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Neutron scattering investigations of α-uranium in the charge-density-wave state

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Below 43 K, α-uranium (the orthorhombic phase stable below 600 °C) develops an incommensurate charge-density wave (CDW) that has a profound effect on almost all physical properties of this element. Previous work at Oak Ridge National Laboratory and the Institut Laue-Langevin has characterized the phonon dispersion curves and various properties of the periodic distortions of the atomic structure. In this paper we review some of these results and present new information giving further details of the CDW state, in particular the temperature and pressure dependence of both the elastic and inelastic (precursor phonon) scattering. Suggestions for new experiments, including those using other techniques, are presented.

I. INTRODUCTION

The complex charge-density-wave (CDW) state appearing in α-uranium (α-U) below 43 K has been the subject of a series of neutron scattering investigations since the discovery of the CDW in 1979.[1] In particular, experiments have been conducted to examine the relationship between the two apparently independent periodic distortions, and to examine the effects of pressure and temperature on both the CDW state and the phonon dispersion curves. Some of these have been presented in conference proceedings; many are new. Our aim in this paper is to present these investigations in a consecutive and connected manner, so that the status of our present knowledge of α-U at low temperature is clear.

II. BACKGROUND INFORMATION

The structure of α-U is shown in Fig. 1. Reviews of the early work on α-U are numerous, and we refer to the volume edited by Freeman and Darby in 1974.[2] A major program to investigate α-U was started at Oak Ridge National Laboratory, using the neutron facilities at the High Flux Isotope Reactor, in the mid 1970s. As a result of using single crystals (grown by E. S. Fisher at Argonne National Laboratory in the late 1950s and with volumes ~ 0.1 cm^3) the complete phonon dispersion curves in the high-symmetry directions were mapped out at room temperature.[3] A large anomaly was found in the Σ_4 branch in the [100] direction. As the temperature decreases the phonon continues to soften and satellites appear near the positions $(h+\frac{1}{2},k,l)$, corresponding to a modulation with wave vector $[q_x\,0\,0]$ with $q_x \simeq 0.5$. Smith *et al.*[1] showed that these satellites occurred commensurate with a slightly larger lattice.

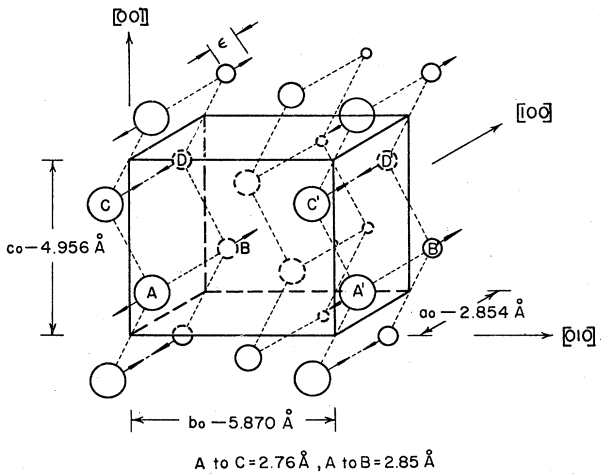

FIG. 1. The orthorhombic unit cell of α-U. Also shown with arrows is an optic displacement of magnitude ϵ along the [100] direction.

Just after the work reported by Smith *et al.*[1] a very important experiment was performed at the Institut Laue Langevin (ILL) by Marmeggi and Delapalme.[4] They discovered a completely new set of satellites corresponding to an incommensurate CDW below 43 K in α-U. Subsequent experiments at the ILL measured the intensities and positions of these satellites, and a complete picture of the atomic displacements has emerged.[5]

An attempt to show a portion of the reciprocal lattice in α-U appears in Fig. 2. It is convenient to refer to the reciprocal-lattice point (2,0,1). The satellites found by Smith *et al.*[1] are marked as open circles close to the positions $(2,0,1)\pm(\sim 0.5,0,0)$. The much stronger (by about a factor of 40 on average) satellites of Marmeggi *et al.*[5] are at the positions corresponding to the solid squares in Fig. 2. The $\vec{q}$ vector of these satellites at 5 K is

$$\vec{q}=\pm 0.500(1)\vec{a}^{*}\pm 0.176(2)\vec{b}^{*}\pm 0.182(2)\vec{c}^{*}\,, \qquad (1)$$

where $\vec{a}^{*}$, $\vec{b}^{*}$, and $\vec{c}^{*}$ are the reciprocal-cell vectors and the figures in parentheses are standard deviations on the least significant figure. The plus-minus signs indicate that one finds satellites at all possible combinations of q_x, q_y, and q_z. Around each fundamental Bragg point hkl there are eight satellite reflections.

Marmeggi *et al.*[5] measured a great number of these first-order satellites and worked out the atomic motions $\vec{u}_{lk}$. There are six important parameters needed to define these atomic motions, three displacements (e_i or ϵ_i if relative values) and three phases (ϕ_i). A least-squares program based on the observed structure factors for the first-order satellites gave the following results:

$$\begin{aligned} e_x&=\epsilon_x a=0.053(1)\ \text{Å},\quad \phi_x=99^{\circ}\pm 3^{\circ}\,,\\ e_y&=\epsilon_y b=0.009(1)\ \text{Å},\quad \phi_y=-24^{\circ}\pm 5^{\circ}\,,\\ e_z&=\epsilon_z c=0.006(1)\ \text{Å},\quad \phi_z=118^{\circ}\pm 10^{\circ}\,, \end{aligned} \qquad (2)$$

with a χ^2 value of 7 and a crystallographic R factor [equal to $\Sigma(|F_{\text{obs}}|-|F_{\text{calc}}|)/\Sigma|F_{\text{calc}}|$] of 0.10. The largest displacement is along $\vec{a}$, and is predominantly optic in motion, i.e., changes sign across the inversion center. A pure optic motion corresponds to $\phi=90^{\circ}$, and a pure acoustic motion, i.e., the same sign across the inversion center, corresponds to $\phi=0^{\circ},180^{\circ}$, etc. Thus $\vec{u}_{lk}$ is almost pure optic in $\vec{\epsilon}_x$ and pure acoustic in $\vec{\epsilon}_y$, and this is exactly the symmetry of the Σ_4 phonon[3] along the [100] direction.

This completes a short survey of the CDW state of α-U as already published in Refs. 1–5. A more complete review of the experimental situation as summarized in this section has been given by one of us at a recent conference.[6]

III. ELASTIC SCATTERING INVESTIGATIONS: AMBIENT PRESSURE

A. Temperature dependence

We show in Fig. 3 the temperature dependence of the satellite reflections from the incommensurate CDW and the nearly commensurate CDW. Note that because the latter is much less intense than the former there is some difficulty in measuring the intensity of the $(1.495,0,-1)$ reflection for $T>35$ K. In particular the softening of the phonon in this temperature range, coupled with the finite resolution of the triple-axis spectrometer, make it difficult to be sure that all intensity is elastic. Indeed, weak elastic scattering is seen at both the reflections plotted in Fig. 3 up to 70 K, but, again, this is thought to be connected

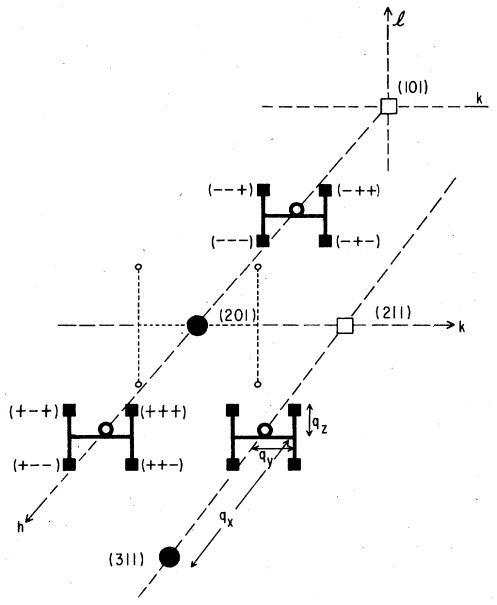

FIG. 2. Schematic diagram of a portion of reciprocal space for α-U. Lattice points are (1,0,1), (2,0,1), and (2,1,1). The C-face centering condition implies no Bragg intensity at (101) and (211) since $h+k$ is odd. The points corresponding to $\vec{q}\,||\,[\sim 0.5\,0\,0]$ are marked as open circles, and those corresponding to the incommensurate CDW with $\vec{q}\,||\,[\pm 0.5\pm q_y\pm q_z]$ are shown as solid squares. The symbols $(+\ +\ +)$, etc., refer to q components from the (201). The second-order satellites, which in principle occur around every lattice point, are shown only around the (201).

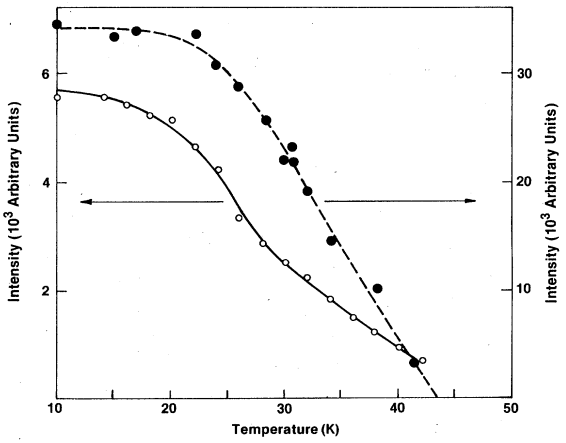

FIG. 3. Temperature dependence of the incommensurate CDW $(2.5,q_y,q_z)$, closed points, and the nearly commensurate CDW $(1.495,0,-1)$, open points. The lines are guides to the eye.

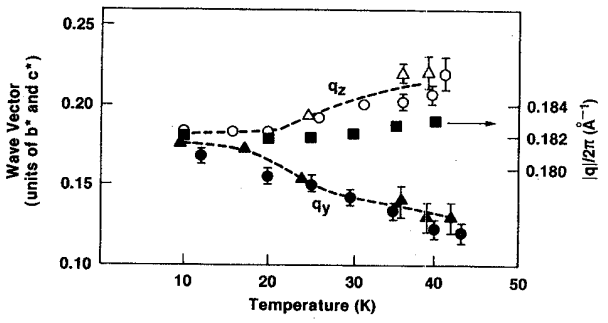

FIG. 4. Temperature dependence of the q_y and q_z components of the incommensurate CDW. Also shown is the absolute value of the $\vec{q}$ vector in $Å^{-1}$. The triangles are from Ref. 5, the circles from the present work.

with the softening of the phonon (see Sec. IV) and the resolution of ~0.2 THz used. These difficulties also prevent us from performing any detailed analysis of the shape of the curves presented in Fig. 3.

The temperature dependence of the q_y and q_z components is shown in Fig. 4. We have also calculated the variation of the absolute value of $\vec{q}$, using the results of Fig. 4 and the known variation with temperature of the lattice constants.[7] This quantity is plotted also in Fig. 4 and varies about 0.7% in the CDW state. Marmeggi and Delapalme[4] proposed that the $\vec{q}$ vector had a constant magnitude, and this does indeed appear to be nearly correct.

B. Analysis of linewidths and positions

We mentioned in Sec. II that the satellites near $\vec{q}=(0.5,0,0)$ were apparently commensurate with a slightly larger lattice. This is described in Ref. 1. However, this effect is so unusual, and at first sight difficult to understand, that it seems worth presenting additional evidence on this point.

The essential point is that the weak satellite reflections occur at positions $((h+\frac{1}{2})(1-\delta), k, l)$. The value of δ can then be found by dividing the observed position of the peak by the quantity $h+\frac{1}{2}$. Representative scans are shown in Ref. 1, but we illustrate the complete determination of δ (at 10 K) in Table I. A number of points are worth making.

(1) The peak profile is sharpest for a low value of the incident energy (i.e., a long wavelength) on a triple-axis

TABLE I. Positions of Bragg (h equals integer) or weak satellites (h equals integer plus 0.5) reflections. Repetition of the same reflections implies an independent measurement with the spectrometer recalibrated between measurements. All determinations are with the sample at 10 K and are made by scanning along the $\vec{a}^*$ axis. Standard deviations refer to the least significant digit.

h,k,l	Position	Mean	h,k,l	Position	Mean
0.5,2,0	0.499±2		2.5,2,0	2.488±2	
0.5,3,0	0.500±2		2.5,3,0	2.496±3	
0.5,2,0	0.498±1		2.5,1,0	2.498±3	
0.5,0,1	0.498±1		2.5,2,0	2.496±2	
0.5,0,3	0.494±3		2.5,2,0	2.493±1	
0.5,0,1	0.499±2	0.498±1	2.5,0,1	2.490±1	
			2.5,0,1	2.491±2	
1.5,2,0	1.493±3		2.5,0,1	2.490±1	
1.5,2,0	1.493±2		2.5,0,1	2.490±1	2.4914±10
1.5,2,0	1.497±2				
1.5,7,0	1.490±4				
1.5,3,0	1.496±2		3.5,3,0	3.497±5	
1.5,1,0	1.498±3		3.5,0,1	3.484±2	
1.5,2,0	1.493±1		3.5,0,1	3.486±3	3.4860±15
1.5,0,3	1.495±1				
1.5,0,1	1.494±1				
1.5,0,1	1.495±1	1.494±1			
2,2,0	1.998±2				
2,2,0	1.997±2				
2,2,0	2.003±2				
2,2,0	2.001±1				
2,2,0	2.001±1	2.001±1			

Mean values

h	Mean position	(mean/h)	
0.5	0.4890±10	0.9960±20	
1.5	1.4940±10	0.9963±7	
			0.9963±4
2.5	2.4914±10	0.9966±4	
3.5	3.4860±15	0.9960±5	

spectrometer. However, one is then unable to reach large values of Q. Clearly the best lattice parameter determinations are done at high Q, so there is a compromise needed.

(2) Normally a triple axis is relatively easily set to ± 0.002 from a Bragg point (see the settings given for a series around the $h=2$ point), so that by $h=3.5$ the discrepancy is large and easily identifiable. It is, of course, must more difficult to see this effect at $h=0.5$.

(3) Note that two different crystals have been used in the determinations shown in Table I, the first giving the scattering plane ($hk0$) and the second giving ($h0l$).

As shown in the lower part of Table I the (mean position)/h is remarkably consistent for the four h values and gives at 10 K

$$\delta=(37\pm4)\times10^{-4}\ .$$

The wave vector is then commensurate with a lattice constant a_s that is *slightly larger* than twice the fundamental lattice a_0,

$$a_s/2a_0=1+\delta=1.0037\pm4\ . \tag{3}$$

The temperature dependence of δ is shown in Fig. 5(a). Figure 5(b) shows the variation of a_0, the a-axis lattice parameter, at low temperature (from Ref. 7). Above this is plotted $(1+\delta)a_0$, which is essentially independent of temperature. The commensurate lattice a_s for the weak periodic distortion at $[\sim0.500]$ is therefore given by $a_s/2=2.855\pm0.001$ Å *at all temperatures* in the CDW state.

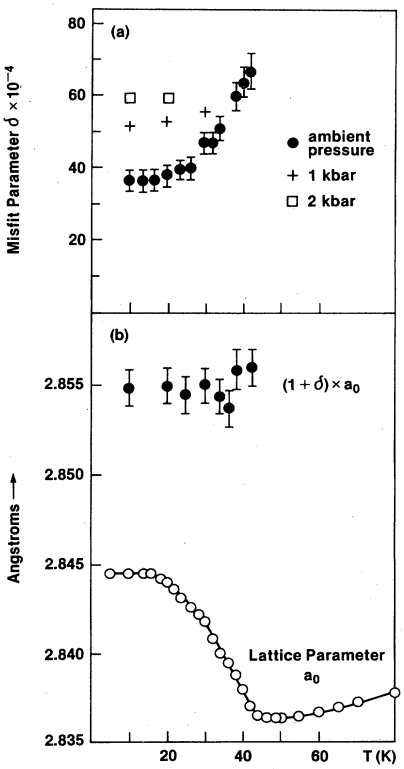

FIG. 5. Variation of temperature of (a) the misfit parameter δ (a few values at pressure are also given), (b) the quantities $(1+\delta)a_0$ and a_0, where the latter is the a-axis parameter as measured by Barrett *et al.* (Ref. 7).

We shall maintain throughout this paper that the principle CDW is associated with the incommensurate $\vec{q}$, and that the nearly commensurate satellites at $[\sim0.500]$ represent either an (as yet) unexplained diffraction effect or (more likely) the result of discommensurations. Under these conditions it is of special interest to study the line shapes of the satellites from the two $\vec{q}$ vectors. These are shown as measured for the three orthogonal directions in Fig. 6. We note that the widths (and shapes) for the incommensurate CDW are always the same as nearby lattice points, i.e., the scattering from this periodic distortion has a coherent length as long as the underlying lattice. These peaks are fitted in Fig. 6 in all directions with Gaussian functions, whose widths are the same as neighboring fundamental Bragg lattice points. On the other hand, for the periodic distortion giving satellites near [0.500] both the widths and the line shapes are unusual. The fits in Fig. 6 are with Lorentzian functions, that are in all cases much wider than the Gaussian peaks shown in the same figure. From the Lorentzian shape we may infer that the weak satellites arise from spatial correlations, rather than true long-range order. We may also define from the half widths of these Lorentzian peaks (suitably deconvoluted

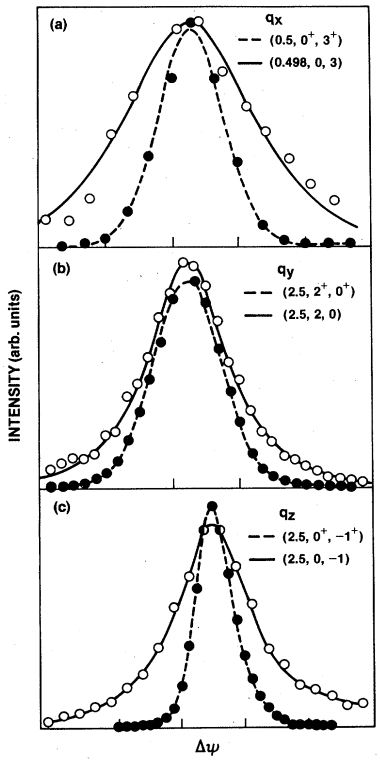

FIG. 6. Profiles of different satellite reflections as a function of the three different orthogonal directions. The incommensurate satellites (solid points) are fitted with the Gaussian curves and are always resolution limited. The nearly commensurate satellites (open points) have been fitted with Lorentzians, which are much wider than the intrinsic resolution. The indexes of the peaks are given in each case, and the scans shown are transverse to the respective Q value. The linewidths are discussed in the text.

with the Gaussian resolution function) the mean correlation length in the three orthogonal directions. We obtain

$$\begin{aligned}\zeta_x &\simeq 170 \text{ Å}, \\ \zeta_y &\simeq 220 \text{ Å}, \\ \zeta_z &\simeq 130 \text{ Å}.\end{aligned} \tag{4}$$

All these correlation lengths are relatively short compared to that of true long-range order, so that it is clear that the distortion wave, which for these satellites is only along q_x, is not well developed in the crystal. This point will be useful in discussing how these satellites possibly arise from discommensurations.

C. Search for higher-order satellite reflections

As discussed in Ref. 5 the structure factors from the displacement waves are given by

$$F(\vec{\tau}+m\vec{q}) = \sum_{\{m\}} 2\cos(2\pi\vec{\tau}\cdot\vec{r} - m_x\phi_x - m_y\phi_y - m_z\phi_z) \times J_{m_x}(\epsilon_x \vec{a}\cdot\vec{Q}) J_{m_y}(\epsilon_y \vec{b}\cdot\vec{Q}) J_{m_z}(\epsilon_z \vec{c}\cdot\vec{Q}), \tag{5}$$

where ϵ_x, etc., are fractional shifts, J_m are Bessel functions of order m, $\vec{r}$ is the atom position, and $\vec{Q}=\vec{\tau}+m\vec{q}$, which corresponds to the location of a satellite of order m with wave vector $\vec{q}$ and measured from a fundamental reciprocal-lattice point $\vec{\tau}=h\vec{a}^*+k\vec{b}^*+l\vec{c}^*$. The summation is over all combinations of m components, i.e., $m_x+m_y+m_z=m$. This form assumes that an inversion operator relates the displacements of the two atoms across the inversion center such that $\phi_i^2=-\phi_i^1$. In Ref. 5 an excellent fit was obtained for a large number of reflections and no improvement in the overall fit could be obtained by dropping the inversion operator, so we assume it still applies in the CDW state. A series of reflections are listed in Table II.

TABLE II. Representative structure factors for fundamental reflections and satellites at the incommensurate wave vector in α-U at 10 K. Calculated values use Eq. (5), see Ref. 5.

Reciprocal point (h,k,l)	Satellite index $(\pm q_x, \pm q_y, \pm q_z)$	First satellite $10^3\lvert F_{obs}\rvert$ (± 2)	First satellite $10^3\lvert F_{calc}\rvert$	Fundamental reflection $T>43$ K $\lvert F_{calc}\rvert$	Fundamental reflection $T<43$ K $\lvert F_{calc}\rvert$	Second satellite $10^3\lvert F_{calc}\rvert$
004	+ + +	7	6	1	1	1.3
	+ + −	8	2			0.5
200	+ + +	18	11	1	0.986	7.3
	− + +	11	7			0.8
201	+ + +	70	73	0	0	2.5
	+ + −	68	70			2.1
	− + +	39	41			0.2
	− + −	43	45			0.4
202	+ + +	13	13	1	0.986	7.9
	+ + −	11	9			6.8
	− + +	14	5			0.6
	− + −	10	9			1.0
241	+ + +	53	53	0.534	0.529	4.7
	+ + −	52	55			4.1
	+ − +	77	75			0.9
	+ − −	69	71			0.9
	− + +	30	30			1.1
	− + −	35	32			1.3
	− − +	30	30			0.5
	− − −	32	34			0.5
226	+ + −	51	56	0.278	0.275	1.9
	+ − −	58	63			0.2
	− + +	30	31			0.4
	− + −	51	48			1.5
	− − +	27	28			0.3
	− − −	51	52			0.2
204	+ + +	13	15	1	0.986	8.5
300	+ + +	17	16	0	0	13.1
	− + +	18	11			3.2
302	+ + +			0	0	13.8
	+ + −					12.3
	− + +	13	13			2.8
	− + −	11	9			3.6
400	− + +	17	16	1	0.946	7.2
401	− + +	92	97	0	0	2.2

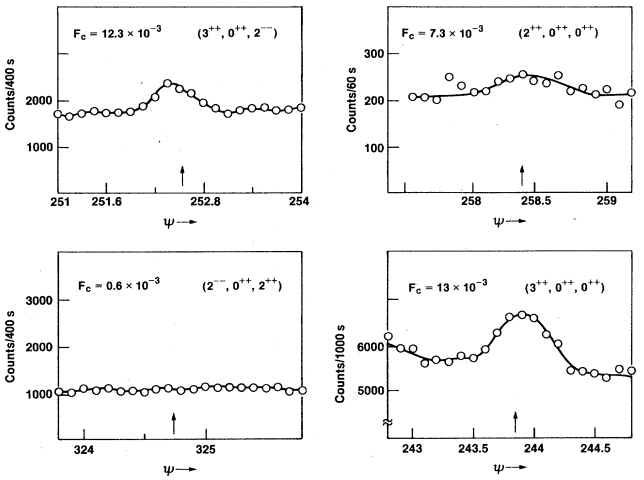

FIG. 7. Profiles of second-order satellites as marked in each panel. The quantity F_c is calculated with Eq. (5) and the square of it should be proportional to the intensity if the displacement wave is purely sinusoidal.

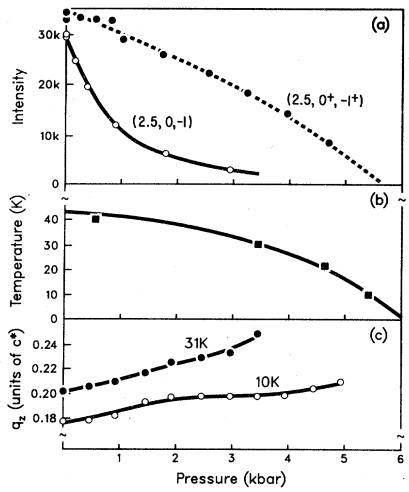

FIG. 8. (a) Pressure dependence of the two satellite systems in α-U at 10 K. (b) P-T existence curve for the incommensurate CDW in α-U. (c) Pressure dependence of the q_z component of the incommensurate CDW at 10 and 31 K.

First, we note that Eq. (5) predicts changes in the intensities of the fundamental ($m=0$) peaks and some of these are shown in the table. Most are very small and impossible to determine accurately in view of changes in extinction[8] that frequently accompany the formation of the CDW.

Equation (5) also predicts the presence of weak second (and higher) -order order satellites because of the displacive nature of the modulation. The second-order satellites are predicted to be very weak. This prediction is based on a simple sine wave for the displacement wave and may not necessarily be correct. We show in Fig. 7 a collection of scans searching for second-order satellites. The calculated structure factors are shown in Table II and on the figures. Based on a weak first-order satellite we find the $(302)^{(3^{++},0^{++},2^{--})}$ integrated intensity equivalent to $F_0=(10\pm1)\times10^{-3}$ so this is a little weaker than predicted. We see that the variation in intensity is approximately given by $|F_{\rm calc}|^2$. These satellites are $\sim10^{-5}$ of the fundamental Bragg peaks, so that determining an accurate absolute scale is extremely difficult, and the intensities of the second-order satellites are within statistics of that predicted in Table II. In $TaSe_2$ the second-order satellites are much stronger than expected for a sinusoidal displacement wave and this additional distortional wave plays a key role in driving the system commensurate.[9] Clearly, this is not the case in α-U.

We have also searched for third-order satellites but have not found any. Such satellites would be associated with a squaring of the sinusoidal modulation. For a pure sine-wave displacement these satellites would be too small to observe.

IV. ELASTIC SCATTERING INVESTIGATIONS: VARIATION OF PRESSURE

Pressure effects have long been known to be important in the low-temperature phase of α-U. For example, the superconducting temperature T_c rapidly increases from a value <0.1 K to over 2 K with application of modest pressures[2] (~8 kbar), the temperature at which the anomalies occur in the elastic constants decreases with increasing pressure,[10] and de Haas–van Alphen oscillations have been seen only with hydrostatic pressures above 6 kbar.[11]

The experimental apparatus and some of the results have been described in a recent conference paper.[12] We show in Fig. 8(a) the pressure dependence of both sets of satellites. These are clearly different, and the weak (nearly commensurate) satellites are essentially unobservable above ~2 kbar. Note also the concave nature of the weak satellite pressure dependence.

The satellites do not simply diminish with applied pressure, there is also a change in position. We have already shown in Fig. 5 the pressure dependence of the misfit parameter δ, which rapidly increases with applied pressure. Apparently the weak satellites do not exist for $\delta>\sim70\times10^{-4}$ and this may be achieved either with pressure or temperature.

The pressure-temperature existence curve for the incommensurate CDW is shown in Fig. 8(b). This phase diagram is in good agreement with the more limited P-T information obtained with elastic constant measurements.[10] Within this phase diagram one can also study the q_x and q_z dependence of the CDW but we have not pursued this fully. In particular, we have not studied the pressure dependence of q_y. That of q_z is given in Fig. 8(c). The lack of any data on q_y means that we cannot be sure that the total amplitude of $\vec{q}$ stays constant under pressure, although this seems a reasonable assumption. There is no change in q_x ($=0.5$) with pressure.

V. INELASTIC SCATTERING INVESTIGATIONS

A. Ambient pressure

We have already discussed the importance of the phonon dispersion curves[1,3] in the condensation of the CDW.

A number of pertinent questions arise.

(1) To what extent are the q_y and q_z components related to soft phonon modes? We show in Fig. 9 scans in the three orthogonal directions around the CDW point. The frequency of the soft mode continues to decrease[1] from 300 to $\sim$50 K. Between 50 and 30 K it is extremely difficult to observe because the energy is low (<0.3 THz) and the best resolution we have used is $\sim$0.2 THz, full width at half maximum. By 12 K the frequency has once again increased to values comparable to those found at 300 K. A number of points are immediately obvious from Fig. 9. Whereas the frequency dependence is extremely sharp in the [100] direction, the minima in the [010] and [001] are not well defined. The CDW positions are certainly consistent with the minima in the Σ_4 response but, except for q_x, are not necessarily defined by the phonon minimum.

(2) To what extent are the displacements in the CDW state related to the Σ_4 phonon? We have already seen that the [100] direction the Σ_4 phonon has predominantly opticlike x motion and acousticlike y motion. (This can be derived directly from Table III of Ref. 3.) As one moves away from the [100] direction and introduces small q_y and q_z components the dynamical matrix becomes more complicated, but the components are optic (x), acoustic (y), and optic (z). These are precisely the major components of the CDW motion as derived from Eq. (2). An attempt has also been made to predict the frequencies of the phonons away from the symmetry axis with the fitting parameters of Ref. 3. However, this was not wholly successful since the frequencies rapidly became negative with the introduction of q_y and q_z components. The transition from the dynamic to the static CDW configuration can thus be regarded as a continuous one, with the symmetry and motions preserved during the condensation.

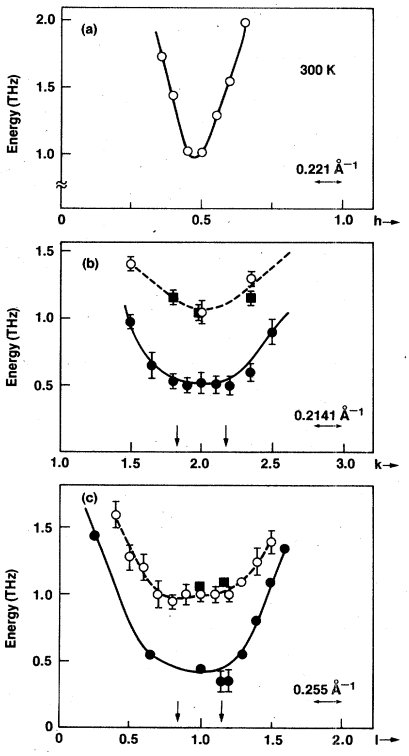

FIG. 9. Spatial dependence of the Σ_4 phonon frequency in the three orthogonal directions around the point at which the CDW occurs. The exact positions of the CDW at low temperatures are marked with arrows. Open circles room temperature; closed circles, 100 K; closed squares, 12 K. A scale, in absolute reciprocal-lattice lengths, is shown on each figure.

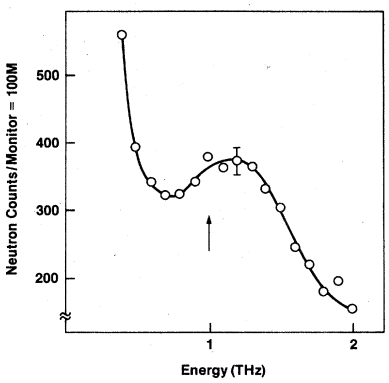

FIG. 10. Neutron counts (per approximately 30 min) at the position (2.48,0,1) showing the frequency of the Σ_4 phonon with an applied hydrostatic pressure of 5.16 kbar. The experimental arrangement was with Be(002)$\rightarrow$Be(002) and a final energy $E'=8$ THz. The position of the phonon at ambient pressure is given by the arrow.

B. Variation of pressure

Pressure has a drastic effect on the CDW in α-U as discussed in Sec. IV. We also expect some effect on the Σ_4 phonon frequency. At room temperature the increased phonon frequency is shown in Fig. 10. The relative shifts are much greater at lower temperatures, as one would expect, but precise data are difficult to achieve because of the decreasing phonon intensity and the background scattering from the pressure vessel. More complete studies of the inelastic scattering as a function of pressure require larger crystals than presently available.

VI. SUMMARY

A. Formation of CDW

The incommensurate CDW is now reasonably well characterized in α-U, but we cannot explain why it forms. This touches on the far more complex question of the stability and structures of the actinide metals. At present the widely held view is that the $5f$ electrons participate in the bonding for U, Np, and Pu, but not for heavier elements.[13] That is one reason why these elements have complex structures and many allotropes.[14] Efforts to calculate the band structure of α-U have not produced any anomalous results in the [100] direction, but this perhaps is not too surprising since it is extremely difficult to include the full details of the electron-phonon interaction in such a calculation.[15] Furthermore, de Haas–van Alphen measurements[11] have yet to yield a complete Fermi surface of α-U.

α-U is the first element to be found that exhibits a spontaneous CDW at low temperature. The orthorhombic α-U structure is itself unique, although at high pressure (56 kbar) cerium adopts this structure,[16] and possibly also Am.[17] Neither of these have been cooled to determine whether a CDW occurs. We should also note that the low-temperature form of Pu, the α phase, shows a variety of anomalies[2] at $T\sim 60$ K that resemble those found in α-U.

B. Possibility of single or multi-$\vec{q}$ states

Many of the systems that exhibit complex CDW states are multi-$\vec{q}$ in nature. For example, in $TaSe_2$ the CDW is described by a triple-$\vec{q}$ state,[9] in which all three $\vec{q}$ vectors exist *simultaneously* in a given crystallite. The question in α-U is whether the true low-temperature state consists of domains of different single $\vec{q}$ states or of a $4\vec{q}$ state given by $\vec{q}_1+\vec{q}_2+\vec{q}_3+\vec{q}_4$, where each $\vec{q}$ is given by a choice of signs in Eq. (1). There are two ways in which a distinction between these two choices can be made. Unfortunately neither is conclusive in the case of α-U. First, we may observe higher-order satellites, as found in $TaSe_2$, but none were found. Second, we may apply uniaxial stress and see if the domain population changes. As discussed in Ref. 5, uniaxial stress (up to 3.5 kbar) was applied along both the $\vec{a}$ and $\vec{b}$ orthorhombic axes at 5 K. In both cases no change in the CDW satellites was observed, although the weak $q_x\simeq 0.5$ satellites rapidly decreased in intensity and could not be observed for stresses >0.5 kbar.

Neither of these observations is conclusive. The higher-order satellites may be weak and we do not know *a priori* the structure factors. Examination of the stress measurement shows that $\vec{a}$ (and $\vec{b}$) make an equal angle with $\vec{q}_i$ (where $i=1$ to 4) so that it is not evident which $\vec{q}$ of a single domain structure would be preferred.

C. The weak $q_x\approx 0.5$ satellites and discommensurations

The incommensurate CDW is apparently almost pure sinusoidal in form with the intensity of the second-order satellites compatible with a simple sine-wave displacement. Despite this apparent simple form, a complex diffraction effect gives rise to weak satellites near $q_x\simeq 0.5$, $q_y=q_z=0$ that are apparently commensurate with a lattice slightly larger than the regular α-U lattice. (See Sec. III.) The "misfit" parameter δ (Fig. 5) varies with temperature, but in such a way to keep $(1+\delta)a_0$, where a_0 is the regular a axis, essentially constant.

A somewhat similar diffraction phenomenon is associated with the precipitation of the ω phase in Zr-Nb alloys.[18] In this case *diffuse* peaks are found between the regular lattice points and appear to sample a different lattice embedded in the host bcc lattice. Considerable effort[19] has been directed at trying to understand the ω-phase precipitation in terms of so-called "stacking solitons" or "discommensurations."

To apply similar ideas to α-U we note the following. The intensities of the satellites measured at $[\sim 0.5\,0\,0]$ are accurately accounted for with $e_x=0.006$ Å, $\phi_x=90°$, and all the other parameters zero in Eq. (5). However, this assumes that the total volume is scattering, but suppose we were to make the assumption that the displacement is really 0.053 Å in these regions as given by Eq. (2), then the volume of this phase α'' would be $\frac{1}{400}$ of the volume of the regions with the α' incommensurate CDW at $[0.5\,q_y\,q_z]$. One can therefore imagine "fault" regions α'' in which the $\vec{q}$ vector is $[0.5\,0\,0]$ and represents a change from $[0.5\,q_y\,q_z]$ to $[0.5\,-q_y\,-q_z]$. The unit-cell volume of this fault region α'' would prefer to be larger than a α' phase but because of inherent stresses this is energetically unfavorable, and the result is discommensurations. Quantitative estimates with this model were attempted by Smith *et al.*,[20] but the parameters determined were very different from those of Horowitz *et al.*,[19] and their physical reality seems somewhat difficult to understand. It should be pointed put that since this model involves domains it assumes a single $\vec{q}$ state.

A comparison between the x-ray and neutron intensities for the two sets of satellites would be useful in case the weaker satellites arise from surface effects. It is known, for example, that all crystals are coated with a thin film of the stable oxide. Discommensurations may also be seen *directly* with electron microscopy[21] and such studies, if possible, of α-U would be of immense value in understanding the details of the CDW state.

Experiments on α-U single crystals with strain gauges some years ago[22] identified the 43-K transition, and two additional, apparently first-order transitions at 23 and 37 K. Heat-capacity measurements[23] also found that in pseudo-single-crystal samples anomalies occurred near 23 and 37 K. On the other hand, the 43-K CDW transition appears in all heat-capacity studies, whatever the form of the sample. In all our neutron experiments we have found no evidence for additional phase transformations. The fact that the effects are not easily seen in a polycrystalline sample suggests that high dislocation density, inherent strains, or small particle size may suppress these transformations. This, in turn, suggests that they are associated with the nearly commensurate CDW. The resolution of our spectrometer is such that apparent jumps in the misfit parameter (δ) in Fig. 5(a) would be hard to observe. This is another area that could be tackled with x-ray techniques. Another possibility is that the CDW periodicity shifts only between these temperatures (i.e., between 23 and 37 K). Here the data of Fig. 4 are inconclusive.

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