Observation of a Charge-Density Wave in α-U at Low Temperature

H. G. Smith, N. Wakabayashi, W. P. Crummett,[a] and R. M. Nicklow
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

and

G. H. Lander and E. S. Fisher
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
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The discovery of a charge-density wave (CDW) in α-U at ~43 K is reported. The mode corresponds to the condensation of a longitudinal-optic phonon near $\vec{q} = [\frac{1}{2},0,0]$ in which the atoms are displaced by ~0.006 Å from their special positions. Large precursor effects are seen in the phonon spectra. The wave vector of the CDW is related to that of the fundamental lattice in a rather complex way, which is discussed in terms of discommensurations between the CDW (α' phase) and the primary α phase.

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Almost twenty years ago anomalies were first reported in the elastic constants of α-U metal at low temperature.[1] Since that time a great variety of experiments have been undertaken to elucidate the nature of the low-temperature phase transition at ~43 K, but with little success, except to present a wealth of seemingly contradictory evidence.[2] In this Letter we present the results from a condensation of a soft LO phonon near $\vec{q} = [\frac{1}{2},0,0]$ at low temperature. We have tentatively associated this periodic lattice distortion (PLD) as evidence of a CDW state, although we do not, at this time, know the electronic origin of this distortion. Interestingly, the wave vector of the CDW appears commensurate with a lattice slightly (0.4%) expanded with respect to the fundamental α-U lattice, but coexisting with the α phase. We do not have a complete explanation of the nature of this coexistence; however, the problem is reminiscent of that found in the ω-phase precipitation in the Zr-Nb alloys,[3] and we have made some progress in understanding the position of the CDW peaks in α-U by using concepts recently advanced to understand the ω-phase alloys.[4,5]

The crystal structure of α-U is orthorhombic *Cmcm* with four atoms in the unit cell (Fig. 1). Below 43 K the volume of the unit cell expands,[6] primarily because the a axis expands by 0.3%. The atom positions at room temperature are $\pm(0, y, \frac{1}{4}), \pm(\frac{1}{2}, \frac{1}{2}+y, \frac{1}{4})$, where $y = 0.1024$. This parameter also varies slightly with temperature, having a minimum near 40 K, but such a variation does not constitute a phase change in a crystallographic sense.[6,7] Since the most dramatic anomalies occur in the elastic constants, specifically c_{11}, the present experimental program started with a neutron inelastic-scattering investigation at Oak Ridge National Laboratory of the phonon dispersion curves along the principal symmetry direction at room temperature.[8] The most interesting are those in the [100] direction and are reproduced in Fig. 2(a). Here we see that the frequency of one of the Σ_4 branches is very low near $\vec{q} = [\frac{1}{2}, 0, 0]$. The eigenvector of this mode is $(u, v, 0; \bar{u}, v, 0)$, i.e., out-of-phase (optic) displacements in the x direction and in-phase (acoustic) displacements in the y direction. The observed neutron intensities near $\vec{q} = [\frac{1}{2}, 0, 0]$ indicate that for this wave vector the mode predominantly consists of opticlike x-direction displacements. With this information, and in particular a knowledge of the phonon structure factors, we were in a position to follow this branch on cooling.

The detailed low-temperature experiments were performed on two single crystals, each with

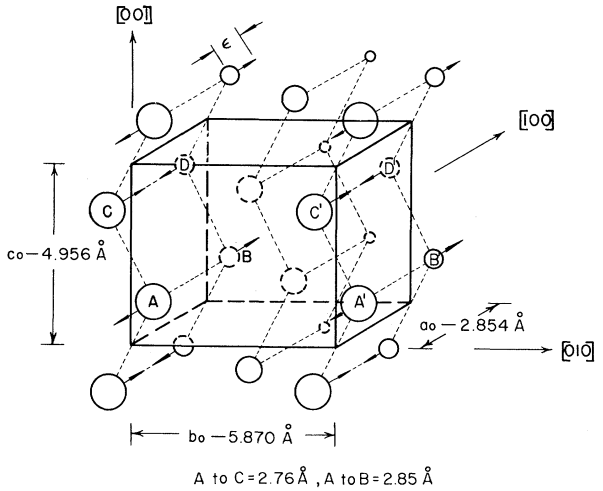

FIG. 1. Modulated structure of α-U at 10.4 K.

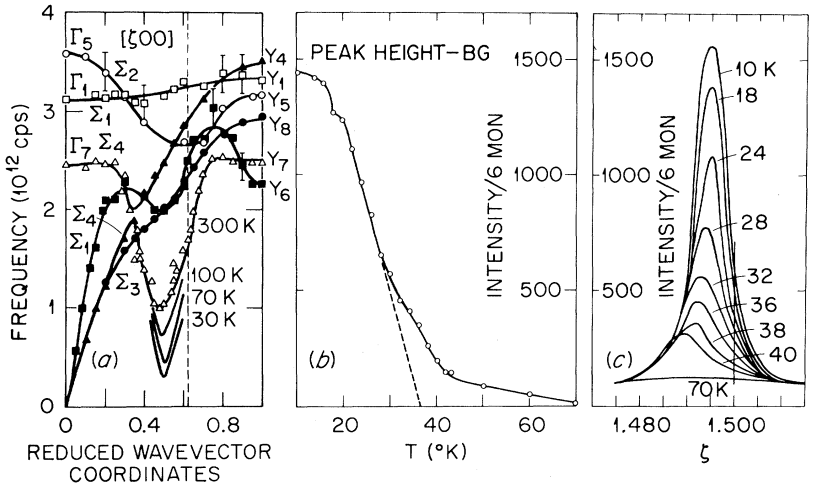

FIG. 2. (a) Dispersion curves in [100] direction. The reduced wave vector coordinate $\zeta = aq/2\pi$. (b) Intensity of (1.495, 0, 1) reflection vs T. (c) Peak shape and position of (1.495, 0, 1) reflection vs T.

a volume of ~0.1 cm^3, on the HB-3 triple-axis neutron spectrometer at the Oak Ridge High-Flux Isotope Reactor. Measurements were made in both the $(hk0)$ and $(h0l)$ zones with two different crystals. Most of the inelastic-scattering measurements were made under rather coarse resolution conditions (utilizing a Be monochromator with either Be or Ge analyzers) to permit neutron groups to be gathered within a reasonable time. The temperature dependence of the lower Σ_4 branch is also shown in Fig. 2(a). A central peak begins to appear around 60 K and grows very rapidly below 40 K; see Fig. 2(b). Under these conditions it becomes very difficult to separate the elastic from the inelastic scattering without employing very good resolution, which, in turn, reduces the intensity. Nevertheless, the indications are that the dip in the Σ_4 LO branch does not collapse to zero energy, but has a minimum at ~0.4 THz (1.6 meV). Measurements of other phonon modes, such as Σ_1 and Σ_3, revealed no anomalies near the zone center at low temperatures.

We shall now confine our attention to the *elastic* scattering. Figure 2(c) shows high-resolution scans near the (1.5,0,1) position as a function of temperature. All the superlattice reflections occur close to the positions $(h+\frac{1}{2},k,l)$ corresponding to the condensation of a phonon mode near $\vec{q} = [\frac{1}{2},0,0]$. The small deviations from a commensurate lattice are significant and are discussed later. We have measured a total of 21 superlattice reflections in the two zones, and found quantitative agreement[9] between the observed and calculated intensities given by the simple formula

$$I_s \propto |F_c|^2 = |4\pi(h+\tfrac{1}{2})\epsilon_x \sin[2\pi(ky+l/4)]|^2. \quad (1)$$

The fundamental reflections are given by

$$I \propto |F_c|^2 = |4(1-\pi^2h^2\epsilon_x^2)\cos[2\pi(ky+l/4)]|^2. \quad (2)$$

This form corresponds to a simple sinusoidal modulation of the displacements in the x direction and requires a doubling of the unit cell in the same direction. The atoms at $x = \pm(0,y,\frac{1}{4})$ are shifted by $\pm\epsilon_x$, and the atoms at $x = \pm(1,y,\frac{1}{4})$, (with respect to the original unit cell) by $\mp\epsilon_x$; see Fig. 1. For convenience we choose the phase so that the atoms at $x = \frac{1}{2}$ are not shifted. The agreement between observed and calculated intensities is obtained with $\epsilon_x = 0.002$. This atomic displacement of 0.006 Å (this is a lower limit based on 100% volume transformation) gives rise to I_s of the order of 10^{-4} of the strongest fundamental reflections. The latter are virtually unaffected (less than one part in 10^4) by the CDW. The appropriate crystallographic description in terms of the new unit cell is space group D_{2h}-$Pmnm$ (origin at center of symmetry), $Z = 8$, with atoms in $4(f)$: $\pm(\epsilon,y_1,\frac{1}{4})$; $\pm(\frac{1}{2}-\epsilon,y_1,\frac{1}{4})$; $2(a)$: $\pm(\frac{1}{4},y_2,\frac{1}{4})$; $2(b)$: $\pm(\frac{1}{4},y_3,\frac{3}{4})$. $\epsilon \equiv \epsilon_x/2$, and, at this stage of the investigation, y_2 and y_3 taken to be $\frac{1}{2}+y_1$, and $\frac{1}{2}-y_1$, respectively. Previous searches[6,7,10] have been confined to the $(h,0,0)$ and $(0,k,0)$ lines, along which the structure factor [Eq. (1)] assures that the superlattice reflections cannot be seen. Our success came simply because the phonon dispersion curves were measured first

and gave the clue on where to expect possible superlattice reflections.

We now turn to the wave vector of the CDW. In Fig. 2(c) the peak position at low temperature is slightly less than (1.5,0.1), i.e., at $(1.5-\frac{3}{2}\delta,0,1)$. If the reflection corresponded to an incommensurate CDW we should expect a peak at $(2.5+\frac{3}{2}\delta,0,1)$ so that the two peaks are equidistant from the point (2,0,1). However, this is *not* found experimentally. Rather, we find the peak at a position $(2.491\pm0.001,0,1)$, i.e., $h<2.5$ (see Fig. 3). These effects have been found in the scattering from two different crystals, one oriented to give the $(hk0)$ zone, the other to give the $(h0l)$ zone. We have measured a variety of reflections to eliminate possible errors for resolution effects and crystal misalignment. In both zones the superlattice positions depend only on the h index. A detailed analysis shows the position of the superlattice reflections to be given by $((h+\frac{1}{2})(1-\delta), k, l)$ so that the wave vector is commensurate, $\vec{q}=[\frac{1}{2},0,0]$, with a lattice whose lattice constant a_s is *slightly larger* than twice the fundamental lattice a_0. In fact $a_s/2a_0=1+\delta=1.0037\pm0.0004$. In terms of the α lattice, the exact positions of the superlattice reflections at 10 K are then given by $h=1.4945$, 2.4908, 3.4871, etc., in agreement with experiment. This is a most unusual situation. One of the simplest explanations would be that the new low-temperature α' phase is formed with the CDW and this is embedded in a matrix of α phase. However, we should then expect a second set of fundamental peaks associated with the α' phase adjacent to the α phase peaks, but high-resolution scans over the fundamental Bragg peaks show no extra peaks or even line broadening above and below the 43-K transition. Similarly, no extra peaks or anomalous profiles were reported in the previous experiments done at low temperature with both x rays[6] and neutrons.[7] We reject, therefore, the idea of the coexistence of two independent and uncorrelated phases, one of which exhibits a CDW.

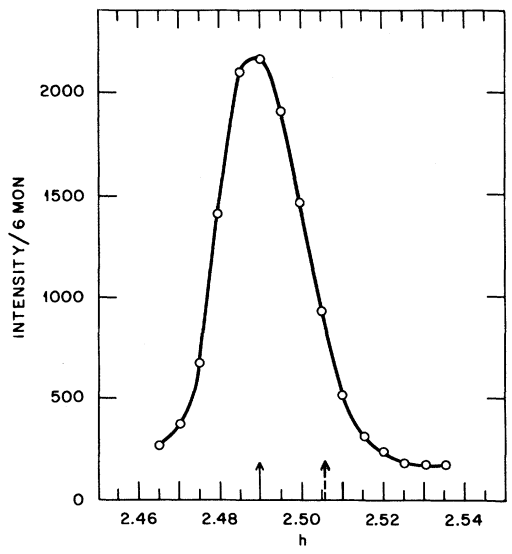

FIG. 3. Peak shape and position of the $(2.5-\frac{5}{2}\delta,0,1)$ superlattice reflection at 10 K. The dotted arrow indicates the expected peak position if the reflection were due to an incommensurate CDW.

The shifts in the weak reflections may be due to discommensurations.[11,12] One such model was used by Horovitz, Murray, and Krumhansl,[4] to explain the rather unusual diffuse scattering observed in some Zr-Nb alloys, in which a diffuse ω phase coexists with the bcc β phase, in terms of *narrow* "stacking solitons." The ω phase is thought to "feel" the perturbating potential of the β phase. We have applied these ideas to the problem of the wave vector in α-U with some success. From our experimental data it appears that the atoms want to be displaced slightly from the crystallographic mirror planes at $x=0$, causing a lattice expansion incommensurate with the α lattice. The results of our model calculations, based on the one-dimensional formalism of Horovitz, Murray, and Krumhansl, is in semiquantitative agreement with the observed data. The weak superlattice reflections are shifted to lower $\vec{q}$ values, in quantitative agreement with the shift δ, and the fundamental peaks are shifted to higher $\vec{q}$ values, but still below the α-phase peaks [$\Delta h=0.005$ for the (2,0,0) reflection]. The value of the parameter λ we used ($\lambda=0.98$) is very different from that used in the ω-phase problem ($\lambda=0.2$), and produces quite different effects. This large value of λ corresponds to *wide* "stacking solitons" and the phase shift varies slowly over many unit cells, rather than over a narrow region as in the Zr-Nb system. The calculations omit any coherent relations between the α and α' regions and, therefore, predict two (2,0,0) peaks slightly separated, contrary to observation. This may merely reflect the limitations of the one-dimensional model. An laternative explanation (unproven here) is that coherent relations exist between the α and α' regions such that they contribute coherently to the fundamental peaks. Such a model would probably involve a more complex arrangement of the discommensurations than has been proposed here. Additional diffuse scattering at low temperatures

also indicates that the structural distortion may be somewhat more complex than has been described above. This has been briefly discussed in Ref. 9.

In conclusion, we believe the present results represent a major step forward in understanding the properties of α-U at low temperature. This material is also a superconductor with $T_c \sim 0.1$ K, but T_c can be raised to ~2 K with modest pressure,[2] which also inhibits the α-α' transition at 43 K. We plan to study the soft mode and superlattice formation as a function of pressure in the near future. Although the formation of a superlattice in α-U is well established, and is discussed in terms of a CDW, the exact relationship of the wave vector to the fundamental lattice is an intriguing and, to the best of our knowledge, new problem.

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[a]Present address: Baptist College of Charleston, Charleston, South Carolina 29411.

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