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## Joint note on the $\beta$-uranium structure.

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Tucker (1950, 1951) and Tucker & Senio (1953) have given the results of detailed studies of the crystal structure of $\beta$-uranium (stable between 660 and 760° C.) based on single crystals retained at room temperature by quenching from the $\beta$-stable region an alloy containing 1·4 atomic % chromium. Thewlis (1952) and Thewlis & Steeple (1954) have also given the results of detailed studies of $\beta$-uranium based on powder data from the unalloyed metal and the 1·4% Cr alloy at 720° C., using both the original structure of Tucker (1950, 1951) and that of Tucker & Senio (1953) as the starting points since it was not possible to index the powder patterns independently. When the results of the single-crystal and powder work were compared it was found that the general features of the $\beta$-uranium structure were confirmed by the powder work but that there were detailed differences which led to bond-length differences of the order of 0·3 Å between the two structures. Differences of this order are not important for most practical purposes but are of paramount importance when it comes to matters of bonding within the structure, because 0·3 Å can mean the difference between a single and a triple bond.

Since the work of Tucker & Senio (1953) represents about the best that can be done with single crystals and that of Thewlis & Steeple (1954) about the best that can be done with powder data, and since there is virtually no chance that really decisive work can be done with single crystals at high temperature, the question naturally arises whether there are really two $\beta$-uranium structures or whether the differences are simply due to experimental uncertainties in one or both of the determinations. Thewlis & Steeple are of the opinion that the possibility of the existence of two $\beta$-uranium structures—a high- and a low-temperature form—remains open, whereas Tucker & Senio are of the opinion that there are serious doubts that powder work can settle the details of a structure involving as many atomic-position parameters as are involved in the $\beta$-uranium structure (13 in Thewlis & Steeple's (1954) non-centrosymmetric structure). Since it is unlikely that the present authors will extend their work on the $\beta$-uranium structure it has seemed useful to clarify the situation by presenting a brief summing-up of their respective positions.

Table 1. *Agreement residuals*

| Source of intensity data | Structure agreement residual | |
|---|---|---|
| Powder pattern of $\beta$-U at 720° C. | Thewlis & Steeple | 20%* |
| Powder pattern of $\beta$-U at 720° C. | Tucker & Senio | 35% |
| Single crystal of $\beta$-U (1·4 atomic % Cr alloy at 20° C.) | Tucker & Senio | 18 % |
| Single crystal of $\beta$-U (1·4 atomic % Cr alloy at 20° C.) | Thewlis & Steeple | 38% |

* This was given as 19% by Thewlis & Steeple (1954). The increase arises from the consideration of a number of reflections with $h = 11$ or 12 which had previously been overlooked.

A natural recourse in a controversy such as this is to examine the agreement residual for the two structures. Confining the single-crystal data to the limited number of reflections which it was possible to observe in the powder data, Table 1 shows the agreement residual for each structure as computed against each set of data.

If there is only one $\beta$-uranium structure, the table certainly offers little possibility for preferring either structure, based on the agreement residual alone. But, in the opinion of Thewlis & Steeple, the table provides evidence that there may well be two different structures. Tucker & Senio, however, maintain, as do Lipson & Cochran (1953), that there are other considerations which can override the agreement residual in assessing the correctness of a structure. For the purpose of discussing this and other points, it seems best to divide the remainder of the note into two parts, representing the diverging views of the respective authors.

### Separate statement by Tucker & Senio

Very complete details of the improved $\beta$-uranium structure of Tucker & Senio (1953) have been published and that work is available for critical examination. Further, Tucker (1954) has discussed that work and the structure of Thewlis & Steeple (1954) in considerable detail so that very few details of the arguments for or against the two structures need be given here; rather a brief review of the main arguments will be given.

Our basic position is that Thewlis & Steeple are extending powder work into the region of rather complex structures and it is widely believed amongst crystallographers that in this region single-crystal methods are clearly superior, owing to inherent weaknesses in powder data. Thus it seems to us that the Thewlis & Steeple position is the reverse of a rather generally held position. Nevertheless, Thewlis & Steeple are convinced of the correctness of their structure, and sound arguments must be produced against it. Our contention is that the details of the structure of Thewlis & Steeple (1954) are much less certain than those of the Tucker & Senio (1953) structure.

A major weakness of the powder data is their incompleteness. Thus Thewlis & Steeple (1954) base their work on only 10–20% of the possible reflections. Further, these reflections are only the stronger ones so that the moderate and weaker reflections which are sensitive to the details of the structure are not available for comparison. In addition, Thewlis & Steeple do not calculate the remaining structure factors to see if there are any reflections which their structure might predict to be observable and which were not observed. In this connection the single-crystal data indicate that there are a

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* The Knolls Atomic Power Laboratory is operated by the General Electric Company for the U.S. Atomic Energy Commission.

number of rather intense reflections which fall in this category. Furthermore, since Thewlis & Steeple maintain in their statement that these reflections are too weak to be observed according to their structure, it is quite possible that there are among the moderate and weaker reflections of the Tucker & Senio structure some reflections which would be sufficiently strong to be observed in the powder data if their intensities were calculated for the Thewlis & Steeple structure. In our opinion it is essential that the intensities of all possible reflections be calculated for the Thewlis & Steeple structure. This point is important in view of the statement of Lipson & Cochran (1953) that 'The only valid basis for the assessment of the correctness (as distinct from accuracy) of a structure lies in the agreement for individual reflections'.

A second major weakness in the powder data is that since the data are confined to the stronger reflections and since the details of the structure are in question, a very high accuracy is required in the intensity measurements. There are two factors which lead us to doubt very strongly that sufficient accuracy has been achieved. First, there is a rather high and variable background on the film used in the powder work. This background and the background of unaccounted lines would make very accurate intensity measurements difficult indeed. Second, there are present in addition to the $\beta$-uranium pattern the patterns of UO and $UO_2$, and these oxide patterns are just as intense as the $\beta$-uranium pattern. This would not be important except for the fact that of the 36 resolved reflections used in the refinement of the powder data, eight either coincide with or are so close to UO and $UO_2$ lines that it is certain, in our opinion, that the oxide lines interfered with accurate intensity measurements. Thus, for the two reasons stated above, we do not believe that the intensity measurements on the powder pattern of $\beta$-uranium are sufficiently accurate to settle the details of the structure.

Thewlis & Steeple raise the point in their statement that there are inconsistencies in our *hkl* and *khl* intensities. These inconsistencies have been apparent in our published data for some time and are undoubtedly due to strong absorption effects. However, in discussing the details of the structure, in particular the puckering of the layers, we have always been careful to compare reflections close together on the film. For such reflections, absorption corrections are unnecessary. Thus the point raised by Thewlis & Steeple concerning the *hkl* and *khl* reflections is not, in our opinion, relevant in regard to the details of the structure.

Finally, the position of Thewlis & Steeple that there may be two $\beta$-uranium structures implies that there is a transformation from one to the other during cooling from 720° C. to room temperature. We know of no independent evidence for such a transformation. Against the transformation is the fact that in a wire 1 mm. in diameter $\beta$-uranium single crystals several centimetres long can be grown and retained by quenching. It seems highly improbable that such large crystals could be retained if there were a transformation. The implication of a transformation therefore seems, to us, highly speculative.

### Separate statement by Thewlis & Steeple

It will, we think, be generally agreed that the structure of a phase existing at high temperature can be determined unequivocally only from data obtained at that temperature. Unfortunately single-crystal X-ray evidence does not exist for $\beta$-uranium in the $\beta$ range and the only data available are the powder data referred to above. It seemed incumbent on us, therefore, to try to extract as much information from the data as we could, incomplete though they are by single-crystal standards. We should certainly not have considered making such an effort had the single-crystal data of Tucker & Senio referred to the structure at high temperature.

In their statement, Tucker & Senio have pointed out the difficulties with which we were faced in undertaking this task. These difficulties we realize and have attempted to overcome, although some weaknesses remain. Thus our data, in common with all powder data, suffer from referring only to relatively strong reflections. We are satisfied, however, that the rather intense reflections, which Tucker & Senio state should have been observed but were not, correspond to calculated intensities (according to our structure and after allowing for the multiplicity factor, absorption factor etc.) which are in no case significantly above the threshold of observability. With regard to the accuracy of the intensity measurements we would say that, in our opinion, no measurements of diffracted X-ray intensity are characterised by 'very high accuracy'. However, we believe that our measurements are as accurate as most. In particular, where interference by oxide lines seemed to us to occur we have (Thewlis & Steeple, 1954) rejected the measurements. It is perhaps relevant to note here that even single-crystal intensity measurements are not entirely free from suspicion. There are, for example, several inconsistencies in the observed intensities of the *hkl* and *khl* reflections listed by Tucker & Senio (1953).

Using the powder data, we considered both the centrosymmetrical and non-centrosymmetrical structures and found that the former was not capable of improvement (agreement residual 32%) whereas the latter was (agreement residual 20%). It seems very unlikely that the powder data can be so incomplete and inaccurate as to reverse the true position, and we therefore conclude that the non-centrosymmetrical structure is to be preferred. The structure differs in the main from that of Tucker & Senio in the nature of the puckering of the atomic layers, and in our view this may well represent a real difference between the structure at room temperature and that at high temperature, although we do not claim to have proved this. Our view is supported by the fact that, as shown by the table in the first part of this joint note, Tucker & Senio's structure shows up badly against our data, and vice versa. In addition, the nature of the puckering in our structure is such as to lead to a reduction in the intensity of the 004 reflection as compared with that at room temperature, a reduction which is indeed observed. The 004 reflection is actually three times as strong on our powder photographs of 'retained' $\beta$-U (1·4 atomic% Cr) at room temperature as on those of $\beta$-U at 720° C. Our use of the agreement residual to assess the correctness of our structure is challenged, however, by Tucker & Senio, who, in their statement above, quote Lipson & Cochran (1953). We are therefore glad to say that Prof. Lipson supports our use of the residual, there being no examples of major discrepancies between the observed and calculated structure factors.

With regard to the last point made by Tucker & Senio, it seems to us that, in view of the relatively small atomic shifts involved, the possibility of a structural transformation on cooling from 720° C. to room temperature is by no means ruled out.

### References

LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*, pp. 146–7. London: Bell.

THEWLIS, J. (1952). *Acta Cryst.* **5**, 790.

THEWLIS, J. & STEEPLE, H. (1954). *Acta Cryst.* **7**, 323.

TUCKER, C. W. (1950). *Science*, **112**, 448.

TUCKER, C. W. (1951). *Acta Cryst.* **4**, 425.

TUCKER, C. W. (1954). *Acta Cryst.* **7**, 752.

TUCKER, C. W. & SENIO, P. (1953). *Acta Cryst.* **6**, 753.

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## A note on celsian.

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X-ray work on the Ba-felspar celsian ($BaSi_2Al_2O_8$) by Taylor, Darbyshire & Strunz (1934) determined the values $a = 8{\cdot}63$, $b = 13{\cdot}10$, $c = 7{\cdot}29$ Å, $\beta = 116°$ (approx.) for the dimensions of a monoclinic cell; they also showed that celsian had the same tetrahedral framework structure as other felspars. Several celsian specimens from different localities have been examined by the author and it is found that the cell described by Taylor *et al.* is only a pseudo-cell. In the true cell the length of the $c$ axis is doubled, for weak reflexions are observed midway between the main layer lines on $c$-axis oscillation photographs. If these weak reflexions are indexed on the basis of the true cell dimensions, their indices are all of the type $(h+k)$ odd, $l$ odd. The strong reflexions on the main layer lines all have $(h+k)$ even, $l$ even; thus the cell is body-centred. These new observations are particularly interesting since they confirm the expected close structural similarity between the Ba-rich members of the K–Ba felspar series and the Ca-rich members of the plagioclases.

The plagioclase series has been investigated in some detail, and suggestions concerning the structural arrangements of the Ca-rich members have been put forward (Gay & Taylor, 1953; Gay, 1954); these are used in the following discussion. The diffraction patterns of celsian (apart from changes in intensity, and some small dimensional changes) are very similar to those of body-centred anorthite. In body-centred anorthite the Si–Al distribution within the tetrahedra of the framework is thought to be ordered; the 14 Å $c$ axis, denoted by a particular class of weak reflexions, is characteristic of this ordering. In the same way, the Si–Al arrangement in celsian is thought to be ordered since the $c$ axis is doubled. In celsian, the reflexions resulting from this doubling are, on the whole, very much weaker (5–10 times) than the corresponding reflexions in anorthite-type structures. This may be in part due to enhancement of reflexions on the main layer lines by the presence of the heavy Ba ions and also to the small but significant differences between the atomic positions in celsian and anorthite. There is also the possibility that the Si–Al ordering is not complete for the particular specimens examined. Some anorthite-rich plagioclases show additional weak reflexions which do not obey the body-centring condition; the character of these reflexions may vary from sharp to very diffuse. These 'primitive' reflexions are dependent on the Ca ions, and the reversible changes in character which they exhibit may be associated with movement of the Ca ions within their interstices in the structure. No traces of similar reflexions have been found for the celsians examined; it might be expected that the larger size of the Ba ions would prevent their occurrence.

Although the main features of the celsian diffraction patterns are in accord with those expected in the light of current views of felspar structures, it should be pointed out that the specimens so far examined contain appreciable amounts (possibly as much as 10%) of potash felspar. Whether this affects the degree of Si–Al order (and consequently the intensities of the weak subsidiary reflexions) and the possible occurrence of additional weak primitive reflexions, such as are found in the plagioclases, can only be determined by an examination of a very pure barium felspar. Further work on this and on other members of the K–Ba felspar series is being carried out.

### References

GAY, P. (1954). *Miner. Mag.* **30**, 428.

GAY, P. & TAYLOR, W. H. (1953). *Acta Cryst.* **6**, 647.

TAYLOR, W. H., DARBYSHIRE, J. A. & STRUNZ, H. (1934). *Z. Kristallogr.* **87**, 464.