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Rapid Note

Inelastic neutron scattering study of the dynamics of the AlNiCo decagonal phase

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Abstract. The dynamics of the decagonal AlNiCo phase has been investigated on a single-grain quasicrystalline sample using inelastic neutron scattering. The decagonal structure can be viewed as a periodic stacking of quasiperiodic planes. The anisotropy between the modes propagating in the periodic and quasiperiodic directions is found to be much weaker than theoretically predicted. A strong resonance splitting is observed at an energy transfer of 15 meV for transverse modes polarized in the quasiperiodic plane.

PACS. 61.44.Br Quasicrystals – 63.20.Dj Phonon states and bands, normal modes, and phonon dispersion

Quasicrystals are long-range ordered structures which lack translational symmetry in at least one dimension. Their collective dynamics is expected to reflect the quasiperiodic nature of the structure (for a review see [1]). Although the Brillouin zone concept only applies to periodic structures, pseudo-zone boundaries (PZB) can be defined around the strong quasicrystalline Bragg reflections which, to some extent, act as zone centers [2]. This induces in principle a hierarchical stacking of gaps in the excitation spectrum. The nature of the eigenstates (localised or critical) in 3D quasiperiodic structures is still a matter of debate [1,3]. However, calculations of the electronic eigenstates on large decagonal approximant structures indicate that some modes have a critical behavior, *i.e.* they are neither localized nor extended, with wave-function maxima located on highly symmetric atomic clusters and a power law decay around each maximum [4]. Experimentally, the dynamics of quasicrystals has been studied on single grain of icosahedral structures such as AlLiCu [5], AlCuFe [6], and AlPdMn icosahedral phases [7]. In the AlPdMn system where large single grains are available, well defined propagating acoustic modes have been observed by inelastic neutron scattering close to strong Bragg peaks. For wave-vectors larger than 0.35 $\mathring{A}^{-1}$, the excitations exhibit an abrupt broadening, and merge into a continuum of dispersionless modes. This broadening occurs for an excitation wavelength which is comparable to the size of the Mackay clusters, the main building block of the AlPdMn icosahedral structure [7]. For the high quality AlPdMn quasicrystal, a comparison with a crystalline approximant has not yet been performed for lack of large single grain samples.

Decagonal phases are thus particularly interesting systems for dynamical studies since they combine structural properties of both periodic (P) and quasiperiodic (QP) materials. They are periodic along the tenfold symmetry axis c and quasiperiodic in a plane orthogonal to it, and allow a direct comparison, on the same sample, of P and QP dynamical properties. Although the decagonal phase is frequently presented as a layered structure, it is nevertheless a close packed structure. Experimentally anisotropies have been observed in the electronic, optical and heat transport properties [8–11]. The phonon contribution to the thermall conductivity is higher along the QP direction, and its temperature dependence is markedly

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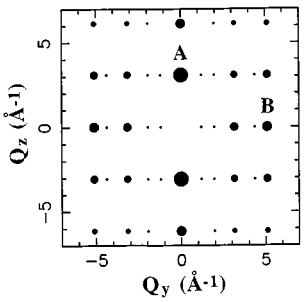

Fig. 1. Experimental (b^*, c^*) diffracting plane containing the periodic and a quasiperiodic direction. Measurements were done around reflections A and B.

anisotropic: there is a conductivity maximum along the periodic direction, as typical for crystals, and an extended plateau along the quasiperiodic directions in agreement with the concept of generalized umklapp processes [11].

Dynamical calculations on decagonal models also predict a strong anisotropy, with a situation similar to what is observed in the icosahedral phases for modes propagating in the quasiperiodic directions and a more structured response for modes propagating along the periodic direction [12].

In this paper, we present an experimental study of the dynamics of a decagonal AlNiCo single grain.

In fact two single grain samples have been used in the experiment. The first one with an approximate size of $3 \times 5 \times 5$ mm^3 was obtained at the Bell Laboratories, and extracted from an ingot slowly cooled from the melt of initial composition $Al_{70}Ni_{15}Co_{15}$. The second sample, about 8 times larger in volume, was produced by the floating-zone technique, and had the composition $Al_{72}Ni_{12}Co_{16}$ [13]. The single grain character of each sample was carefully checked by neutron and hard X-ray Laue diffraction in order to probe the bulk of the samples. Both samples have a periodic lattice constant c equal to 4.1 Å. As for most AlNiCo decagonal phases we observed a large amount of diffuse scattering located in the quasiperiodic reciprocal planes at nc^* and $nc^*/2$ (n integer) as well as commensurate satellites reflections corresponding to a super-structure on the 4D decagonal unit cell [14].

Excitations have been measured in the QP plane (a^*, b^*) and in the (b^*, c^*) plane which contains a QP and the P direction. Most of the measurements have been carried out around the A and B reflections, with 5D indices (00002) and $(11\bar{1}\bar{1}0)$ respectively, according to Steurer's convention [15] (Fig. 1). The experiment was carried out on the thermal three-axis spectrometer IN8, at the ILL. Excitations were first measured at room temperature, and then at 600 K to take advantage of the Bose occupation factor. We did not observe any changes in the excitation spectrum, but for a 3% decrease of the sound velocity at 600 K. Low energy acoustic modes were measured at room temperature on the ILL cold-guide three-axis spectrometer IN14.

Because of the high incoherent cross-section of Co and Ni, there is a significant incoherent inelastic background related to the generalized vibrational density of state [16].

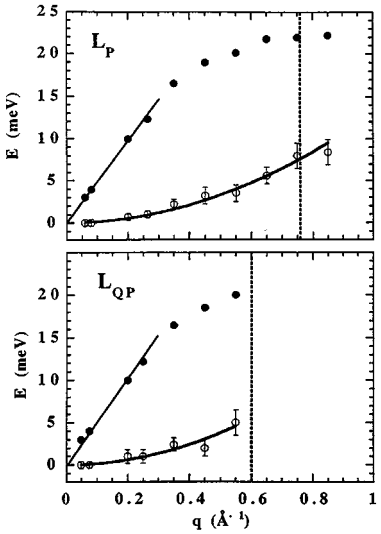

Fig. 2. Dispersion relation for the periodic (top) and quasi periodic (bottom) longitudinal excitations. The vertical dashed line indicate the position of the Brillouin ZB and of the main PZB. The open symbols refer to excitations linewidths. They increases as q^2 as shown by the solid line.

After subtraction of the incoherent background, the position and width of the measured excitations were fitted with a damped harmonic oscillator model convoluted with the instrumental resolution. As for any kind of solid state matter, in the long-wavelength acoustic limit the intensity of the measured inelastic signal scales as

$$I \sim |F_{el}|^2 \, Q^2/\omega^2 \tag{1}$$

where $|F_{el}|$ is the elastic structure factor, Q the position in reciprocal space and ω the phonon frequency. When measuring phonons near a strong Bragg reflection it is thus convenient to consider the normalized inelastic intensity $I\,\omega^2$ which should remain constant as long as the signal remains acoustic.

Longitudinal excitations should in principle show the largest degree of anisotropy, since both propagation and polarization vectors are parallel either to a P or QP direction. Due to the large longitudinal sound velocity, the effective instrumental energy resolution is poor (2 to 4 meV). For wavevector values $q < 0.45$ Å^{-1}, similar results are found for both P and QP directions. The measured excitations linewidths are resolution limited, and start to show a broadening for $q > 0.3$ Å^{-1}. The dispersion relation is linear up to $q = 0.25$ Å^{-1}, with a sound velocity of 7000 ± 150 m/s in both directions (Fig. 2). This is very close to the value in pure Al, to values in Al based icosahedral phases and also in good agreement with elastic constants determined by Chernikov *et al.* [17]. For $q > 0.25$ Å^{-1}, the dispersion relation is no longer linear but the intensity of the signal follows expression (1), *i.e.* the excitation remains acoustic in character. However the width of the measured signal increases progressively.

For wavevectors larger than 0.45 Å^{-1} an anisotropy develops. Whereas the longitudinal QP excitation broadens

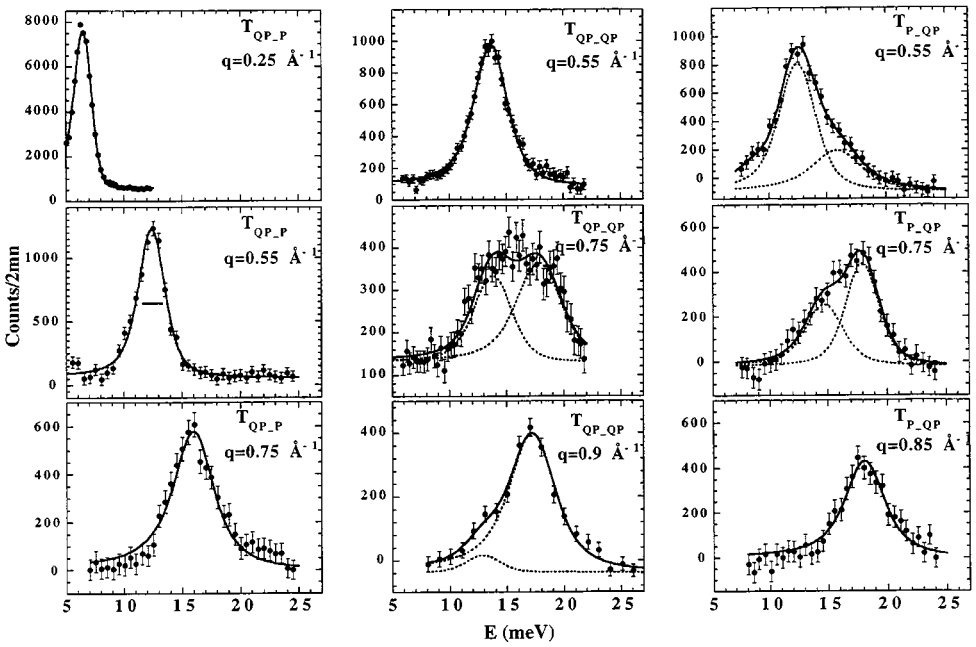

Fig. 3. Experimental profiles for transverse excitations T_{QP-P}, T_{QP-QP} and T_{P-QP} (from left to right). The solid line is a fit with one or two damped harmonic oscillators convoluted with the instrumental resolution (shown as an horizontal line on the left panel). There is a clear broadening of the T_{QP-P} modes. For $q = 0.75$ Å^{-1} a level repulsion is observed between the acoustic T_{QP-QP}, T_{P-QP} branches and a resonant mode. The two contributions are indicated by dashed lines.

rapidly and essentially vanishes at $q > 0.6$ Å^{-1}, the longitudinal P excitation could be followed up to $q = 0.85$ Å^{-1}. However, its normalized intensity (1) shows a discontinuity at $q = 0.65$ Å^{-1}: the signal becomes extremely broad and a fit with a single excitation leads to an integrated intensity which is twice as large as what is measured at lower q values. Thus the dominant character of this periodic excitation is no longer acoustic. In both P and QP directions the excitation linewidth seems to increase as q^2, as shown by the solid line in Figure 2.

Three different type of transverse acoustic modes were measured, which are called hereafter T_{P-QP}, T_{QP-P}, T_{QP-QP}, where the first subscript indicates the propagation direction and the second one the polarization vector. The TA modes have been measured on IN14 with a resolution of 0.7 meV ($q < 0.25$ Å^{-1}) and on IN8 with a resolution of 1.5 to 2 meV ($q > 0.25$ Å^{-1}).

For the transverse modes T_{QP-P}, we found results similar to those observed in the icosahedral AlPdMn phase: below $q = 0.35$ Å^{-1}, excitations are well defined and have a width limited by the instrumental resolution. The dispersion relation is linear with a sound velocity equal to 4100±150 m/s in good agreement with ultrasonic measurement [17]. For wavevectors in the range 0.35 to 0.8 Å^{-1}, the signal broadens and the dispersion curve starts to saturate (Figs. 3 and 4). A damped harmonic oscillator function well reproduces the shape of the signal, with an integrated intensity following expression (1). For q larger than 0.8 Å^{-1}, the signal is very broad (larger than 8 meV) and probably corresponds to a mixing of several excitations up to a maximum energy of 22 meV.

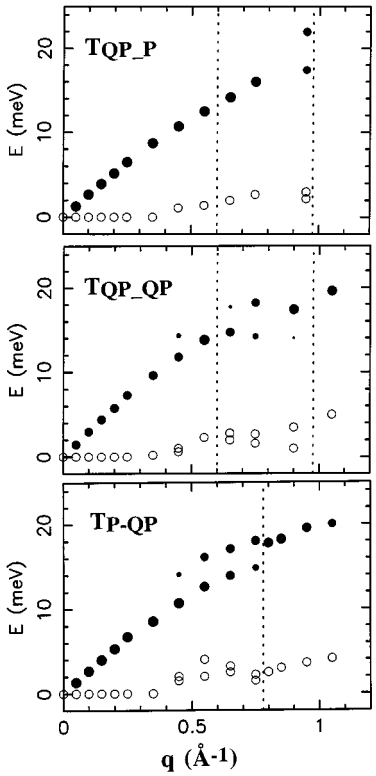

Fig. 4. Dispersion relations for transverse branches. The size of the dots is proportional to the normalized intensity (see text). The open symbols refer to excitation linewidths. The vertical dashed line indicate the position of the Brillouin ZB and of the main PZB.

Similarly the T_{P-QP} and T_{QP-QP} modes are resolution limited for $q < 0.35$ Å^{-1}. The dispersion relation is linear with transverse sound velocities equal to 4100 ± 150 and 4600 ± 150 m/s for T_{P-QP} and T_{QP-QP} respectively, again in good agreement with ultrasonic measurements. As noticed by Chernikov [17] the anisotropy between the two sound velocities (related to the C_{66} and C_{44} elastic constants) is rather weak, in agreement with the close packed nature of the decagonal phase. At higher wavevectors an additional excitation clearly shows up in both directions, at an energy around 15 meV. This excitation is a resonant mode which is mainly observable when its energy is close to the one of the acoustic mode. At this point, the total integrated intensity increases (see $q = 0.75$ Å^{-1} in Fig. 3). At higher q's the signal diminishes, and only the acoustic phonon remains with a normalized intensity which is again equal to the low q acoustic value. There is a level repulsion between the acoustic and the resonant mode as shown on Figure 3. Results are summarized in Figure 4 where the size of the dots is proportional to the normalized intensity of the excitations. Such a strong resonance splitting in quasicrystalline samples has never been reported previously .

When comparing the present results with calculations based on a realistic decagonal model the agreement is quite poor [12]. Whereas theoretical calculations predict a strong anisotropy, we only observe weak differences. Moreover the calculations predict a difference between the T_{QP-QP} and T_{QP-P} excitations with a situation similar to icosahedral phases in the former case and a strong coupling with L_P modes in the latter case, leading to a flattening of the dispersion curve. Experimentally we observe the reverse, since there is a mere broadening of T_{QP-P} excitations, similar to measurement in the i-AlPdMn case and a resonance splitting behavior for T_{P-QP} and T_{QP-QP} modes near 15 meV. The rather poor resolution of the theoretical calculation along the periodic direction makes it difficult to compare our T_{P-QP} dispersion with the theoretical predictions.

The resonance splitting could be due to the opening of a gap at the Brillouin ZB (along the P direction) or PZB (along QP directions). The ZB and the two main PZB are shown as vertical dashed line in Figure 4; their positions do not match the position where the intensity of both acoustic and optic modes are equal, as would be expected for a gap opening. Moreover, along the P direction, because of the non-symmorphic space group of the decagonal structure, the optic and acoustic branch should be degenerated at the ZB [18], which does not correspond to the observed data.

The resonance splitting is much more similar to what is observed in disordered alloys, as reported for instance in the AlCu0.018 alloy in the presence of Guinier-Preston zones [19]. Indeed the structured diffuse scattering observed so far in decagonal phases, is the signature of short range correlations, which may well influence their excitation spectrum. One peculiar aspect of the resonant splitting we observed is that it occurs only for transverse modes polarized in the QP direction. Our experimental resolution would not be sufficient to detect such an effect along longitudinal branches, if present, but it is clearly absent for T_{QP-P} excitations. A simple mass defect theory would thus not reproduce our observations as the resonance splitting would be isotropic in that case. The precise nature of the resonant mode remains thus to be elucidated, but we note that the diffuse scattering appears as thin sheets located in QP reciprocal planes with an extremely sharp intensity distribution along the P direction.

Summarizing, excitations in the decagonal AlNiCo phase show a rather small anisotropy between the periodic and the quasiperiodic directions, even for rather large wavevectors. For longitudinal modes the only difference lies in the fact that the L_P signal can be followed at least up to $q = 0.85$ Å^{-1}, whereas the L_{QP} mode becomes washed out for $q > 0.6$ Å^{-1}. The corresponding wavelength (12 Å) is comparable to the diameter of the columnar clusters which constitute the main building block of the decagonal structure [15]. Transverse acoustic modes remain resolution limited for $q < 0.35$ Å^{-1}. Whereas there is a mere broadening at higher q's for T_{QP-P} excitations, we observe a resonance splitting behavior for transverse mode polarized in the QP direction. We suggest that it is related to structural disorder.

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