ESRF	**Experiment title:** A study of the momentum dependence of high-energy phonons in single-crystal CaC_6	**Experiment number**: HS 3761
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Shifts: 18	**Local contact(s)**: Dr Mathieu LE TACON, Dr Alexei BOSSAK	*Received at ESRF:*

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Report:

Since the discovery of superconductivity in YbC_6 and CaC_6 at temperatures over an order of magnitude higher than previously found in graphite intercalation compounds (GICs) [1,2], the properties of these two compounds has been extensively studied. Although initially an exotic superconducting mechanism was proposed involving acoustic plasmons [3], more recent density functional theory approaches [4,5] have suggested that the superconducting mechanism can be understood via a weak-coupling, BCS-like description, with electron-phonon (e-ph) coupling occurring approximately equally with graphitic phonons and calcium phonons.

In contrast to this model, a large Ca isotope effect (α(Ca) ~ 0.5) has been measured in CaC_6 [6], suggesting that calcium phonons are exclusively involved in the e-ph coupling. In addition to this discrepancy, recent ARPES measurements on CaC_6 [7] suggest that there is far stronger e-ph coupling to the high-energy graphite phonons than the DFT calculations predict. These surprising discrepancies provided the motivation for us to carry out a detailed study of the phonons in CaC_6, to help us to clarify which phonons are involved in e-ph coupling and which are not.

Before this experiment on ID28, we had measured the phonons in CaC_6 at Sector 3 at the Advanced Photon Source, USA, on CaC_6 samples made using highly-ordered pyrolytic graphite (HOPG). CaC_6 samples made from HOPG are reasonably well-ordered perpendicular to the graphene sheets (mosaic ~ 4°), but parallel to the graphene plane (in the ab-plane) the samples are powder-like with crystallite size typically less than 1 μm. These samples allowed us to measure the detailed dispersion of the low-energy phonons in CaC_6 which propagate perpendicular to the graphene sheets, but could only give a powder average of the phonons propagating in the ab-plane [8].

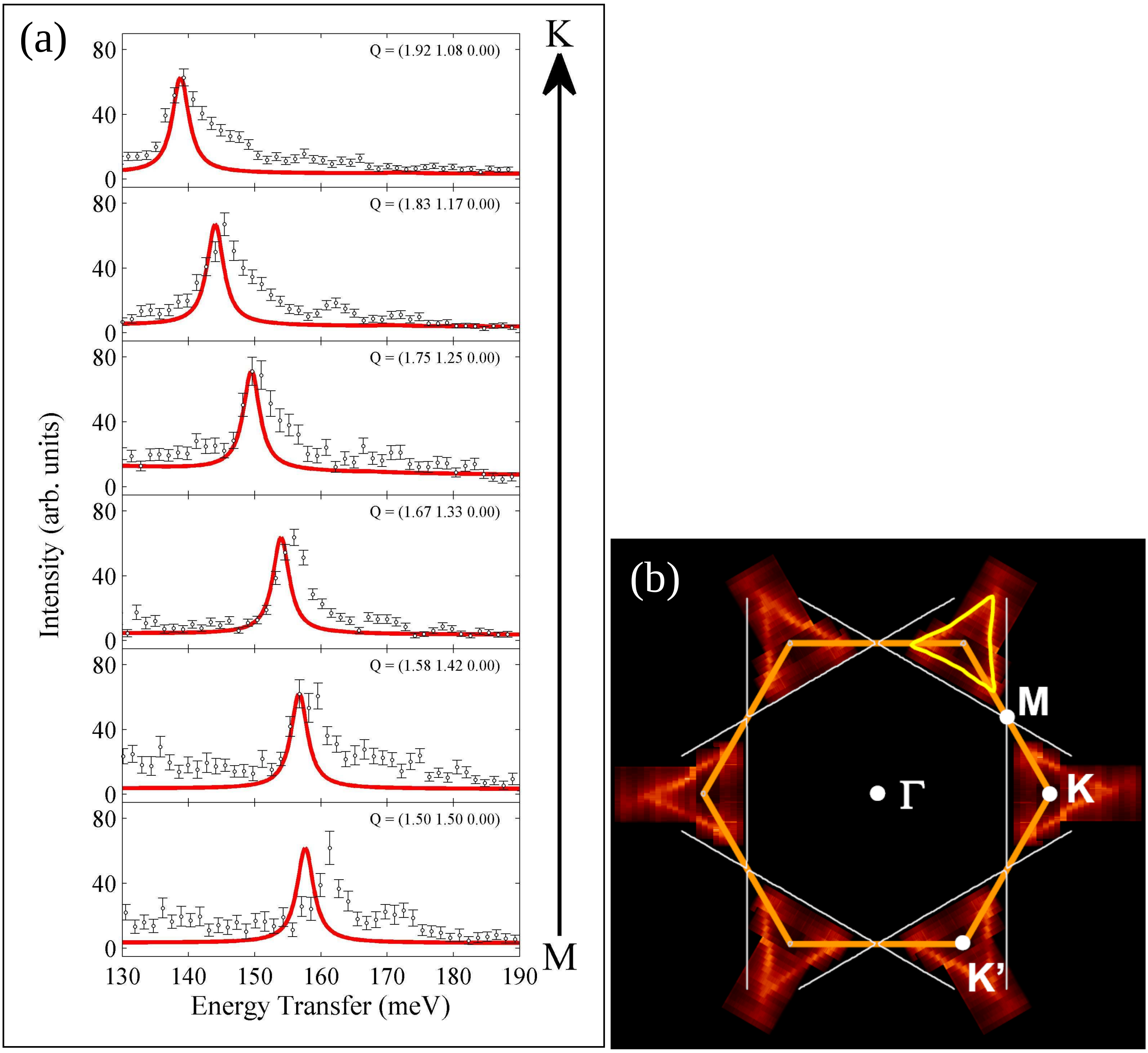

Figure 1: (a) Raw inelastic x-ray scattering data (black) measured at ID28 on CaC_6, measured parallel to the graphene sheets. Each dataset is labelled with its reduced Q and plotted with the appropriate DFT-based calculation (red) of the expected phonon intensity [9]. (b) ARPES measurement of the Fermi surface in CaC_6 [7].

More recent developments in sample preparation have allowed the production of single-crystal CaC_6 samples using natural flake graphite. In our beamtime at ID28 we used these single-crystal samples to enable us to study the phonons as a function of momentum within the ab-plane.

In preparation for the ID28 experiment, we mounted four such samples in different orientations inside a sealed Beryllium dome, in order for all possible areas of momentum to be accessible at ID28. In this beamtime we measured the high-energy phonons in the range from 100 meV to 200 meV over a very large range of momenta in the ab-plane. Although originally we also planned to study the phonons in the Γ-X direction, which is approximately 30° out of the ab-plane, we eventually decided to stay within the ab-plane, since we saw a good deal of phononic signal which was not anticipated by DFT calculations.

A subset of the data is plotted in Figure 1(a). This is a selection of energy scans made at various fixed momenta. These scans were chosen as each energy scan was made at a different point along the M-K line as labelled within the graphite Brillouin zone. Figure 1(b) is the measured Fermi surface of CaC_6 as measured by ARPES [7]. From the ARPES measurements we expect e-ph coupling to occur around the corners of the 'triangles' of the Fermi surface, one of which lies on the M-K line. There is a strong suggestion of broadening of the measured phonon at ~145 meV in the Q = (1.83 1.17 0) scan, which could be a direct result of this phonon coupling to the electronic π^* band.

In conclusion, we have successively measured the high-energy phonons in CaC_6 at room temperature at different momenta within the graphene plane using single crystals. This is the first time to our knowledge that phonons have been measured in unique directions in the graphene plane in any GIC. We have found some tentative evidence for e-ph coupling to one of these modes, and with careful analysis of our large dataset we will look for further evidence for strong e-ph coupling to these modes, as has been claimed in the recent ARPES work [7].

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