CDW-gaps, soft-phonons and physical transitions in bulk single crystal of alpha-Uranium

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Abstract. An overview of three decades of studies of the low temperature structural behaviour of the bulk of alpha-Uranium (α-U) is presented. Combining high-resolution elastic and inelastic neutron scattering made it possible to observe and study, down to 5 K, the structural and lattice dynamical aspects of a series of three charge-density waves (CDWs) transition (43, 37 and 22 K). However at lower temperatures several physical quantities show anomalies such as a controversial superconductivity transition. This stresses the need for extra structural data down to very low temperatures. While this would be a challenge with neutrons due to fission sample heating, a new opportunity is offered by low temperature Laue diffraction with hard X-rays. For example a full locking of the periodic lattice distortion (PLD) can be expected related to the evolution of the CDW and/or the appearance of a SDW, this might help understand the physical behaviour of the material and clarify the role of sample impurities.

1. Diffraction and charge-density-wave transitions

The low-temperature phase of uranium metal (see [1] for a review) is called the alpha phase (α-U) and is stable below 935 K. We consider here the bulk material at ambient pressure. Others put the focus on thin film [2] or epitaxial [3] samples that exhibit a substantially different behavior e.g. due to intrinsic strain, dominating surface effect, skin effect, etc. Thus the comparison is hazardous and a global discussion of both bulk and film results is out of our scope.

α-U crystallizes in the orthorhombic system with space group Cmcm (A20) and exhibits a series of three periodic lattice distortions (PLDs) at low temperature. In the case of a metal these are known to be responsible for the lowering of the energy of the electron states thus opening a gap at the Fermi level. At ambient pressure a modulation wave vector (q) with respect to the equilibrium phase appears below $T_0 \approx 43$ K (: $\alpha_1$ with $<q_x, q_y, q_z>$), changes to (: $\alpha_2$ with $<1/2, q_y, q_z>$) at 37 K and then to (: $\alpha_3$ with $<1/2, 1/6, q_z>$) at 22 K. α-U is the only element, so far, which exhibits such a series of transitions. These true PLDs with ±q components were observed for the first time on the neutron Laue-diffractometer S42 on α-U single crystals first and then on polycrystals [4, 5]. The single crystals were produced by Fisher [6] using a grain coarsening method. In fact, white-beam neutron diffraction was

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well suited for this study because a Laue pattern is the image of a large part of the reciprocal space. On the contrary, with monochromatic diffraction, scans along high symmetry directions are very likely to miss the corresponding Bragg peaks since the modulation wave vector is incommensurate with the lattice of the reference structure. However, the very weak elastic peaks observed (~ 0.01% of fundamental reflections) and referred as ’Smith’ in [1] are not related to a true PLD (i.e. no ±q pair).

Back-reflection neutron Laue patterns showed satellites up to \(\sin \theta/\lambda > 0.075 \text{ nm}^{-1}\) while the measured magnetic form factor of \(\alpha\)-U is zero for \(\sin \theta/\lambda > 0.05 \text{ nm}^{-1}\) [7]. This ruled out the old hypothesis of a spin-density wave (SDW) and demonstrated that the superstructure has a crystalline origin, a result that supports the hypothesis of a long-range order (LRO), i.e. a three-dimensional 2\(k_F\) charge-density wave (CDW).

In the following, the set of modulation vectors \(<q^n>\) is related to the Laue pattern by:

\[
h = H + \Sigma M_n q^n \quad \text{with} \quad H = H_\alpha^* + K b^* + L c^* \quad \text{and} \quad q = q_x a^* + q_y b^* + q_z c^*
\]

where \(H\) and \(h\) are the Miller indices of main and satellite reflections respectively, \(a^*, b^*, c^*\) are the reciprocal lattice parameters, \(M_n\) are integers with \(1 \leq n \leq d\) and \(d\) the order of the modulation.

The main Bragg reflections and satellites (~ 1% of the intensity of the main reflections) being recorded simultaneously, this made it possible to observe that the main Bragg reflections remain fixed in position while satellites reflections move in the temperature range 36 to 22 K. The projection of \(q\) \(<q = 1/2 a^* + q_i(T)>\) in the plane perpendicular to \(a^*\) rotates away from the \(c^*\) axis by an angle which tops 12° at 22 K. At this temperature, the projection \(q_i\) is thus almost parallel to \(<011>\). In other words, this disclosed a floating incommensurate structure [4].

The discovery of this set of incommensurate charge-density-waves (ICDWs) by means of white neutron beam diffraction opened the road for extra studies using monochromatic neutron diffraction. The first goal was to widen the range of observation in \(q\) and detect as many weak high-order satellites as possible. The 4-circle diffractometer D10 of the ILL made it possible for the observation of satellites up to the 9th order and with intensities down to \(10^{-6}\) of the main Bragg peaks. Since only satellites with odd orders \((1, 3, 5, 7 \& 9)\) were observed, the shape of the distortion modulation is in the form of a square wave. In other words, the offset of atoms in the modulated structure from their ‘average’ position in the parent structure follows a square wave [8].

An attempt was made to obtain a single domain sample by applying a uniaxial stress along the [011] axis. The achieved domain population was partially modified but diffraction measurements unambiguously showed that the only coupling observed amongst the four components \(q_1, q_2, q_3, q_4\) of the CDW of \(\alpha\)-U are: \(q_1 \pm q_4\) and \(q_2 \pm q_3\) [9].

Thus long-range structural information on \(\alpha\)-U available so far from neutron diffraction is:

i) proposed crystallographic path for the three successive phase transitions [10]:

- undistorted phase: Cmcm above 43 K
- \(\alpha_1\): C2/m11 (\(q_x, q_y, q_z\)) for the interval 43 K > \(T\) > 37 K;
- \(\alpha_2\): P211 (1/2, \(q_y, q_z\)) for the interval 37 K > \(T\) > 22 K;
- \(\alpha_3\): P211 (1/2, 1/6, \(q_z\)) for the interval 22 K > \(T\) > 5 K;
- \(\alpha_4\): still unobserved.

ii) the distortion modulation of the CDW is a partially squared wave from 37 K since no even-order satellites were observed, and the squaring increases down to 5 K (\[8\], table III). This is indicated by the dependence in \(n\) (the odd order index) of the satellite structure factors either observed: \(F_\alpha(n)\) or calculated for a pure square-wave mode: \(F_{\alpha}^{\text{sw}}(n)\). The product \(F_\alpha(n) \times n\) decreases with \(n\) while it should be constant for a pure square modulation. Furthermore, the observed width of satellites increases with \(n\) (\[8\], table III) thus indicating a decrease of the coherence length in the real space.
2. Inelastic neutron scattering around \( T_0 = 43 \) K

Inelastic neutron scattering (INS) investigations were initiated at the High Flux Isotope Reactor of the Oak Ridge National Laboratory (1979 to 1984, [11]). Phonon dispersion curves were measured along the orthorhombic high-symmetry directions [100], [010], [001] only, first at room temperature and then in the temperature range 70 to 100 K. This showed a significant LO phonon softening, sharp along [100] but broad along [010] and [001] with minima not well defined.

When CDW peaks were discovered in 1980 [4], the interest switched to a study of a modulation (\( q_{\text{CDW}} \)) incommensurate with the undistorted structure. This raised the hypothesis that the transition at \( T_0 = 43 \) K involves a soft phonon condensing at (or near) the CDW position in the Brillouin zone, hence the importance of precisely locating the phonon minimum (\( q_{\text{min}} \)). However, the measured phonon intensity being proportional to the phonon population at a given frequency, both a high resolution and a high neutron flux were essential. Even on the cold neutron 3-axis spectrometer IN14 measurements were difficult because the Bose factor strongly lower the intensity at low temperature.

The IN14 measurements ([12], 1999) showed phonon groups for two values of momentum transfer \( Q \) of the soft mode in the Brillouin zone (2 0 1). Since \( Q = k_i - k_f = \tau_{(hkl)} + q \) with \( \tau_{(hkl)} \) the diffraction vector these phonons can be noted as:

\[
Q_c = [1.5, 0, 1] \quad \text{and} \quad Q_s = [2 - q_x (T), 0 + q_y (T), 1 + q_z (T)]
\]
(see figure 1)

For the two families of momentum transfer, the square of the energy of the mode was fitted with a Curie law for the temperature range 120 K to \( T_0 \):

\[
\begin{align*}
(E_c)^2 &= (hf_c)^2 = 3.2 + 0.085(3)^*(T - T_0) \quad \text{hence} \quad (hf_c)_0 = 1.788 \text{ meV} \\
(E_s)^2 &= (hf_s)^2 = 0.75 + 0.107(2)^*(T - T_0) \quad \text{hence} \quad (hf_s)_0 = 0.866 \text{ meV}.
\end{align*}
\]

Figure 1 shows that phonon frequencies at \( Q_s \) (\( hf_s = 0.866 \) meV) are roughly half than those at \( Q_c \) that is along a high symmetry axis [11]. In other words, the minimum of the soft mode is clearly offset from the high symmetry axes but, since (\( hf_s)_0 \) is not zero, there is still something unexplained.

The driving force for the formation of the CDW being the gain in electronic energy, \( \alpha-U \) is pushed to the state of a modulated electronic density below its Peierls transition at 43 K. A PLD, an ICDW with the same wave vector \( q_{\text{CDW}} = 2k_F \), takes place at a typical 2nd-order phase transition. Figure 1 shows a signature of the latter since, according to the Landau theory, there is an absolute ratio of about
2 between the slopes of $Q_s$ in the ordered phase ($T < T_0$, long-range order CDW) and then in the parent phase ($T > T_0$). It is worth noting that $T_0$ coincides with the condensation of the compressional moduli $c_{11}$ & $c_{44}$ that exhibit a clear lambda type change in slope at the 43 K transition [13].

In figure 1, the crosses correspond to the best-fit frequencies obtained via a more complete analysis of the same $Q_s$ data, namely a convolution of the 4-dimensional resolution ellipsoid with the soft-mode dispersion surface expanded quadratically in $q_x$, $q_y$, and $q_z$ around its minimum:

$$(E_{min})^2 = (hf_{min})^2 = 0.113(2)\times(T - 43.65)\text{ meV}^2 \quad \text{with } T_0 = 43.65\text{ K}.$$  

A further experimental effort was made to map a complete 3-dimensional phonon dispersion surface slightly above $T_0 = 43\text{ K}$.

A first set of measurements was performed at 44 K ([12], 2001) in the vicinity of the point at which the CDW condenses, i.e. at:

$$Q_{CDW}(44\text{ K}) = [1.515(5), 0.13(1), 1.21(1)]$$

This result from inelastic scattering is in agreement with the value of $q_{CDW}$ from diffraction.

A second set of 30 energy scans were performed at 48 K at different $q$ values [14]. These were analysed using a 4D convolution to map the surface dispersion with a quadratic development around the minimum at $q = q_0 + q(T) = 0.485 a^* + q_u + q_v$ with $u$ and $v$ two orthogonal unit vectors and:

$$q_u = \cos\alpha q_x + \sin\alpha q_z \quad \text{and} \quad q_v = -\sin\alpha q_x + \cos\alpha q_z$$

where $\alpha = (b^*, u)$ according to the model,

$$(hf)^2(q, T) = (hf_0)^2(q_{0\text{,o}}, T) + \lambda_x(q_x - q_{0\text{,o}})^2 + \lambda_\perp(q_{\perp})^2 + \mu_\parallel(q_{\parallel})^4$$

where $(hf_0)^2(q_{0\text{,o}}, T) = (hf_0)^2$ (cf. above), $q = q_{0\text{,o}} a^* = 0.485 a^*$, $q_{min}(48\text{ K}) = [0.495, 0.147, 0.231]$. The best-fit parabolic parameter values ($T = 48\text{ K}$) were obtained for a $\chi^2 = 0.46$:

$$\lambda_x = 1385, \lambda_\perp = -43.7, \mu_\parallel = 116.7, \lambda_\perp = 66.4 \text{ in meV}^2\text{.rlu}^{-2} \text{ with } \alpha = 58.6^\circ.$$  

While the fit (figure 2) showed a reasonable agreement with observed phonons, the saddle point (secondary minimum) at $T = 48\text{ K}$ is at $q_x = 0.495$ i.e. not exactly at $q_x = 0.5$ as expected but slightly offset along the $x$-axis towards the location of the true minimum. In other words, the observed saddle point is at $Q = [1.505, 0, 1]$ opposite to 1.5 (the commensurate position) with respect to [1.494, 0, 1] the position of the 'Smith' weak reflections observed in early neutrons experiments [15]. This implies that, in the range $90>T>44\text{ K}$, the phonon is already sensing the instability before it occurs. From 65 K to 44 K, a clockwise rotation of the projection of $q_{min}$ in the plane perpendicular to $a^*$ (referred above as $q_x$) was also observed, which is in the right direction with the rotation of $q_{CDW}$ from 43 K to 22 K. For both sides of the transition the value of $q_{min}$ remains similar to that of $q_{CDW}$ at $T_0 = 43\text{ K}$.

In other words, the results of [12, 14] are consistent with an electron-phonon coupling driving up the modulation vector of the CDW.

**3. CDW and the controversial superconductivity transition**

Both the CDW and superconductivity clues ($T_{SC} = 0.78$ to 0.48 K) coexist but in a temperature range which depends on the quality of samples [16]. This raises the question of how they are interwoven as a function of temperature since their driving forces may be opposite. Up to now little is known in that field and even the cell dimensions of $\alpha$-U at $T \leq T_{SC}$ are still unknown.

A trial experiment was performed on D10 [17] to investigate the superconducting transition of depleted $\alpha$-U by means of neutron diffraction at very low temperature. However, the cooling power of the helium-flow cryostat of D10 [18] was not enough to overcome the sample heating due to both neutron capture and induced fission reactions. The latter was estimated to 3 $\mu$W for a sample of about 0.1 cm$^3$ (~ 2 gr) containing 0.4% of $^{235}\text{U}$.  

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Both the a.c. susceptibility $\chi$ measured on Fisher’s samples [19] and the electrical resistivity $R$ measured on McPheeters ones [16] exhibit abrupt drops at low temperature, which suggests a superconducting transition (figure 3). Fisher’s samples were grown using a grain coarsening method [6]. The observed transition temperature (half height of the diamagnetic drop) is $<T_{SC}> = 0.48$ K. McPheeters samples grown by the electrochemical technique are relatively strain free. These exhibit a higher critical temperature $T_{SC}$ at about 0.78 K. This difference is probably related to the impurity level in the samples. On the contrary, $\chi$ and $R$ both exhibit a broad anomaly at about 0.36 K (arrows F and M respectively) almost at the same temperatures despite they were measured on samples with different purity levels. While [16] thinks that M is a measurement artifact, the coincidence is striking and this may be the hint of a crystallographic transition, such as the locking of the $q_z$ component of the CDW, a phenomenon that might be less sensitive to the purity level.

The study of the CDW phases down to temperatures lower than $T_{SC}$ should offer new opportunities to gain insights in the crystallography of $\alpha$-U in the temperature range of the controversial superconductivity transition. However, this implies measuring in the bulk since free surfaces of $\alpha$-U...
crystals rapidly oxidize and the $q$ vector is different in the bulk and in the skin [21]. This was considered only feasible with neutrons but hard X-rays are a good alternative. In fact, they can penetrate millimeter thick samples and they induce no fission reaction and hence no such heating.

Preliminary experiments showed that a hard X-ray facility such as the one at the ILL [22] would be well suited for such measurements (figure 4). Therefore investigating with hard X-ray diffraction down to the interval ($T_{SC}/15 < \Delta T < 15xT_{SC}$) on bulk $\alpha$-U samples seems now a realistic goal. If a locking of the $q_z$ component of $q$ can be observed (see the last paragraph of section 1), then comparing the locking temperature with the critical temperature $T_{sc}$ for samples from different origins should help understand the role of defects/impurities on the material properties. Furthermore it should be possible to collect extra useful structural data, such as cell parameters at very low temperature.

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