ESRF	**Experiment title:** ***Phonon dispersion in the new graphite intercalated superconductor CaC_6***	**Experiment number**:
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Report: Although graphite is one of the most studied materials known, it continues to provide scientists with new and interesting challenges as recently testified by a wide range of novel discoveries in the field, as an integer quantum Hall effect [1-3], and superconductivity [4,5].
Superconductivity in graphite compound can be stabilised by introducing metal atoms between the layers, which allow both tuning of the interlayer spacing and charging of the graphite host. For long time it was believed that the maximum critical temperature obtainable in GIC [6] was of less than 1K. Recently high temperature superconductivity has been discovered [4,5] in two intercalated compounds: YbC_6 and CaC_6 with unprecedented high transition temperatures, 6.5K and 11.5K respectively.

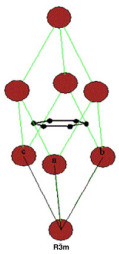

Fig. 1 CaC6 structure [4].

By using the functional density theory, it has been shown that superconductivity in CaC_6 is due to an electron-phonon mechanism [7]. This coupling is mainly associated to the vibrations perpendicular to the planes of graphite for the atoms of carbon, and parallel, for those of calcium. Since the electron-phonon coupling of these modes is activated by the presence of the intercalating metal (Ca) Fermi surface, the occurrence of superconductivity in inserted graphite requires an incomplete ionization of intercalating ion [7]. This is in contrast with the previous picture where intercalated ions are considered just a charge donor to the graphene plane.
In order to validate this new and original point of view, it is necessary to measure the dispersion of the phonons and the electronic bands structure of CaC_6, and compare the experiment with the numerical results.

The measurements has been conducted on a polycrystalline sample of highly oriented pyrolytic graphite intercalated with Ca. In this kind of sample a crystal direction is well defined, corresponding to the c axes of the hexagonal structure in graphite, and to the <1 1 1> family in the rombohedral structure of CaC_6 (see Fig. 1). In this configuration, one can follow the phonon dispersion for the longitudinal modes with momentum parallel to the <1 1 1> direction. But in the reciprocal space planes corresponding to the graphite a^*b^* plane,

the measurement for a given momentum modulus Q will be an average over a circle of radius Q, as shown in Fig. 2, left panel. The volume of the sample we measured was enough for a measurement of the longitudinal phonon dispersion along <1 1 1> using Inelastic Neutron Scattering (INS), but the signal from the *in-plane* average was way too weak for neutron, while strong enough for Inelastic X-ray Scattering (IXS). Therefore we decided to couple the two probes in order to achieve an extensive insight on the phonon structure of CaC_6.

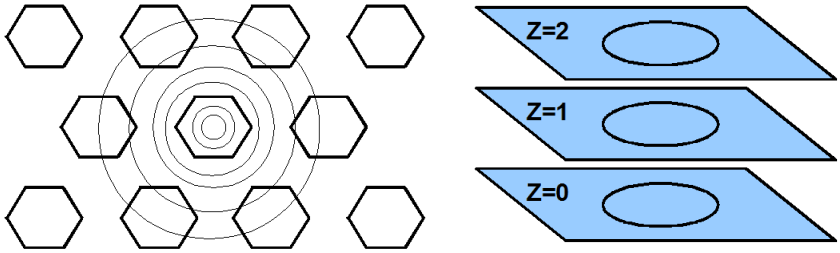

*Fig. 2 Left panel: section of the rombohedric reciprocal space corresponding to the a*b* plane of the graphite sub- lattice in CaC_6. Circle corresponds to fixed Q lines in the plane. Right panel: the circles can be shifted in different Brillouin zones along the graphite c*, adding a component z(1 1 1).*

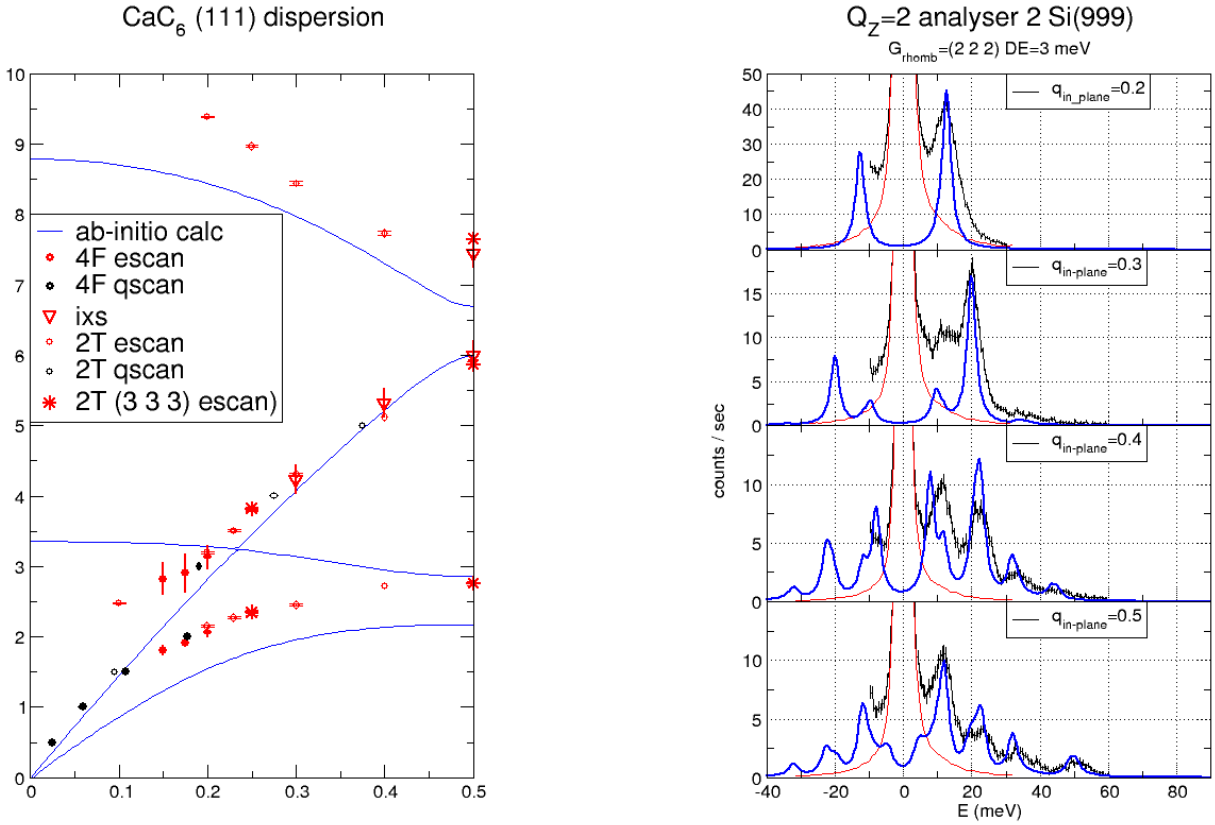

Fig. 3 Left panel: phonon dispersion along the <1 1 1> direction. Red and black circles indicate, respectively, constant energy and constant Q INS scan. Data has been collected on cold source 4F 3-axes spectrometer and thermal source 2T. Red triangles represent IXS constant energy scan. Blue line represents ab-initio calculated phonon dispersion.
Right panel: examples constant Q, in-plane phonon density of state obtained using IXS (black line) compared to ab-initio calculations (blue lines) plus an experimental elastic contribution. The scans are obtained at G+q where G=z(1 1 1) and z=2, while q lies in-plane and we give its modulus for each spectra.

The results obtained in this way are shown in Fig. 3 for the dispersion of longitudinal modes along c* (left panel), and for the partial, constant Q, *in-plane* phonon density of state (right panel). Let's review first the results on the left panel, for the longitudinal dispersion along <1 1 1>. The the phonon energy for the

longitudinal acoustic mode, clearly start in agreement with the expected dispersion. Then, suddenly, bend at around 2 THz (~ 8 meV) and q ~ 0.15, reaching the zone boundary around 2.8 THz (~ 12 meV), close to the energy of the first transverse optical mode. A symmetric bending at higher energy (4 THz 16-18 meV) and lower q of the acoustic longitudinal branch end up again in an unidentified mode at low q and about 2.5 THz (~ 10 meV). This strongly suggests an anti-crossing behaviour, where the longitudinal acoustic mode interacts with an unknown mode. In this region the data are from INS only, as the strong elastic line, due to the disorder of the system, make IXS difficult. One can see that close to the zone boundary IXS and INS data match nicely. In a recent paper on a similar sample of CaC_6 [8], using IXS only, Upton and co-workers assign the flat band at ~10 meV to the first transverse optical mode. This is due to the fact that they lack both a symmetry analysis of their calculated modes as well as the resolution necessary to see the details of the anti-crossing.
From our data it is clear that the mode can not be interpreted that way, even taking into account a symmetry breaking allowing transverse mode to be seen in longitudinal configuration.

At present, we can only suggest some possible hypothesis for the origin of this additional contribution. A first possibility is the presence of an impurity mode coming from the presence of lithium in the preparation of these samples. This hypothesis is supported by a strong XPS signal for the lithium ion. However, there are indications that the Li impurities do not enter the CaC6 structure but are concentrated on the grain boundaries of our polycrystalline sample. A second possibility would be an additional mode coming from an electronic excitation, namely a plasmon. However the 10 meV energy of the peak would be surprisingly low for a plasmon. More data are necessary in order to investigate the origin of this additional mode, possibly in a single crystal CaC_6 sample without impurities.

The second set of data, consist in constant Q phonon density of state, with a propagation vector q lying in the plane perpendicular to the <1 1 1> direction and corresponding to the a^*b^* plane of graphite. In first Brillouin zone this partial density of state has contribution only from few longitudinal modes, and strongly resembles a longitudinal dispersion, but, unfortunately, our experimental configuration did not allow these measurements. For this reason we compared the spectra obtained to simulation taking into account all the modes as shown, *e.g.*, in Fig. 3, right panel. We found a general agreement between our data and the simulation, but an extra intensity is measured at about 10 meV for some of the spectra in this and other configuration. The possible origin of this unexpected intensity could be from the additional, flat mode for which we have evidence on our longitudinal dispersion along <1 1 1>, but, as the information from *in-plane* modes is averaged, we can not draw direct conclusion. We note that in Ref. [8], the data are compared directly to calculated dispersion, and not to partial density-of-state, with no analysis of the mode symmetry. The conclusion of Ref. [8] based on the *in-plane* mode at 10 meV, are not confirmed, as our data show an intensity in that energy band which does not correspond to the model.

References

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