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The Status of the β-Uranium Structure

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The non-centrosymmetric structure for β-uranium based on powder pattern data recently proposed by Thewlis & Steeple is compared with the (probably) centrosymmetric structure of Tucker & Senio, which was based on single-crystal data. It is shown that, when compared on an equal basis, the reliability factor for the two structures is the same, namely, 18%. Further, the Thewlis & Steeple structure, which leans heavily on the stronger reflections, clearly contradicts the moderate and weaker single-crystal intensity data of Tucker & Senio regarding certain critical reflections which establish the puckering of the subsidiary layers. Also, the *z* parameters of the Thewlis & Steeple structure for the main layers spoil the agreement obtained for the critical reflections by puckering the subsidiary layers, thus indicating that the centrosymmetric structure is more probably correct. The differences in bond lengths between the two structures are of the order of 0·3 Å, and therefore the bonding is entirely different in the two structures. It is held that the bond lengths and valencies given by Thewlis & Steeple are, therefore, incorrect. The two structure determinations are discussed.

Introduction

In a recent paper, Thewlis & Steeple (1954) give a non-centrosymmetric structure for β-uranium which they claim to be superior to the (probably) centrosymmetric one given by Tucker & Senio (1953). The basis for Thewlis & Steeple's contention is that their reliability factor is 19% whereas Tucker & Senio's was 31%. It is the purpose of this paper to show that, when compared on an equal basis, the reliability factors for the two structures are the same, to show that the puckering of the subsidiary and main layers suggested by Thewlis & Steeple is not in agreement with the single-crystal data of Tucker & Senio, and to discuss the two structure determinations more generally.

The reliability factor

Owing to the large size of the β-uranium unit cell, there are a very large number of reflections in the region of reciprocal space explored by Cu $K\alpha$ radiation. Thus the overall reliability factor of 31% obtained by Tucker & Senio (1953) was based on 422 separately observed *hkl* reflections, nearly all possible reflections available by rotation about the a_0 axis. The reliability factor of 19% computed by Thewlis & Steeple (1954), however, was based on 65 powder lines to which 101 (one hundred and one) *hkl* reflections contributed. Thus only about one fourth of the possible reflections were considered by Thewlis & Steeple.

In order to make a fair comparison of the two reliability factors, it is necessary to calculate the reliability factor for the same reflections in both cases. To do this, it was necessary to neglect eleven of Thewlis & Steeple's lines because they contained *hkl* data in which h and k were simultaneously greater than 5. These reflections were not observed by Tucker & Senio (except for *hk*0). This left 54 lines to which 74 planes contributed. The reliability factor for the 54 lines was calculated from Thewlis & Steeple's data and gave 18%. The reliability factor for the 74 planes involved was calculated from Tucker & Senio's data and also gave 18%! *That is, when the reliability factors are calculated on an equal basis, there are in fact no grounds for preferring either structure based on the reliability factor alone.*

The reason why Tucker & Senio's overall reliability factor of 31% appears unfavorable compared to the Thewlis & Steeple value of 19% is easy to find. The Thewlis & Steeple data based on a powder pattern using a single film (on which the strongest lines are of measurable intensity) must necessarily include only the stronger reflections. Thus of the 74 planes which contribute to the 54 lines mentioned in the previous paragraph, the data of Tucker & Senio show that 40 (or 54%) have $|F|_o \geqslant 70$. On the other hand, Tucker & Senio's *hkl* data on 422 reflections have 87 (or only 21%) reflections with $|F|_o \geqslant 70$. Since reflections with $|F|_o = 70$ are still moderately strong, it is clear that the Thewlis & Steeple data contain two and one-half times the normal proportion of strong lines. Now it is well known that inclusion of the weaker lines spoils the apparently good reliability factor which arises from consideration of only the stronger lines. Therefore, it is clear that the 19% value given by Thewlis & Steeple only appears better than the 31% value of Tucker & Senio because the Thewlis & Steeple data are heavily weighted in favor of the strong reflections.

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The atoms in the subsidiary layers

One of the features of the β-uranium structure which was quite firmly established by the structure of Tucker & Senio (1953) was the puckering of the subsidiary layers. Thewlis & Steeple state that the puckering of the subsidiary layers is the same as that of Tucker & Senio's structure but of opposite sense. This statement is not precisely correct but is qualitatively correct. The subsidiary layers in the Thewlis & Steeple structure are defined by two sets of 4 atoms (c) in the space group *P4nm* (*Internationale Tabellen*, 1935) with position parameters $x = y = 0{\cdot}290$, $z = 0{\cdot}00$ and $x = y = 0{\cdot}690$, $z = 0{\cdot}48$, while for the Tucker & Senio structure the corresponding parameters in terms of the same space group are $x = y = 0{\cdot}3183$, $z = -0{\cdot}020$ and $x = y = 0{\cdot}6817$, $z = 0{\cdot}520$. The differences in the x, y parameters for the two structures will be discussed later. The difference between the z parameters in the two structures leads to entirely different bonding of the atoms in the subsidiary layers and is therefore quite significant. For example, the bonds between atoms in adjacent subsidiary layers are 2·723 and 2·947 Å (corrected for thermal expansion) for the Thewlis & Steeple structure, while the corresponding bond lengths are 3·042 and 2·592 Å, respectively, in the Tucker & Senio structure. The differences in bond lengths are 0·319 and 0·355 Å, respectively, differences of great importance when it comes to interpreting bonding in the structure.

The z parameters of the atoms in the subsidiary layers in the structure of Tucker & Senio are, as previously mentioned, quite firmly established. The basis for these z parameters is the widespread agreement they produce in a number of violations of the flat layer intensity relation

$$I_{hk1} = I_{hk3} = I_{hk5} \ldots$$

found in the β-uranium structure (Tucker & Senio, 1953). The pairs (013)(015), (513)(515), (813)(815), and (913)(915) were pointed out particularly as demonstrating the good agreement given by the Tucker & Senio structure. In order to test the z parameters of the atoms in the subsidiary layers of the Thewlis & Steeple structure, the structure factors of the above pairs were calculated for that structure and are compared with the Tucker & Senio values, both calculated and observed, in Table 1 and Fig. 1(*a*). (Direct comparison could not be made with the Thewlis & Steeple observed or calculated values because none of the reflections was observed without interference in that work.) Examination of Table 1 and Fig. 1(*a*) shows that the Tucker & Senio values follow the observed values very well while the Thewlis & Steeple values do not. In fact, the reliability factor for these eight reflections (the squares of the structure factors have been normalized to the same value) is 35% for the Tucker & Senio structure, but is 84% for the Thewlis & Steeple structure.

It is felt that the failure of the Thewlis & Steeple structure to give the same z parameters for the atoms in the subsidiary layers and thus account for the flat-layer violations, which occur so extensively in the

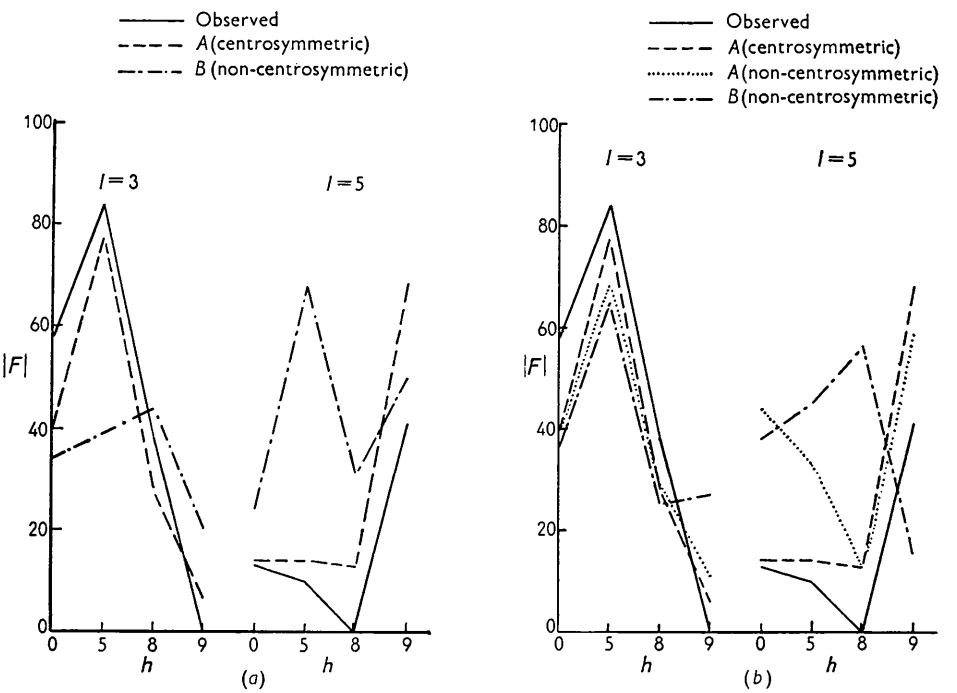

Fig. 1. (*a*) Puckering of subsidiary layers. (*b*) Effect of puckering main layers. A = Tucker & Senio; B = Thewlis & Steeple.

Table 1. *Puckering of subsidiary layers*

	$l = 3$			$l = 5$		
	Thewlis & Steeple (non-centro-symmetric)		Tucker & Senio (centro-symmetric)	Thewlis & Steeple (non-centro-symmetric)		Tucker & Senio (centro-symmetric)
hk	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$
01	34	57	39	24	13	14
51	39	84	78	68	10	14
81	44	38	28	31	0	13
91	20	0	6	50	41	68

Table 2. *Puckering of main layers based on Tucker & Senio centrosymmetric structure*

	$l = 3$				$l = 5$			
	Thewlis & Steeple *z* parameters	Tucker & Senio (non-centro-symmetric)	Tucker & Senio (centro-symmetric)		Thewlis & Steeple *z* parameters	Tucker & Senio (non-centro-symmetric)	Tucker & Senio (centro-symmetric)	
hk	$\|F\|_c$	$\|F\|_c$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_c$	$\|F\|_c$	$\|F\|_o$
01	36	39	39	57	38	44	14	13
51	65	68	78	84	45	33	14	10
81	25	29	28	38	56	13	13	0
91	27	11	6	0	15	59	68	41

*hk*1, *hk*3, *hk*5, ... single-crystal data of Tucker & Senio (1953), demonstrates the incorrectness of the *z* parameters for the atoms in the subsidiary layers derived by Thewlis & Steeple (1954). Further, the Thewlis & Steeple *z* parameters lead to entirely different bonding of these atoms, so that the differences between the two structures is significant and not a minor detail.

In addition to the difference between the *z* parameters of the atoms in the subsidiary layers, there are important differences between the *x* and *y* parameters of these atoms. Thewlis & Steeple find the rows formed by these atoms in the c_0 direction to be staggered, the projection of the staggering on the (001) plane amounting to 0·30 Å. There was no evidence for staggering of this magnitude in the Fourier *hk*0 projection of Tucker & Senio (1953), and that projection was performed using 38 independently observed *hk*0 reflections. This difference also serves to show that the two structures lead to entirely different bonding, with differences in the interatomic distances of the order of 0·3 Å.

The *z* parameters for the main layers

In order to test the validity of the Thewlis & Steeple *z* parameters for the atoms in the main layers, the structure factors of the (013)(015), (513)(515), (813)(815), and (913)(915) pairs were calculated for the Tucker & Senio (1953) structure but with the Thewlis & Steeple *z* parameters for the atoms in the main layers. The structure factors for the same reflections were also calculated using the *z* parameters for the atoms in the main layers that were obtained when a Fourier refinement of the intensity data of Tucker & Senio (1953) was made in terms of the non-centrosymmetric space group. These calculations are of interest because the average deviation of the atoms in the Thewlis & Steeple structure from the ideal flat layer positions is 0·254 Å (0·045 units) while in the Tucker & Senio structure it is only 0·085 Å (0·015 units). That is, the puckering is only one-third as great in the Tucker & Senio structure. The results of the calculations are given in Table 2 and Fig. 1(*b*). For comparison purposes the structure factors for the Tucker & Senio centrosymmetric structure are included. The squares of the structure factors have been normalized to the value for the observed structure factors.

Examination of Table 2 and Fig. 1(*b*) shows that the structure factors based on the Thewlis & Steeple *z* parameters do not follow the observed values at all. In fact, the reliability factor for these eight reflections is 91%. The structure factors for the Tucker & Senio *z* parameters for their non-centrosymmetric structure is definitely better (reliability factor 57%) than for the Thewlis & Steeple *z* parameters. However, the agreement is rather poor for the (015) and (515) reflections and it is seen that the values for the Tucker & Senio centrosymmetric structure are definitely better for these reflections. In fact, the reliability factor for the Tucker & Senio centrosymmetric structure is 35%, much better than either of the non-centrosymmetric structures.

Since the reliability of the structure (as determined by the eight reflections in Table 2) decreases as the magnitude of the puckering of the main layers increases, one concludes that, at least for the two cases chosen, the centrosymmetric structure of Tucker & Senio (1953) is definitely favored. However, since there may still be *some* set of puckered *z* parameters for the main layer atoms which will not spoil the established

effect of the puckering of the subsidiary layers, it is not claimed that the foregoing argument proves that the structure is centrosymmetric. But the argument does show that the main layers are *not* puckered according to the z parameters of Thewlis & Steeple (1954). Also, since the average deviation from flatness of the main layers of the Thewlis & Steeple structure is so large (0·25 Å), it is clear that this structure leads to entirely different bonding than the Tucker & Senio (1953) structure. Therefore, the interatomic distances and valencies given by Thewlis & Steeple (1954) should be viewed in the light of the foregoing discussion and are, in fact, incorrect since they are not consistent with the single-crystal data from β-uranium.

Discussion of the two structure determinations

Any discussion of structure determination eventually concerns itself with the intensity measurements. The multiple-film method used by Tucker & Senio (1953) is well established. It is generally agreed that this method can cover intensities over a range of several thousand to one with an accuracy adequate for most purposes in structure work. The major questions which arise concern certain corrections to the observed intensities; namely, Lorentz, polarization, temperature, absorption, and extinction corrections. The Lorentz and polarization corrections are standard and cause no particular concern. There was no clear necessity in the data of Tucker & Senio (1953) for the application of a temperature correction and this is reasonable since the atoms are heavy and the patterns were obtained at room temperature. Extinction corrections are desirable for the strong reflections but are difficult to make and are not usually regarded as necessary for the moderate and weaker reflections. The absorption correction in uranium, however, is admittedly severe, and evidences of its importance can be seen in the single-crystal patterns of β-uranium. However, the evidence for puckering of the subsidiary layers in the Tucker & Senio structure (1953) comes from intensity measurements on reflections of moderate and weak intensity close together on the film, and therefore the relative intensities involved are not subject to serious question regarding any of the corrections mentioned above.

The data on which the structure of Thewlis & Steeple (1954) is based were obtained using a recording microphotometer on a single powder pattern film. This method is likewise considered very reliable. However, it is necessary to convert density of the film to intensity, using the characteristic curve of the film for the radiation used. Thewlis & Steeple do not go into this matter and it would be pertinent to know if this was done. Another factor of great importance is that the Thewlis & Steeple data were obtained using a single- rather than a multiple-film technique. Since the strongest reflections in the pattern were recorded at a measurable level, it is clear that moderate and weaker reflections, in general, could not be measured accurately. This is because the range of accurate intensity measurements by means of the photographic emulsion is for densities in the range 0·05–1·7. That is, lines whose intensities are one-fiftieth that of the strongest line (and less) cannot be measured accurately. In terms of the data of Tucker & Senio (1950) lines for which $|F|_o \leqslant 60$ could not in general be measured accurately by the microphotometer method on the Thewlis & Steeple film. Further, the background density in the print of the β-uranium pattern (kindly furnished by Dr Thewlis) is so high over much of the region studied as to make absolutely necessary the conversion of densities (line and background) to intensities through the characteristic curve for the film used, if reasonable accuracy is to be claimed. Thewlis & Steeple do not state whether such conversions of density to intensity were made.

In regard to the various corrections which must be made to the measured intensities (or to the calculated intensities) of Thewlis & Steeple, the absorption and extinction corrections are the most difficult. While accepted absorption corrections have been given for powder patterns from a cylinder, there is additional absorption due to the UO_2 and UO films on the specimen which actually give patterns about as strong as the β-uranium pattern. Also, since the Thewlis & Steeple structure leans so heavily on the stronger lines it is clear that extinction corrections should be made, although this is admittedly difficult. The remaining corrections, namely, temperature, Lorentz, and polarization, seem adequate.

To summarize, the work of Tucker & Senio (1953) found the absorption and extinction corrections the most difficult to make. However, since the argument concerning the puckering or non-puckering of the main and subsidiary layers is based on moderate and weak reflections close together on the film, the Tucker & Senio z-parameters for the atoms in the subsidiary layers are firmly established.

The Thewlis & Steeple (1954) structure leans quite heavily on the more intense reflections, and therefore the precision of their intensity values comes much more into question, particularly in regard to the puckering or non-puckering of the main and subsidiary layers. The fact that the intensities of the strongest lines were measurable, places a lower limit (about one-fiftieth of the intensity of the strongest line) to the weakest lines measurable, since a single film was used. On the other hand, the Tucker & Senio data cover a much larger intensity range (weakest reflection about one-thousandth of the strongest). That is, the Thewlis & Steeple data can say practically nothing about the moderate and weaker reflections whose intensities are much more sensitive to puckering of the layers, but rather must depend on precision measurement of the stronger reflections. The questions which can be raised concerning the Thewlis & Steeple intensity data involve absorption and extinction corrections, determination of intensities by the microphotometer method

(this method requires the use of the characteristic curve for the emulsion, especially in the region of high background), and the large number of lines which they ignored and which might change some of their intensity values (since they considered only about one-quarter of all possible reflections).

Conclusions

When the Thewlis & Steeple (1954) non-centrosymmetric structure for β-uranium is compared on an equal basis with the Tucker & Senio (1953) (probably) centrosymmetric structure, the reliability factors are precisely the same, 18%. The superiority claimed by Thewlis & Steeple for their structure is only apparent, and is due to the fact that they compared their overall reliability factor of 19% (heavily weighted in favor of the stronger reflections) with the 31% value of Tucker & Senio for about four times as many reflections with the normal concentrations of strong and weak reflections.

The Thewlis & Steeple z parameters for the atoms in the subsidiary layers are quite different from the firmly established values of Tucker & Senio, contradict the single-crystal intensity data, and lead to differences in bond lengths of 0·3 Å, that is, entirely different bonding of these atoms. The x and y parameters of these atoms are also in disagreement to about the same extent.

The z parameters for the atoms in the main layers in the structure of Thewlis & Steeple also contradict the single-crystal data of Tucker & Senio, lead to differences in bond lengths of about 0·3 Å, and therefore to entirely different bonding in the structure.

In view of the quite different bonding in the two structures and the failure of the Thewlis & Steeple z parameters for the main and subsidiary layers to agree with the single-crystal data, it is held that the interatomic distances and valencies computed by Thewlis & Steeple (1954) are incorrect.

After discussing the two structure determinations, it is concluded that the Tucker & Senio intensities are subject to uncertainties in the absorption and extinction corrections. However, the moderate and weaker intensities, which are much more sensitive to z-parameter variations, are not strongly involved in these corrections (relatively) and it is held that the z parameters for the atoms in the subsidiary layers are firmly established. The Thewlis & Steeple intensity values are also subject to uncertainties in absorption and extinction effects. In addition, it is pointed out that their conditions of measurement require the use of the characteristic curve for the photographic emulsion used and in any case are only valid down to lines whose intensities are one-fiftieth of the intensity of the strongest line. However, the data of Tucker & Senio go down to reflections whose observed intensities are one-thousandth of that of the strongest reflection, and therefore include the moderate and weaker reflections which clearly reveal the presence of the puckered subsidiary layers. The data of Thewlis & Steeple, therefore, do not go down to the reflections which are quite sensitive to puckering of the layers. The details of their structure depend strongly on the precision measurement of the intensities of the stronger lines, which are just those most subject to errors in measurement and in absorption and extinction corrections.

It is concluded that the Tucker & Senio structure follows the single-crystal data to much lower intensities than does that of Thewlis & Steeple and has, therefore, a higher probability of being correct. Further, the fact that puckering of the main layers spoiled the agreement of certain sensitive reflections in the two cases studied makes it more probable that the main layers are flat, as suggested by Tucker & Senio (1953). However, the work so far done does not preclude the possibility that some puckering of the main layers may be found which will not spoil the puckering of the subsidiary layers established by Tucker & Senio. In any case, the puckering of the layers is not that given by Thewlis & Steeple.

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