Determination of the incommensurately modulated structure of α-uranium below 37 K

Sander van Smaalen* and Thomas F. George
Departments of Physics and Astronomy and Chemistry, State University of New York at Buffalo, 239 Fronczak Hall, Buffalo, New York 14260
(Received 10 November 1986)

The modulated structure of α-uranium is analyzed with use of the neutron scattering data of Marmeggi *et al.* [Solid State Commun. **43**, 577 (1982)]. The results of the refinements are given for all the superspace groups compatible with the neutron diffraction pattern. Fits to the experimental data of equal quality are obtained for different structure models (different symmetries), thus prohibiting the determination of the structure from neutron scattering alone. Together with the recently reported results of electron microscopy, the refinements lead to a unique assignment of a superspace group to the incommensurately modulated structure of α-uranium below $T=37$ K, with the tentative symbol $P2/m\,11(\frac{1}{2}\beta\gamma)$. The values of the structural parameters, as follow from the refinements, are also reported.

I. INTRODUCTION

The low-temperature physical properties and structure of α-uranium have been studied extensively over the past three decades. Although considerable progress has been made, a complete understanding of the changes in α-uranium occurring at low temperature has yet to be obtained.

At room temperature, α-uranium is believed to crystallize in the orthorhombic space group $Cmcm$ (D_{2h}^{17}). The first structure determination was performed in 1937 by Jacob and Warren,[1] and it has been confirmed on many occasions.[2,3] For $T<18$ K the lattice parameters are, $a=2.8444$ Å, $b=5.868$ Å, and $c=4.9316$ Å.[2] There is one independent atom on a fourfold position $\pm(0,y,\frac{1}{4})$, $\pm(\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$, with $y=0.102$ (Fig. 1).

Major steps in the understanding of the low-temperature behavior came with the preparation of large single crystals by Fisher and McSkimmin,[4] and subsequently the measurement of the elastic constants down to $T=1.5$ K. These experiments clearly showed an anomaly at $T=43$ K, and therefore indicated a phase transition at this temperature. Later, Steinitz *et al.*[5] were able to show, by means of thermal expansion measurements, the existence of three low-temperature phase transitions, respectively at 43, 37, and 23 K. Only around 1980 it became clear that the 43-K transition is connected with the formation of an incommensurately modulated structure, presumably due to a charge-density wave (CDW).[6–9]

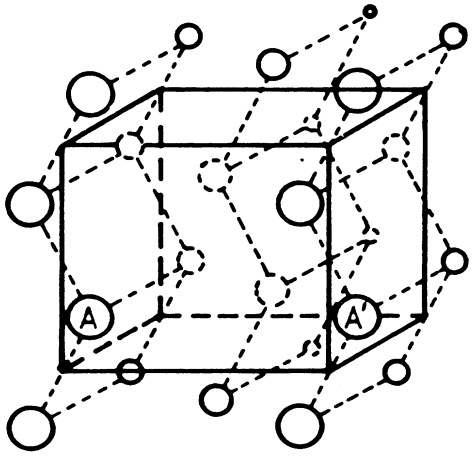

FIG. 1. Perspective drawing of the C-centered orthorhombic unit cell of α-uranium.

Inelastic neutron scattering at room temperature revealed a softening in the Σ_4 phonon branch at a wave vector at $0.5\mathbf{a}^*$.[6] Low-temperature elastic neutron scattering indicated the occurrence of satellite reflections below a temperature of 43 K. One set can be described as commensurate satellites [$\mathbf{q}=(0.5,0,0]$ with respect to a slightly expanded lattice.[7] The other, much intenser, set consists of incommensurate satellites at positions $(\pm\frac{1}{2},\pm q_y,\pm q_z)$, with $q_y=0.176$ and $q_z=0.182$ at $T=5$ K.[8,9] These reflections gave the conclusive proof that the phases below 43 K have an incommensurately modulated structure. Both sets of satellites were measured in neutron diffraction between 5 and $\sim$43 K,[10] however, the transitions at 23 and 37 K could not be observed. A review of this earlier neutron scattering work is given by Smith and Lander.[10,11]

The diffraction pattern of both main reflections and incommensurate satellites shows *mmm* symmetry.[3,9] Marmeggi *et al.*[9] noted that this could be interpreted as satellites coming from a single domain multiple-$\mathbf{q}$ structure or from a multidomain single-$\mathbf{q}$ structure. However, their analysis of the intensity data was restricted to the four-domain single-$\mathbf{q}$ structure, which has triclinic symmetry. In an earlier paper,[12,13] it was argued that the correct description of the symmetry of α-uranium should make use of the superspace groups developed by De Wolff, Janner, and Janssen.[14,15] A complete list of all 16 possible superspace groups was derived, which arises when all possibilities for dividing the diffraction pattern in subsets coming from different domains are considered.[12,13] On the basis of the experimental data available at that time (most notably the fact that the first component of the

modulation wave vectors was found to be exactly one-half),[9] the orthorhombic superspace group $Pmcm(\frac{1}{2}\beta\gamma)$ was assigned to the structure as the most probable one, although it was recognized that structure refinements and/or other experiments are necessary for a reliable determination of the symmetry.[12,13]

Recently, transmission electron microscopy (TEM) experiments were performed.[16] These clearly show that the incommensurate satellites and the commensurate satellites come from different regions in the crystal. This supports the assumption that both sets of satellites can be considered independently, at least as far as a description of the structure is concerned. In this paper we shall confine the analysis to the incommensurate domains.

In TEM all three low-temperature phase transitions are observed.[16] The 23-K transition is found to be connected with the onset of the growth of the incommensurate domains at the expense of the commensurate domains. Around 37 K almost the whole crystal consists of incommensurate domains. The 37-K transition is connected with a change within the incommensurate domains. At $T\approx 43$ K the satellites, and therefore the modulation, disappear. It is noted that TEM experiments are done with very thin samples, and that the observed effects need not reflect the bulk properties. Based on the satellite intensities in neutron scattering, it is believed that the incommensurate domains comprise the largest part of the crystal at any temperature.[10,17]

For the incommensurate domains below $T=37$ K, the TEM experiments show one domain with modulation wave vector $\mathbf{q}^1=(\frac{1}{2},q_y,q_z)$ and a second with $\mathbf{q}^3=(\frac{1}{2},q_y,-q_z)$.[16] Also, the presence of main reflections with $h+k=$odd indicate a loss of the high-temperature C-centering. As noted by Walker,[18] the symmetry of each of these domains is then given by the monoclinic superspace group $P2/m11(\frac{1}{2}\beta\gamma)$, or one of its acentric maximal subgroups.[12,13] The nature of the incommensurate domains between 37 and 43 K is less clear. The observation in TEM is that domains with $\mathbf{q}^3$ ($\mathbf{q}^1$) start to grow within the $\mathbf{q}^1$ ($\mathbf{q}^3$) domains. A discussion of the possible interpretations is deferred to Sec. V.

The transition at 43 K is believed to be second order, whereas the 37- and 23-K transitions are first order.[4,5] Based on the presumption of a second-order phase transition at $T=43$ K, and a high-temperature symmetry $Cmcm$, Walker[18] has performed a Landau-theory analysis for the transition to the incommensurate domains. It appeared that a second-order phase transition is only possible to a modulated structure in which the first component of the modulation wave vector is also incommensurate.[18] This is easily understood when we recognize that in the superspace groups where $q_x=\frac{1}{2}$, the modulation can be described with respect to the C-centered cell by one or two incommensurate wave vectors $\mathbf{q}^1$ and $\mathbf{q}^2=(\frac{1}{2},-q_y,q_z)$, and a commensurate wave vector $\mathbf{q}^5=(1,0,0)$. It is known that for a second-order phase transition to be possible only wave vectors belonging to one star of the high-symmetric phase can occur. $(\mathbf{q}^1,\mathbf{q}^2)$ and $\mathbf{q}^5$ belong to different stars of the space group $Cmcm$. The description given by Walker[18] for low-temperature behavior is then a second-order phase transition at $T=43$ K to a structure with superspace group $C2/m11(\alpha\beta\gamma)$, $\alpha\neq 0.5$, followed by a lockin transition at $T=37$ K to a structure with symmetry $P2/m11(\frac{1}{2}\beta\gamma)$. Although this series of transitions might quite well be possible, there is at present no positive experimental evidence to support it. In particular, deviations of q_x from $\frac{1}{2}$ have not been observed.[10,16] Also, we like to point out that already at room temperature some reflections are observed in neutron diffraction at positions forbidden by the C-centering.[2,19] This would indicate a high-temperature symmetry $Pmcm$. In that case a second-order phase transition to a noncentered structure is possible, and in fact these symmetries (orthorhombic and a-axis unique monoclinic) are the only ones which need to be considered.

In this paper we present the results of the refinements of the structural parameters on the neutron intensity data of Marmeggi *et al.*,[9] for each of the possible superspace groups listed in Ref. 12. The a-axis incommensurate superspace groups suggested by Walker[18] reduce to one of the groups given in Ref. 12 if $q_x=\frac{1}{2}$. Since there are as yet no experimental indications that $q_x\neq\frac{1}{2}$, or, if so, what the deviation will be, these a-axis incommensurate superspace groups will not be considered here. Moreover, the intensity data collection was done at $T=10$ K,[9] for which there is ample experimental evidence that $q_x=\frac{1}{2}$.[9,16] To show the insensitiveness of the quality of the fit to the particular structure model, we give results for all 16 superspace groups, rather than only the a-axis unique monoclinic ones. In fact, it will appear that one of the orthorhombic superspace groups gives a fit of equal quality as the best fit for an a-axis unique monoclinic superspace group.

To understand the various structure models, the definitions of the superspace groups need to be known. In Secs. II and III we review the derivation of the various superspace groups and their consequences for the structure as given in Refs. 12 and 13. In Sec. IV the results of the refinements will be presented. In Sec. V the consequences of the structure model will be evaluated, and the possible interpretations for the modulated structure above 37 K will be discussed. Finally, conclusions are presented in Sec. VI.

II. SUPERSPACE GROUPS

By analysis of a neutron or x-ray diffraction pattern, i.e., by determination of its point symmetry and of the extinction conditions, the number of possible space groups for a particular structure can be reduced to but a few. Often, only one centrosymmetric group and its maximal acentric subgroups need to be considered. The analysis for ordinary structures (leading to a spacegroup) and for modulated structures (resulting in a superspace group) is completely analogous. For α-uranium the diffraction pattern alone is not sufficient to determine if it originates in one domain or in more. This leads to an additional ambiguity for the symmetry. In Ref. 12, all the possibilities for the superspace group of α-uranium, compatible with the neutron diffraction results, were derived, which we shall review here.

The incommensurate satellites occur at positions

$(\pm\frac{1}{2},\pm q_y,\pm q_z)$ as measured from the nonextinct main reflections in the C-centered lattice.[9] In the superspace group description of modulated structures all reflections are characterized by a set of $(3+d)$ integers, defining the diffraction wave vector as[15]

$$\mathbf{S}=h\mathbf{a}^*+k\mathbf{c}^*+l\mathbf{c}^*+\sum_{j=1}^{d} m_j\mathbf{q}^j . \tag{1}$$

The modulation wave vectors are chosen such that a minimum number, d, is needed to describe all reflections. d is called the dimension of the modulation. $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ are the reciprocal-lattice vectors of the average structure, and for α-uranium they are equal to those of the high-temperature space group $Cmcm$. The superspace group is determined by considering the point symmetry of the diffraction pattern and the extinction conditions for the indices h, k, l, m_j $(j=1,2,\ldots,d)$.

First, consider the whole diffraction pattern as coming from one domain. Then only two wave vectors are needed to describe the satellites. A possibility is

$$\begin{aligned}\mathbf{q}^1&=(\tfrac{1}{2},q_y,q_z) ,\\ \mathbf{q}^2&=(\tfrac{1}{2},-q_y,q_z) .\end{aligned} \tag{2}$$

Other possibilities include a choice from the wave vectors

$$\begin{aligned}\mathbf{q}^3&=(\tfrac{1}{2},q_y,-q_z) ,\\ \mathbf{q}^4&=(\tfrac{1}{2},-q_y,-q_z) .\end{aligned} \tag{3}$$

Note that there are now satellites belonging to present main reflections and belonging to main reflections forbidden by the C centering. This means that in the single domain structure the centering is lost. Alternatively, the symmetry of this structure can be described by a centered superspace group, if an additional modulation wave vector $\mathbf{q}^5=(1,0,0)$ is used (or any choice of three vectors from the set $\{\mathbf{q}^1,\mathbf{q}^2,\mathbf{q}^3,\mathbf{q}^4\}$). This latter description would lead to a superspace group which is a combination of a two-dimensional incommensurate and one-dimensional totally commensurate modulation, and which is a more complicated analogue of the totally commensurate one-dimensional superspace groups.[12,20] Such a description would show the resemblance of the a-axis commensurate superspace groups with the a-axis incommensurate superspace groups proposed by Walker[18] for the $T>37$ K phase. However, in the analysis presented here, we have chosen to describe the loss of the centering by the use of a primitive unit cell.

A. Orthorhombic symmetry

The point symmetry of a diffraction pattern for an orthorhombic (super)space group is always mmm. It is then easily shown that by starting from one satellite, all the others are generated. Therefore, the complete diffraction pattern originates in one domain. This does not mean that the crystal has only one domain, but only states that all domains give identical diffraction patterns. In fact, noncentrosymmetric structures always have two different domains, whereas the loss of the C centering also leads to two different domains, which are related by a translation over a vector $\mathbf{a}$.[18] The Bravais class can now be established as $Pmmm(\frac{1}{2}\beta\gamma)$, No. 2-51 in the tables of Janner *et al.*[15]

To analyze the extinction conditions, it is advantageous to make a transformation to a larger basic unit cell, such that the commensurate components of the modulation wave vectors disappear.[14] The required new unit cell is $(2a\times b\times c)$, in which the modulation is described by the two wave vectors

$$\begin{aligned}\mathbf{q}_i^1&=(0,q_y,q_z) ,\\ \mathbf{q}_i^1&=(0,-q_y,q_z) .\end{aligned} \tag{4}$$

The transformation of the indices is,

$$\begin{aligned}H&=2h+m_1+m_2 ,\\ K&=k ,\\ L&=l ,\\ m_1,&m_2 \text{ unchanged} .\end{aligned} \tag{5}$$

In the larger unit-cell reflections with $H+m_1+m_2=$odd are absent, which correspond to a centering translation

$$\mathbf{ct}=(\tfrac{1}{2},0,0,\tfrac{1}{2},\tfrac{1}{2}) . \tag{6}$$

The first three components give the translations along the new basic unit-cell vectors $2\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$. The last two components give translations along the two extra coordinates defined by the two modulation wave vectors.

For the main reflections, one extra extinction condition is given by: $l=$odd is absent for the $(h\,0\,l)$ reflections.[2,3] For the satellites it can be deduced from the reflection set[9,10] that there are no extinction conditions. Therefore, for the complete diffraction pattern one extinction condition: $L=$odd is absent for the $(H\,0\,L\,0\,0)$ reflections. This represents a translation component of $(0\,0\,\frac{1}{2}\,0\,0)$ for the mirror plane perpendicular to the y axis.

The extinction condition representing the C-centering of the average structure then states that $H+2K\neq 4n$ is absent for the $(H\,K\,L\,0\,0)$ reflections (n is the integer). There is no symmetry element in the Bravais class $Pmmm(\frac{1}{2}\beta\gamma)$ which can account for this condition. In fact, considering the description based on a C-centered lattice discussed earlier, some of the second-order satellites (e.g., $\mathbf{q}^1+\mathbf{q}^4$) are at the positions of reflections forbidden by the C-centering. In neutron diffraction some of them have been observed by Marmeggi *et al.*,[19] and in TEM they were observed by Chen and Lander.[16] Other second-order satellites, of the form $2q$, were observed by Smith and Lander.[10]

An element of a $(3+d)$-dimensional point-group operation consists of a three-dimensional part R, a d-dimensional part represented by a $d\times d$ matrix ε, and a $(d\times 3)$ matrix $\underline{G}$ built from d reciprocal-lattice vectors of the basic unit cell. For every three-dimensional operator R and each given set of modulation wave vectors $\{\mathbf{q}^j\}$ $(j=1,\ldots,d)$, the ε matrix and $\underline{G}$ can be determined from the relation[15]

$$R\underline{Q}-\varepsilon\underline{Q}=\underline{G} , \tag{7}$$

where $\underline{Q}$ is a $d\times 3$ matrix formed by the d wave vectors $\mathbf{q}^j$. In addition, the demand has to be fulfilled that the set of transformations (R,ε) forms a group. For the choice of modulation wave vectors given in Eqs. (2) or (4) a set of ε matrices is obtained, denoted by ε_1 in Table I. For the other choices of the pair of modulation wave vectors it is possible that another set of ε matrices is obtained (ε_2 in Table I). Next to the point-group part, each element of a superspace group contains a translation vector of length $(3+d)$. For α-uranium the translation components are derived above from the extinction conditions. The complete set of symmetry operators for the two-dimensional superspace groups of α-uranium is given in Table I. Rather than develop an *ad hoc* notation for them, we will denote each superspace group element by its three-dimensional part, bearing in mind that the complete operator given in Table I is meant.

Now, the superspace groups for all possible orthorhombic symmetries can be determined. There is one centrosymmetric and there are four acentric superspace groups. They are given in Table II.

One complicating feature should be noted. For the centrosymmetric group we are free to choose any pair of modulation wave vectors to describe the structure (except, of course, combinations as $\mathbf{q}^1$ with $\mathbf{q}^4$, which are rationally dependent). However, for the noncentrosymmetric groups we are restricted to a choice of pairs of wave vectors which can be transformed into each other by the elements of that noncentrosymmetric superspace group. It is not possible to make always a choice such that the ε_1 matrices can be used. The pair of wave vectors used in the rest of this paper, as well as the set of ε matrices which should be used, is included in Table I. Such a complication does not occur for one-dimensional modulated structures.

B. Monoclinic symmetry, *a*-axis unique

The diffraction pattern of a structure with monoclinic symmetry has point symmetry $2/m$. There are three possibilities for a monoclinic symmetry, with, respectively, the unique axis along **a**, **b**, and **c** of the high-temperature orthorhombic unit cell. These will be considered in this and subsequent subsections.

By application of each of the symmetry elements 2, m, or i, to each modulation wave vector $\pm\mathbf{q}^j$ $(j=1,2,3,4)$, it is easily shown that in the case of monoclinic symmetry the satellites divide into two subsets, originating in different domains. Again, the real number of domains might also be four or eight, where then two, respectively, four domains give identical diffraction results.

For the Laue group $2/m11$, one set of satellites can be described by $\mathbf{q}^1$ and the other set of $\mathbf{q}^2$. Again, satellites occur for both present and extinct main reflections, indicating a loss of the C-centering. The Bravais class is $P2/m\,(\frac{1}{2}\beta\gamma)$, No. 1-3 in the tables of Janner *et al.*[15] The

TABLE I. The (3 + 2)-dimensional superspace group elements.

R	Point-group element[a,b] ε_1	ε_2	Translation component	Remarks
m_x	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$		
m_y	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$	$(0,0,\frac{1}{2},0,0)$	
m_z	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$		located at $(x,y,\frac{1}{4})$
^2x	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$		
^2y	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$		located at $(0,y,\frac{1}{4})$
^2z	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\bar{1}\\\bar{1}&0\end{bmatrix}$	$(0,0,\frac{1}{2},0,0)$	
i	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$	$\begin{bmatrix}\bar{1}&0\\0&\bar{1}\end{bmatrix}$		

[a]For definitions of R and ε, see the text.

[b]ε_1 matrices are obtained for example for the following pairs of modulation wave vectors: $\mathbf{q}^1=(\frac{1}{2},q_y,q_z)$ with $\mathbf{q}^2=(\frac{1}{2},-q_y,q_z)$; $\mathbf{q}^3=(\frac{1}{2},q_y,-q_z)$ with $\mathbf{q}^4=(\frac{1}{2},-q_y,-q_z)$. ε_2 matrices are obtained for the pairs of modulation wave vectors, $\mathbf{q}^1=(\frac{1}{2},q_y,q_z)$ with $\mathbf{q}^3=(\frac{1}{2},q_y,-q_z)$; $\mathbf{q}^2=(\frac{1}{2},-q_y,q_z)$ with $\mathbf{q}^4=(\frac{1}{2},-q_y,-q_z)$.

modulation is now one-dimensional. Transforming to the $(2a \times b \times c)$ cell, analogous to Eq. (5), makes it possible to determine the extinction condition that $L=$odd is absent for the $(H\,0\,L\,0)$ reflections. This corresponds to a c glide perpendicular to the y axis. Because such a symmetry element is not present, this observed extinction condition cannot be accounted for by symmetry. The centrosymmetric and the two acentric possibilities for the superspace group are given in Table II. For the one-dimensional incommensurate superspace groups a complete list and a notation is given by De Wolff *et al.*[14] This alternative symbol is given in Table II, instead of specifying the set of ε values, thus also defining the superspace group. To facilitate the comparison with the average structure and with the other superspace groups, we shall use the incomplete symbol given in the first column of Table II in this paper.

C. Monoclinic symmetry, *b*-axis unique

Starting with a spot at $\mathbf{q}^1$ as measured from a present main reflection, it can be shown that one subset of the satellites is given by $\mathbf{q}^1$ and $\mathbf{q}^2$, but measured from the present main reflections only. The other domain gives rise to the satellites at $\mathbf{q}^3$ and $\mathbf{q}^4$. The extinction conditions are the same as in the orthorhombic case, except that now all $(H\,K\,L\,m_1\,m_2)$ reflections with $H+K=$odd are absent. The C-centering of the high-temperature structure remains present. The $(3+2)$-dimensional Bravais class is $C2/m\,(\alpha\beta\gamma)$, No. 2-17 in the tables of Janner *et al.*[15] The three possible superspace groups are given in Table II. Note that for these groups $\alpha=\frac{1}{2}$ cannot be a consequence of the symmetry.

D. Monoclinic symmetry, *c*-axis unique

The derivation for this case is completely analogous to that for the Laue group $1\,2/m\,1$. The diffraction pattern of one of the domains is now given by the $\mathbf{q}^1$ and $\mathbf{q}^3$ satellites, as measured from the present main reflections only. The structure is C-centered, and the Bravais class is given by $C2/m\,(\alpha\beta\gamma)$, No. 2-17 in Ref. 15. The three possible superspace groups are listed in Table II.

E. Triclinic symmetry

For a triclinic group, the only symmetry of the diffraction pattern is given by the inversion operator i. The diffraction pattern splits into four subsets, each one arising from a different domain. Each subset is characterized by one of the four modulation wave vectors $\mathbf{q}^j$ $(j=1,2,3,4)$, and only satellites belonging to the present main reflections are found. The modulation is one-dimensional, and the Bravais class is $P\bar{1}(\alpha\beta\gamma)$, No. 1-1 in Ref. 15. The two possible superspace groups are given in Table II. Of course the extinction condition that $L=$odd is absent for $(H\,0\,L\,0)$ reflections cannot be accounted for by symmetry.

To conclude this section, we would like to mention the following. It is possible to divide the satellite reflections into subsets coming from the different domains. However, for the main reflections such a disentangling is not possible. Therefore, to make a complete structure determination possible in, for example the a-axis unique superspace groups, a data collection must be performed on a crystal with unequal populations of the different domains.

III. STRUCTURAL PARAMETERS

In the high-temperature ($T>43$ K) space group *Cmcm*, there is one independent atom on a fourfold special position $\pm(0,y,\frac{1}{4})$, $\pm(\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$. All experimental data indicate that these remain the average positions in the modulated phases to a good approximation.[2,3,19] Therefore, we shall assume that no large structural changes occur at low temperature.

The modulation in α-uranium is of the displacive type. Then, the positions of the atoms are given as the sum of an average position, $\mathbf{r}^0$, and a modulation function, $\mathbf{u}(\bar{x}_4,\bar{x}_5,\ldots,\bar{x}_{3+d})$,

$$\mathbf{r}=\mathbf{r}^0+\mathbf{u}(\bar{x}_4,\bar{x}_5,\ldots,\bar{x}_{3+d})\,. \tag{8}$$

$\bar{x}_{3+j}=\mathbf{q}^j\cdot\mathbf{r}^0 (j=1,2,\ldots,d)$ represent additional coordinates of the atoms, related to the d-independent modulation wave vectors. The function $\mathbf{u}(\bar{x}_4,\bar{x}_5,\ldots,\bar{x}_{3+d})$ is periodic in each of its arguments with period one.[21] The superspace group elements operate in the $(3+d)$-dimensional space defined by the coordinates x_1,x_2,x_3 of $\mathbf{r}^0$ and the additional coordinates $\bar{x}_4,\bar{x}_5,\ldots,\bar{x}_{3+d}$. The average positions have the symmetry given by the three-dimensional part of the operators in the superspace group, and thus they form a three-dimensional lattice with a unit cell defined as the average structure or basic structure unit cell. Except for the possible absence of the C-centering, this unit cell is identical to that of the high-temperature structure. The actual position of an atom is different in each unit cell, due to the incommensurability of the modulation, i.e., $\mathbf{u}(\bar{x}_4,\bar{x}_5,\ldots,\bar{x}_{3+d})$ assumes a different value in each unit cell.

The special positions in the average structure ($\mathbf{r}^0$) follow from the average structure space-group elements. This space group is a subgroup of the high-temperature structure space group *Cmcm*, and therefore the restrictions on the average structure parameters may be less than in *Cmcm*. In particular, the original fourfold position may split up in two twofold or four single positions. For example, loss of the C-centering makes the atoms on $\pm(0,y,\frac{1}{4})$ independent from those on $\pm(\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$. Moreover, the originally restricted parameters $x=0$ and $z=\frac{1}{4}$, may become free, due to the loss of the corresponding symmetry elements. All the special positions for α-uranium are listed in Table II.

Each independent atom has its own modulation function [Eq. (8)]. The number of modulation functions to be considered is therefore limited to a small amount; one to four for the different possible symmetries. However, the only requirement for $\mathbf{u}(\bar{x}_4,\bar{x}_5,\ldots,\bar{x}_{3+d})$ is that it be periodic. To be able to determine this function we need some model for it. For example, the modulation functions can be expanded in their Fourier series,

TABLE II. The different possible symmetries for the modulated phase of α-uranium. Indicated are the dimension of the modulation, the wave vectors which are used in the definition of the modulation functions, and the set of ε matrices which applies to that particular choice. The first wave vector is always $\mathbf{q}^1=(\frac{1}{2},q_y,q_z)$, which is the only one for the one-dimensional modulations, and the superspace group symbol is given in the notation of Ref. 14. The last column gives the average positions of the atoms. Each line corresponds to one independent atom. For the centered groups, additional atoms are found at positions $(\frac{1}{2},\frac{1}{2},0)+$.

Superspace group	Dimension of the modulation	Second modulation wave vector	Set of ε matrices (Table I)	Number of independent atoms	Average position of the atoms
Orthorhombic					
(1) $Pmcm(\frac{1}{2}\beta\gamma)$	2	$\mathbf{q}^2$	ε_1	2	(1) $(0,y,\frac{1}{4})$, $(0,-y_1,-\frac{1}{4})$ (2) $(\frac{1}{2},y_2,\frac{1}{4})$, $(\frac{1}{2},-y_2,-\frac{1}{4})$
(2) $P222_1(\frac{1}{2}\beta\gamma)$	2	$-\mathbf{q}^3$	ε_1	2	(1) $(0,y_1,\frac{1}{4})$, $(0,-y_1,-\frac{1}{4})$ (2) $(\frac{1}{2},y_2,\frac{1}{4})$, $(\frac{1}{2},-y_2,-\frac{1}{4})$
(3) $Pmc2_1(\frac{1}{2}\beta\gamma)$	2	$\mathbf{q}^2$	ε_1	2	(1) $(0,y_1,z_1)$, $(0,-y_1,z_1-\frac{1}{2})$ (2) $(\frac{1}{2},y_2,z_2)$, $(\frac{1}{2},-y_2,z_2-\frac{1}{2})$
(4) $P2cm(\frac{1}{2}\beta\gamma)$	2	$\mathbf{q}^2$	ε_1	2	(1) $(x_1,y_1,\frac{1}{4})$, $(x_1,-y_1,-\frac{1}{4})$ (2) $(x_2,y_2,\frac{1}{4})$, $(x_2,-y_2,-\frac{1}{4})$
(5) $Pm2m(\frac{1}{2}\beta\gamma)$	2	$\mathbf{q}^3$	ε_2	4	(1) $(0,y_1,z_1)$ (2) $(0,y_2,z_2)$ (3) $(\frac{1}{2},y_3,z_3)$ (4) $(\frac{1}{2},y_4,z_4)$
Monoclinic					
(6) $P2/m11(\frac{1}{2}\beta\gamma)$	1		$A^{P2/m}_{\bar{1}\ 1}$	2	(1) $(0,y_1,z_1)$, $(0,-y_1,-z_1)$ (2) $(\frac{1}{2},y_2,z_2)$, $(\frac{1}{2},-y_2,-z_2)$
(7) $P211(\frac{1}{2}\beta\gamma)$	1		$A^{P2}_{\bar{1}}$	2	(1) (x_1,y_1,z_1), $(x_1,-y_1,-z_1)$ (2) (x_2,y_2,z_2), $(x_2,-y_2,-z_2)$
(8) $Pm11(\frac{1}{2}\beta\gamma)$	1		A^{Pm}_{1}	4	(1) $(0,y_1,z_1)$ (2) $(0,y_2,z_2)$ (3) $(\frac{1}{2},y_3,z_3)$ (4) $(\frac{1}{2},y_4,z_4)$
(9) $C12/c1(\alpha\beta\gamma)$	2	$\mathbf{q}^2$	ε_1	1	$(0,y,\frac{1}{4})$, $(0,-y,-\frac{1}{4})$
(10) $C121(\alpha\beta\gamma)$	2	$-\mathbf{q}^2$	ε_2	2	(1) $(0,y_1,\frac{1}{4})$ (2) $(0,y_2,-\frac{1}{4})$
(11) $C1c1(\alpha\beta\gamma)$	2	$\mathbf{q}^2$	ε_1	1	(x,y,z), $(x,-y,z-\frac{1}{2})$
(12) $C112_1/m(\alpha\beta\gamma)$	2	$-\mathbf{q}^3$	ε_1	1	$(x,y,\frac{1}{4})$, $(-x,-y,-\frac{1}{4})$
(13) $C112_1(\alpha\beta\gamma)$	2	$-\mathbf{q}^3$	ε_1	1	$(x,y,\frac{1}{4})$, $(-x,-y,z-\frac{1}{2})$
(14) $C11m(\alpha\beta\gamma)$	2	$\mathbf{q}^3$	ε_2	2	(1) $(x_1,y_1,\frac{1}{4})$ (2) $(x_2,y_2,-\frac{1}{4})$
Triclinic					
(15) $C\bar{1}(\alpha\beta\gamma)$	1		$P^{P\bar{1}}_{\bar{1}}$	1	(x,y,z), $(-x,-y,-z)$
(16) $C1(\alpha\beta\gamma)$	1		P^{P1}_{1}	2	(1) (x_1,y_1,z_1) (2) (x_2,y_2,z_2)

$$\mathbf{u}^{\mu}(x_4,x_5,\ldots,x_{3+d})=\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_d=0}^{\infty}\mathbf{A}^{\mu}_{n_1n_2\cdots n_d}\cos[2\pi(n_1\bar{x}_4+n_2\bar{x}_5+\cdots+n_d\bar{x}_{3+d})]$$
$$+\mathbf{B}^{\mu}_{n_1n_2\cdots n_d}\sin[2\pi(n_1\bar{x}_4+n_2\bar{x}_5+\cdots+n_d\bar{x}_{3+d})]\ , \tag{9}$$

where μ labels the independent atoms, and $n_1=n_2=\cdots=n_d=0$ is excluded from the summation. Now $\mathbf{A}^{\mu}_{n_1n_2\cdots n_d}$ and $\mathbf{B}^{\mu}_{n_1n_2\cdots n_d}$ can be used as parameters to be determined in the refinement on the diffraction data. It follows that we have an infinite set of parameters for only a finite set of data. Fortunately, it can be shown that the intensity of satellites of the mth order ($m=|m_1|+|m_2|+\cdots+|m_d|$) is mainly determined by the Fourier components up to the mth order.[22] For α-uranium only the first-order satellites were measured, so that only the first harmonics can be determined. This leads to $6d$ modulation structural parameters for each independent atom.

Symmetry restrictions on the modulation function can be obtained from

$$(R,\varepsilon)\mathbf{u}(\bar{x}_4,\bar{x}_5,\ldots,\bar{x}_{3+d})=\mathbf{u}(\bar{x}_4,\bar{x}_5,\ldots,\bar{x}_{3+d})\ , \tag{10}$$

for each superspace group operator (R,ε), for which the three-dimensional part R leaves the average position invariant. The atom on $(0,y,\frac{1}{4})$ is left invariant under the operators m_x, 2_y, and m_z. The atom on $(\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$ is left invariant under m_z and under the combination of operators $\mathbf{a}m_x$ and $\mathbf{a}2_y$. For the determination of the restrictions on $\mathbf{u}$, the $(3+1)$-dimensional and $(3+2)$-dimensional superspace groups need to be considered separately.

A. Two-dimensional modulation

To analyze the symmetry restrictions we work in the larger $2a\times b\times c$ unit cell, where $\underline{G}$ for each operator is zero. The translation over $\mathbf{a}$ becomes the centering translations $\mathbf{ct}=(\frac{1}{2},0,0,\frac{1}{2},\frac{1}{2})$ in this larger unit cell [Eq. (6)]. The restrictions for all symmetry elements and for both possibilities of the set of ε matrices are given in Table III. Note that for the higher-order harmonics the restrictions can be different. The various superspace groups listed in Table II may contain only a subset of the operators given in Table III. Also, the independent atoms may vary for the different possibilities. Therefore, the actual restrictions are different for each superspace group. They are summarized in Table IV. The given restrictions apply to the atom with average position given as the first entry in Table II.

B. One-dimensional modulation

For the triclinic groups, only the inversion can be present as point symmetry. Therefore, there are no restrictions on the modulation parameters. For the a-axis unique monoclinic groups, restrictions can only be derived from m_x and $\mathbf{a}m_x$. Transformation to the $(2a\times b\times c)$ unit cell now let $\mathbf{a}$ correspond to the centering translation $(\frac{1}{2}\,0\,0\,\frac{1}{2})$. The restrictions are given in Table IV.

TABLE III. Restrictions on the first-order harmonics of the modulation functions for the symmetry operators which leave atom 1 on $(0,y,\frac{1}{4})$ or atom 2 on $(\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$ of the average structure invariant. The fourth and fifth operation refer to the subsequent application of a point group element and the centering translation (Eq. 6). Note that the restrictions on the higher harmonics will be different. For the sine part of the modulation (B), the set of ε_1 matrices and the set of ε_2 matrices give rise to different restrictions. Both restrictions are given, respectively, in the third and fourth columns.

Operator	Restrictions for both matrices	For ε_1 matrices	For ε_2 matrices
(m_x,ε_{mx})	$A_{10x}=A_{01x}=0$	$B_{10x}=B_{01x}=0$	
$(2_y,\varepsilon_{2y})$	$A_{10x}=-A_{01x}$	$B_{10x}=B_{01x}$	$B_{10x}=-B_{01x}$
	$A_{10y}=A_{01y}$	$B_{10y}=-B_{01y}$	$B_{10y}=B_{01y}$
	$A_{10z}=-A_{01z}$	$B_{10z}=B_{01z}$	$B_{10z}=-B_{01z}$
(m_z,ε_{2z})	$A_{10x}=A_{01x}$	$B_{10x}=-B_{01x}$	$B_{10x}=B_{01x}$
	$A_{10y}=A_{01y}$	$B_{10y}=-B_{01y}$	$B_{10y}=B_{01y}$
	$A_{10z}=-A_{01z}$	$B_{10z}=B_{01z}$	$B_{10z}=-B_{01z}$
$\mathbf{ct}(m_x,\varepsilon_{mx})$	$A_{10y}=A_{01y}=0$	$B_{10y}=B_{01y}=0$	
	$A_{10z}=A_{01z}=0$	$B_{10z}=B_{01z}=0$	
$\mathbf{ct}(2_y,\varepsilon_{2y})$	$A_{10x}=A_{01x}$	$B_{10x}=-B_{01x}$	$B_{10x}=B_{01x}$
	$A_{10y}=-A_{01y}$	$B_{10y}=B_{01y}$	$B_{10y}=-B_{01y}$
	$A_{10x}=A_{01z}$	$B_{10z}=B_{01z}$	$B_{10z}=B_{01z}$

TABLE IV. Symmetry restrictions on the modulation functions and final values for the structural parameters for each of the possible superspace groups. The number and atom number correspond to the numbers given, respectively, in the first and last column of Table II. Restrictions only occur for parameters belonging to the same component (x, y, or z) of the modulation function. They are always of the form $A[\cos(2\pi\bar{x}_4)\pm\cos(2\pi\bar{x}_5)]$ or $B[\sin(2\pi\bar{x}_4)\pm\sin(2\pi\bar{x}_5)]$. The plus or minus combination is indicated by (+) or (−) in the column following the free parameter. The other restriction is that the particular component of the modulation function is zero, which is indicated as such. An asterisk means that the parameter is kept zero in the refinement to fix the phase of the modulation wave. The parameters refer to modulation functions of the form given in Eq. (9). The values given, which should be multiplied by 10^{-4}, are relative coordinates with respect to the lattice parameters of the ($a\times b\times c$) unit cell. Uncertainties are indicated within the parentheses.

	Atom	X				Y				Z			
Number	number	$\cos(2\pi\bar{x}_4)$	$\cos(2\pi\bar{x}_5)$	$\sin(2\pi\bar{x}_4)$	$\sin(2\pi\bar{x}_5)$	$\cos(2\pi\bar{x}_4)$	$\cos(2\pi\bar{x}_5)$	$\sin(2\pi\bar{x}_4)$	$\sin(2\pi\bar{x}_5)$	$\cos(2\pi\bar{x}_4)$	$\cos(2\pi\bar{x}_5)$	$\sin(2\pi\bar{x}_4)$	$\sin(2\pi\bar{x}_5)$
1	1	0	0	0	0	−16(1)	+	32(2)	−	23(2)	−	−10(2)	+
	2	−27(1)	+	−178(1)	−	0	0	0	0	0	0	0	0
2	1	24(2)	−	*	+	−14(1)	+	33(1)	−	26(1)	−	−12(2)	+
	2	27(1)	+	174(1)	−	28(2)	−	−2(2)	+	32(3)	+	17(3)	−
3	1	0	0	0	0	22(3)	−38(3)	44(2)	−14(2)	26(3)	−38(3)	−47(3)	16(3)
	2	−179(3)	167(3)	55(2)	*	0	0	0	0	0	0	0	0
4	1	−9(3)	+	*	−	−13(1)	+	25(2)	−	26(1)	−	−4(2)	+
	2	−26(1)	+	−176(1)	−	10(2)	+	−33(2)	−	−37(3)	−	16(2)	+
5	1	0	0	0	0	−22(3)	+	−44(2)	+	−26(3)	−	47(3)	−
	2	0	0	0	0	−38(3)	+	−14(3)	+	39(3)	−	−16(3)	−
	3	179(3)	+	−55(2)	+	0	0	0	0	0	0	0	0
	4	169(3)	+	*	+	0	0	0	0	0	0	0	0
6	1	0		0		−16(1)		32(2)		23(2)		−10(2)	
	2	−27(1)		−178(1)		0		0		0		0	
7	1	24(2)		*		−14(1)		33(1)		26(1)		−12(2)	
	2	−27(1)		−174(1)		28(2)		−2(2)		−32(3)		16(3)	
8	1	0		0		−4(3)		−9(3)		4(4)		−5(3)	
	2	0		0		−53(4)		29(3)		4(4)		−59(3)	
	3	180(3)		−58(3)		0		0		0		0	
	4	166(4)		*		0		0		0		0	
9		−89(1)	−	13(1)	+	8(1)	+	−16(1)	−	−11(1)	−	6(1)	+
10	1	−25(1)	−	−81(1)	−	16(1)	+	−12(1)	+	−21(2)	−	−2(1)	−
	2	*	−	93(1)	−	4(1)	+	−24(1)	+	19(2)	−	18(1)	−
11		28(1)	*	90(1)	−84(1)	−11(1)	19(1)	−22(1)	7(1)	−13(2)	19(2)	23(1)	−8(1)

TABLE IV. (*Continued*).

Number	Atom number	X				Y				Z			
		$\cos(2\pi\bar{x}_4)$	$\cos(2\pi\bar{x}_5)$	$\sin(2\pi\bar{x}_4)$	$\sin(2\pi\bar{x}_5)$	$\cos(2\pi\bar{x}_4)$	$\cos(2\pi\bar{x}_5)$	$\sin(2\pi\bar{x}_4)$	$\sin(2\pi\bar{x}_5)$	$\cos(2\pi\bar{x}_4)$	$\cos(2\pi\bar{x}_5)$	$\sin(2\pi\bar{x}_4)$	$\sin(2\pi\bar{x}_5)$
12		−89(1)	+	13(1)	−	8(1)	+	−16(1)	−	−11(1)	−	6(1)	+
13		28(1)	*	89(1)	84(1)	−11(1)	19(1)	−22(1)	7(1)	−13(2)	19(2)	23(1)	−8(1)
14	1	−29(1)	+	−90(2)	+	2(1)	+	5(2)	+	−2(2)	−	3(2)	−
	2	*	+	83(2)	+	27(1)	+	−15(2)	+	2(2)	−	29(1)	−
15		89(1)		−14(1)		−3(1)		7(1)		6(1)		3(1)	
16	1	95(1)		−31(1)		0(1)		15(1)		0(1)		−11(1)	
	2	−77(1)		*		4(1)		0(1)		−10(1)		7(1)	

IV. REFINEMENTS

Refinements of the first-order harmonic parameters of the modulation functions were performed on the 243 independent satellite reflections measured by Marmeggi *et al.*[9] The computer program REMOS, written by Yamamoto, was used.[23,23] The average structure parameters could not be refined, because only satellite reflections were available. They were fixed at the values found in earlier investigations of the average structure alone ($x=0$, $y=0.1018$; $z=\frac{1}{4}$).[3] As pointed out in Sec. II, an analysis of the main reflections for the monoclinic and triclinic symmetries is only possible if measurements are performed on single crystals with different populations of the various domains. Zero-temperature factors were used, which should be a good approximation at the temperature of measurements (10 K).[9]

First, refinements in the centrosymmetric superspace groups were performed. Starting with a small offset of one of the parameters for the x component of the modulation function, and the remaining parameters zero, the R (reliability) factor converged to a minimum in 5 to 10 cycles. The reliability factor based on the square of the structure factors (R_{F^2}) was used for minimization. Refinements in the acentric superspace groups were performed, with the results of the refinement in the corresponding centrosymmetric group as initial values. Now, one of the parameters of u_x was kept zero to fix the phase of the modulation wave. (In the centrosymmetric groups the phase is fixed by the inversion center.) The convergence was slower, and 15 to 30 cycles were necessary to reach the final fit. All reliability factors for the final parameter sets are given in Table V. The values of the corresponding parameters are listed in Table IV.

From Table V it follows that a much better fit is obtained for the acentric superspace groups than for the centrosymmetric groups. Such an improvement could have

TABLE V. Reliability factors of the best fit of each of the symmetries. $R_F=\sum\big||F_c|-|F_0|\big|/\sum|F_0|$; $R_{F^2}=[(\sum|F_c-F_0|^2)/\sum F_0^2]^{1/2}$.

Superspace group	R_F (%)	R_{F^2} (%)
(1) $Pmcm(\frac{1}{2}\beta\gamma)$	9.5	10.6
(2) $P222_1(\frac{1}{2}\beta\gamma)$	6.5	7.1
(3) $Pmc2_1(\frac{1}{2}\beta\gamma)$	6.6	7.2
(4) $P2cm(\frac{1}{2}\beta\gamma)$	6.6	7.2
(5) $Pm2m(\frac{1}{2}\beta\gamma)$	6.6	7.2
(6) $P/2m11(\frac{1}{2}\beta\gamma)$	9.6	10.6
(7) $P211(\frac{1}{2}\beta\gamma)$	6.5	7.1
(8) $Pm11(\frac{1}{2}\beta\gamma)$	7.7	8.2
(9) $C12/c1(\alpha\beta\gamma)$	9.5	10.6
(10) $C121(\alpha\beta\gamma)$	6.6	7.2
(11) $C1c1(\alpha\beta\gamma)$	6.6	7.2
(12) $C112_1/m(\alpha\beta\gamma)$	9.5	10.6
(13) $C112_1(\alpha\beta\gamma)$	6.6	7.2
(14) $C11m(\alpha\beta\gamma)$	7.6	8.2
(15) $C\bar{1}(\alpha\beta\gamma)$	10.1	11.3
(16) $C1(\alpha\beta\gamma)$	7.0	8.1

its origin in an insufficient correction for extinction, where the extra structural parameters introduced by the loss of the centering then account for the extinction correction. However, it is supposed that the satellites are not much affected by extinction, because they are very weak.[17] We therefore have to conclude that the difference in R factor between centric and acentric groups is significant, although we do not want to entirely rule out the possibility of a centrosymmetric group.

The most striking result is that identical R factors are obtained for completely different structure models. For example, within the set of centrosymmetric groups, No. 9 $C12/c1(\alpha\beta\gamma)$ has only one independent atom, whereas No. 1 $Pmcm(\frac{1}{2}\beta\gamma)$ has two independent atoms, of which one has no displacement along x and of which the other has a displacement only along x (Table IV). The R factors of both parameter sets are identical (Table V). Analogous large differences in structure which give fits of the same quality are observed within the set of acentric groups.

The lowest R factor (best fit) is obtained for more than one structure model. It is therefore impossible to determine the correct symmetry from the structure refinements only. It is possible to rule out some of the superspace groups. First, it is noted that all differences observed in R_{F^2} (Table V) are significant by Hamilton's test on a level much better than 99%, except for the difference between 7.1% and 7.2%.[25] Moreover, all acentric groups involve 12 parameters of which 11 were varied in the refinement. Hence it is unlikely that the lower R factor of one model with respect to another is caused by systematic errors (e.g., extinction) in the intensity data. The conclusion is that these differences are structurally significant, and the superspace groups $8.Pm11(\frac{1}{2}\beta\gamma)$, $14.C11m(\alpha\beta\gamma)$, and $16.C1(\alpha\beta\gamma)$ can be ruled out as possibilities for the correct structure model. It is interesting that $Pm11(\frac{1}{2}\beta\gamma)$ was also ruled out by Walker on the basis of a Landau theory analysis of the phase transitions.[18] We are left with eight possible superspace groups.

The recently performed TEM experiments[16] indicate a Bravais class $P2m11(\frac{1}{2}\beta\gamma)$ (No. 1-3 in Ref. 15) for the incommensurate domains below $T=37$ K.[18] Together with the refinements presented here, this leads to the conclusion that the symmetry of this phase is $P211(\frac{1}{2}\beta\gamma)$, or $A^{P\frac{2}{1}}$ in the notation of Ref. 14. This superspace group is one with the lowest R factor (7.1%), although this difference with structure models with $R=7.2\%$ is thought of as insignificant. However, there is one other superspace group, No. 2 $P222_1(\frac{1}{2}\beta\gamma)$, with an equally low R factor. Table IV shows that $P222_1(\frac{1}{2}\beta\gamma)$ and $P211(\frac{1}{2}\beta\gamma)$ also result in the same values for the parameters, although the structure models are quite different. In $P222_1(\frac{1}{2}\beta\gamma)$ each parameter refers to a modulation function of the form $\cos(2\pi\bar{x}_4)\pm\cos(2\pi\bar{x}_5)$, whereas in $P211(\frac{1}{2}\beta\gamma)$ there are two different domains, one modulated according to $\cos 2\pi\bar{x}_4$ and another according to $\cos 2\pi\bar{x}_5$. Clearly, the refinement is not able to distinguish between those two models.

Marmeggi *et al.*[9] did a structure refinement on the same intensity data as used in this paper. The structure model used by those authors can be identified with the triclinic superspace groups used in this paper.[12,13] For the centrosymmetric group $C\bar{1}(\alpha\beta\gamma)$, we find the same R_F factor as in Ref. 9 (10%). However, Marmeggi *et al.*[9] fail to find an improvement of the fit for the acentric group, while we find a significant lowering of the R_F factor to 7.0% (Table V). We do not have an explanation for this discrepancy.

To compare our structure model for the $C\bar{1}(\alpha\beta\gamma)$ superspace group with the results of Marmeggi *et al.*,[9] we rewrite our results in the form

$$u_\alpha(\bar{x}_4)=\nu_\alpha\sin(2\pi\bar{x}_4+\psi_\alpha) \tag{11}$$

for the three components $\alpha=x,y,z$ of the modulation function. The values for $\nu_\alpha a_\alpha$ and ψ_α are given in Table VI, together with the results obtained by Marmeggi *et al.*[9] It follows that our refinement leads to the same phases as in Ref. 9 (ψ_α,ϕ_α), but that we find amplitudes which are only half as large. (The relative values of the amplitudes are the same as in Ref. 9.) We found that it was possible to obtain the same amplitudes with an identical R factor as in Table V by adjusting the scale of the satellites. In fact, the amplitudes were found exactly proportional to the scale factor. We do not know if the scale used in this paper [$F(004)=1$ per atom], which is supposed to be the same as published in Refs. 9 and 10, or the scale apparently used by Marmeggi *et al.*[9] is correct. If the latter should be correct, all amplitudes in Table IV have to be multiplied by two in order to obtain the correct values.

The refinement of Marmeggi *et al.*[9] and the one presented here for $C\bar{1}(\alpha\beta\gamma)$ seem to give the same fit (apart from the scale factor). However, Marmeggi *et al.*[9] report that their parameters refer to a cosine function, whereas we find the same values but now for a sine function. This discrepancy can be explained when it is assumed that the results of Marmeggi *et al.*[9] pertain to the presence of a $(3+1)$-dimensional symmetry operator $(i\,\bar{1}\,|\,000\frac{1}{2})$ in the origin. Centers of inversion of the three-dimensional (3D) modulated structure then are on lattice points $(x\,00)$ with $x=\pm1,\pm3,\pm5,\ldots$. The choice of origin used in this paper implies that 3D inversion centers occur on positions $(x\,00)$ with $x=0,\pm2,\pm4,\ldots$, i.e., there is a real 3D inversion center at the origin of the coordinate system.

TABLE VI. Final structural parameters for the triclinic superspace group $C\bar{1}(\alpha\beta\gamma)$. The values of this work are obtained from Table IV and $u_\alpha=\nu_\alpha\sin(2\pi\bar{x}_4+\psi_\alpha)$. The parameters obtained from Ref. 9 refer to a modulation function $u_\alpha=\varepsilon_\alpha\cos(2\pi\bar{x}_4+\phi_\alpha)$. a_α is the lattice parameter for $\alpha=x$, y, or z. Uncertainties are given within parentheses.

	This work		Ref. 9	
α	$\nu_\alpha a_\alpha$ (Å)	ψ_α (deg)	$\varepsilon_\alpha a_\alpha$ (Å)	ϕ_α (deg)
x	0.026	99	0.053(1)	99(3)
y	0.004	−25	0.009(1)	−24(5)
z	0.003	113	0.006(1)	118(10)

V. DISCUSSION

The various structure models have one aspect in common: the major part of the modulation is always found to be a displacement along the a axis (Table IV). An interesting point, raised by Marmeggi *et al.*,[9] is how the static modulation below 43 K relates to the symmetry of the deformation of the soft phonon observed at room temperature at wave vector $(\frac{1}{2},0,0)$ in the Σ_4 optical phonon branch.[6] The latter has opposite displacements along **a** of the two atoms at $\pm(0,y,\frac{1}{4})$ across the inversion center.[6] The soft phonon at $(\frac{1}{2},0,0)$ is commensurate, so that a corresponding static displacement will give a structure with the three-dimensional periodicity again. In particular, the inversion centers at the nodes of the original lattice are preserved. Therefore the two atoms across each lattice point at $\mathbf{L}\pm(0,y,\frac{1}{4})$ will always have opposite displacements. The static deformation found in the modulated phase below 43 K is incommensurate. In real space, only the periodicity along **a** is preserved. Then, the actual displacements of two atoms across a lattice point are not simply related. Due to the incommensurability, a unit cell can always be found in which the displacements of those atoms are opposite and one can be found in which the displacements are equal. A simple picture as given in Fig. 1 of Ref. 9 is therefore not sufficient to show the optic character of the displacement along x.

In fact, it is very difficult to determine the character of a phonon from the displacements of the atoms.[26] If we identify, as in Ref. 9, the optic phonon with a modulation function given by a sine, it follows that the displacements along x found in the centrosymmetric orthorhombic and a-axis unique monoclinic groups (Nos. 1 and 6) resemble the optic phonon displacements indeed, but the displacements in the other centrosymmetric superspace groups (Nos. 9, 12, and 15) are just 90° out of phase (Table IV). The superspace group No. 7 $P211(\frac{1}{2}\beta\gamma)$, which gives the symmetry of the incommensurate domains below 37 K, also has the major part of the displacement along x given by a sine function. This does not change when another parameter is kept zero in the refinement. For example, making the now largest parameter (Table IV) zero will cause the other atom to have the largest amplitude which again belongs to the sine part of the modulation function.

For other superspace groups, however, such a simple interpretation is not possible. For example, in No. 3 $Pmc2_1(\frac{1}{2}\beta\gamma)$, the choice of a different phase causes the large amplitude to move from the cosine part of the sine part of the modulation function (Table IV).

The TEM experiments[16] clearly show that the Bravais class for the incommensurate domains is $P2/m11(\frac{1}{2}\beta\gamma)$. This is at variance with the neutron scattering work of Lander and Mueller.[3] In those experiments, which involved the main reflections only, the extinction conditions of the group *Cmcm* were observed also below 37 K. For $P2/m11(\frac{1}{2}\beta\gamma)$ one should expect to find intensity both at the points forbidden by the C centering and at the points $(h\,0\,l\,0)$ with $l=$odd, forbidden by the original c glide. Reflections belonging to the latter set have not been observed until now, but reflections at positions forbidden by the C centering were found by Marmeggi *et al.*[19] In fact, those authors as well as Barrett *et al.*[2] observed those reflections already at room temperature, indicating that the room-temperature structure is also noncentered with the space group *Pmcm*.[19]

The 37- and 23-K transitions have not been observed in either x-ray or neutron scattering experiments. Measurements of the neutron diffraction as a function of temperature showed no abrupt changes in intensity or in positions of the reflections at those temperatures.[10] All detailed low-temperature scattering experiments have been performed well below 37 K. Data collection of the main reflection intensities in Ref. 3 have been done at 11 K, the satellites were measured in Ref. 9 at 10 K, and in Ref. 19 the temperature of measurement was 23 K. We can therefore safely assume that the analysis in this paper pertains to the state of the incommensurate domains below 37 K. It should be noted that the only reasonable explanation for the intensity ratio between the incommensurate and commensurate satellites is that the latter arise from domains that occupy much less volume than the incommensurate domains, although the TEM experiments suggest differently.

The 23-K transition is, according to TEM, related to the onset of the growth of incommensurate domains at the expense of the commensurate domains.[16] Therefore, one does not expect sudden changes within the set of incommensurate satellites, as is found indeed.[10] However, the transition at 37 K is related to a change within the incommensurate domains. TEM shows that each domain [e.g., $(\frac{1}{2},q_y,q_z)$] breaks up and that smaller portions of the other domain [e.g., $(\frac{1}{2},-q_y,q_z)$] start to grow within the first.[16] Unfortunately, Chen and Lander[16] do not give much details about these observations and also no photographs are published of this temperature region. A possible explanation for these observations is that they show a yet incomplete transition to a phase with an orthorhombic superspace group symmetry. For the $T<37$ K superspace group being $P211(\frac{1}{2}\beta\gamma)$, the most likely candidate for the $T>37$ K phase is the superspace group No. 2 $P222_1(\frac{1}{2}\beta\gamma)$. The fact that both $P211(\frac{1}{2}\beta\gamma)$ and $P222_1(\frac{1}{2}\beta\gamma)$ give fits to the scattering data of the same quality (Table V) then also explains why this phase transition is not observed in the neutron scattering intensities. Hysteresis for phase transitions involving modulations were recently observed in TEM for a number of other compounds,[27–29] and it appeared that the hysteresis can easily exceed 6 K, i.e., the whole existence region of the 37 $\mathrm{K}<\mathrm{T}<43$ K phase. For the 37-K transition in α-uranium a hysteresis of 3 K was observed in magnetic susceptibility measurements.[5] In this respect, it would be extremely interesting if TEM is done on lowering the temperature through the 43-K transition, instead of raising the temperature through the 37-K transition as in Ref. 16.

Another possibility for the symmetry of the 37 $\mathrm{K}<T<43$ K phase was recently proposed by Walker[18] on the basis of a Landau theory analysis. Based on the presumption that the 43-K transition is of second order and that the high-temperature symmetry is *Cmcm*, it was found that the only possibilities are modulations with also an incommensurate first component $(q_x\neq\frac{1}{2})$.[18] Tentative superspace group symbols are for example $Cmcm(\alpha\beta\gamma)$

(three-dimensional modulation) and $C2/m11(\alpha\beta\gamma)$ (two-dimensional modulation). The 37-K transition then is of the lockin type to the $P211(\frac{1}{2}\beta\gamma)$ symmetry. [Note that Walker cannot determine whether $P211(\frac{1}{2}\beta\gamma)$ or $P2/m11(\frac{1}{2}\beta\gamma)$ is the correct group, but that the Landau theory rules out $Pm11(\frac{1}{2}\beta\gamma)$ as possibility.[18]] The so-called a-axis incommensurate superspace groups all preserve the high-temperature C-centering. Such a recreation of the centering going through the 37-K transition is, however, not reported by Chen and Lander in their TEM experiments.[16] On the contrary, Marmeggi *et al.*[19] report an absence of the centering already at room temperature. Then, a second-order phase transition is possible to one of the noncentered orthorhombic groups (Nos. 1–5 in Table IV). The most crucial test of whether the $T > 37$ K symmetry is a-axis incommensurate or is given by $Pmcm(\frac{1}{2}\beta\gamma)$ or one of its acentric subgroups, is the measurement of the first component of the modulation wave vector. It should not be too difficult in x-ray or neutron scattering to determine whether q_x is exactly one-half or not. Again, it is important that the measurements be performed on a sample obtained by cooling and not on a sample obtained by heating.

A third possibility is that the domains found for $T > 37$ K remain large enough, so that the symmetry of the now smaller domains above 37 K is again given by $P211(\frac{1}{2}\beta\gamma)$.

Finally, we want to emphasize that for neither of the possibilities for the symmetry of the 37 K $< T <$ 43 K phase considered here, is there sufficient experimental evidence to support it.

VI. CONCLUSIONS

In this paper we have presented the results of refinements on the neutron scattering data of Marmeggi *et al.*,[9] of the structure models corresponding to the various possibilities for the superspace group symmetry of the incommensurate domains below 37 K. From the refinements only, it is not possible to select one symmetry as giving the best fit to the experimental data, although several possibilities are ruled out on the basis of the reliability factors (R factors). There are two superspace groups which lead to the lowest R_{F^2} factor, and there are six more groups which have a slightly but not significantly higher R factor (Table V).

Recently performed TEM experiments indicate a Laue symmetry of $2/m11$ for the incommensurate domains below 37 K, as well as an absence of the C centering.[16,18] Combined with the neutron diffraction refinements, this leads to the superspace group No. 7 $P211(\frac{1}{2}\beta\gamma)$ as the symmetry for the structure. The R-factor difference between $P211(\frac{1}{2}\beta\gamma)$ and $P2/m11(\frac{1}{2}\beta\gamma)$ is large and certainly significant. However, the structure determination involves only the satellites and not the main reflections, so that we do not want to entirely rule out $P2/m11(\frac{1}{2}\beta\gamma)$ as the possible correct symmetry. A new x-ray or neutron scattering experiment, which includes both satellites and main reflections, as well as a proper correction for absorption and secondary extinction, would therefore be extremely useful in determining the exact values of all the parameters. (The analysis of satellites only is not able to determine the changes in average structure parameters.)

The phase transition at 37 K, previously not observed in neutron scattering, is clearly seen in TEM.[16] Several models for the symmetry of this phase are discussed, neither of which is sufficiently supported nor challenged by the experiment. It is suggested that TEM of the 37 K $< T <$ 43 K phase, obtained by cooling through the 43-K transition, as well as an accurate determination of the first component of the modulation wave vector, can be helpful in determining the symmetry of this domain.

ACKNOWLEDGMENTS

We are greatly indebted to G. H. Lander for making the satellite intensities available. One of us (S.V.S.) thanks G. H. Lander for a very useful correspondence concerning the experiment on α-uranium. This research was supported by the Office of Naval Research, United States Navy and the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract No. F49620-86-C-0009.

*Present address: Laboratory of Inorganic Chemistry, University of Groningen, Nijenborgh 16, NL-9747 AG Groningen, The Netherlands.

[1]C. W. Jacob and B. E. Warren, J. Am. Chem. Soc. **59**, 2588 (1937).
[2]C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).
[3]G. H. Lander and M. H. Mueller, Acta Cryst. B **26**, 129 (1970).
[4]E. S. Fisher and H. J. McSkimmin, Phys. Rev. **124**, 67 (1961).
[5]M. O. Steinitz, C. E. Burleson, and J. A. Marcus, J. Appl. Phys. **41**, 5057 (1970).
[6]W. P. Crummet, H. G. Smith, R. M. Nicklow, and N. Wakabayashi, Phys. Rev. B **19**, 6028 (1979).
[7]H. G. Smith, N. Wakabayashi, W. P. Crummet, R. M. Nicklow, G. H. Lander, and E. S. Fisher, Phys. Rev. Lett. **44**, 1612 (1980).
[8]J. C. Marmeggi and A. Delapalme, Physica **102B**, 309 (1980).
[9]J. C. Marmeggi, A. Delapalme, G. H. Lander, C. Vettier, and N. Lehner, Solid State Commun. **43**, 577 (1982).
[10]H. G. Smith and G. H. Lander, Phys. Rev. B **30**, 5407 (1984).
[11]G. H. Lander, J. Magn. Magn. Mater. **29**, 271 (1982).
[12]S. van Smaalen, Ph.D. thesis, University of Groningen, 1985.
[13]S. van Smaalen and C. Haas, Solid State Commun. **55**, 1027 (1985).
[14]P. M. de Wolff, T. Janssen, and A. Janner, Acta Cryst. A **37**, 625 (1981).
[15]A. Janner, T. Janssen, and P. M. de Wolff, Acta Cryst. A **39**, 658 (1983).

[16]C. H. Chen and G. H. Lander, Phys. Rev. Lett. **57**, 110 (1986).
[17]G. H. Lander (private communication).
[18]M. B. Walker, Phys. Rev. B **34**, 6830 (1986).
[19]J. C. Marmeggi, E. Roudant, D. Fruchart, and P. Wolfers, Solid State Commun. **46**, 277 (1983).
[20]S. van Smaalen, Acta Cryst. A **43**, 202 (1987).
[21]The crystallographic convention $\mathbf{a}\cdot\mathbf{a}^*=1$ is used.
[22]W. van der Aalst, J. den Hollander, W. J. A. M. Peterse, and P. M. de Wolff, Acta Cryst. B **32**, 47 (1976).
[23]REMOS: a computer program for the refinement of modulated structures by Akiji Yamamoto, National Institute for Reseach in Inorganic Materials, Sakura-Mura, Niihari-Gun, Ibaraki, Japan 1982 (unpublished).
[24]Akiji Yamamoto, Acta Cryst. A **38**, 87 (1982).
[25]W. C. Hamilton, Acta Cryst. **18**, 502 (1965).
[26]O. Madelung, *Introduction to Solid State Theory* (Springer, Berlin, 1978).
[27]K. K. Fung, J. Phys. C **18**, L489 (1985).
[28]J. Mahy, J. Van Landuyt, S. Amelinckx, Y. Uchida, K. D. Bronsema, and S. Van Smaalen, Phys. Rev. Lett. **55**, 1188 (1985).
[28]H. Bestgen, Solid State Commun. **58**, 197 (1986).