3, values of $(B^T-B^0)_{hkl}$ have been obtained by means of the formula

$$(B^T-B^0)_{hkl} = (\lambda^2/\sin^2\theta)\,\log_e\left(F^0/F^T\right)\,. \qquad (4)$$

where B^0 is the zero-point energy correction, inclusive of errors of extrapolation. These values are recorded in Table 4, together with the corresponding values of $(B^T-B^0)'_{hkl}$ obtained using F_1^0 instead of F^0.

If the (B^T-B^0) values are plotted along directions making angles φ (see Tables 1 or 2) with [001], as in

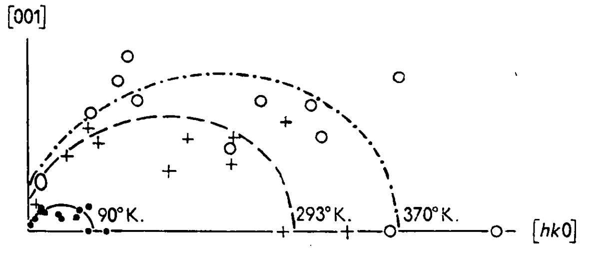


Fig. 2. Radial distribution of values of (B^T-B^0), from Table 4, with 'average curves' for T = 90, 293 and 370° K. Dots: 90° K.; crosses: 293° K.; circles: 370° K.

Fig. 2, it will be found that they are scattered about curves of the type

$$B^T-B^0 = A+B\cos^2\varphi\,,$$

where

Table 4. $(B^T-B^0)_{hkl}$ *values deduced from experimental, extrapolated F curves*

$(B^T-B^0)'$ refers to a curve artificially flattened at temperatures below 90° K., (B^T-B^0) to the curve extrapolated to 0° K. without flattening. (All $\times 10^{16}$.)

hkl	$(B^{90}-B^0)$	$(B^{293}-B^0)$	$(B^{370}-B^0)$	$(B^{90}-B^0)'$	$(B^{293}-B^0)'$	$(B^{370}-B^0)'$
013	0·11	0·44	0·76	0·05	0·38	0·70
023	0·25	1·28	2·08	0·10	1·13	1·93
112	0·43	2·06	3·16	0·17	1·79	2·99
123	0·39	1·83	2·74	0·19	1·62	2·54
133	0·41	1·72	2·66	0·22	1·53	2·48
121	0·56	2·89	4·22	0·19	2·51	3·83
221	0·90	3·57	4·92	0·52	3·19	4·54
301	1·08	4·49	6·44	0·63	4·04	5·98
031	1·02	4·39	6·36	0·54	3·91	5·88
131	0·57	2·22	3·26	0·36	1·98	3·04
401	0·81	3·51	5·14	0·47	3·17	4·79
041	0·80	3·28	4·63	0·48	2·96	4·31
330	0·96	4·06	5·78	0·58	3·68	5·40
220	1·25	5·07	7·48	0·73	4·64	6·96

$$\begin{aligned}
(B^{90}-B^0)10^{16} &= 1{\cdot}02-0{\cdot}92\cos^2\varphi = 0{\cdot}10+0{\cdot}92\sin^2\varphi\,,\\
(B^{293}-B^0)10^{16} &= 4{\cdot}25-3{\cdot}75\cos^2\varphi = 0{\cdot}50+3{\cdot}75\sin^2\varphi\,,\\
(B^{370}-B^0)10^{16} &= 5{\cdot}9\;\;-5{\cdot}2\;\;\cos^2\varphi = 0{\cdot}7\;\;-5{\cdot}2\;\;\sin^2\varphi\,.
\end{aligned}$$

The $(B^T-B^0)'$ values give similar curves but with somewhat lower values of the coefficients.

It is quite clear, however, that the application of an anisotropic temperature factor of this simple form, although better than an isotropic factor, would introduce serious errors for some reflexions. It would imply, for example, that all *hk*0 reflexions should have the same *B* factor. This would be true only if all vibrations normal to [001] were isotropic. If, however, the molecule is oscillating so that the N and H atoms have a large anisotropic temperature vibration normal to [001] as compared with C and O (as Vaughan & Donohue deduce), then those *hk*0 reflexions to which the N contribution is largest will also have a temperature factor larger than that of the *hk*0 reflexions where the scattering is due to C and O. Using sufficient reflexions, it may indeed be possible to deduce the anisotropic temperature factors for individual atoms of a known structure. This would be especially useful in the case of a structure having a number of atoms in special positions. It has not been attempted in the present paper because the number of reflexions actually measured (12) is statistically insufficient for accurate results and because the known atomic parameters are themselves dependent upon assumptions made about thermal vibrations.

Comparison of the $(B^T—B^0)$ values with *B* values deduced from Vaughan & Donohue's X-ray structure analysis, and hence an estimate of zero-point energy

Vaughan & Donohue (1952) have given not only atomic co-ordinates (see Table 6) but also the following equations for the anisotropic temperature factors for the atoms, deduced from Fourier contours and least-squares refinements (the factor for the hydrogen atoms was assumed to be isotropic):

$$\left.\begin{aligned}
&\text{hydrogen:}\\
&\qquad B_{\mathrm{H}}\times 10^{16} = 4;\\
&\text{carbon and oxygen:}\\
&\qquad B^{293}_{\mathrm{C,O}}\times 10^{16} = 3{\cdot}9\sin^2\varphi-1{\cdot}9\cos^2\varphi\\
&\qquad\qquad\qquad\qquad = 1{\cdot}9-2{\cdot}0\sin^2\varphi;\\
&\text{nitrogen:}\\
&\qquad B^{293}_{\mathrm{N}}\times 10^{16} = 1{\cdot}9+\sin^2\varphi(2{\cdot}0+5{\cdot}7\sin^2\psi);
\end{aligned}\right\}\quad(5)$$

where φ has the meaning previously given and ψ si the angle in the plane (001) between [110] and the projected normal to the plane (*hkl*). (Note that the angle with $[1\bar{1}0]$ is $90°-\psi$.)

These data apply only at room temperatures, presumed to be 293° K. Since Vaughan & Donohue's $|F_c|$ values contain an error (private communication), Grenville-Wells (1956) has given recalculated values of $|F_c^{293}|$, using Vaughan & Donohue's own atomic coordinates and temperature factors, but with a different scaling factor for $|F_o|$, and has obtained a reliability factor $R = \Sigma||F_c|-|F_o||\div\Sigma|F_o|$ of 0·061, as compared with their 0·099. Using the same atomic co-ordinates but omitting the temperature factors, gives F_R^{293}. Hence, from equation (3), values of B_{hkl}^{293} can be obtained for as many reflexions as have been measured. Table 5 shows values B_1^{293} and B_2^{293} obtained as follows:

$$B_1^{293} = (\lambda^2/\sin^2\theta)\log_e(F_R^{293}/F_o^{293})\,, \tag{6}$$

$$B_2^{293} = (\lambda^2/\sin^2\theta)\log_e(F_R^{293}/F_c^{293})\,. \tag{7}$$

Figs. 3(*a*) and 3(*b*) compare B_1 and B_2 respectively with our $(B^{293}-B^0)$ and $(B^{293}-B^0)'$. The parallelism of the results is better for B_2 than for B_1, which is to be expected, for the F_R^{293} values refer to atomic coordinates which are consistent with $|F_c^{293}|$. The discrepancies between $|F_c|$ and $|F_o|$, which are random, are carried back into F_R^{293} and lead to bigger random errors in B_1.

The parallelism between B_2 and either set of $(B^{293}-B^0)$ is amazingly good.

If B_2^{293} were identical with our B^{293} then the mean difference, ΔB_2, between the two sets of values B_2^{293}

Table 5. *Debye factors* ($B^{293}\times 10^{16}$) *deduced from Vaughan & Donohue's F data, with* ΔB *values as follows*: $\Delta B_1 = B_1^{293} - (B^{293} - B^0)$, $\Delta B_1' = B_1^{293} - (B_2^{293} - B^0)'$ etc.

hkl	$\lvert F_o^{293}\rvert$*	$\lvert F_c^{293}\rvert$†	$\lvert F_R^{293}\rvert$†	B_1^{293}	ΔB_1	$\Delta B_1'$	B_2^{293}	ΔB_2	$\Delta B_2'$
013	7·19	7·56	9·56	2·65	2·21	2·27	2·15	1·71	1·77
023	5·07	5·32	7·36	2·82	1·54	1·69	2·45	1·17	1·32
112	5·56	5·00	6·26	1·96	(−0·20)	0·17	3·30	1·26	1·53
123	5·62	5·80	8·74	3·15	1·32	1·53	2·92	1·09	1·30
133	5·39	5·56	4·69	3·27	1·55	1·74	3·10	1·38	1·57
121	5·63	5·50	6·52	2·92	0·03	0·41	3·39	0·50	0·88
221	10·50	10·54	14·49	4·38	0·81	1·19	4·33	0·76	1·14
301	6·85	6·80	10·90	5·72	1·28	1·74	5·80	1·36	1·82
131	8·48	8·44	11·96	3·85	1·63	1·87	3·91	1·69	1·93
401	6·02	6·14	11·34	4·64	1·24	1·57	4·50	1·10	1·43
330	8·54	9·20	18·50	5·50	1·44	1·82	4·97	0·91	1·29
220	9·98	10·82	16·14	9·68	2·61	3·04	6·39	1·32	1·73
				$\Delta\bar{B}$ =	1·42	1·64		1·19	1·48

* The $\lvert F_o^{293}\rvert$ values given by Vaughan & Donohue have been multiplied by a scaling factor 0·965.

† Recalculated by Grenville-Wells (1956) from Vaughan & Donohue's atomic co-ordinates, with and without their temperature factors, using James & Brindley's f factors, as they did.

Table 6. *Various sets of atomic parameters*

I. Vaughan & Donohue's published data.
II. The same including a Cox correction (Cox, Cruickshank & Smith, 1955) to the x parameter of the nitrogen atom.
III. Values leading to the molecular dimensions given by neutron diffraction data (Peterson & Levy, reported by Levy (1954)).
IV. Parameters giving the slightly different intra- and inter-molecular spacings shown in Table 10.
V. See text.

	C(z)	O(z)	N(x)	N(z)	$H_1(x)$	$H_1(z)$	$H_2(x)$	$H_2(z)$
I	0·3308	0·5987	0·1429	0·1848	0·253	0·287	0·137	0·972
II	0·3308	0·5987	0·1445	0·1848	0·253	0·287	0·137	0·972
III	0·331	0·592	0·145	0·180	0·259	0·282	0·141	0·970
IV	0·314	0·584	0·146	0·167	0·259	0·282	0·141	0·970
V	0·332	0·598	0·142	0·186	0·253	0·287	0·137	0·972

and ($B^{293} - B^0$) would be a measure of the average zero-point energy.

Even apart from errors of extrapolation, however, the values of B_2^{293} and B^{293} are not identical. B_2^{293} compares the thermally vibrating structure at 293° K. with a structure *at rest at the same temperature.* Our B^{293} compares the thermally vibrating structure at 293° K. with the structure, as yet unknown, *at rest at* 0° K.

Atomic parameters at 0° K.

At present we have no means of estimating the atomic parameters at absolute zero, nor have we sufficient diffraction data to obtain them even at 90° K. As an exercise, however, we may take three other sets of atomic parameters (Table 6) (slightly different from those of Vaughan & Donohue), assume that these apply at 0° K. and by comparing the F_R^0 obtained from them with the same $\lvert F_c^{293}\rvert$, still using James & Brindley's f factors, we may calculate new sets of B and ΔB values (all given $\times 10^{16}$ from now on) by means of the formula

$$B_{\mathrm{II}}^{293} = (\lambda^2/\sin^2\theta)\log_e(F_{R\,\mathrm{II}}^0/F_c^{293})\,. \tag{8}$$

These Debye factors are plotted against ($B^{293} - B^0$) in Figs. 3(c), (d) and (e).

On the whole there would be little to choose between the Debye factor agreement for set I (Fig. 3(b)) and set II, although it will be noticed that the small change in N(x) does make an appreciable difference in the Debye factors of certain reflexions. The set III give an agreement which is not quite so good, but set IV gives Debye factors which diverge very markedly from our measured ($B^{293} - B^0$) data. Since the Debye factors are so sensitive to change of the atomic positional parameters, it does seem likely that for urea these parameters cannot in fact differ much at 0° K. from their values at 293° K., so that the values of B^{293} derived from equations (3) and (4) are, in fact, approximately equal in this case. It does not follow that they will usually be so. The identity of ΔB_2 with B^0 may still, however, depend upon the conditions assumed for the calculation of $\lvert F_c^{293}\rvert$. In particular, the use of James & Brindley's f factors is probably erroneous and the substitution of McWeeny f factors may alter both the scaling factor and the individual atomic thermal vibration factors (Grenville-Wells, 1956).

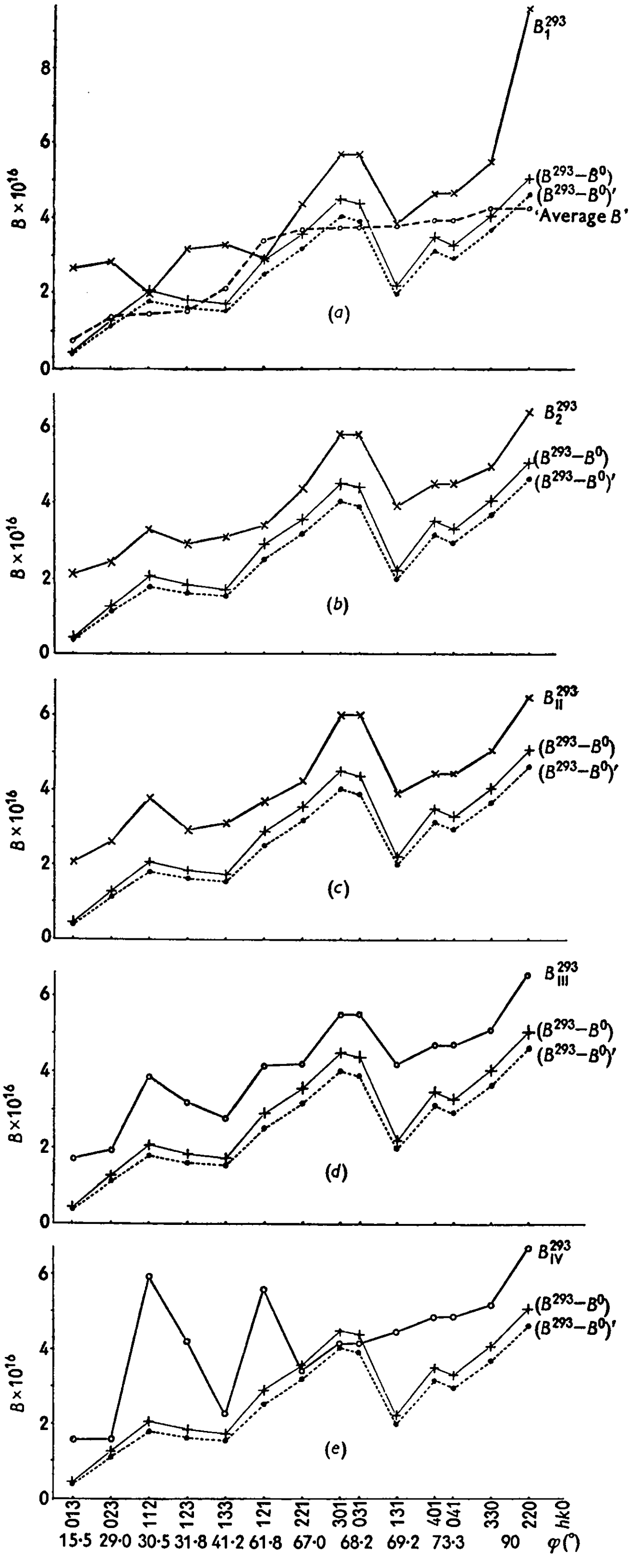
Let us now begin in another way. Suppose we take our values of ($B^{293} - B^0$) for all 12 planes and add to each what seems a *reasonable* value of B^0. We can obtain such a value as follows: For simple cubic crystals containing only one kind of atom:

$$B^T = \frac{6h^2}{mk\Theta}\left\{\frac{\varphi(x)}{x} - \frac{1}{4}\right\},\ \text{where } x = \Theta/T$$

and

$$B^0 = \frac{6h^2}{mk\Theta}\cdot\frac{1}{4} \text{ is the zero-point energy.} \qquad (9)$$

The function $\varphi(x)/x$ has been tabulated for a wide range of Θ/T values.



A formula of this kind holds reasonably well for the alkali halides and for other simple ionic compounds; that is to say, it leads to values of Θ, the Debye temperature, which are consistent with those obtained by other methods, provided that the vibrating atoms are assumed to have a mass m which is the arithmetic mean of those of all the atoms present.

In the case of urea we do not know whether to treat the molecule as a single oscillator of molecular weight 60, or to regard the atoms as vibrating entirely independently. Nor do there appear to be any independent estimates of Θ. Indeed, the Debye temperature may be expected to vary with temperature; and the Debye temperature, the average mass of the vibrating unit and the zero-point energy may all be expected to vary from one direction to another in the crystal. Nevertheless we can make an estimate of zero-point energies as follows.

Substituting for known constants, we may write

$$B^T - B^0 = \frac{11500}{M\Theta}\,\frac{\varphi(x)}{x} \times 10^{-16}, \qquad (10)$$

$$B^0 = \frac{2875}{M\Theta} \times 10^{-16}, \qquad (11)$$

where M is the mass of the vibrator in atomic units. If we take $M = 5, 10, 15, 30, 60$ (molecular weight of urea), then for each of these values the range, 0·1–7·5, of our observed $(B^T - B^0)$ limits the possible values of Θ and B^0, as shown in Table 7.

Table 7

M	Range of Θ (°K.)	Range of $B^0 \times 10^{16}$
5	800–300	0·72–1·92
10	600–220	0·48–1·31
15	520–180	0·37–1·07
30	400–140	0·24–0·68
60	300– 90	0·16–0·50

On the whole $M = 30$, $\Theta = 400-140°$ K. seem the most reasonable values to assume, although these lead to B^0 values much lower than those found for ΔB (Table 5).

In Table 8 are given the calculated values of B^0 and $(B^T - B^0)$ corresponding to $M = 10$, $M = 30$ and various values of Θ.

It will be seen that the relative values of the calculated $(B^T - B^0)$ in Table 8 compare reasonably well with the observed values in Table 4 for $T = 90$, 293 and 370° K. Table 9 gives the values of B^0 for $M = 30$ that would correspond with our observed values of $(B^{293} - B^0)$ for the different hkl reflexions. These are

Fig. 3. (*a*) B_I^{293}, $(B^{293}-B^0)$ and $(B^{293}-B^0)'$ for our 12 reflexions, arranged in order of increasing inclination of normals to [001]; together with the 'average values' corresponding to $(0{\cdot}5+3{\cdot}75\sin^2\varphi)$. (*b*) B_2^{293}, $(B^{293}-B^0)$ and $(B^{293}-B^0)'$, (*c*) B_{II}^{293}, $(B^{293}-B^0)$ and $(B^{293}-B^0)'$, (*d*) B_{III}^{293}, $(B^{293}-B^0)$ and $(B^{293}-B^0)'$, (*e*) B_{IV}^{293}, $(B^{293}-B^0)$ and $(B^{293}-B^0)'$ for the same 12 reflexions as in (*a*).

obtained from Table 8 by interpolation. Hence a value of B^{293} is found for each reflexion *hkl*. This, when applied to Vaughan & Donohue's $|F_o^{293}|$, gives $|F_o^{0/R}|$ for the structure at rest at 0° K.

If sufficient data were available, it would be possible now to determine the structure, by Fourier analysis or least-squares refinement, that would best correspond with these data. Although twelve reflexions are not sufficient for this purpose, trial-and-error methods can be used to test possible sets of parameters and atomic scattering factors. Dr Grenville-Wells (1956) has carried out such calculations for us, in the course of a longer investigation concerning the general accuracy of refinement methods. She has shown that the same set of atomic parameters (Table 6, (I)) that Vaughan & Donohue have given for room temperatures do give very good agreement at 0° K. also ($R = 4{\cdot}26\%$ for these twelve planes) when used with the McWeeny scattering factors for all atoms, provided that a scaling factor ×1·16 is applied. Her $|F_c^{0/R}|$ values are also given in Table 9. Using sets of atomic parameters II or III, good agreement is also obtained ($R = 4{\cdot}49$, $4{\cdot}63\%$ respectively) and indeed it is clear that a number of sets of slightly differing atomic parameters will give $R \sim 5\%$.

If the set of B^0 values for $M = 10$ are applied in the same way, a set of slightly larger $|F_o^{0/R}|$ values are obtained, requiring a slightly smaller scaling factor (×1·105). The same atomic parameters still give the best agreement, but with slightly higher R values (4·69% instead of 4·25% for the set I, for example).

We may again conclude that the atomic parameters at 0° K. cannot differ much, if at all, from those at 293° K., in spite of the considerable expansion of the unit cell.

Revised atomic temperature factors

In their calculations, Vaughan & Donohue used James & Brindley's *f* factors, and their scaling factor and temperature factors were adjusted to give the best agreement in these circumstances. Using the McWeeny *f* factors, including the effect of the directed bond for oxygen, Dr Grenville-Wells finds the following thermal anisotropies to be necessary in order to obtain good agreement with $|F_o^{293}|$:

for carbon:

$$B_{\mathrm{C}}^{293}\times10^{16} = 1{\cdot}5-1{\cdot}8\sin^2\varphi\,;$$

for oxygen:

$$B_{\mathrm{O}}^{293}\times10^{16} = 0{\cdot}6+2{\cdot}9\sin^2\varphi\,;$$

for nitrogen:

$$B_{\mathrm{N}}^{293}\times10^{16} = 1{\cdot}5-\sin^2\varphi(1{\cdot}4-4{\cdot}6\sin^2\psi)\,;$$

for hydrogen:

$$B_{\mathrm{H}}^{293}\times10^{16} = 1{\cdot}9-\sin^2\varphi(2{\cdot}0-5{\cdot}7\sin^2\psi)\,. \qquad (12)$$

Table 8. *Calculated values of B^0 and B^T-B^0 for various combinations of Θ and M*

	$M = 10$				$M = 30$			
Θ (°K.)	B^0	$(B^{90}-B^0)$	$(B^{293}-B^0)$	$(B^{370}-B^0)$	B^0	$(B^{90}-B^0)$	$(B^{293}-B^0)$	$(B^{370}-B^0)$
600	0·48	0·07	0·56	0·79	—	—	—	—
500	0·58	0·12	0·87	1·21	—	—	—	—
450	0·64	0·16	1·12	1·55	—	—	—	—
400	0·72	0·22	1·49	2·04	0·24	0·07	0·50	0·68
350	0·84	0·34	2·08	2·81	0·28	0·11	0·70	0·93
300	0·96	0·51	2·91	3·85	0·32	0·17	0·97	1·29
250	1·15	0·84	4·35	5·75	0·39	0·28	1·45	1·92
200	1·44	1·50	7·07	9·28	0·48	0·50	2·35	3·20
150	—	—	—	—	0·64	1·00	4·40	5·70
100	—	—	—	—	0·96	2·61	10·31	13·26

Table 9. *Correction of $|F_o^{293}|$ values to give $|F_o^{0/R}|$ values, using our measured $(B^{293}-B^0)$ data and B^0 values corresponding to $M = 30$*

(B values × 10^{16}.)

hkl	$(B^{293}-B^0)_{\text{obs.}}$	$B^0(M=30)$	B^{293}	$\lvert F_o^{293}\rvert$	$\lvert F_o^{0/R}\rvert\times1{\cdot}16$	$\lvert F_c^{0/R}\rvert$
013	0·44	0·24	0·68	7·45	9·30	9·64
023	1·28	0·35	1·63	5·25	7·55	7·62
112	2·06	0·44	2·50	5·76	7·78	7·25
123	1·83	0·42	2·25	5·82	9·25	8·82
133	1·72	0·42	2·14	5·59	9·52	9·75
121	2·89	0·50	3·39	5·83	8·01	6·99
221	3·57	0·55	4·12	10·88	17·07	16·33
301 031	4·49 4·39	0·60	5·04	7·10	12·40	12·10
131	2·22	0·45	2·67	8·77	12·90	13·54
401 041	3·51 3·28	0·55	3·95	6·24	12·40	12·18
330	4·06	0·58	4·64	8·85	19·69	19·72
220	5·07	0·65	5·72	10·34	17·13	18·56

These are intermediate between the Vaughan & Donohue values of the individual Debye factors (equation (5)) and those reported by Peterson & Levy (Levy, 1954) as obtained from neutron-diffraction data. Their application improves the reliability factor for our 12 planes, at 293° K., to $R = 3\cdot44\%$. Fig. 4(*a*) shows the Debye factors for these 12 reflexions from the equation

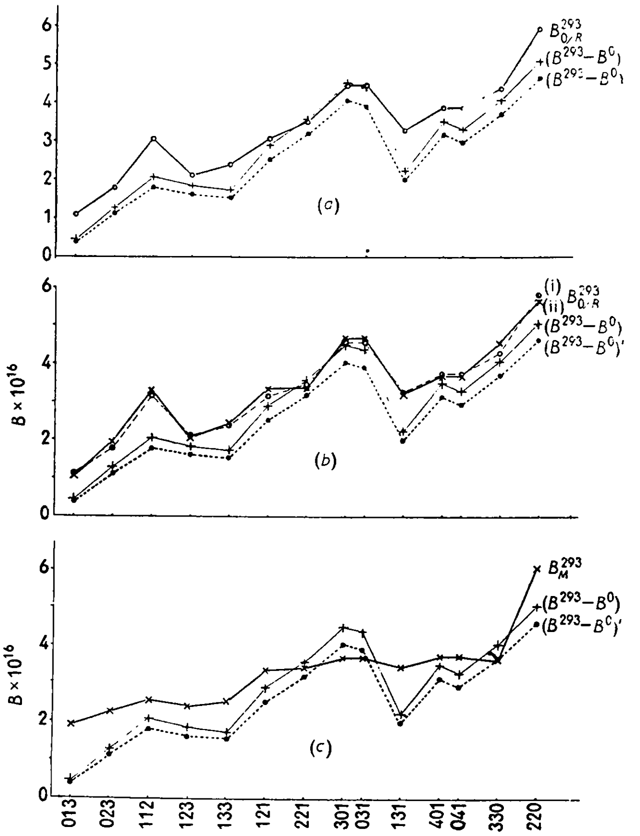


Fig. 4. (*a*) Debye factors $B^{293}_{0/R}$ using parameters set I, McWeeny *f* factors and temperature factors from equations (12), as compared with $(B^{293}-B^0)$ and $(B^{293}-B^0)'$. (*b*) Debye factors $B^{293}_{0/R}$ using parameters set V, (i) without, (ii) with the Cox correction, as compared with $(B^{293}-B^0)$ and $(B^{293}-B^0)'$. (*c*) Debye factors for a 'flapping molecule' as compared with $(B^{293}-B^0)$ and $(B^{293}-B^0)'$.

$$B^{293}_{0/R}\times10^{16} = \lambda^2/\sin^2\theta \log_e (F_c^{0/R}/F_c^{293}), \qquad (13)$$

using set I parameters at both temperatures. Refinement using these thermal parameters and the McWeeny *f* factors also leads to a slightly different set of atomic parameters V (Table 6), and Fig. 4(*b*) (i) shows the corresponding Debye factors for $F_c^{0/R}/F_c^{293}$ for this set of parameters assuming that they apply at both temperatures. Fig. 4(*b*) (ii) shows the result of applying the Cox correction to the parameters at rest. Although the parallelism for either (i) or (ii) with our $(B^{293}-B^0)$ values is good, it is extremely doubtful whether the accuracy of intensity measurement justifies a selection between parameter sets I and V.

Dr Grenville-Wells has also considered the possibility of a urea molecule which is vibrating to and fro as a whole (flapping) rather than oscillating about the C=O direction. The structure factors calculated for such a model do not give good agreement either in respect of the reliability factor or for the Debye factors (Fig. 4(*c*)). This means that it is possible to distinguish between different types of molecular movement by purely structural methods.

Bond distances at 293° K. and at 90° K.

The inter- and intra-molecular distances corresponding to the sets of atomic parameters I–V are given in Table 10.

It will be seen that set IV, which gave no Debye factor agreement, differs from the others by less than 1% in bond lengths, but retains at 90° K. the same type of hydrogen bond difference that occurs at room temperature.

The remaining sets, all of which lead to good reliability factors using appropriate Debye factors, and which seem to apply at both temperatures, imply a tendency to equalization of the hydrogen bond lengths at low temperatures.

In all cases the change in the C–N bond length appears to be about 1·2% as against 0·3–0·4% for C=O, for a temperature change of 200° K. This difference may be related to the large difference in amplitude of thermal vibrations.

Amplitudes of thermal vibration for various atoms

If we assume the model of a simple vibrator, then the mean square amplitudes of vibration of any individual atom along three orthogonal directions, *X*, *Y* and *Z* are given by

$$B_X = 8\pi^2\overline{u_X^2} \quad \text{etc.},$$

Table 10. *Inter- and intra-molecular bond distances and angles for various sets of atomic parameters at 293 and 90° K.*

	I		II		III		IV		V	
Bond	293° K.	90° K.	293° K.	90° K.	293° K.	90° K.	293° K.	90° K.	293° K.	90° K.
C=O (Å)	1·262	1·258	1·262	1·258	1·230	1·225	1·273	1·268	1·254	1·249
C–N (Å)	1·335	1·321	1·345	1·330	1·362	1·345	1·357	1·342	1·329	1·312
$NH_1\cdots O$ (Å)	3·035	2·993	3·022	2·981	3·039	2·996	3·067	3·025	3·040	2·998
$NH_2\cdots O$ (Å)	2·989	2·972	2·994	2·975	3·004	2·985	2·986	2·966	2·995	2·976
N–C–N (°)	117·9	117·6	118·4	118·0	116·9	116·4	118·6	118·2	117·6	117·2

Table 11. *Values of* $u^2_{[uvw]}$ *and of* $\sqrt{(\overline{u^2_{[uvw]}})}$ *for individual atoms at* 293° K.

	$\overline{u^2_{[001]}}$	$\overline{u^2_{[1\bar{1}0]}}$	$\overline{u^2_{[110]}}$	$\sqrt{u(^2_{[001]})}$	$\sqrt{(\overline{u^2_{[1\bar{1}0]}})}$	$\sqrt{(\overline{u^2_{[110]}})}$
C	0·019 Å^2	0·042 Å^2	0·042 Å^2	0·14 Å	0·20	0·20
O	0·008	0·044	0·044	0·09	0·21	0·21
N	0·019	0·095	0·037	0·14	0·31	0·19
H	0·024	0·122	0·037	0·16	0·35	0·19

the total mean square amplitudes $\overline{u^2}$ being given by

$$\overline{u^2} = \overline{u^2_X} - \overline{u^2_Y} - \overline{u^2_Z} \,.$$

For an isotropic vibration,

$$\overline{u^2_X} = \overline{u^2_Y} = \overline{u^2_Z} = \overline{u^2}/3 \,.$$

and the expression is then often written as

$$B = 8\pi^2\overline{u^2}/3;$$

but we are interested in actual amplitudes in given directions [*uvw*], corresponding to the anisotropic Debye factors in various crystal directions. Table 11 shows the values of $\sqrt{(\overline{u^2}_{uvw})}$ along the [001], [1$\bar{1}$0] and [110] directions for individual atoms at 293° K., as derived from the Debye factors given in equations (12).

The zero-point energy B^0 given in Table 9, as corresponding to a vibrator of $M = 30$, varies from $0{\cdot}24\times10^{-16}$ to $0{\cdot}65\times10^{-16}$. The former value would imply a minimum component $\sqrt{(\overline{u^2_X})} = 0{\cdot}055$ Å and the latter a maximum component 0·09 Å. The values of B^0 deduced from ΔB, the difference shown in Figs. 3 and 4 between B^{293}_{hkl} and $(B^{293}-B^0)$ or $(B^{293}-B^0)'$, though very much dependent upon the precise atomic parameters, *f* factors etc. used in calculation, are of the same order of magnitude. It follows that the zero-point amplitudes of vibration are comparable with the amplitudes of thermal vibration and must form a considerable part of the total vibration, especially at low temperatures.

Diffuse X-ray scattering in relation to thermal vibration

The root-mean-square amplitudes of vibration calculated from the Debye factors and shown in Table 11 refer to all frequencies. In general, thermal vibrations are capable of being regarded, relative to the oncoming X-rays, as a system of stationary waves superimposed upon the crystal, because the thermal frequencies are low relative to X-ray frequencies. (This is not true for neutrons, however.) The thermal waves of maximum amplitude are those which correspond to low frequencies and long wavelengths.

Ramachandran & Wooster (1951) have shown that for simple structures it is possible to determine the elastic constants of the crystal by quantitative measurements of the intensity of diffuse X-ray scattering. Bones (1954) found that this was not possible

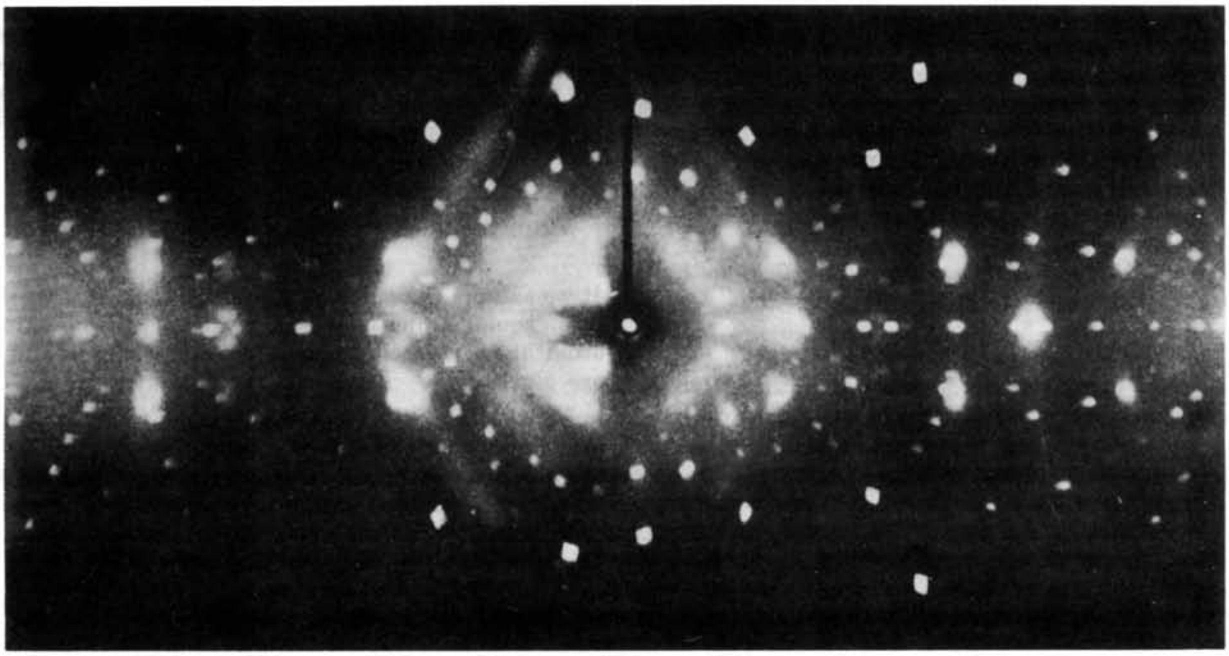


Fig. 5. Laue photographs of urea, [100] vertical, X-rays 10° off [001], showing strong diffuse scattering.

for urea; in other words, our treatment of the urea molecule as a simple unit is a gross over-simplification. Bones obtained a fairly complete representation of the diffuse scattering of urea in reciprocal space (Figs. 5 and 6). There is intense scattering along sheets perpendicular to [110] and [1$\bar{1}$0] not only near to reciprocal-lattice points, but right across from one reciprocal-lattice point to its neighbours. This means that the molecular oscillations are of relatively high frequency and short wavelength, or, in other words, that they are not highly synchronized from one unit cell to the next, but are, to a certain extent at least, independent.

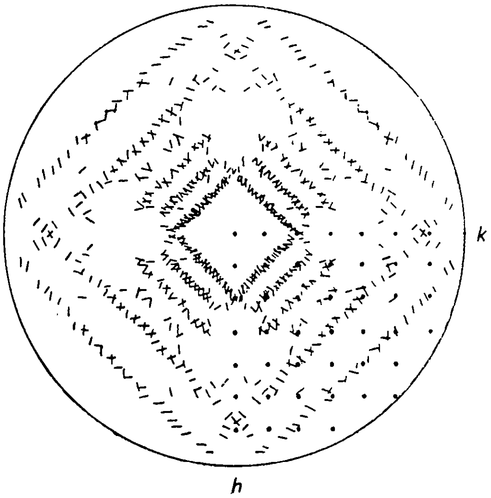


Fig. 6. Reciprocal net (001) of diffuse scattering, plotted from a series of Laue photographs such as that shown in Fig. 5. The reciprocal-lattice points $hk0$ are shown in one quadrant.

We hope, by taking diffuse scattering (Laue) photographs at different temperatures and relating these to the changes of Bragg intensity, to be able to trace the changes of distribution of thermal frequencies for different reflexions and hence, perhaps, for different individual atoms.

Distribution of Debye factors in the crystal

Meanwhile it is of interest to examine the distribution of the B^{293}_{hkl} factors for all reflexions $\{hkl\}$, and for the $\{hk0\}$ zone in particular. Our own results (Fig. 2) are not sufficient to indicate any distribution in the $\{hk0\}$ zone and may not necessarily be typical of $\{hkl\}$ in general.

The Debye factors given in equations (12) have therefore been used by Dr Grenville-Wells (1956, Figs. 2 and 3) to calculate B^{293}_{hkl} for all planes, graphically, using set V of the atomic parameters both for $|F_c^{293}|$ and $|F_c^{0/R}|$, with the McWeeny scattering factors (Grenville-Wells, 1956, Table 3 (*22*)). The results are given in Table 12 and are plotted in Fig. 7.

Two noticeable features emerge from Fig. 7(*a*). The first is that the B factors for reflexions with $h+k$ odd are, on the whole, considerably larger than those for $h+k$ even. The $h+k$ odd reflexions do not include any contribution from C and O, since the individual C and O atoms occur at the corners and centre of the projection and have (or are assumed to have) isotropic thermal vibrations in the (001) projection. The fact that the $h+k$ odd Debye factors are large is in itself evidence that the thermal vibrations of N are of larger amplitude than those of C and O.

The second feature is that there is a steady average increase of B_{hk0} in going from B_{h00} to B_{hh0}. Although the crystal is tetragonal, the B_{hk0} factors are by no means distributed about a circle. As might be expected, even the various orders of reflexion from a single set of planes have varying Debye factors. Since in simple structure determination such sets (say from axial planes) are often used in trial-and-error determination of parameters, it is important to realize that this effect exists.

Fig. 7(*b*) shows the distribution of Debye factors for all hkl reflexions plotted in a way similar to that used for our 12 planes in Fig. 2. The curve corresponding to our $B^{293}-B^0 = 0\cdot5+3\cdot75\sin^2\varphi$ has been marked in, but no attempt has been made to calculate an improved formula of the type $B^{293} = A+B\sin^2\varphi$, because it is clear that such an approximation, although better than an isotropic B, is certainly extremely bad.

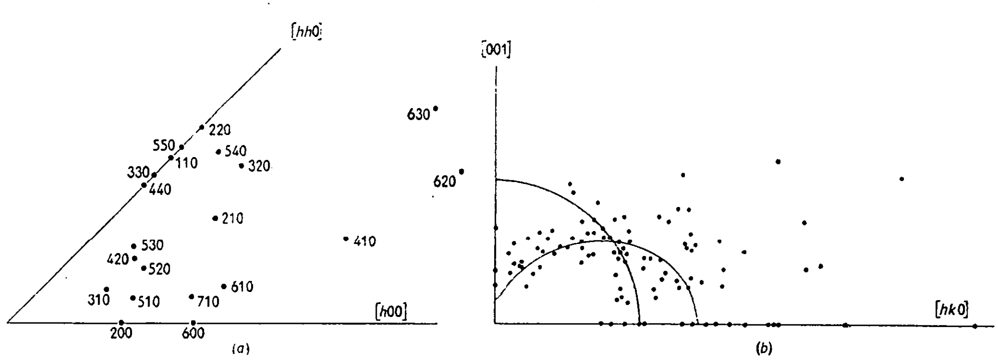


Fig. 7. (*a*) Radial distribution of B^{293} for $hk0$, from Table 12. (*b*) Distribution of B^{293}_{hkl}, plotted radially, from Table 12. The circle indicates the 'statistical B'; the curve is $B^{293}-B^0 = 0\cdot5+3\cdot75\sin^2\varphi$.

Table 12. *B values for reflexions hkl corresponding to the parameters (set* V), *the McWeeny scattering factors and the temperature factors (equations* (12)) *given by Grenville-Wells* (1956, *Table* 3 (22)), *as best fitting the observed intensity data at* 293° K.

*hk*0	ψ (°)	*B*	*hkl*	φ (°)	*B*	*hkl*	φ (°)	*B*
200	45	2·4	301	68·2	4·5	325	31·0	2·3
400	45	—	602	68·2	4·3	112	30·5	3·2
600	45	3·9	532	67·6	2·7	224	30·5	2·1
710	36·9	3·9	221	67·0	3·5	203	29·0	1·8
610	35·5	4·6	442	67·0	4·3	315	27·7	3·3
510	33·7	2·7	522	65·9	3·4	225	25·2	2·1
410	31·0	7·3	512	64·8	4·5	214	25·0	1·3
310	26·6	2·2	502	64·3	—	102	22·6	1·4
620	26·6	~ 10	432	64·3	3·0	204	22·6	1·3
520	23·2	3·1	211	61·8	3·1	113	21·4	1·4
210	18·4	4·9	422	61·8	2·9	215	20·4	1·9
420	18·4	3·0	412	59·8	6·8	621	79·2	4·1
630	18·4	~ 10	613	59·3	3·1	611	78·8	3·9
530	14·0	3·1	201	59·0	2·9	601	78·7	2·6
320	11·3	5·9	402	59·0	4·2	531	78·4	4·4
430	8·1	—	332	59·0	4·7	441	78·0	2·3
540	6·3	5·7	533	58·3	3·3	521	77·4	3·4
110	0	4·9	443	57·5	4·5	511	76·7	4·2
220	0	5·8	322	56·3	4·1	501	76·5	4·9
330	0	4·4	523	56·2	3·1	431	76·5	3·9
440	0	4·1	413	48·8	2·4	513	54·7	3·4
550	0	5·2	524	48·2	3·3	503	54·2	2·2
			403	48·0	3·0	433	54·2	2·5
hkl	φ (°)	*B*	514	46·7	2·8	312	52·8	3·0
711	80·4	2·8	504	46·1	2·5	302	51·3	5·0
551	80·4	3·4	323	45·0	2·7	423	51·1	2·9
701	80·3	4·8	212	43·0	3·0	111	49·7	3·5
631	79·8	6·6	424	43·0	2·2	222	49·7	3·5
541	79·4	6·9	313	41·3	2·4	333	49·7	~8·5
421	75·0	3·6	334	39·8	2·1	114	16·4	1·3
331	74·2	2·7	101	39·8	3·3	103	15·5	1·1
411	73·9	5·4	202	39·8	2·8	104	11·8	—
401	73·3	3·7	303	39·8	1·0	105	9·5	1·5
321	71·6	6·8	404	39·8	1·9	001	0	—
632	70·3	~ 9	223	38·1	1·5	002	0	2·0
542	69·4	5·0	324	36·9	1·3	003	0	2·0
311	69·2	3·3	314	33·3	1·8	004	0	0·8
622	69·2	4·4	304	32·0	2·1	005	0	1·1
612	68·4	3·7	213	31·8	2·1			

Note.—For planes of small intensity *B* sometimes calculates as negative. These values have been omitted. Values over 7 are also probably untrustworthy.

Conclusion

This preliminary study, which has been reported in far more detail than will be necessary in respect of subsequent investigations of the same kind, does seem to make certain points clear:

(1) That it is possible to use intensity measurements at different temperatures to measure Debye factors directly with relatively simple experimental effort, and with reasonable accuracy.

(2) That Debye factors for individual atoms, obtained by a structure refinement at one temperature only, can be compared with the above by calculating the structure factors for the atomic arrangement with and without atomic vibrations and hence obtaining Debye factors for the various *hkl* reflexions.

(3) Whether these two sets of Debye factors, independently determined, are the same (apart from zero-point energy) depends mainly upon the changes of atomic parameters with temperature.

(4) It is therefore highly desirable, in order that full use shall be made of the available data, that complete intensity measurements shall be made, at least for simple organic compounds, at more than one temperature, and that a complete structure refinement (including anisotropic atomic *B* factors) shall be carried out *at each temperature*. In the following paper, Dr Grenville-Wells emphasizes the necessity of introducing anisotropic atomic *B* factors at an early stage in the refinement, say when an *R* factor of about 0·20 is reached. Such measurements would enable a proper comparison of Debye factors determined by both methods to be made, would lead to a proper estimate of zero-point energies and would provide data about changes in inter- and intra-molecular bond lengths with temperature, as well as about changes in molecular orientation etc., for use by theoretical chemists and physicists interested in crystal or molecular properties.

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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 $R = \Sigma\{|F_c|-|F_o|\} \div \Sigma|F_o|$ 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 $R(hkl) = 0{\cdot}071$. 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 $R(hkl) = 0{\cdot}178$ 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 ($P\bar{4}2_1m$, $a = 5{\cdot}661$, $c = 4{\cdot}712$ Å, 2 molecules of $CO(NH_2)_2$ 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