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The β-Uranium Structure

By J. Thewlis

Atomic Energy Research Establishment, Harwell, Didcot, England

and H. Steeple

Physics Department, College of Technology, Manchester 1, *England*

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The non-centrosymmetrical structure put forward by Tucker and the centrosymmetrical one proposed by Tucker & Senio are refined, using the X-ray powder intensities of Thewlis, by a method of trial. It is concluded that the non-centrosymmetrical structure is correct, with an agreement residual of 19% as against 32%, but that both the main and subsidiary layers of atoms in the structure are puckered. In this respect the proposed structure may be considered as a combination of the previous two.

A feature of the structure is the binding together of neighbouring main layers by short bonds, 2·53 Å in length, between certain atoms. This bonding, together with the pairing of neighbouring atoms along the 'vertical' chains which run through the structure, suggests a tendency towards the formation of U_2 molecules. A similar tendency is noted in α-neptunium.

Atoms appear to be present in the structure in four different electronic states, with valencies of 3, 4, 5 and 6 respectively. These are the valencies exhibited by uranium in its compounds. Analysis of the structure, based on this valency allocation, shows that the short inter-layer bonds are intermediate in character between double and triple bonds, and that the short bonds along the chains are intermediate in character between single and double bonds.

Introduction

An acceptable structure for β-uranium (tetragonal with 30 atoms in the unit cell) was first proposed by Tucker (1950, 1951) on the basis of the X-ray examination of single crystals of an alloy containing 1·4 atomic % of chromium, quenched from the β region. In the light of intensity differences between powder photographs of a similar alloy and of β-uranium itself at temperatures within the β range, one of the present writers (Thewlis, 1951, 1952) suggested that further refinement of the structure, which was indeed necessary since the agreement residual of Tucker's approximate structure was found to be about 30%, should be carried out on β-uranium itself and not on the alloy. Tucker (1952) gave some suggested reasons for the intensity differences referred to and in a later paper (Tucker & Senio, 1952, 1953) it was shown that new single-crystal intensity data for the alloy were in essential agreement with the powder intensities found by Thewlis for β-uranium. In view of this and the work of Tucker (1952) on a series of alloys with decreasing chromium content this agreement must now be accepted, although it is somewhat unsatisfactory that none of the reasons put forward by Tucker to explain the discrepancies between powder photographs of the alloy and of β-uranium itself appears to hold.

In the work referred to, Tucker & Senio (1952, 1953) present the results of a Fourier refinement of the β-uranium structure based on the new data, which lead to the conclusion that the main layers of the structure, previously found to be puckered, are flat, whereas the subsidiary layers, previously found to be flat, are puckered. The present paper contains the results of a refinement of both structures, using the intensity data of Thewlis (1952), carried out by a method of trial. The conclusion reached is that both layers are puckered.

Tucker's two structures

The first structure proposed by Tucker was a non-centrosymmetrical layer structure (space group C_{4v}^4–$P4nm$) with main layers of distorted hexagons perpendicular to the c axis at $\frac{1}{4}c_0$ and $\frac{3}{4}c_0$. Midway between these layers, at 0 and $\frac{1}{2}c_0$, were subsidiary layers of atoms not in contact within the layer. The main layers were slightly puckered but the atoms in each subsidiary layer were at exactly the same height.

In the course of the refinement of this structure Tucker & Senio (1952, 1953) found that it was not possible to reconcile it with the observed intensities by any alteration of the z parameters of the atoms in the main layers and they then considered space group D_{4h}^{14}–$P4/mnm$, a centrosymmetrical space group which confines the atoms in the main layers to planes at 0 and $\frac{1}{2}c_0$ but permits the subsidiary planes to be puckered The structure based on this space group gave a better agreement between observed and calculated intensities than that based on C_{4v}^4–$P4nm$, and was accepted as the correct structure. Even so, the agreement residual was stated to be 31%.

If the second structure were indeed correct it ought

Table 1. *Atomic parameters in the structures of Tucker and Tucker & Senio*

Group	No. of atoms	Layer	x		y		z	
			T.	T. & S.	T.	T. & S.	T.	T. & S.
I	2	Main	0*	0*	0*	0*	0·66	0·50*
II	4	Main	0·11	0·1033	0·11	0·1033	0·23	0·25*
III	4	Subsidiary	0·32	0·3183	0·32	0·3183	0·00	0·9800
IV	4	Subsidiary	0·68	0·6817	0·68	0·6817	0·50	0·5200
V	8	Main	0·56	0·5608	0·24	0·2354	0·25	0·25*
VI	8	Main	0·38	0·3667	0·04	0·0383	0·20	0·25*

* Value set by space-group.

to be possible to derive it from the first by a suitable process of refinement, since the centrosymmetrical space group D_{4h}^{14}–$P4/mnm$ is a special case of the non-centrosymmetrical one C_{4v}^{4}–$P4nm$. When Dr Tucker very kindly sent the results of his and Senio's work to one of the present writers (J.T.) such a refinement had indeed been completed and the conclusion had been reached that the subsidiary layers were probably puckered. The main layers, however, also remained puckered, and, as will be seen below, the intensity agreement worsened if the centrosymmetrical structure were assumed.

It may be of interest at this stage to list the parameters of the atoms in the structures of Tucker and Tucker & Senio, referring both structures to the non-centrosymmetrical space group for convenience. This is done in Table 1. There are six groups of structurally equivalent atoms in the structure. Atoms (III) and (IV) are also structurally equivalent in the centrosymmetrical space group.

The refinement

(*a*) *The non-centrosymmetrical structure*

In order to refine the structure only the measured resolved reflexions, of which there were 36, were utilized. The method adopted is an unpublished one used by Dr I. G. Edmunds of the Physics Department, College of Technology, Manchester. The partial derivatives of the structure factors of each of the 36 reflexions were calculated on the assumption that one only of the atomic parameters was variable, and the change, δF_c, in the value of each calculated structure factor was then determined for an arbitrary small change, ε, in the value of the atomic parameter under consideration. It was thus possible to obtain $\Sigma||F_o|-|F_c||$ for a number of values of ε, where F_o is the observed structure factor and the summation is over the 36 reflexions; the value of ε which corresponded to the lowest obtained value of $\Sigma||F_o|-|F_c||$ was assumed to be the required correction in the atomic parameter. The procedure was repeated for each of the 13 variable parameters, but in view of the fact that there were only 36 available reflexions it was thought that the corrections might not be independent. Accordingly, before proceeding with the calculation of the partial derivatives required for the determination of the correction to a further parameter, new values of all the structure factors were calculated, using the previously corrected parameters.

At the completion of the refinement the value of the overall agreement residual (i.e. the value that includes all the reflexions and not merely the resolved ones), calculated in the usual way, had been reduced from 30% to 19%; no further improvement was effected by a second refinement, and the new values of the atomic parameters are given in Table 2.

Table 2. *Preliminary atomic parameters in present work*

Group No.	No. of atoms	Layer	x	y	z
I	2	Main	0	0	0·66
II	4	Main	0·11	0·11	0·23
III	4	Subsidiary	0·30	0·30	0·00
IV	4	Subsidiary	0·68	0·68	0·48
V	8	Main	0·55	0·23	0·27
VI	8	Main	0·37	0·04	0·18

These values are seen to be not very different from those for Tucker's first structure, but puckering of the subsidiary layers now occurs in view of the change in the *z* parameter of atoms (IV).

The square roots of the calculated intensities (used in obtaining the agreement residual), both of the resolved and of the overlapping reflexions, which were obtained from these parameters are shown in the fourth column of Table 4 and the square roots of the observed intensities are shown in the second column. Owing to the presence of oxide lines the experimental data obtained from the reflexions 973 to 964 inclusive were considered unreliable, and are therefore not included in the table.

A further improvement in the parameter values was later obtained by drawing the graphs of the agreement residual for the resolved reflexions only against the atomic parameter in the regions of the respective minima, the value of each parameter at the corresponding minimum being taken as correct. This procedure also enabled an estimate to be obtained of the errors in the values of the atomic parameters, referred to an arbitrarily chosen acceptable increase in the overall agreement residual. The maximum acceptable increase so chosen was in fact 2–3%, corresponding to a change in the overall agreement residual of about 0·2% for each parameter. The final corrected values of the atomic parameters with the estimated 'error' in each case (i.e. the change in parameter that will give a

Table 3. *Final atomic parameters in present work*

Group No.	No. of atoms	Layer	x	y	z
I	2	Main	0	0	$0{\cdot}68 \pm 0{\cdot}03$
II	4	Main	$0{\cdot}105 \pm 0{\cdot}010$	$0{\cdot}105 \pm 0{\cdot}010$	$0{\cdot}22 \pm 0{\cdot}01$
III	4	Subsidiary	$0{\cdot}290 \pm 0{\cdot}010$	$0{\cdot}290 \pm 0{\cdot}010$	$0{\cdot}00 \pm 0{\cdot}02$
IV	4	Subsidiary	$0{\cdot}690 \pm 0{\cdot}008$	$0{\cdot}690 \pm 0{\cdot}008$	$0{\cdot}48 \pm 0{\cdot}02$
V	8	Main	$0{\cdot}547 \pm 0{\cdot}004$	$0{\cdot}227 \pm 0{\cdot}004$	$0{\cdot}27 \pm 0{\cdot}01$
VI	8	Main	$0{\cdot}367 \pm 0{\cdot}005$	$0{\cdot}041 \pm 0{\cdot}002$	$0{\cdot}18 \pm 0{\cdot}01$

change of 0·2% in the overall agreement residual) are given in Table 3.

It will be seen that the departure from flatness of the subsidiary layers is the same as that found by Tucker & Senio. It is, however, not outside the 'error' limit and it cannot be stated beyond all doubt, therefore, that these layers are puckered, although this seems very likely.

Some of the values in Table 3 differ slightly from those obtained at the completion of the first stage, but in view of the labour involved it was considered that the changes did not justify yet another calculation of all the structure factors. Substitution of the final values of the parameters should result in a slight improvement in the value of the overall agreement residual but improvement beyond this is not to be expected with the experimental data at present available.

As has already been stated, in the refinement process the corrected structure factors were calculated after each adjustment in the value of a parameter. This entailed considerable labour since the structure was non-centrosymmetrical; the possibility that the arithmetical work might have been reduced was tentatively explored by comparing the fully refined x and y parameters for the atoms (IV) and (V) with the values obtained when these parameters were refined quite independently, those groups being chosen for testing purely by chance. The fully refined values, as given above, are $x = y = 0{\cdot}690$ and $x = 0{\cdot}547$, $y = 0{\cdot}227$; whereas the independently refined values are $x = y = 0{\cdot}692$ and $x = 0{\cdot}550$, $y = 0{\cdot}226$. It appears, therefore, that even with 13 variables and only 36 resolved reflexions the parameters could have been refined independently with a consequent saving of much time and labour.

Comparison with previous work.—For the purpose of comparison, the third column of Table 4 shows the square roots of the calculated intensities obtained from the atomic parameters published by Tucker (1950, 1951). Although there are instances in which the agreement between observed and calculated values is made slightly worse when the refined values of the parameters are substituted for the approximate values, there are others in which the agreement is better and, in general, the effect is one of improvement.

Tucker & Senio (1952, 1953), in the work which led to the rejection of the non-centrosymmetrical structure, obtained a Fourier (0*kl*) projection of this structure from data derived from a single crystal of the

Table 4. *Comparison of* $\sqrt{I_o}$ *and* $\sqrt{I_c}$

		$\sqrt{I_c}$	
hkl	$\sqrt{I_o}$	Approximate structure	Refined structure
002	3·2	4·4	3·9
400	2·0	0	0·8
112	2·4	2·2	1·8
410	8·4	8·8	9·8
330	7·3	6·0	6·8
202	6·4	5·5	6·2
212	6·9	8·7	8·3
411	10·0	10·5	10·9
331	7·6	7·7	7·2
222	4·5	4·4	5·8
312	4·4	2·8	3·5
322	3·3	1·7	2·0
431; 501	3·0	2·4	2·9
511	3·0	3·0	4·2
432	3·3	1·7	3·4
512 223	3·7	3·2	4·4
522 621	5·0	5·0	5·1
541	3·1	2·2	2·3
532 631	5·3	6·6	7·1
413	6·7	6·6	5·5
333 602	6·3	7·9	5·5
612	6·5	3·9	5·1
720	6·1	7·1	6·6
551; 711	4·4	4·4	5·1
622	4·1	2·2	2·4
542 641	4·6	3·9	3·6
004 730	3·6	4·4	3·7
314 820	4·9	6·4	6·3
613	2·4	1·7	2·3
821	*	—	—
414	5·4	6·2	5·7
802	4·7	4·2	4·3
742; 812	4·7	7·3	4·8
703	3·0	1·4	3·0
822 553; 713	4·1	3·3	4·7
841	3·2	1·4	3·5
723 911	4·5	3·0	2·3
851	4·2	2·2	2·7
305 762; 922	2·2	2·8	4·3
315 823 941	3·0	3·5	3·3
932 663 10,1,1	4·9	7·2	5·3

Table 4 (*cont.*)

hkl	$\sqrt{I_o}$	$\sqrt{I_c}$ Approximate structure	$\sqrt{I_c}$ Refined structure
415 10,2,1	4·7	4·0	2·7
554; 714	4·4	3·2	3·7
724	6·0	7·0	5·3
772 843 10,3,1	*	—	—
862; 10,0,2 913	3·9	4·4	4·7
960	4·2	3·5	4·3
952 961	5·0	3·7	4·3
804	4·9	2·5	2·7
10,5,0	4·5	4·8	4·3
10,5,1	4·8	4·4	5·4
664 970	4·2	4·0	2·1
545 962	3·6	4·0	3·7
216 635	4·3	5·5	5·3
10,2,3	4·0	1·4	4·2
844	5·6	3·0	4·5
705 10,5,2 10,6,1	3·6	3·6	3·8
645 882	3·9	5·1	3·9
972	4·0	2·2	2·8
10,7,0	4·5	~0	2·7
10,7,1	4·7	1·0	2·9
516	3·0	5·0	5·9
10,5,3 864; 10,0,4	4·2	6·5	4·9
825 10,1,4	3·7	4·7	5·1
526 982	3·2	3·5	4·0
973	†	—	—
835 10,7,2	†	—	—
606	†	—	—
626 845	†	—	—
915	†	—	—
964	†	—	—
556; 716	5·5	3·3	5·6
10,5,4 726	6·5	11·1	6·3

* Not measured.

† Data unreliable owing to presence of oxide lines.

low-chromium alloy of uranium. Although the agreement residual was as high as 30% it is stated that the synthesis showed no spurious peaks and that there was good agreement between the assumed atomic positions and their associated peaks. Consequently it was thought of interest to produce another synthesis of this projection by combining the phase angles resulting from the refined values of the atomic parameters obtained in the present paper for pure β-uranium with the improved observed structure factors obtained by Tucker & Senio from their single crystal of the alloy. This synthesis is shown in Fig. 1 and it will be seen that the agreement between the peaks and the assumed atomic positions (marked by crosses) is quite good although there are present some areas of spurious intensity distribution. An exact projection, however, is not to be expected because, owing to the difficulties involved, Tucker & Senio's corrections for the absorption, polarization and Lorentz factors are only approximate.

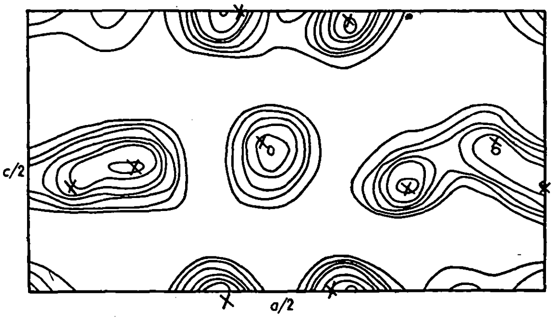

Fig. 1. Fourier (0*kl*) projection when Tucker & Senio's corrected observed intensities are combined with the phase angles of the refined non-centrosymmetrical structure. Assumed atomic positions are marked by crosses.

(*b*) *The centrosymmetrical structure*

Although, as stated above, the centrosymmetrical structure, if correct, might have been expected to arise naturally in the course of the refinement of the non-centrosymmetrical structure, a refinement of the structure of Tucker & Senio (1952, 1953) was undertaken. Utilizing their values of the atomic parameters the agreement residual for the measured resolved reflections was found to be about 35%, whereas, as already mentioned, the value obtained by Tucker from his single-crystal work was 31%. Refinement was carried out as for the non-centrosymmetrical structure, after which process the value of the agreement residual for the resolved reflexions was 30%; after consideration of the overlapping reflexions the value was 32%. Even after allowing for the fact that, according to Wilson (1950), a non-centrosymmetrical structure would be expected to give a lower agreement residual than a centrosymmetrical one, this value of 32% compares very unfavourably with that of 19% which was obtained for the non-centrosymmetrical structure. Accordingly, it is concluded that the latter structure is correct.

Discussion of the structure

(*a*) *Interatomic distances*

The structure can, in some respects, be regarded as a combination of the two structures discussed by Tucker & Senio, in that both types of atomic layer are puckered. The nature of the puckering in the main layers is similar to that in Tucker's first structure, as will be seen from a comparison of the *z* values, but the puckering in the subsidiary layers is in the opposite sense from that in Tucker & Senio's structure. The interatomic distances are as follows:

Each of two atoms (I) has 4 neighbours at 3·023 Å, 2 at 3·053, 4 at 3·353 and 2 at 3·447, i.e. 12 neighbours.

Each of four atoms (II) has 2 neighbours at 2·911 Å, 1 at 3·053, 1 at 3·077, 2 at 3·182, 1 at 3·196, 2 at 3·447, 2 at 3·571, 2 at 3·651 and 2 at 3·907, i.e. 15 neighbours.

Each of four atoms (III) has 1 neighbour at 2·732 Å, 2 at 2·926, 1 at 2·957, 2 at 2·983, 1 at 3·077, 2 at 3·231, 1 at 3·352, 2 at 3·664 and 2 at 3·907, i.e. 14 neighbours.

Each of four atoms (IV) has 1 neighbour at 2·732 Å, 2 at 2·951, 1 at 2·957, 2 at 3·295, 2 at 3·329, 1 at 3·352, 2 at 3·411, 1 at 3·447 and 2 at 3·571, i.e. 14 neighbours.

Each of eight atoms (V) has 1 neighbour at 2·531 Å, 1 at 2·831, 1 at 2·926, 1 at 2·951, 1 at 3·023, 1 at 3·071, 1 at 3·182, 1 at 3·231, 1 at 3·295, 1 at 3·439, 1 at 3·487 and 1 at 3·651, i.e. 12 neighbours.

Each of eight atoms (VI) has 1 neighbour at 2·531 Å, 1 at 2·831, 1 at 2·911, 1 at 2·983, 1 at 2·995, 1 at 3·071, 1 at 3·329, 1 at 3·411, 1 at 3·487, 4 at 3·533 and 1 at 3·664, i.e. 14 neighbours.

A feature of this structure is the very small interatomic distance of 2·531 Å, which occurs between atoms (V) and (VI) in adjacent layers. As Tucker & Senio (1952) point out, each atom of neptunium in the α-Np structure has no fewer than four close neighbours, one at 2·60 Å and three at 2·63 or 2·64 Å, and it is not surprising to find similar short bond lengths in uranium. The next shortest distance observed is one of 2·732 Å. This is the distance between the pairs of nearest atoms along the chains of (III) and (IV) atoms which run through the structure parallel to the *c* axis. The occurrence of these two short bond lengths, especially the 2·531 Å bond between atoms in adjacent main layers, suggests a tendency for some atoms to form U_2 molecules. Fig. 2, a section of the structure taken through the (110) plane, which also shows those atoms which are immediately adjacent to the plane and between it and the observer, illustrates how the 2·531 Å bonds serve to bind the main layers together.

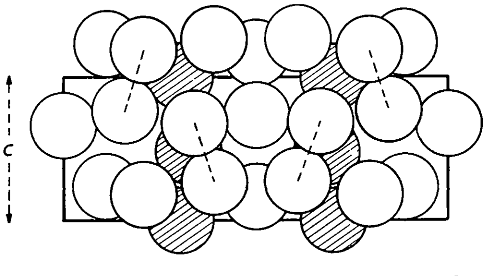

Fig. 2. Section through the (110) plane of the β-uranium structure, showing atoms in and adjacent to this plane. Open circles: atoms in main layer; shaded circles: atoms in subsidiary layer; broken lines: short inter-layer bonds of 2·53 Å.

(*b*) *Valency*

The differences between the environments of the atoms belonging to the various crystallographically equivalent groups in β-U suggest that atoms with different electronic configurations occur in the structure. A calculation of the bond order of the various bonds in the structure, following Pauling (1947, 1949) would, of course, indicate whether this were so, and, if the single bond radius of uranium were known, would permit the valency states of the various groups of atoms to be elucidated. Such a calculation is, however, not feasible if one wishes to avoid making unwarranted assumptions, but it is possible (Thewlis, 1954) to approach the problem in a slightly different way that will lead to an allocation of valency to each atom in the structure without any assumption as to the single-bond radius of uranium. When this is done it is found that no fewer than four valency states occur in β-uranium, being distributed among the various groups as follows:

Group	I	II	III	IV	V	VI
Valency	3	3	5	4	6	6

These are precisely the valencies which are exhibited by uranium in its compounds. They are consistent with a valency of 4 for α-uranium and one of 3 for γ-uranium. The single-bond radius works out at 1·376 Å, which is in good agreement with that obtained from α-uranium, namely 1·368 Å, a value which is presumably more accurate.

An analysis of the structure based on this valency allocation indicates that each of the short bonds between atoms in neighbouring main layers is intermediate in character between a double and a triple bond, the number of electron pairs involved being 2·7 out of the 6 available. Similarly the short bonds along the 'vertical' chains of atoms are intermediate in character between single and double bonds, the number of electron pairs involved in each such bond being 1·25 out of the 5 available for (III) atoms and the 4 available for (IV) atoms.

A similar calculation, made for the four short bonds in α-neptunium, shows that each of these is approximately a single bond, the four together taking up 85% of the electron pairs available for each atom. When it is remembered that the number of bonds per atom is 12 or 14 in all cases, the figures show the marked extent to which the tendency towards the formation of molecules occurs in both β-U and α-Np.

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A Fundamental Set of Structure-Factor Inequalities

BY P. M. DE WOLFF

Technisch Physische Dienst T.N.O. en T.H., Delft, The Netherlands

AND J. BOUMAN

Laboratorium voor Technische Physica, Technische Hogeschool, Delft, The Netherlands

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Among all inequalities between the structure factors related by a given restriction on the indices, the fundamental set is defined as a set of independent inequalities from which all others can be derived. The present paper deals with the problem of finding this set for the structure factors U_H, $U_{H'}$, U_{2H}, $U_{2H'}$, $U_{H-H'}$ and $U_{H+H'}$ for a centrosymmetric structure. Starting from a more restricted problem, viz. to establish relations between some known inequalities, a new inequality is found:

$$(U_{H+H'}+U_{H-H'}-2U_HU_{H'})^2 \leqq (1+U_{2H}-2U_H^2)(1+U_{2H'}-2U_{H'}^2).$$

It is shown that various known inequalities containing the same U's can be derived from this relation combined with three different versions of Harker & Kasper's inequality $(U_H \pm U_{H'})^2 \leqq (1\pm U_{H+H'})(1\pm U_{H-H'})$.

The general problem is solved by calculating the extreme values of $U_{H+H'}$ for arbitrary variations of a positive charge distribution in the unit cell, provided the other five U's remain constant. The above four inequalities are found anew, so these constitute the fundamental set.

A convenient graphical representation is obtained by plotting the extreme values of $U_{H+H'}$ as a function of $U_{H-H'}$ for given values of the other U's. Finally Karle & Hauptman's inequality $(U_{H\pm H'}-U_HU_{H'})^2 < (1-U_H^2)(1-U_{H'}^2)$ is discussed, and is found to be the analogue of the new inequality for the asymmetric case.

1. Introduction

Since Harker & Kasper (1948) derived the first inequalities between structure factors, many new inequalities have been found. The diversity of these relations leads to the following questions:

Let us consider inequality relations, based on the positiveness of the electron density, between structure factors belonging to a given set.

(*A*) Can all possible relations of this kind be enumerated in an explicit way? This question will be treated in a forthcoming paper, using Karle & Hauptman's (1950) method of generating inequalities (cf. also § 5).

(*B*) Are the explicitly known inequalities independent of each other? If one of them can be derived from another, clearly this one can be discarded.

(*C*) Can a set of independent inequalities be found from which all others can be derived? This set will obviously be of considerable importance, so we shall call it the *fundamental set* of inequalities for the given structure factors. This set may, of course, be stated in algebraically different forms. The limits which it imposes on U-values are, however, unique (cf. also § 4), so the above definition is essentially unambiguous.

Grison (1951) has given an answer to question (*B*), and his answer, though erroneous in itself, will lead us to a new way of tackling this problem. An approach to (*C*) has led to the development of a theory which confirms and strengthens the results which have been derived in answering (*B*).

We consider unitary structure factors, U_H, defined by

$$U_H = \sum_i n_i \exp 2\pi i(hx_i+ky_i+lz_i) = \sum_i n_i \exp 2\pi i(\mathbf{h}, \mathbf{r}_i),$$

where n_i is the atomic number of the ith atom, divided