3D phonon dispersion surface of incommensurate phases of alpha-U metal

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Abstract. The experimental data on incommensurate phase versus temperature, as they have been obtained by high resolution inelastic neutron scattering, are compared to theoretical models. In the experiments reported we have set out to examine the phonon dispersion surface to verify that the charge-density wave (CDW) state is present continuously at temperature even above $T_{\text{CDW}}$. The position of the phonon minimum ($q_{\text{min}} = q_{\text{CDW}}$), as well as the detailed shape of the dispersion surface of phonon modes over an extended areas in the $(E, q)$ space, is important in view of the debate on the origin of the CDW at the Peierls transition (2$^{nd}$ order phase) and gives rise to a further modulation of the structure. This work confirms that the CDW state has precursor effects before the phase transition, there is a strong coupling between phonon and electronic states and that a 'soft-mode transition' occurs at $T_{\text{CDW}}$. This result is compared to theories discussing the origin of the CDW state.

1. Introduction

Although there are several measurements of good single crystal data by Inelastic Neutron Scattering (INS) techniques there’s no complete measurement of dispersion surface in alpha-U. Phonon dispersion curves were carried against their wave vector along the principal symmetry direction for the structure. A deep minimum was in the $\Sigma_4$ branch at $q = [1/2, 0, 0]$. Furthermore, this minimum phonon frequency shows a classical soft mode behavior with temperature. It does not collapse to zero energy, but has a minimum at $\approx 0.4$ THz (1.6 meV) [1]. A review of this earlier work is given by Smith and Lander (1984); the investigations of the phonons were limited to the symmetry axes.

A new way was opened using extremely high resolution 3-axis experiment (IN14 at ILL) to investigate more appreciable minima forms at $[1/2, q_y, q_z]$ than near the saddle point at $[1/2, 0, 0]$, partial results are appeared from 1999 to 2001 given by Marmeggi and al. [2] as precursory data who have needed more investigations around the incommensurate components of $q = [q_x, q_y, q_z]$. The experimental phonon softening [2] which is accompanied by large changes in cell parameters at $T_0$, is dependent on $q_x(T)$, $q_y(T)$. At $T_0 = 43$ K the modulation wave vector of the incommensurate low-temperature condensing soft mode is $q_{\text{min}} = [0.497 (1), 0.13 (1), 0.21 (1)] \approx q_{\text{CDW}}$. From the collection of the three dimensional surface dispersion the minimum position $q_{\text{min}}$ is reached where low-frequency damped phonons (Kohn anomaly) soften exactly at the incommensurable charge density wave (ICDW) positions.
2. Inelastic neutron scattering

The determination of crystal phonon frequencies through experiments of coherent INS has been used. Conservation of crystalline momentum implies that one-phonon processes of absorption (emission) for a mode, with wave vector \( \mathbf{q} \) (-\( \mathbf{q} \)), can be observed only at scattering vector \( \mathbf{Q} \), such that \( \mathbf{Q} + \mathbf{q} \) is a reciprocal vector \( \tau_{hkl} \). Hence at different \( \mathbf{Q} \) values, the repetition of measurements, allows one in principle, to determine the phonon branches \( \varpi(\mathbf{q}) \): \( \mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f = \tau_{hkl} \pm \mathbf{q} \); where \( \mathbf{q} \) is the phonon vector, defined with the respect to the nearest reciprocal-lattice point \( \tau_{hkl} \). An energy scan, called a constant-Q scan with such a scattering will show two signals, due to the creation and the annihilation of a phonon. A characteristic feature of phonons is the presence of Kohn anomalies structure in the dispersion surface, for phonon wave vector \( \mathbf{q} \), corresponding to: \( \mathbf{Q} + \tau_{hkl} = 2\mathbf{k}_F \), where \( \mathbf{k}_F \) is the Fermi momentum of the electrons.

3. Temperature behavior of the soft mode frequency from both side of the transition

INS have been performed at the cold source on 3-axis spectrometer (IN14), using a PG (002) monochromator and an elastically bent perfect Si (111) analyser to improve the resolution and eliminate second-order contamination. Figure 1 of a previous paper ([2], 1999), reported below, has shown phonon groups for two values \( \mathbf{Q}_c = [1.5, 0, 1] \) and \( \mathbf{Q}_s = [2 - q_x(T), q_y(T), 1 + q_z(T)] \) of momentum transfer. The square of the frequency of the mode for the two families of momentum transfer, as a function of temperature gives respectively, from 120 K to \( T_0 \), the Curie laws:

\[
(E_0)^2 = (h\nu_c)^2 = 3.2 + 0.085(3)(T - T_0) \quad \text{hence} \quad (h\nu_c)_0 = 1.788 \text{ meV}
\]

\[
(E_0)^2 = (h\nu_s)^2 = 0.75 + 0.107(2)(T - T_0) \quad \text{hence} \quad (h\nu_s)_0 = 0.866 \text{ meV}
\]

From figure 1, it is clear that the phonon frequency is smaller at \( \mathbf{Q}_s \) compared to \( \mathbf{Q}_c \); \( \mathbf{Q}_c \) coexists with \( \mathbf{Q}_s \). The minimum energy of \( h\nu_c \) (0.866 meV) for \( T_0 \) has been divided by two compared to \( (h\nu_c)_0 \).

![Figure 1.](image1.png)  
**Figure 1.** The square of the phonon frequency, \( h\nu = E_0 \), plotted as a function of \( T \) at the momentum transfer \( \mathbf{Q}_c = [1.5, 0, 1] \) (open circles) and \( \mathbf{Q}_s = [1.5, q_y, 1 + q_z] \) (closed circles). The triangles correspond to values at \( \mathbf{q}_{min} = (q_x, q_y, q_z) \) that minimize \( h\nu \).

![Figure 2.](image2.png)  
**Figure 2.** (color online) A 3D view of the dispersion surface at \( T = 48 \text{ K} \) projected along an oblique direction, of the lowest energy path for \( q_x \) & \( \mathbf{q}_z \), in order to show \( \mathbf{q}_{min} \). Open and closed circles show the measured phonon frequencies above and below the fitted map.

The driving force for the formation of the CDW state is the gain in electronic energy. Below the Peierls transition temperature, alpha-U is pushed into the state of modulated electronic density and a
periodic lattice distortion of the same wave vector equal to: $q_{CDW} = 2k_F$, takes place as a second-order phase transition for incommensurable CDW state. In addition on the figure 1, it is observed for $Q_s$ that the absolute value of the slope ratio between the ordered phase ($T<T_0$, CDW long-range order) and the disordered phase ($T>T_0$) is around 2 as a new signature for this second-order phase transition.

In figure 1, the triangles correspond to the best-fit frequencies obtained via a more complete analysis of the same $Q_s$ data (convolution of the four-dimensional resolution ellipsoid with the soft-mode dispersion surface expanded quadrically in $q_x$, $q_y$, and $q_z$ about its minimum):

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

The square of the phonon energy, $(E)^2$, obeys a Curie law which states that $(E)^2$ rises from zero at $T_0$ and increases linearly with temperature. Hence it has been shown that the temperature dependence of the mode frequency associate to $Q_s$ writes: $hf_{\text{min}} \approx |T - T_0|^{1/2}$.

The softening of transverse optic (TO) mode monitors the structural phase transition at $T_0$. This coincides with the condensation for the compressional moduli $c_{11}$ & $c_{44}$ (shaped with a clear lambda type change in slope at 43 K transition [3]).

Below $T_0$, a point of interest concerning satellite Bragg reflections is the variation of the satellite (1.5, $q_y$, 1 + $q_z$) intensity as a function of temperature: after a rapid increase between $T_0$ and $\approx 20$ K, a saturation is observed on the satellite reflection that is among the strongest measured, its intensity is still $\approx 1/500$ compared with a strong fundamental Bragg reflection such as (2, 0, 0). In previous experiments, reported elsewhere [5], a large set of fundamental and satellite reflections were collected at 20 K, using the four-circle diffractometer D10. With an incident neutron $\lambda = 2.36$ Å, and after averaging over equivalent reflections, the ratio of the two integrated intensities was found to be:

$$I(2, 0, 0) / I(1.5, q_y, 1 + q_z) = 550 \pm 26.$$

Near 44 K, an experimental effort was made to map a complete 3-dimensional phonon dispersion surface ([2], 2001) over the region of $Q$ near to the point at which the charge-density wave condenses $q_{CDW}(T_0 = 43 \text{ K}) = [0.490, 0.131, 0.225]$ as determined by neutron diffraction experiments [4]. The value of the real minimum $q_{\text{min}}(44 \text{ K}) = [0.485(5), 0.13(1), 0.21(1)]$, (cf. [2], 2001), with statistical accuracy of INS, corresponding to:

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

is indistinguishable from $q_{CDW}$.

The data, now at 48 K, was obtained on a total of 30 energy scans with different $q$’s; the analysis has been established by a 4D convolution to map the surface dispersion response, in figure 2, with a quadratic development around the minimum $q_s = q_x + q_i(T) = q_{00}a^* + q_iu + q_jv$ with:

$$q_x = \cos \alpha q_y + \sin \alpha q_z$$
and
$$q_i = - \sin \alpha q_y + \cos \alpha q_z$$
where $\alpha = (j, u) \equiv (b^*, u)$ following the model,

$$(hf)^2(q_s, T) = (hf_{\text{min}})^2(q_{00}, T) + \lambda_x(q_x - q_{00})^2 + \lambda_y(q_y)^2 + \lambda_z(q_z)^2$$

with $(hf_{\text{min}})^2(q_{00})$ (cf. above), $q_i = q_{00}a^* = 0.485 a^*$, $q_{\text{min}}(48 \text{ K}) = [0.495, 0.147, 0.231]$ and the following best-fit parabolic parameters values ($T = 48 \text{ K}$):

$$\lambda_x = 4138, \lambda_y = - 43.7, \lambda_z = 116.7, \alpha = 66.4 \text{ all in meV}^2\text{.ru}^{-2} \text{ with } \alpha = 1.023 \text{ rd, where } \chi^2 = 0.46.$$ 

The experimental fit shows a reasonable agreement with the measured phonons, and the saddle point (secondary minimum) in figure 2 at $T = 48 \text{ K}$ is not exactly at the $q_s = 0.5$, but displaced along the $x$ axis towards the value of the main minimum, i.e. at $q_s = 0.495$, and this corresponds to the position $Q = [1.505, 0, 0]$; at the opposite side compared to 1.5 where the position (1.494, 0, 0) [1] of the weak satellite Bragg reflection occurs at $T < T_0$. This implies that the phonon is already sensing the instability before it occurs. Such an interaction is almost certainly a signature of the Fermi-surface instability. The phonon anomaly is present at a temperature even above $T_0$ as consequence of a real coupling between the electron and phonon states. Finally, at $T = 90 \text{ K}$ the phonon dispersion surface has been collected but the shape is relatively flat; at this temperature, the energy associated to the momentum transfer $Q_s (= 2.35 \pm 0.02 \text{ meV})$ joins with those of the $Q_c$.

4. Theory takes the hand: analysis and conclusion

In 1993, Yamada [6] proposed a theory in which the weak additional peaks at $q = [1/2, 0, 0]$ were a consequence of strain in boundary region between the different domains of the main CDW distortion,
occurring at \( q_{\text{CDW}} \). The fact that \( q_{\text{CDW}} \) had finite components in \( q_x, q_y \) and \( q_z \) was viewed as another consequence of the coupling of the CDW displacements with the strain. From figure 1, it is clear that the phonon frequency is smaller at \( Q_s \) compared to \( Q_c \); since \( q_x = 1/2 \) in both \( Q_s, Q_c \), and Yamada’s theory propounds that the frequency should depend on \( q_x \) only, this part of the theory is clearly incorrect.

More recently, the mechanism of the phase transition in alpha-U at 43 K (\( \alpha_1 \)) has been investigated by Fast et al. [7] using as guide line low temperature scattering experimental probes sufficiently accurate, identified as the CDW state. At \( T_0 = 43 \) K, \( q_{\text{CDW}} \) is known to be totally incommensurate in the \( x, y, z \) components from the experimental point of view. Fast et al, have shown that applying the full Local Density Approximation calculations (limited to the commensurate \( q = [1/2, 0, 0] \)), in consideration with a full-potential schema at the first phase transition (\( \alpha_1 \)), gives some calculated energy gain as a function of the CDW distortion parameter. But the amplitude of the periodic lattice deformation (responsible of the filled electron states of the conduction band) increases on decreasing temperature; for all that, the experimental value [5] established at \( T = 5 \) K and the theoretical [7] estimated at 43 K suffer the comparison, and nevertheless this figure is of the order to be expected. In this connection it is of particular interest to notice that although uranium is an f-electron element, Fast et al. are able to account for the CDW phase \( \alpha_1 \), which involves minute energy changes and puts extremely high demands on the theoretical treatment.

5. Conclusion

At the issue of ours experimental works on phonon-dispersion, an expansion of the soft-mode frequency in powers of \( q(T) \) around \( q_{\text{min}} \) has been given mapping the inelastic response over an extended areas in the \( (E, q) \) space. By comparison the relationship is not yet reproduced by theory of lattice dynamics on the calculated phonon spectra around the 43 K (\( \alpha_1 \)) transition. Finally it is also of interest to note that another f-element, such as Pu, shows physical anomalies at 60 K perhaps a CDW state exists, this affirmation is confirmed by preliminary results [8] up to the recent “local” structural studies by EXAFS [9]; but sufficiently refined low temperature experimental probes are necessary for this detection as guide line for future theoretical work. To conclude, an ideal way for the detection of additional superlattice reflections at phase transitions undiscovered remains (with hard X-rays to reduce the absorption of Pu) the “white beam” Laue diffraction technique, useful to investigate in a wide solid angle of the reciprocal space, as for \( \alpha \)-U (1980, Marmeggi and Delapalme [10], start of a long story), unique metallic element known as having an incommensurately-modulated crystal structure at ambient pressure.

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