Modulated phases of α-uranium: Theoretical considerations

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The modulated phases of α-uranium consistent with a Landau-type theory are described in detail and analyzed in terms of their superspace symmetry. It is suggested that the phase transition at 43 K is to a phase which is incommensurate both parallel and perpendicular to the a axis, that the phase transition at 37 K is to a phase which is commensurate along the a axis but incommensurate in a perpendicular direction, and that the transition at 23 K is to a purely commensurate phase.

I. INTRODUCTION

The observation by neutron diffraction of weak satellites near $\mathbf{q}=(\pm\frac{1}{2},0,0)$ by Smith *et al.*[1] and of stronger satellites at $\mathbf{q}=(\pm\frac{1}{2},\pm\beta,\pm\gamma)$ (where β and γ are nonzero) by Marmeggi and Delapalme[2] indicate that the phase transition discovered at 43 K in C-centered orthorhombic α-uranium by Fisher and McSkimin[3] is due to the appearance of a modulation of the basic structure. Lander[4] has given a detailed review of these and related works.

In a measurement of the atomic displacements associated with the $\mathbf{q}=(\pm\frac{1}{2},\pm\beta,\pm\gamma)$ reflections Marmeggi *et al.*[5] assumed that the modulated phase was a single-$\mathbf{q}$ state and that a given crystal contained equal populations of the four single-$\mathbf{q}$ domains [the four domains correspond to $\mathbf{q}=\pm(\frac{1}{2},\beta,\gamma)$, $\pm(\frac{1}{2},-\beta,\gamma)$, $\pm(\frac{1}{2},-\beta,-\gamma)$, and $\pm(\frac{1}{2},\beta,-\gamma)$]. However, Smith and Lander[6] have raised the possibility that the modulated phase might be a multi-$\mathbf{q}$ state and van Smaalen and Haas[7] and van Smaalen[7] claim to have given, by making use of superspace groups,[8–10] "a complete list of all possibilities along with their consequences for the structure." They[7] have also identified a preferred possibility [$Pmcm(\frac{1}{2}\beta\gamma)$] for the modulated structure of α-uranium; their preferred possibility is, in the language of this paper, a quadruple-$\mathbf{q}$ state.

It is important to note that there are three, and not just one, low-temperature phase transitions in α-uranium (at temperatures of 43, 37, and 23 K) as shown by the thermal expansion measurements of Steinitz *et al.*[11] Thus, to fully understand the modulated phases of α-uranium, one must understand the differences between the modulated phases in each of the three temperature regions.

Very recently, Chen and Lander[12] have performed electron microscopy studies which have clearly identified different coexisting phases in α-uranium; this coexistence of different phases, indicating that the phase transitions do not go to completion, is at least part of the reason a detailed understanding of the modulated phases has been difficult to obtain. Chen and Lander find that below 23 K the nearly commensurate phase [a phase which gives diffraction at wave vectors close to $\mathbf{q}=(\frac{1}{2},0,0)$ but not at the incommensurate wave vectors] grows at the expense of the incommensurate phase. Furthermore, they find that the incommensurate phases which occur between 23 and 37 K and between 37 and 43 K are $2-\mathbf{q}$ states (in the language of this paper), which would appear to rule out the preferred state of van Smaalen and Haas[7] as being the explanation of either of the incommensurate phases.

This paper develops a Landau-type theoretical model for the incommensurate phases. This approach not only allows an identification of a number of possible different modulated phases, but also gives information on the phase changes which might be expected as a function of temperature. For example, the model allows a second-order phase transition to various modulated phases described by $\mathbf{q}=(\pm\alpha,\pm\beta,\pm\gamma)$; in general there is no reason for α to equal one-half immediately below the second-order phase transition temperature, although a phase transition from a state with $\alpha\neq\frac{1}{2}$ to one with $\alpha=\frac{1}{2}$ is predicted to occur at lower temperatures for certain model parameters and is thus a possibility for the transition at 37 K.

The work of van Smaalen and Haas,[7] which is based on symmetry considerations only, describes in addition to some of the phases obtained here, phases which I have not obtained. This is not surprising, since a Landau theory adds restrictions due to energetic considerations to the requirements of symmetry. On the other hand, I find a number of phases not described by them, which is surprising in view of their claim to have given a "complete list of all possibilities."

The satellites found by Smith *et al.*[1] close to $\mathbf{q}=(\pm\frac{1}{2},0,0)$ occur at positions $((h+\frac{1}{2})(1-\delta),k,l)$, i.e., they have the unusual property of appearing to be reflections from a lattice with a lattice constant a_s, which is slightly larger than twice the fundamental lattice constant a_0; also, the space-group symmetry of the superlattice was found to be $Pmnm$. Smith *et al.*[1] rejected the idea that the superlattice peaks which they observed represented a new phase which occupied a small fraction of the total sample volume because high-resolution scans of the fundamental Bragg peaks failed to detect evidence for the two sets of Bragg peaks which would be expected for two coexisting phases. Instead, they[1,4] attributed the shift of the satellite positions from $\mathbf{q}=(\pm\frac{1}{2},0,0)$ to the presence of discommensurations. In this article, I examine the commensurate phases resulting from a Σ_4 normal-mode distortion for which $\mathbf{q}=(\frac{1}{2},0,0)$ and show that one of the two possible phases has space-group symmetry $Pmnm$ in

agreement with that observed. This observation coupled with the electron microscopic observations of Chen and Lander[12] (of nearly commensurate phase domains embedded in the incommensurate phase) mentioned above support the conclusion that the satellites near $\mathbf{q}=(\frac{1}{2},0,0)$ represent scattering from commensurate phase domains embedded in incommensurate phase material having a slightly different average lattice constant.

Two shortcomings of this article are that we have ignored the possibility that "the structure [of α-uranium] at room temperature may be non centered,"[13] and that we have ignored the striations observed by Chen and Lander.[12]

Sections II–IV of this article are devoted to a discussion of the incommensurate phases which produce satellites at $\mathbf{q}=(\pm\alpha,\pm\beta,\pm\gamma)$, Sec. V describes the relevant commensurate phases which produce satellites at $\mathbf{q}=(\pm\frac{1}{2},0,0)$, and some conclusions are noted in Sec. VI.

II. SYMMETRY CONSIDERATIONS AND FREE ENERGY FOR THE INCOMMENSURATE PHASES

Basal-plane projections of the C-centered orthorhombic structure of α-uranium and of the associated Brillouin zone are shown in Figs. 1(a) and 1(b).

The wave vectors $\mathbf{q}_j$ $(j=1,2,3,4)$ are defined by

$$\begin{aligned}&\mathbf{q}_1=(\alpha,\beta,\gamma),\quad \mathbf{q}_2=(\alpha,-\beta,\gamma)\ ,\\ &\mathbf{q}_3=(\alpha,-\beta,-\gamma),\quad \mathbf{q}_4=(\alpha,\beta,-\gamma)\ ,\end{aligned}\tag{2.1}$$

where $(\alpha,\beta,\gamma)\equiv\alpha\mathbf{a}^*+\beta\mathbf{b}^*+\gamma\mathbf{c}^*$. At temperatures below 43 K, diffraction experiments have observed[2] satellites

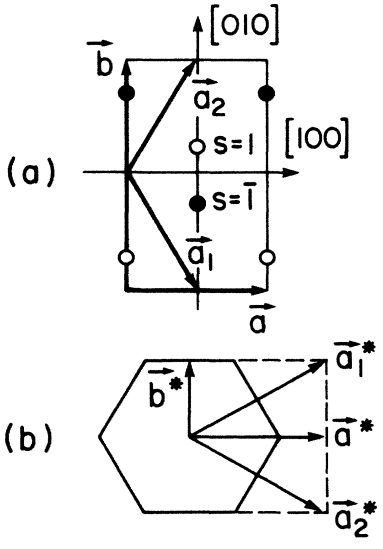

FIG. 1. (a) Basal plane projection of the C-centered orthorhombic unit cell of the α-uranium structure. The vectors $\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3$ and $\mathbf{a},\mathbf{b},\mathbf{c}$ are basis vectors describing the primitive and conventional unit cells, respectively; the vectors $\mathbf{a}_3=\mathbf{c}$ are normal to the plane of the paper. The open and solid circles represent uranium ions in the planes $z=c/4$ and $z=-c/4$, respectively. (b) Basal plane projection of the Brillouin zone showing various reciprocal lattice vectors; $\mathbf{a}_3^*=\mathbf{c}^*$ is normal to the plane of the paper.

with wave vectors $\mathbf{q}_j$ relative to the α-uranium reciprocal-lattice vectors. The parameter $\alpha=\frac{1}{2}$ to within experimental error.

The form of the normal-mode distortion for a given $\mathbf{q}_j$ has been determined by Marmeggi *et al.*[5] However, it is important for this work to establish definitions which relate the normal modes with different $\mathbf{q}_j$ to one another and to show how the different normal modes transform into one another under the operations of the space group *Cmcm* (D_{2h}^{17}).

The column vectors

$$e(\mathbf{q},s,\alpha)=N^{-1/2}\sum_l e^{i\mathbf{q}\cdot\mathbf{R}(l,s)}e(l,s,\alpha)\tag{2.2}$$

are a convenient set of basis vectors for a description of the normal modes of wave vector $\mathbf{q}$. Here l labels the particular primitive unit cell, s [$=1$ or $\bar{1}$, see Fig. 1(a)] labels the two atoms in the primitive unit cell, and $\alpha=x,y$ or z. $\mathbf{R}(l,s)$ is the position of the atom labeled by l and s, and $e(l,s,\alpha)$ is a column vector with unity in the row labeled by (l,s,α) and zero elsewhere; the crystal is assumed to contain N unit cells, so all column vectors have $N\times2\times3$ rows. In a translation of the crystal by a Bravais lattice vector $\mathbf{R}(l)=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3$, these basis vectors transform according to

$$\{E\mid\mathbf{R}(l)\}e(\mathbf{q},s,\alpha)=e^{-i\mathbf{q}\cdot\mathbf{R}(l)}e(\mathbf{q},s,\alpha)\ .\tag{2.3}$$

The basic normal-mode eigenvectors for this work are defined to be

$$\begin{aligned}e(\mathbf{q}_1^0)&=i\sum_\alpha a_\alpha[e^{i\theta_\alpha}e(\mathbf{q}_1^0,1,\alpha)+e^{-i\theta_\alpha}e(\mathbf{q}_1^0,\bar{1},\alpha)]\ ,\\ e(\mathbf{q}_2^0)&=-i\sum_\alpha(\sigma_y a_\alpha)[e^{-i\theta_\alpha}e(\mathbf{q}_2^0,1,\alpha)+e^{i\theta_\alpha}e(\mathbf{q}_2^0,\bar{1},\alpha)]\ ,\\ e(\mathbf{q}_3^0)&=-i\sum_\alpha(C_{2x}a_\alpha)[e^{-i\theta_\alpha}e(\mathbf{q}_3^0,1,\alpha)+e^{i\theta_\alpha}e(\mathbf{q}_3^0,\bar{1},\alpha)]\ ,\\ e(\mathbf{q}_4^0)&=i\sum_\alpha(\sigma_z a_\alpha)[e^{i\theta_\alpha}e(\mathbf{q}_4^0,1,\alpha)+e^{-i\theta_\alpha}e(\mathbf{q}_4^0,\bar{1},\alpha)]\ .\end{aligned}\tag{2.4}$$

Here the $\mathbf{q}_j^0$ are given by Eq. (2.1) with $\alpha=\frac{1}{2}$ and the a_α and θ_α are real. Also $\sigma_y(a_x,a_y,a_z)=(a_x,-a_y,a_z)$, $C_{2x}(a_x,a_y,a_z)=(a_x,-a_y,-a_z)$, and $\sigma_z(a_x,a_y,a_z)=(a_x,a_y,-a_z)$.

The transformation properties of the eigenvectors under a set of generators of the space group *Cmcm* are

$$\begin{aligned}&\{I\mid\mathbf{0}\}e(\mathbf{q}_j^0)=e^*(\mathbf{q}_j^0)\ ,\\ &\{C_{2x}\mid\mathbf{0}\}e(\mathbf{q}_j^0)=-e(C_{2x}\mathbf{q}_j^0)\ ,\\ &\{\sigma_z\mid\tfrac{1}{2}\mathbf{c}\}e(\mathbf{q}_j^0)=\exp(i\mathbf{q}_j^0\cdot\mathbf{c}/2)e(\sigma_z\mathbf{q}_j^0)\ .\end{aligned}\tag{2.5}$$

Since the little group of a given wave vector $\mathbf{q}_j^0$ contains only the identity element, only time-reversal symmetry restricts the form of the eigenvectors. The consequences of time-reversal symmetry are reflected in the first of Eqs. (2.5), which fixes the phases of the eigenvectors. The four eigenvectors $e(\mathbf{q}_j^0)$ together with their complex conjugates, form a basis of an irreducible corepresentation of *Cmcm*.

In this work, I consider distortions from the basic α-uranium structure which have the form of a liner com-

bination of the normal modes given in Eq. (2.4). The distorted state is specified in terms of the column vector

$$u=\mathrm{Re}\left[\sum_{j=1}^{4}\psi_j(\mathbf{r})e(\mathbf{q}_j^0)\right], \tag{2.6}$$

where the order parameter $\psi_j(\mathbf{r})$ is a complex slowly varying function of $\mathbf{r}$ to be determined. The atomic displacements $u(l,s,\alpha)$ for the state described by Eq. (2.6) are found by taking the scalar product of $e(l,s,\alpha)$ with u and evaluating the result at $\mathbf{r}=\mathbf{R}(l,s)$. For example, in a case considered below, $\psi_j(\mathbf{r})$ has the form

$$\psi_j(\mathbf{r})=|\psi_j|e^{i(\mathbf{p}\cdot\mathbf{r}+\phi_j)}, \tag{2.7}$$

and the αth component of the displacement of atom (l,s) is given by

$$\begin{aligned}u(l,s,\alpha)=a_\alpha|\psi_1|\cos[\mathbf{q}_1\cdot\mathbf{R}(l,s)+s\theta_\alpha+\tfrac{1}{2}\pi+\phi_1]+(\sigma_y a_\alpha)|\psi_2|\cos[\mathbf{q}_2\cdot\mathbf{R}(l,s)-s\theta_\alpha-\tfrac{1}{2}\pi+\phi_2]\\ +(C_{2x}a_\alpha)|\psi_3|\cos[\mathbf{q}_3\cdot\mathbf{R}(l,s)-s\theta_\alpha-\tfrac{1}{2}\pi+\phi_3]+(\sigma_z a_\alpha)|\psi_4|\cos[\mathbf{q}_4\cdot\mathbf{R}(l,s)+s\theta_\alpha+\tfrac{1}{2}\pi+\phi_4]\end{aligned} \tag{2.8}$$

where, as above, s is 1 or $\bar{1}\equiv-1$ and

$$\mathbf{q}_j=\mathbf{q}_j^0+\mathbf{p}\,. \tag{2.9}$$

Given Eq. (2.6) and the transformation properties [Eq. (2.5)] of the normal-mode eigenvectors, the transformation properties of the order parameter can be determined (for example, under the inversion operation $\{I\,|\,\mathbf{0}\}$, $\psi_j\rightarrow\psi_j^*$). The Ginzberg-Landau free-energy density which must be invariant with respect to the transformations of the *Cmcm* space group, can now be shown to be

$$\begin{aligned}F=&\sum_{j=1}^{4}\psi_j^*(\mathbf{r})A_j(-i\nabla)\psi_j(\mathbf{r})+B_1\left[\sum_{j=1}^{4}|\psi_j|^2\right]^2+B_2(|\psi_1|^2|\psi_3|^2+|\psi_2|^2|\psi_4|^2)\\ &+B_3(|\psi_1|^2|\psi_2|^2+|\psi_3|^2|\psi_4|^2)+B_4(|\psi_1|^2|\psi_4|^2+|\psi_2|^2|\psi_3|^2)+\tfrac{1}{2}B_5(\psi_1\psi_3\psi_2^*\psi_4^*+\text{c.c.})\\ &+\tfrac{1}{4}C[(\psi_1^2\psi_3^2+\psi_2^2\psi_4^2)+\text{c.c.}]+\tfrac{1}{2}D(\psi_1\psi_2\psi_3\psi_4+\text{c.c.})\,,\end{aligned} \tag{2.10}$$

where c.c. stands for the complex conjugate of the other terms inside the same bracket.

The quantities $A_j(\mathbf{p})$ are assumed to have their minimum at $\mathbf{p}=\delta\mathbf{a}^*$, independent of j. Furthermore, at temperatures T close to the assumed second-order phase-transition transition temperature $T_c\approx 43$ K, A_j will be assumed to vary as

$$A_j(\delta\mathbf{a}^*)=k(T-T_c)\,, \tag{2.11}$$

where k is a positive constant. Thus, just below the transition temperature, the distorted state will be characterized by an order parameter of the form of Eq. (2.7) (some of the $|\psi_j|$'s may be zero) and wave vectors of the form given by Eq. (2.9) with $\mathbf{p}=\delta\mathbf{a}^*$; i.e., the $\mathbf{q}$'s have the form given by Eq. (2.1) with $\alpha=\frac{1}{2}+\delta$. In all experiments to date, α was found to be $\frac{1}{2}$ to within experimental error. However, there is no symmetry argument which requires δ to be zero; therefore it must be assumed to be nonzero.

III. POSSIBLE MODULATED STATES OF α-URANIUM

As pointed out at the end of the preceding section, immediately below the transition temperature T_c the order parameter has the form given by Eq. (2.7), with one or more of the $|\psi_j|$'s nonzero, and the modulation is characterized by the wave vectors $\mathbf{q}_j$ of Eq. (2.1) with $\alpha=\frac{1}{2}+\delta$ and $\delta\neq 0$. Since $\delta\neq 0$, these states are incommensurate in the **a**-axis direction. For such states the terms proportional to C and D in the free-energy density of Eq. (2.10) give zero contribution to the free energy, since they average to zero when integrated over the entire crystal. On the other hand, if states for which ψ_j is independent of $\mathbf{r}$ are considered, i.e., states characterized by wave vectors $\mathbf{q}_j^0$ which are commensurate in the **a**-axis direction, it can be shown that the terms in C and D give a negative contribution to the free energy if the relative phases of the ψ_j are appropriately chosen. When the temperature is lowered sufficiently below T_c, the fourth-order terms in the free energy have the dominant effect in determining the equilibrium state, and one can show that for appropriately chosen values of the model parameters (the B_i's, C, and D) a phase transition to an **a**-axis commensurate state can occur so as to take advantage of the terms in C or D (or both) in the free energy.

A. {1}, {2}, {3}, and {4} a-axis incommensurate states

The parameter B_1 will always be assumed to be sufficiently positive to assure an absolute minimum of the free energy with bounded $|\psi_j|$'s. If, in addition to $B_1>0$, the parameters B_2, B_3, and B_4 are positive, and B_5 is sufficiently small, the minimum free energy is obtained when only one of the $|\psi_j|$'s is nonzero. Such a state is called a single-$\mathbf{q}$ state and is denoted by {1}, {2}, {3}, or {4}, depending on whether ψ_1, ψ_2, ψ_3, or ψ_4 is nonzero. The single-$\mathbf{q}$ states must always be **a**-axis incommensurate because the terms in C and D in the free energy which stabi-

lize the **a**-axis commensurate phases do not exist if only a single ψ_j is nonzero.

B. {1,3} and {2,4} states

A {1,3} state has ψ_1 and ψ_3 nonzero and $\psi_2=\psi_4=0$. An **a**-axis incommensurate {1,3} state can be shown to give the minimum free energy if $B_2<0$, $B_3>0$, $B_4>0$, B_5 is sufficiently small, and T is sufficiently close to T_c; the minimum occurs for ψ_1 and ψ_3 having equal magnitudes, i.e., $|\psi_1|=|\psi_3|$; as always for **a**-axis incommensurate states the **r** dependence of ψ_j is given by Eq. (2.7) with $\mathbf{p}=\delta\mathbf{a}^*$. The phases ϕ_j of ψ_j [see Eq. (2.7)] are undetermined by the free energy and will be written $\phi_1=-\mathbf{q}_1^0\cdot\mathbf{r}_0$ and $\phi_3=-\mathbf{q}_3\cdot\mathbf{r}_0$ where the vector $\mathbf{r}_0$ is restricted to lie in the plane containing $\mathbf{q}_1$ and $\mathbf{q}_3$; note that $\mathbf{r}_0$ thus has only two independent components corresponding to the two independent phases ϕ_1 and ϕ_3. When the phases ϕ_j are written as $\phi_j=-\mathbf{q}_j\cdot\mathbf{r}_0$, the arguments of the cosine functions in Eq. (2.8) can be seen to contain the terms $\mathbf{q}_j\cdot[\mathbf{R}(l,s)-\mathbf{r}_0]$, thus showing that a change in the vector $\mathbf{r}_0$ by an amount $\delta\mathbf{r}_0$ corresponds to a translation of the modulation pattern by $\delta\mathbf{r}_0$. An identical interpretation of $\mathbf{r}_0$ applies to all cases considered below. The {2,4} state is defined in an analogous manner and is degenerate with the {1,3} state.

The term in C in the free-energy density can stabilize the **a**-axis commensurate {1,3} state at temperatures sufficiently below T_c. For this state the ψ_j ($j=1,3$) are given by Eq. (2.6) with $\mathbf{p}=0$, the ψ_j for $j=3,4$ are zero, and the free energy contains a term proportional to

$$C\,|\psi_1|^2\,|\psi_3|^2\cos2(\phi_1+\phi_3)\ . \tag{3.1}$$

If $C<0$, the minimum of Eq. (3.1) is obtained for $\phi_1+\phi_3=n\pi$ with n an integer whereas for $C>0$, $\phi_1+\phi_3=(n+\frac{1}{2})\pi$. For representative states for each case, I make the following choices: for case (i),

$$\begin{aligned} &C<0,\ \ \phi_1+\phi_3=0\ ,\\ &\phi_1=-\mathbf{q}_1\cdot\mathbf{r}_0,\ \ \phi_3=-\mathbf{q}_3^0\cdot\mathbf{r}_0\ , \end{aligned} \tag{3.2}$$

and for case (ii),

$$\begin{aligned} &C>0,\ \ \phi_1+\phi_3=\tfrac{1}{2}\pi\ ,\\ &\phi_1=\tfrac{1}{2}\pi-\mathbf{q}_1^0\cdot\mathbf{r}_0,\ \ \phi_3=-\mathbf{q}_3^0\cdot\mathbf{r}_0\ . \end{aligned} \tag{3.3}$$

Here, $\mathbf{r}_0$ is taken to be a one-dimensional vector parallel to $\mathbf{d}^*\equiv\beta\mathbf{b}^*+\gamma\mathbf{c}^*$ (for comparison recall $\mathbf{q}_1^0=\frac{1}{2}\mathbf{a}^*+\mathbf{d}^*$ and $\mathbf{q}_3^0=\frac{1}{2}\mathbf{a}^*-\mathbf{d}^*$). That $\mathbf{r}_0$ has only one component is consistent with the fact that $\phi_1+\phi_3=$const so that there is only one independent phase. Furthermore, note that $\mathbf{r}_0$ cannot have an $\mathbf{a}^*$ component (since $\phi_1+\phi_3=$const) and that any component of $\mathbf{r}_0$ perpendicular to both $\mathbf{a}^*$ and $\mathbf{d}^*$ does not enter Eqs. (3.3) and thus need not be considered. The atomic displacements are given by Eq. (2.8) with $\mathbf{q}_j$ replaced by $\mathbf{q}_j^0$ since this state is **a**-axis commensurate.

C. The {1,2} and {3,4} states

The {1,2} state has $\psi_j\neq0$, $j=1,2$ and $\psi_j=0$, $j=3,4$. It is always **a**-axis incommensurate since there is no term in the free energy which would stabilize an **a**-axis commensurate state. The two independent phases are written $\phi_j=-\mathbf{q}_j\cdot\mathbf{r}_0$, $j=1,2$ where $\mathbf{r}_0$ is confined to the plane containing both $\mathbf{q}_1$ and $\mathbf{q}_2$. The {3,4} state is degenerate with the {1,2} state. These are the lowest energy **a**-axis incommensurate states if $B_3<0$, $B_2>0$, $B_4>0$, and B_5 is sufficiently small.

D. The {1,4} and {2,3} states

The {1,4} state is always **a**-axis incommensurate, has phases $\phi_j=-\mathbf{q}_j\cdot\mathbf{r}_0$, $j=1,4$ (where $\mathbf{r}_0$ lies in the plane containing $\mathbf{q}_1$ and $\mathbf{q}_4$) and is degenerate with the {2,3} state. These are the lowest energy **a**-axis incommensurate states if $B_4<0$, $B_2>0$, $B_3>0$, and B_5 is sufficiently small.

E. The {1,2,3,4} states

The {1,2,3,4} states have $\psi_j\neq0$ for all j. It can be shown that a minimum of the free energy is obtained for the case where the magnitude of ψ_j, $|\psi_j|$, is independent j, and model parameters can be found for which this is an absolute minimum. The free energy for an **a**-axis incommensurate state contains the term

$$B_5\,|\psi_1\psi_2\psi_3\psi_4|\cos(\phi_1+\phi_3-\phi_2-\phi_4)\ . \tag{3.4}$$

If $B_5<0$, the minimum of Eq. (3.4) is obtained for

$$\phi_1+\phi_3=\phi_2+\phi_4+2n\pi\ ,$$

whereas for $B_5>0$,

$$\phi_1+\phi_3=\phi_2+\phi_4+(2n+1)\pi\ .$$

For representative states for each case, I make the following choices: for case (i),

$$B_5<0,\ \ \phi_j=-\mathbf{q}_j\cdot\mathbf{r}_0\ , \tag{3.5}$$

and for case (ii),

$$\begin{aligned} &B_5>0,\ \ \phi_j=\mathbf{q}_j\cdot\mathbf{r}_0\ \text{ if } j\neq1\ ,\\ &\phi_1=\pi-\mathbf{q}_j\cdot\mathbf{r}_0\ . \end{aligned} \tag{3.6}$$

Here $\mathbf{r}_0$ is a three-dimensional vector and its three independent components correspond to the fact that there are three independent phases.

The free energy for the **a**-axis commensurate states contains a term proportional to

$$\begin{aligned} &B_5\cos(\phi_1+\phi_3-\phi_2-\phi_4)+D\cos(\phi_1+\phi_2+\phi_3+\phi_4)\\ &\qquad+\tfrac{1}{2}C\{\cos[2(\phi_1+\phi_3)]+\cos[2(\phi_2+\phi_4)]\}\ . \end{aligned} \tag{3.7}$$

A minimization of this term with respect to the phases yields the following possible minima: Case (i),

$$\phi_1+\phi_3=(m+n)\pi,\ \ \phi_2+\phi_4=(n-m)\pi\ ; \tag{3.8a}$$

case (ii),

$$\phi_1+\phi_3=(n+m+1)\pi,\ \ \phi_2+\phi_4=(n-m)\pi\ ; \tag{3.8b}$$

case (iii),

$$\phi_1+\phi_3=(n+m+\tfrac{1}{2})\pi,\ \ \phi_2+\phi_4=(n-m+\tfrac{1}{2})\pi\ ; \tag{3.8c}$$

case (iv),

$$\phi_1+\phi_3=(n+m+\tfrac{1}{2})\pi,\quad \phi_2+\phi_4=(n-m-\tfrac{1}{2})\pi\ . \tag{3.8d}$$

Here n and m are integers. For $B_5>0$, Fig. 2 shows the region of stability of the different cases. As representative states for each case, I make the following choices: For case (i):

$$\phi_j=-\mathbf{q}_j^0\cdot\mathbf{r}_0\ . \tag{3.9a}$$

For case (ii):

$$\phi_1=\pi-\mathbf{q}_1^0\cdot\mathbf{r}_0;\quad \phi_j=-\mathbf{q}_j^0\cdot\mathbf{r}_0,\quad j\neq 1\ . \tag{3.9b}$$

For case (iii):

$$\begin{aligned}&\phi_j=\tfrac{1}{2}\pi-\mathbf{q}_j^0\cdot\mathbf{r}_0,\quad j=1,2\ ;\\ &\phi_j=-\mathbf{q}_j^0\cdot\mathbf{r}_0,\quad j=3,4\ .\end{aligned} \tag{3.9c}$$

For case (iv):

$$\begin{aligned}&\phi_1=\tfrac{1}{2}\pi-\mathbf{q}_1^0\cdot\mathbf{r}_0,\quad \phi_2=-\tfrac{1}{2}\pi-\mathbf{q}_2^0\cdot\mathbf{r}_0\ ;\\ &\phi_j=-\mathbf{q}_j^0\cdot\mathbf{r}_0,\quad j=3,4\ .\end{aligned} \tag{3.9d}$$

It follows from Eq. (3.8) that $\mathbf{r}_0$ must be perpendicular to $\mathbf{a}^*$; its two independent components correspond to the fact that there are two independent phases.

States with exactly three ψ_j not equal to zero could conceivably play a role in the properties of α-uranium. My (incomplete) investigations did not find any set of model parameters for which such states gave an absolute minimum of the free energy and they are thus not considered in this article. A complete investigation of these states is hampered by the fact that the three ψ_j will have unequal magnitudes.

IV. SUPERSPACE-GROUP SYMMETRY OF THE MODULATED STATES

For all of the modulated structures considered in the preceding section, the phase ϕ_j of Eq. (2.7) is written in the form

$$\phi_j=\phi_{j0}-\mathbf{q}_j\cdot\mathbf{r}_0\ . \tag{4.1}$$

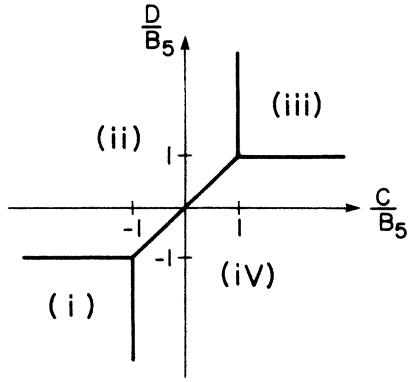

FIG. 2. The regions of stability of the four different {1,2,3,4} a-axis commensurate phases are shown.

The state vector u of Eq. (2.6) then has the form

$$u(\mathbf{r}_0)=\mathrm{Re}\left[\sum_j|\psi_j|e^{i(\phi_{j0}-\mathbf{q}_j\cdot\mathbf{r}_0)}e(\mathbf{q}_j)\right], \tag{4.2}$$

where the $\mathbf{a}^*$ component of the $\mathbf{q}_j$ is $\alpha\neq\frac{1}{2}$ for the a-axis incommensurate states and $\alpha=\frac{1}{2}$ for the a-axis commensurate states. The free energy is independent of $\mathbf{r}_0$ and a change of $\mathbf{r}_0$ by $\delta\mathbf{r}_0$ corresponds to a displacement of the modulation by $\delta\mathbf{r}_0$.

By operating on $u(\mathbf{r}_0)$ with one of the elements $\{P\mid\mathbf{w}\}$ of the space group *Cmcm* and using Eq. (2.5), one obtains a new-state vector describing a state with the same energy. If this new state is the same as the old state except for a change of $\mathbf{r}_0$, the two states will be said, for the purposes of this article, to be the same state. Thus, in looking for transformations which leave the state invariant, one looks for transformations which satisfy

$$\{P\mid\mathbf{w}\}u([P\mid\mathbf{v}]^{-1}\mathbf{r}_0)=u(\mathbf{r}_0)\ . \tag{4.3}$$

Here, the new $\mathbf{r}_0$ is written in the form of the inverse of a Seitz space-group operator operating on $\mathbf{r}_0$; square brackets and curly brackets distinguish Seitz operators operating on $\mathbf{r}_0$ and on the basis vectors $e(\mathbf{q}_i)$, respectively. The set of transformations satisfying Eq. (4.3) form a group called the superspace group of the structure,[8-10] and the element of the group corresponding to the transformation of Eq. (4.3) is written

$$g=(\{P\mid\mathbf{w}\},[P\mid\mathbf{v}])\ , \tag{4.4}$$

so that

$$\begin{aligned}gu(\mathbf{r}_0)&=(\{P\mid\mathbf{w}\},[P\mid\mathbf{v}])u(\mathbf{r}_0)\\ &\equiv\{P\mid\mathbf{w}\}u([P\mid\mathbf{v}]^{-1}\mathbf{r}_0)\ .\end{aligned} \tag{4.5}$$

The result of applying first transformation g_1 and then transformation g_2 is

$$g_2g_1=(\{P_2\mid\mathbf{w}_2\}\{P_1\mid\mathbf{w}_1\},[P_2\mid\mathbf{v}_2][P_1\mid\mathbf{v}_1])\ . \tag{4.6}$$

Because

$$([P_2\mid\mathbf{w}_2][P_1\mid\mathbf{v}_1])^{-1}=[P_1\mid\mathbf{v}_1]^{-1}[P_2\mid\mathbf{v}_2]^{-1}\ ,$$

the use of the inverse operator $[P\mid\mathbf{v}]^{-1}$ in the definition of Eq. (4.5) achieves in a natural way the correct result that in two successive transformations, the transformation operators are applied to $\mathbf{r}_0$ in reverse order.

The analysis of this section allows a comparison of my results with those of van Smaalen and Haas[7] and also allows a description of the different domains having the same energy for a given modulated phase.

In this Sec. I follow the ideas of superspace groups of de Wolff, Janner, and Janssen[8-10] but with a notation adapted to the needs of this article.

A. {1,2,3,4} a-axis incommensurate states

For the {1,2,3,4} a-axis incommensurate states, $\mathbf{r}_0$ is a three-dimensional vector. Also note that the vectors

$$\mathbf{b}_1^*\equiv\mathbf{q}_1,\quad \mathbf{b}_2^*\equiv-\mathbf{q}_4,\quad \mathbf{b}_3^*\equiv\mathbf{q}_3\ , \tag{4.7}$$

form a basis of a body-centered orthorhombic lattice in reciprocal space of which the face-centered orthorhombic direct lattice has the basis

$$\mathbf{b}_1=\frac{1}{2}\left[\frac{\mathbf{a}}{\alpha}+\frac{\mathbf{b}}{\beta}\right],$$
$$\mathbf{b}_2=\frac{1}{2}\left[\frac{-\mathbf{b}}{\beta}+\frac{\mathbf{c}}{\gamma}\right], \tag{4.8}$$
$$\mathbf{b}_3=\frac{1}{2}\left[\frac{\mathbf{a}}{\alpha}-\frac{\mathbf{b}}{\beta}\right];$$

these vectors satisfy

$$\mathbf{b}_i\cdot\mathbf{b}_j^*=2\pi\delta_{ij}. \tag{4.9}$$

It can now be shown that the translations

$$(\{E\mid\mathbf{a}_i\},[E\mid-\mathbf{a}_i]^{-1})$$

and

$$(\{E\mid\mathbf{0}\},[E\mid\mathbf{b}_i]^{-1}) \tag{4.10}$$

satisfy Eq. (4.3), where $i=1,2,3$; the $\mathbf{a}_i$ are the primitive basis vectors of the C-centered α-uranium lattice defined in Fig. 1(a) and the $\mathbf{b}_i$ are given by Eq. (4.8). The translations of Eq. (4.10) can also be represented by the notation

$$A_i=(\mathbf{a}_i,-\mathbf{a}_i),\quad i=1,2,3,$$
$$A_{3+i}=(\mathbf{0},\mathbf{b}_i),\quad i=1,2,3. \tag{4.11}$$

Here, the two vectors in a given bracket are the translation parts of the two translation operators defining the corresponding superspace-group translation of Eq. (4.10). The A_i are said to describe translations in superspace. The set of all combinations of the A_i with integer coefficients defines the superspace Bravis lattice. A basis for the superspace reciprocal lattice is

$$A_i^*=(\mathbf{a}_i^*,\mathbf{0}),\quad i=1,2,3,$$
$$A_{3+i}^*=(\mathbf{b}_i^*,\mathbf{b}_i^*),\quad i=1,2,3. \tag{4.12}$$

These superspace vectors satisfy

$$A_i\cdot A_j^*=2\pi\delta_{ij}, \tag{4.13}$$

where the scalar product of two superspace vectors is defined by

$$(\mathbf{r}_1,\mathbf{r}_2)\cdot(\mathbf{q}_1,\mathbf{q}_2)=\mathbf{r}_1\cdot\mathbf{q}_1+\mathbf{r}_2\cdot\mathbf{q}_2.$$

To proceed further, a given element $\{P\mid\mathbf{w}\}$ of *Cmcm* is applied to $u(\mathbf{r}_0)$, as in Eq. (4.3), and one tries to find a $\mathbf{v}$ for which Eq. (4.3) is satisfied. If such a $\mathbf{v}$ can be found, then one has found a transformation which leaves $u(\mathbf{r}_0)$ invariant, i.e., one has found an element of the superspace group. If no such $\mathbf{v}$ can be found, then the transformation $\{P\mid\mathbf{w}\}$ generates a different state of the same energy; different states of the same energy can coexist and give a domain structure.

In the way just described, the generators of the superspace group for the case where the $\phi_{j0}=0$ are found to be, for case (i),

$$\phi_{j0}=0,$$
$$g_1=(\{I\mid\mathbf{0}\},[I\mid\mathbf{0}]^{-1}),$$
$$g_2=(\{C_{2x}\mid\mathbf{0}\},[C_{2x}\mid\tfrac{1}{2}(\mathbf{b}_1+\mathbf{b}_2+\mathbf{b}_3)]^{-1}), \tag{4.14}$$
$$g_3=(\{\sigma_z\mid\tfrac{1}{2}\mathbf{c}\},[\sigma_z\mid\tfrac{1}{2}\mathbf{c}]^{-1}),$$

whereas for the other case [case (ii)] they are

$$\phi_{10}=\pi,\quad \phi_{j0}=0,\quad j=2,3,4,$$
$$g_1=(\{I\mid\mathbf{0}\},[I\mid\mathbf{0}]^{-1}),$$
$$g_2=(\{C_{2x}\mid\mathbf{0}\},[C_{2x}\mid\tfrac{1}{2}\mathbf{b}_1]^{-1}), \tag{4.15}$$
$$g_3=(\{\sigma_z\mid\tfrac{1}{2}\mathbf{c}\},[\sigma_z\mid\tfrac{1}{2}(\mathbf{c}+\mathbf{b}_1+\mathbf{b}_2)]^{-1}).$$

The superspace-group transformations given in Eqs. (4.10), (4.14), and (4.15) can be written in the form given in Eq. (4.4) by using the result

$$[P\mid\mathbf{v}]=[P^{-1}\mid-P^{-1}\mathbf{v}]^{-1}, \tag{4.16}$$

but are usually more conveniently used in the form given.

Since all of the elments of *Cmcm* generate elements of the superspace group in both of the cases described by Eqs. (4.11) and (4.12), there is only one distinct state in each case.

The states just described were not considered by van Smaalen and Haas.[7] I believe that they would have used the notation $Cmcm(\alpha\beta\gamma)$ to describe both superspace groups; the capital C denotes the fact that the $\mathbf{a}_i$, $i=1,2,3$ entering the definition [Eq. (4.11)] of the superspace Bravais lattice describes a C-centered orthorhombic Bravais lattice; the *mcm* part of the symbol describes the space group generated by the elements $\{I\mid\mathbf{0}\}$, $\{C_{2x}\mid\mathbf{0}\}$, and $\{\sigma_z\mid\frac{1}{2}\mathbf{c}\}$, which are the first parts of the transformations in both Eq. (4.14) and Eq. (4.15); the $(\alpha\beta\gamma)$ part of the symbol gives one of the incommensurate wave vectors $\mathbf{q}_1=\alpha\mathbf{a}^*+\beta\mathbf{b}^*+\gamma\mathbf{c}^*$. Notice that the two superspace groups differ in the fractional translations associated with the elements $[P\mid\mathbf{v}]$ and that this difference is not accounted for in the symbol $Cmcm(\alpha\beta\gamma)$. It should be emphasized therefore that a precise definition of a particular superspace group is given in this paper by stating the superspace Bravais lattice and the generators, as in Eqs. (4.11) and (4.14) above; the corresponding label [in this case $Cmcm(\alpha\beta\gamma)$] is not necessarily either unique or complete, but allows a comparison with the work of Ref. 7.

B. {1,2,3,4} a-axis commensurate states

For the purpose of this section, I define

$$\mathbf{b}_1=\frac{1}{2}\left[\frac{\mathbf{b}}{\beta}+\frac{\mathbf{c}}{\gamma}\right],\quad \mathbf{b}_1^*=\beta\mathbf{b}^*+\gamma\mathbf{c}^*,$$
$$\mathbf{b}_2=\frac{1}{2}\left[-\frac{\mathbf{b}}{\beta}+\frac{\mathbf{c}}{\gamma}\right],\quad \mathbf{b}_2^*=-\beta\mathbf{b}^*+\gamma\mathbf{c}^*, \tag{4.17}$$

so that $\mathbf{b}_i\cdot\mathbf{b}_j^*=\delta_{ij}$; $i,j=1,2$. By making use of the form of $u(\mathbf{r}_0)$ for the $\{1,2,3,4\}$ a-axis commensurate states given in Sec. III E, one can show that sets of basis vectors for the superspace Bravais lattice and reciprocal lattice for this case are

$$A_1=[\mathbf{a},-\tfrac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)],\quad A_1^*=(\mathbf{a}^*,0)\,,$$
$$A_2=(\mathbf{b},-\mathbf{b}),\quad A_2^*=(\mathbf{b}^*,0)\,,$$
$$A_3=(\mathbf{c},-\mathbf{c}),\quad A_3^*=(\mathbf{c}^*,0)\,, \tag{4.18}$$
$$A_4=(0,\mathbf{b}_1),\quad A_4^*=(\mathbf{q}_1^0,\mathbf{b}_1^*)\,,$$
$$A_5=(0,\mathbf{b}_2),\quad A_5^*=(\mathbf{q}_2^0,\mathbf{b}_2^*)\,.$$

Note that the C-centering is lost since the vectors **a**, **b**, and **c** appearing in the A_i are a basis for a primitive orthorhombic lattice.

The generators of the superspace-group transformations can be found for the four $\{1,2,3,4\}$ **a**-axis commensurate cases described in Sec. III E and are now given, as is a symbol giving at least a partial description of the superspace symmetry as described above. For case (i):

$$\phi_{j0}=0,\quad Pmcm(\tfrac{1}{2}\beta\gamma)\,,$$
$$g_1=(\{I\,|\,0\},[I\,|\,0]^{-1})\,,$$
$$g_2=(\{C_{2x}\,|\,0\},[C_{2x}\,|\,-\tfrac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)]^{-1})\,, \tag{4.19}$$
$$g_3=(\{\sigma_z\,|\,\tfrac{1}{2}\mathbf{c}\},[\sigma_z\,|\,\tfrac{1}{2}\mathbf{c}]^{-1})\,.$$

For case (ii):

$$\phi_{10}=\pi,\quad \phi_{j0}=0\ \text{ for } j\neq 1, P\tfrac{2}{m}11(\tfrac{1}{2}\beta\gamma)(\tfrac{1}{2}\bar{\beta}\gamma)$$
$$g_1=(\{I\,|\,0\},[I\,|\,0]^{-1})\,, \tag{4.20}$$
$$g_2=(\{C_{2x}\,|\,0\},[C_{2x}\,|\,\tfrac{1}{2}\mathbf{b}_2]^{-1})\,.$$

For case (iii):

$$\phi_{10}=\phi_{20}=\tfrac{1}{2}\pi,\quad \phi_{30}=\phi_{40}=0,\quad P2cm(\tfrac{1}{2}\beta\gamma)\,,$$
$$g_1=(\{C_{2x}\,|\,0\},[C_{2x}\,|\,\tfrac{3}{4}(\mathbf{b}_1+\mathbf{b}_2)]^{-1})\,, \tag{4.21}$$
$$g_2=(\{\sigma_z\,|\,\tfrac{1}{2}\mathbf{c}\},[\sigma_z\,|\,\tfrac{1}{2}\mathbf{c}+\tfrac{1}{4}(\mathbf{b}_1+\mathbf{b}_2)]^{-1})\,.$$

For case (iv):

$$\phi_{10}=\tfrac{1}{2}\pi,\quad \phi_{20}=-\tfrac{1}{2}\pi,\quad \phi_{30}=\phi_{40}=0,\quad P222_1(\tfrac{1}{2}\beta\gamma)\,,$$
$$g_1=(\{C_{2x}\,|\,0\},[C_{2x}\,|\,\tfrac{3}{4}\mathbf{b}_1+\tfrac{1}{4}\mathbf{b}_2]^{-1})\,, \tag{4.22}$$
$$g_2=(\{C_{2y}\,|\,\tfrac{1}{2}\mathbf{c}\},[C_{2y}\,|\,\tfrac{1}{2}\mathbf{c}-\tfrac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)]^{-1})\,.$$

Since $\{E\,|\,\mathbf{a}_1\}$, where $\mathbf{a}_1$ is defined in Fig. 1, is an element of *Cmcm* but does not generate an element of the superspace symmetry group for any of the above four cases, $\{E\,|\,a_1\}$ operating on $u(\mathbf{r}_0)$ must generate a new distinct state in each case. Since $\{\sigma_z\,|\,\frac{1}{2}\mathbf{c}\}$ does not generate a superspace group symmetry element in case (ii), $\{\sigma_z\,|\,\frac{1}{2}\mathbf{c}\}$ operating on $u(\mathbf{r}_0)$ gives a state which is different from that described by $u(\mathbf{r}_0)$; this new state is, however, the same as that generated by operating on $u(\mathbf{r}_0$ with $\{E\,|\,\mathbf{a}_1\}$. Detailed study shows that in each of the above four cases there are exactly two distinct states with the same energy (i.e., two domains), differing from one another by a translation of $\mathbf{a}_1$.

van Smaalen[7] lists structures having superspace groups labeled $Pmcm(\frac{1}{2}\beta\gamma)$, $P2cm(\frac{1}{2}\beta\gamma)$, and $P222_1(\frac{1}{2}\beta\gamma)$ which would appear to correspond to my cases (i), (iii), and (iv). However, I find that the displacements given by my Eqs. (2.8) for these structures are not in agreement with those given by him, if I have understood his notation correctly. Furthermore, I find that all three structures have two domains, while he finds that the $Pmcm(\frac{1}{2}\beta\gamma)$ structures has only a single domain and that the other two have two domains. In addition, my case (ii), which I have labeled $P\frac{2}{m}11(\frac{1}{2}\beta\gamma)(\frac{1}{2}\bar{\beta}\gamma)$, does not appear to have been discussed by him.

C. 2−q a-axis incommensurate states

To describe the superspace symmetry of the $\{1,3\}$ state, the vectors $\mathbf{b}_1^*$ and $\mathbf{b}_2^*$ are defined by $\mathbf{b}_1^*=\mathbf{q}_1$ and $\mathbf{b}_2^*=\mathbf{q}_3$. Also, $\mathbf{b}_1$ and $\mathbf{b}_2$ are defined as lying in the same plane as $\mathbf{b}_1^*$ and $\mathbf{b}_2^*$ and satisfying $\mathbf{b}_i\cdot\mathbf{b}_j^*=2\pi\delta_{ij}$. The superspace Bravais and reciprocal lattice basis vectors are then found to be

$$A_i=(\mathbf{a}_i,-[\mathbf{a}_i]),\quad A_i=(\mathbf{q}_i^*,0),\quad i=1,2,3\,,$$
$$A_{3+i}=(0,\mathbf{b}_i),\quad A_{3+i}^*=(\mathbf{b}_i^*,\mathbf{b}_i^*),\quad i=1,2\,, \tag{4.23}$$

where $[\mathbf{a}_i]$ is the part of $\mathbf{a}_i$ lying in the plane containing $\mathbf{b}_1$ and $\mathbf{b}_2$. The generators of the superspace group are

$$g_1=(\{I\,|\,0\},[I\,|\,0]^{-1})\,,$$
$$g_2=(\{C_{2x}\,|\,0\},[C_{2x}\,|\,\tfrac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)]^{-1})\,, \tag{4.24}$$

and the group is labeled $C\frac{2}{m}11(\alpha\beta\gamma)$. There are exactly two domains, these domains being the $\{1,3\}$ and $\{2,4\}$ states.

The superspace Bravais and reciprocal lattices of the $\{1,2\}$ **a**-axis incommensurate state are described by Eq. (4.23), provided that $\mathbf{b}_1^*$ and $\mathbf{b}_2^*$ are defined by $\mathbf{b}_1^*=\mathbf{q}_1$ and $\mathbf{b}_2^*=\mathbf{q}_2$. The generators of the superspace group are

$$g_1=(\{I\,|\,0\},[I,0]^{-1})\,,$$
$$g_2=(\{\sigma_y\,|\,\tfrac{1}{2}\mathbf{c}\},[\sigma_y\,|\,-\tfrac{1}{2}[\mathbf{c}]-\tfrac{1}{2}(\mathbf{b}_1+\mathbf{b}_2)]^{-1})\,. \tag{4.25}$$

There are exactly two domains corresponding to the $\{1,2\}$ and $\{3,4\}$ states and the group is labeled $C1\frac{2}{m}1(\alpha\beta\gamma)$.

For the $\{1,4\}$ state, if $\mathbf{b}_1^*$ and $\mathbf{b}_2^*$ are defined by $\mathbf{b}_1^*=\mathbf{q}_1$ and $\mathbf{b}_2^*=\mathbf{q}_4$, then Eq. (4.23) is valid, and the generators are

$$g_1=(\{I\,|\,0\},[I,0]^{-1})\,,$$
$$g_2=(\{\sigma_z\,|\,\tfrac{1}{2}\mathbf{c}\},[\sigma_z\,|\,\tfrac{1}{2}\mathbf{c}]^{-1})\,. \tag{4.26}$$

There are exactly two domains, these being the $\{1,4\}$ and $\{2,3\}$ states.

van Smaalen[7] has noted the existence of states similar to the second and third cases studied in this section, but not the first.

D. The $\{1,3\}-\{2,4\}$ a-axis commensurate states

To analyze the $\{1,3\}$ states, $\mathbf{d}^*$ is defined by $\mathbf{d}^*=\beta\mathbf{b}^*+\gamma\mathbf{c}^*$; **d** is parallel to $\mathbf{d}^*$ and satisfies $\mathbf{d}\cdot\mathbf{d}^*=2\pi$. Bases for the Bravais and reciprocal lattices are then

$$\begin{aligned} &A_1=(\mathbf{a},-\tfrac{1}{2}\mathbf{d}),\quad A_1^*=(\mathbf{a}^*,\mathbf{0}),\\ &A_2=(\mathbf{b},-\beta\mathbf{d}),\quad A_2^*=(\mathbf{b}^*,\mathbf{0}),\\ &A_3=(\mathbf{c},-\gamma\mathbf{d}),\quad A_3^*=(\mathbf{c}^*,\mathbf{0}),\\ &A_4=(\mathbf{0},\mathbf{d}),\quad A_4^*=(\mathbf{q}_1^0,\mathbf{d}^*). \end{aligned} \tag{4.27}$$

The two energetically different cases of $\{1,3\}$ states are discussed in Sec. III B. The generators are

$$\begin{aligned} &\phi_{10}=\phi_{30}=0,\quad P_m^2 11(\tfrac{1}{2}\beta\gamma),\\ &g_1=(\{I\mid\mathbf{0}\},[I\mid\mathbf{0}]^{-1}),\\ &g_2=(\{C_{2x}\mid\mathbf{0}\},[C_{2x}\mid\tfrac{1}{2}\mathbf{d}]^{-1}); \end{aligned} \tag{4.28}$$

in case (i), and

$$\begin{aligned} &\phi_{10}=\tfrac{1}{2}\pi,\quad \phi_{30}=0,\quad P211(\tfrac{1}{2}\beta\gamma),\\ &g=(\{C_{2x}\mid\mathbf{0}\},[C_{2x}\mid\tfrac{3}{4}\mathbf{d}]^{-1}), \end{aligned} \tag{4.29}$$

in case (ii).

Each of the above cases represents a state for which there are exactly four domains. Starting with a given $\{1,3\}$ state, one can translate it by $\mathbf{a}_1$ to get a second $\{1,3\}$ state, operate on it with $\{\sigma_z\mid\frac{1}{2}\mathbf{c}\}$ to get a $\{1,4\}$ state, and translate the $\{1,4\}$ state by $\mathbf{a}_1$ to get the fourth domain.

van Smaalen[7] also finds states which he labels by $P_m^2 11(\frac{1}{2}\beta\gamma)$ and $P211(\frac{1}{2}\beta\gamma)$ but he is in disagreement with us in asserting that the $P_m^2 11(\frac{1}{2}\beta\gamma)$ state has only two domains.

E. The single-q states

There are four domains associated with the $\{1\}$, $\{2\}$, $\{3\}$, and $\{4\}$ states, the generator of the superspace group is

$$g=(\{I\mid\mathbf{0}\},[I\mid\mathbf{0}]), \tag{4.30}$$

and the group is labeled $C\bar{1}(\alpha\beta\gamma)$.

V. THE LOW-TEMPERATURE COMMENSURATE PHASE

Following the observation[14] of a pronounced dip at approximately $\mathbf{q}=(\frac{1}{2},0,0)$ in the Σ_4 branch of the phonon dispersion relation, Smith *et al.*[1] observed weak superlattice reflections at positions $((h+\frac{1}{2})(1-\delta),k,l)$. These reflections correspond to reflections from a superlattice which has space group *Pmnm* and whose a-axis lattice constant a_s is slightly larger than twice the fundamental lattice constant a. I assume that these weak reflections arise from domains which occupy a certain fraction (probably small for the samples used in the neutron experiments since the reflections are weak) of the sample, and that within these domains, there is a modulation which is commensurate with the underlying lattice of the domain. The lattice constant of this commensurate phase will of course be different from that of the incommensurate phase which occupies the rest of the sample.

In terms of the basis vectors defined by Eq. (2.2), the Σ_4 eigenvector at $\mathbf{q}=(\frac{1}{2},0,0)$ is written

$$e_4=e(\mathbf{q},1,x)-e(\mathbf{q},\bar{1},x)+ig[e(\mathbf{q},1,y)+e(\mathbf{q},\bar{1},y)], \tag{5.1}$$

where g is a real constant. The Σ_4 eigenvector of Crummett *et al.*[14] contained an additional phase factor not contained in Eq. (5.1) (possibly due to a neglect by them of time-reversal symmetry). The transformation properties of e_4 under a set of generators of *Cmcm* are

$$\begin{aligned} &\{C_{2x}\mid\mathbf{0}\}e_4=-e_4,\\ &\{\sigma_z\mid\tfrac{1}{2}\mathbf{c}\}e_4=e_4,\\ &\{I\mid\mathbf{0}\}e_4=e_4^*. \end{aligned} \tag{5.2}$$

This section focuses on modulated phases described by the column vector

$$u=\mathrm{Re}(\psi e_4). \tag{5.3}$$

A knowledge of the transformation properties of the order parameter ψ follows from Eq. (5.2) and allows the construction of the appropriate Ginzburg-Landau free-energy density, which is

$$F=\psi^* A(-i\nabla)\psi+B\mid\psi\mid^4+B'(\psi^4+\psi^{*4}), \tag{5.4}$$

where a detailed knowledge of $A(-i\nabla)$ is not necessary in this section.

In the commensurate phase, ψ is independent of $\mathbf{r}$ and is written $\mid\psi\mid\exp(i\phi)$. The phase-dependent contribution to F is then

$$F_4=2B'\mid\psi\mid^4\cos(4\phi), \tag{5.5}$$

which is minimized by

$$\begin{aligned} &4\phi=2n\pi\ \text{ for } B'<0,\\ &4\phi=(2n+1)\pi\ \text{ for } B'>0. \end{aligned} \tag{5.6}$$

The space groups of the structures corresponding to these solutions are *Pmnm* and *Pbnm*, respectively. Thus, the solution corresponding to $B'<0$ gives a structure with a space group in agreement with that of the superlattice as determined by Smith *et al.*[1]

A description of the incommensurate phases of α-uranium could be attempted in terms of the free-energy density of Eq. (5.4) and an order parameter having the form

$$\psi(\mathbf{r})=\sum_{i=1}^{4}\psi_{i0}e^{i\mathbf{k}_i\cdot\mathbf{r}},$$

where $\mathbf{k}_1=(\delta,\beta,\gamma)$, $\mathbf{k}_2=(\delta,-\beta,\gamma)$, $\mathbf{k}_3=(\delta,-\beta,-\gamma)$, and $\mathbf{k}_4=(\delta,\beta,-\gamma)$ but will not be carried out since this approach is less general than that pursued in Sec. IV.

VI. CONCLUSIONS

The Landau-type models described in this article were shown to give rise to modulated phases which are incommensurate in the **a**-axis direction (as well as in at least one of the directions normal to the **a**-axis direction), phases which are commensurate in the **a**-axis direction (but incommensurate normal to the **a** axis) and to phases which are purely commensurate.

The observations of Chen and Lander [12] indicate that the phases which occur between 43 and 37 K and between 37 and 23 K are both $2-\mathbf{q}$ states which I call $\{1,3\}$ states (or equivalently $\{2,4\}$ states). My analysis says that the initial transition at $T_c = 43$ K must be to an **a**-axis incommensurate state, but the model contains an interaction which, for a $\{1,3\}$ state, allows a lock-in phase transition to an **a**-axis commensurate state at some temperature below the initial transition temperature. This suggests that the 37-K phase transition is a lock-in transition, and high-resolution diffraction studies to see if the satellite wave vectors have an incommensurate **a** component between 43 and 37 K would be a useful test of this suggestion. The evidence[12] that the state which exists between 37 and 43 K is a $2-\mathbf{q}$ state is perhaps not conclusive, and other **a**-axis incommensurate possibilities should also be considered.

There are two different **a**-axis commensurate $\{1,3\}$ phases. These are labeled $P\frac{2}{m}11(\frac{1}{2}\beta\gamma)$ and $P211(\frac{1}{2}\beta\gamma)$, lack the C-centering as indicated by the initial capital P (primitive) in the label, and differ by the presence or absence of a center of inversion symmetry. Which of these two occurs in an α-uranium between 23 and 37 K remains to be determined.

Finally, it is suggested that the so-called nearly commensurate phase which produces satellites near $\mathbf{q}=(\frac{1}{2},0,0)$ may be simply a commensurate phase with an average lattice constant slightly different from that of the incommensurate phase. The observations of Chen and Lander[12] show that the nearly commensurate and the incommensurate phases coexist; also, these phases must have different lattice constants since they are different phases; the remaining question is the quantitative one of whether or not the difference in lattice constants is big enough to account for positions of the nearly commensurate satellites. The fact that one of the two commensurate phases obtained from the model of Sec. V has the correct *Pmnm* space group required to account for the observed[1] superlattice reflections favors the interpretation of the nearly commensurate phase as an ordinary commensurate phase.

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