



HAL
open science

Phonon dispersion and low energy anomaly in CaC₆.

Matteo d'Astuto, Matteo Calandra, Nedjma Bendiab, G. Loupiau, Francesco Mauri, Shuyun Zhou, Jeff Graf, Alessandra Lanzara, N. Emery, C. Herold, et al.

► **To cite this version:**

Matteo d'Astuto, Matteo Calandra, Nedjma Bendiab, G. Loupiau, Francesco Mauri, et al.. Phonon dispersion and low energy anomaly in CaC₆.. 2009. hal-00431291v1

HAL Id: hal-00431291

<https://hal.science/hal-00431291v1>

Preprint submitted on 11 Nov 2009 (v1), last revised 3 Mar 2010 (v4)

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Phonon dispersion and low energy anomaly in CaC_6 .

Matteo d'Astuto,^{*} Matteo Calandra, Nedjma Bendiab,[†] Geneviève Loupiau, and Francesco Mauri
*Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC),
Université Pierre et Marie Curie - Paris 6, case 115, 4, place Jussieu, 75252 Paris cedex 05, France[‡]*

Shuyun Zhou, Jeff Graf, and Alessandra Lanzara
*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA and
Department of Physics, University of California Berkeley, CA 94720, USA*

Nicolas Emery,[§] Claire Hérold, and P. Lagrange
*Institut Jean Lamour - UMR 7198 CNRS - Nancy-Université - UPV-Metz - Département
Chimie et Physique des Solides et des Surfaces - Faculté des Sciences et Techniques,
B.P. 70239 - 54506 Vandoeuvre-lès-Nancy Cedex- France*

Daniel Petitgrand
Laboratoire Léon Brillouin, CEA-CNRS, CE-Saclay, 91191 Gif sur Yvette, France

Moritz Hoesch[¶]
*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble cedex, France
(Dated: November 11, 2009)*

We report measurements of phonon dispersions in CaC_6 using inelastic X-ray and neutron scattering. We found good overall agreement, particularly in the 50 meV energy region, between the data and the first-principles density-functional-theory calculations. However, on the longitudinal dispersion along the c-axis of the hexagonal representation, we found an unexpected anti-crossing with an additional longitudinal mode, at about 11 meV. At a comparable energy, we observe also unexpected intensity on the in plane direction. This result could help to explain the incorrect interpretation of previous measurements of phonon dispersion in CaC_6 , which assign a longitudinal character to a transverse mode in the same energy range. By calculating the electron susceptibility from first principles we show that this longitudinal excitation is unlikely to be due to a plasmon and consequently it is probably due to defects or vacancies present in the sample.

PACS numbers: 74.70.Ad, 74.25.Kc, 63.20.Dj, 63.20.Kr, 78.70.Ck, 71.15.Mb

I. INTRODUCTION

Intercalation of foreign atoms in graphite can stabilize superconductivity by introducing metal atoms between the layers, which allow both tuning of the inter-layer spacing and charging of the graphite host. For long time it was believed that the maximum critical temperature obtainable at ambient pressure in graphite intercalation compound (GIC) [1] was of less than 2 K. The discovery of high temperature superconductivity in two intercalated compounds: YbC_6 [2] and CaC_6 [2, 3] with

unprecedented high transition temperatures, 6.5 K and 11.5 K respectively, has raised renewed interest about the role of phonons in GICs.

The role of the in-plane and out-of-plane phonon modes in CaC_6 has been controversial. By using the density functional theory, it has been shown that superconductivity in CaC_6 is due to an electron-phonon mechanism [4, 5, 6]. The electron-phonon coupling is mainly associated to the Carbon vibrations perpendicular to the planes of graphite (C_z), and Calcium vibrations parallel to the graphite planes (Ca_{xy}). However specific heat measurements suggest [7] that the contribution of C_z vibrations is even larger than what was predicted by density functional theory (DFT). Consequently, it would be desirable to measure the phonon dispersion of CaC_6 in order to see if there is actually a disagreement between theory and experimental data.

In this work we measure c-axis phonons in CaC_6 using inelastic X-ray and neutron scattering (IXS and INS respectively). Furthermore, in order to assess the precision of DFT calculation we compare the calculated and measured in-plane averaged IXS structure factor.

On the longitudinal dispersion along the c-axis of the hexagonal representation, we found an unexpected anti-

^{*}Electronic address: matteo.dastuto@impmc.upmc.fr

[†]present address: Laboratoire de Spectrométrie Physique, Université Joseph Fourier - 140 Av. de la physique, BP 87 - 38402 Saint Martin d'Hères

[‡]Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), CNRS UMR 7590, Campus Boucicaut, 140 rue de Lourmel, 75015 Paris, France

[§]present address: University of Aberdeen, Chemistry Department, Meston Walk, Aberdeen, AB24 3UE, Scotland

[¶]present address: Diamond Light Source, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, England

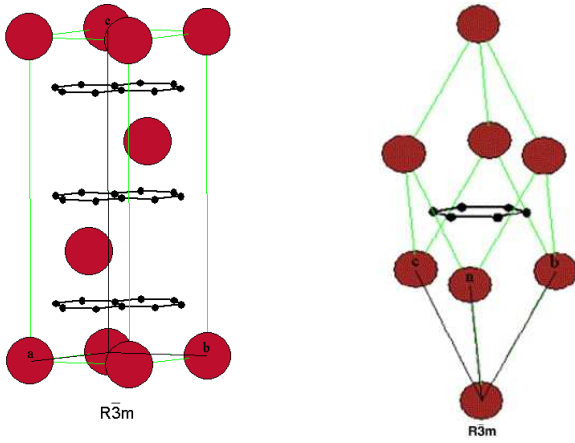


FIG. 1: (Color online) Right panel: rhombohedral crystal structure of CaC_6 . Large red circles correspond to calcium ions, small black ones to carbon atoms. Left panel: The corresponding hexagonal unit cell. The 3- rhombohedral c -axis is perpendicular to the honeycomb graphene planes.

crossing with an unidentified additional mode, at about 11 meV. At the same energy, we observe also unexpected intensity on the in plane direction.

Previous measurements of phonon dispersion in CaC_6 [8] assign a longitudinal character to a mode in the same energy range, but the mode is transverse. Here we show that an additional mode appears in the same energy region, and interacts with the longitudinal acoustic mode. This result could help to explain this apparently incorrect mode assignment.

II. METHOD

The measurements have been conducted on a polycrystalline sample of highly oriented pyrolytic graphite intercalated with Ca, prepared by liquid-solid synthesis method in lithium-based alloys [9]. Phonon measurements in graphite are a classical example of comparison of IXS with INS as shown at the very beginning of the IXS technique by E. Burkel [10]. The IXS approach is particularly favorable for high energy modes as it is the case in graphite and GICs where some optical band involving carbon ions are in the 170 meV energy range.

In this kind of sample the polycrystalline domains are actually aligned along a crystal direction, corresponding to the c axes of the hexagonal unit cell, and to the $(1\ 1\ 1)$ family in the rhombohedral structure of CaC_6 [11] (see Fig.1). As a consequence, the phonon dispersion of the longitudinal modes, with momentum parallel to this direction, can be measured. The different Carbon layers in the sample are randomly rotated respect to the common c -axis so that the IXS measurement for a given momentum modulus Q in the a^*b^* plane will be an average over a circle of radius Q , as shown in Fig. 2, top panel. The volume of the sample we measured was enough for a mea-

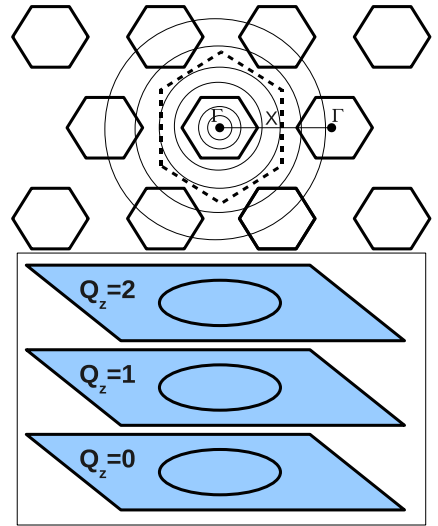


FIG. 2: (Color online) Top panel: section of the rhombohedral reciprocal space corresponding to the a^*b^* plane of the graphite sub-lattice in CaC_6 . Circle corresponds to fixed Q lines in the plane. Two zone center Γ are shown, there are one in each small hexagon, with a line parallel to $(1\ -1\ 0)$ connecting them. The large, dashed hexagon indicate the projection of the rhombohedral Brillouin Zone, with X the zone boundary along $(1\ -1\ 0)$. Bottom panel: the circles can be shifted in different Brillouin zones along the graphite c^* , adding a component $Q_z \times (1\ 1\ 1)$. The L point lies halfway between two planes, at $Q_z \times (1\ 1\ 1) + (0.5\ 0.5\ 0.5)$.

surement of the longitudinal phonon dispersion along $(1\ 1\ 1)$ using INS, but the signal from the in-plane average was way too weak for neutron, while strong enough for IXS. Therefore we decided to couple the two probes in order to achieve an extensive insight on the phonon structure of CaC_6 .

The IXS experiment was carried out on the undulator ID28 beam-line at the ESRF. We have chosen to work with the Si $(9\ 9\ 9)$ [12] reflection, with a wave-length of $0.6968\ \text{\AA}^{-1}$ (17794 eV) and an energy resolution $\Delta E = 3.0 \pm 0.2\ \text{meV}$ [13]. Additional spectra were collected using the Si $(11\ 11\ 11)$ reflection, with a wave-length of $0.5701\ \text{\AA}^{-1}$ (21747 eV) and an energy resolution $\Delta E = 1.5 \pm 0.1\ \text{meV}$. The back-scattered beam is focused on the sample position by a gold-coated toroidal mirror, which provides a focal spot of $h \times v = 0.270 \times 0.090\ \text{mm}$ FWHM. Further details of the used configuration are described in Ref. 14. We measured a platelet of a thickness of $\sim 0.25\ \text{mm}$ in hexagonal c^* direction, and a width of $4.2 \times 0.9\ \text{mm}$ of CaC_6 . The sample was held in a Lindemann glass capillary, sealed in a glove box.

The inelastic neutron-scattering experiment was carried out on the cold source 4F2 and thermal source 2T triple-axis spectrometer at the Laboratoire Léon Brillouin in Saclay, France. Harmonic contribution from the monochromator were reduced using a standard graphite filter, so final neutron wave-number was typically of $1.975\ \text{\AA}^{-1}$ for 4F2, and of $2.662\ \text{\AA}^{-1}$ or $4.100\ \text{\AA}^{-1}$ for 2T al-

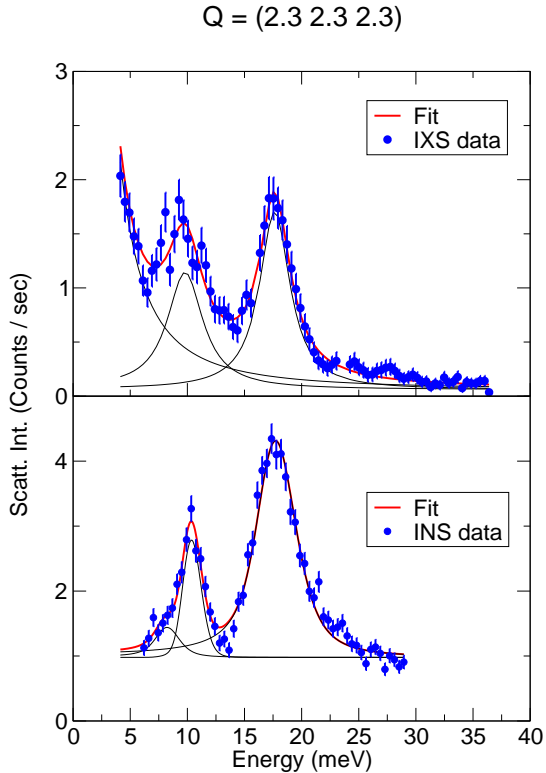


FIG. 3: (Color online) Inelastic energy loss spectra with X-ray (top panel) and neutron (bottom panel) at $\mathbf{Q} = \mathbf{G} + \mathbf{q} = 2 \times (1, 1, 1) + (0.3, 0.3, 0.3)$, corresponding to a longitudinal phonon polarization along 0.6 of the $\Gamma-L$ line. Data are fitted using a convolution of instrumental function with harmonic oscillator.

though some scan at 1.975 \AA^{-1} was taken for comparison sake or for averting artifacts from monochromator harmonics. Collimation were of 60° -open-sample-open-open, and with a horizontally focusing monochromator and a vertically focusing analyzer. Several platelets, of about 6 mm width and for a total of 2 mm thickness, were kept together in an aluminum foil. The sample was sealed in a aluminum can, sealed in a glove box, using an Indium gasket.

A comparison of the IXS and INS data is shown for a point along the $\Gamma-L$ line in Fig. 3.

In parallel to IXS and INS data we carried out first-principles density functional theory in the linear response [15, 16]. We use the generalized gradient approximation [17] and ultrasoft pseudo-potentials [18]. All the technical details are the same as in refs. [4, 19].

III. EXPERIMENTS AND DISCUSSION

Figure 4, top panel, shows the measured phonon dispersion along the c -axis using IXS and INS, as compared with first principles calculations. The low-energy phonons dispersion along $(1\ 1\ 1)$ are in general agreement with theoretical calculations, with two notable ex-

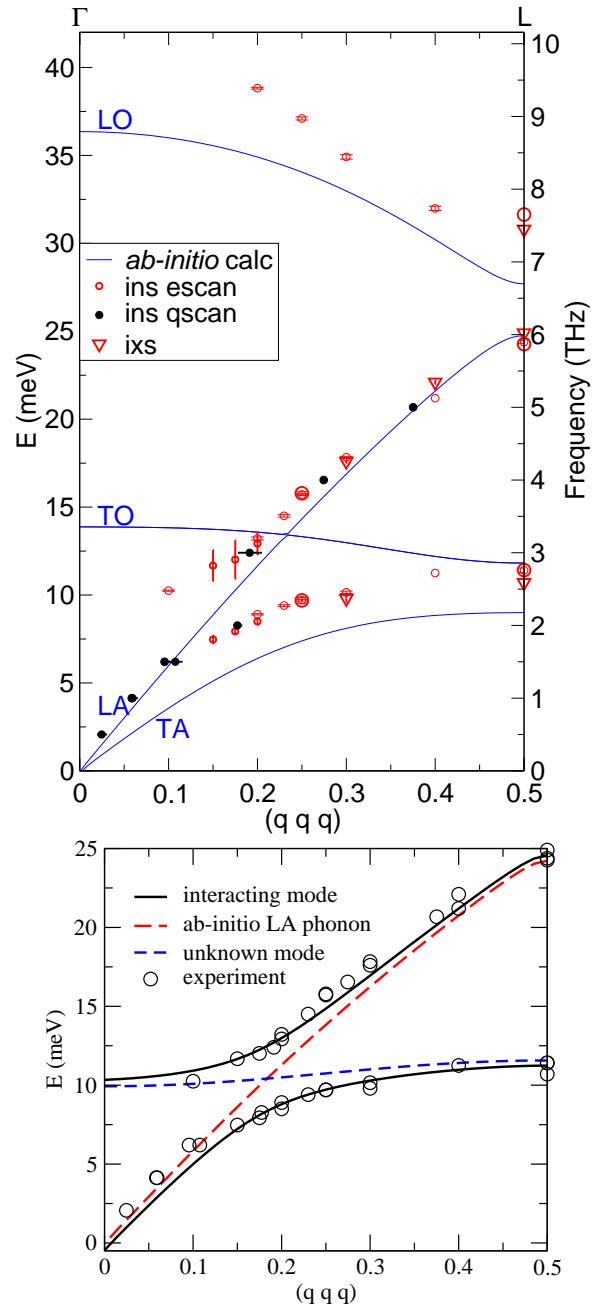


FIG. 4: (Color online) Top panel: Phonon dispersion along the $(1\ 1\ 1)$ direction. Hollow and filled circles indicate, respectively, constant Q and constant energy INS scan. Triangles represent IXS constant Q scan. Lines represent *ab-initio* calculated phonon dispersion. The scans are of type $Q_z \times (1\ 1\ 1) + (q\ q\ q)$ with and $Q_z=1,2,3$, in rhombohedral lattice. Using standard notation, we label as LA and TA longitudinal and transverse acoustic modes respectively, and with LO and TO longitudinal and transverse optic modes. Bottom panel: Zoom on the low energy part of the above dispersion data. Circles indicate the experimental points (all kind together). Dashed lines show the dispersion of the *ab-initio* longitudinal acoustic phonon, of the unknown mode. Continuous lines show the dispersion of the interacting mode described by Eq. (2), fitted to the experimental data.

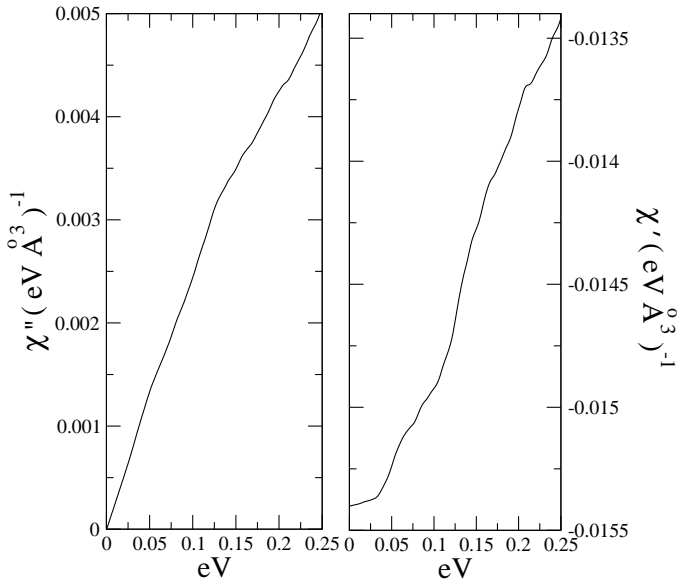


FIG. 5: Real and Imaginary part of the susceptibility for CaC_6 .

ceptions. First, the longitudinal optical mode is hardened in experiments (the hardening is 7 meV at zone border). Furthermore, although the sound velocity of the longitudinal acoustic mode is in good agreement with DFT calculations, above $q = 0.1$ and about 8 meV, the longitudinal acoustic branch (LA) suddenly bends, and its energy at the zone boundary is 11.4 ± 0.1 meV, according to INS, which is very close to that of the calculated first transverse optical mode at the zone boundary L (labeled TO in Fig.4, top panel), at 11.8 meV. The same behavior can be observed on the high energy section of the LA mode. Close to the zone boundary, from $q = 0.5$ to $q = 0.3$, the dispersion, as measured with both INS and IXS, reproduces very well the calculated one. Then it starts departing from the expected one going towards the middle of the zone, below $q = 0.3$ and 16 meV, and it bends to an apparently flat mode close to the zone center, with an energy of about 10 meV, slightly lower than what observed at L. Note, that the calculated energy for the TO mode at the zone center Γ is higher instead, at 13.9 meV.

This behavior is reminiscent of an avoided crossing, or anti-crossing, where the longitudinal acoustic mode interacts with an unknown mode. To analyze the experimental data, we suppose that the dispersion of the unknown mode is described by:

$$\epsilon(q) = a + b \cos(2\pi q) \quad (1)$$

where a and b are fitting parameters and (q, q, q) , is the momentum in the rhombohedral coordinates. We consider a q -independent coupling Δ with the longitudinal acoustic phonon. Within this model, the excitation energies, observed in the inelastic experiments, are the eigen-

values of a 2×2 matrix:

$$\begin{pmatrix} \epsilon(q) & \Delta \\ \Delta & \hbar\omega_{\text{LA}}(q) \end{pmatrix}, \quad (2)$$

where $\hbar\omega_{\text{LA}}(q)$ is the longitudinal acoustic phonon energy, as calculated using DFT. By minimizing the mean square error between the computed and observed energies, we obtain a good fit with $a = 10.75$ meV, $b = -0.82$ meV and $\Delta = 2.06$ meV, see Fig. 4 (bottom panel). As a consequence the detected anomaly can be explained by the coupling of the longitudinal acoustic mode with a longitudinal excitation or defect mode of unknown origin.

A first possibility would be that the first optic, which is transverse supposing $R\bar{3}m$ symmetry, and so silent in this configuration, would be activated by some symmetry breaking scattering, as from impurities, which would mix different polarizations for this mode. However, the dispersion, flat within error bars, or even slightly negative, is not compatible with the negative one of the first optic.

A second possibility, in the case of coupling to a longitudinal excitation, would be the occurrence of a low energy plasmon. In another layered material, MgB_2 , an acoustic plasmon mode was indeed detected at surprisingly low energy [20]. To address this issue we calculate the $\mathbf{G} = \mathbf{0}$ and $\mathbf{G}' = \mathbf{0}$ bare susceptibility, namely

$$\chi_{\mathbf{q}}(\omega) = \chi_{\mathbf{q}}(\mathbf{G} = \mathbf{0}, \mathbf{G}' = \mathbf{0}, \omega) = \frac{1}{N_{\mathbf{k}}\Omega} \times \sum_{\mathbf{k}, nm} \frac{|\langle \psi_{\mathbf{k}n} | e^{-i\mathbf{q}\cdot\mathbf{r}} | \psi_{\mathbf{k}+\mathbf{q}m'} \rangle|^2 (f_{\mathbf{k}n} - f_{\mathbf{k}+\mathbf{q}m})}{\epsilon_{\mathbf{k}n} - \epsilon_{\mathbf{k}+\mathbf{q}m} + \omega - i\eta} \quad (3)$$

where $\Omega = 496.38 a_0^3$ is the unit cell volume with $a_0 = \frac{\hbar^2}{me^2} = 0.53 \text{ \AA}$ is the Bohr radius, and $f_{\mathbf{k}n}$ is the Fermi function for a band energy $\epsilon_{\mathbf{k}n}$. Since the calculation of Eq. 3 requires a very accurate sampling of the Brillouin zone, we calculate the matrix-element using first-principles calculations on a $6 \times 6 \times 6$ grid and then we interpolate it all over the Brillouin zone using Wannier interpolation [21, 22, 23]. In order to obtain a good description of the CaC_6 first principles bands, we use 7 Wannier functions. Then we interpolate the matrix element and the band structure over a $N_k = 150 \times 150 \times 300$ k-points grid and calculate $\chi_{\mathbf{q}}(\omega)$ at $q = (0.25, 0.25, 0.25)$, close to where the anti-crossing occurs, as a function of ω . The temperature in the Fermi function was chosen to be $T = 300\text{K}$ and the lorentzian smearing is $\eta = 4\text{meV}$. The results for the real (χ') and imaginary (χ'') part of the susceptibility are shown in Fig. 5.

A peak in the imaginary part of $\chi_{\mathbf{q}}(\omega)$ would signal the occurrence of a plasmon excitation. In our case the imaginary part of the susceptibility is featureless and thus no plasmon excitations are then present in CaC_6 . To cross-check our result we also consider the case of MgB_2 where a plasmon was found [20]. In the MgB_2 case we reproduce the occurrence of an acoustic plasmon mode

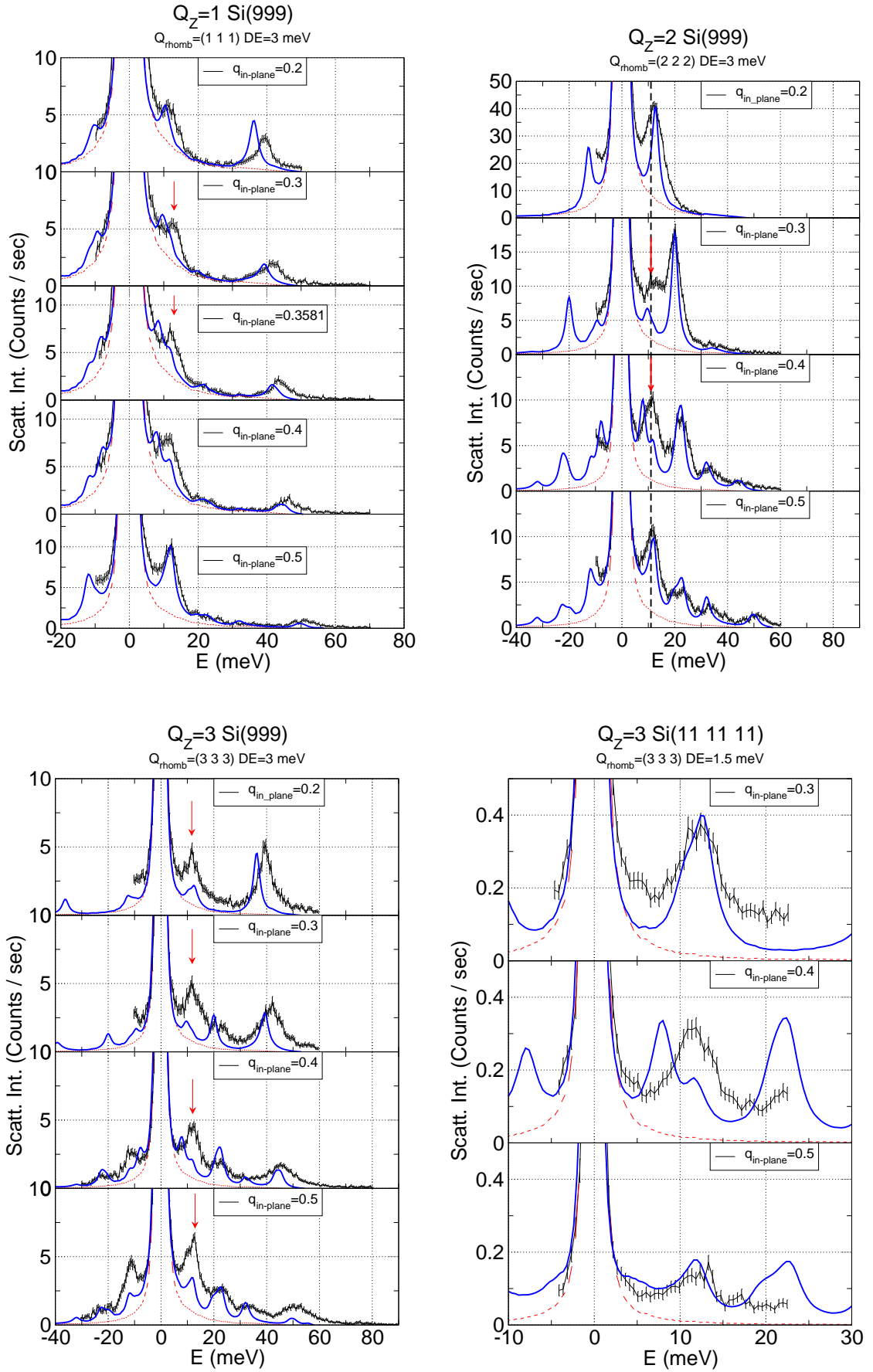


FIG. 6: (Color online) Examples constant Q , in-plane phonon density of state obtained using IXS (line with error bars) compared to *ab-initio* calculations (thick lines) plus an experimental elastic contribution (thin lines). The scans are obtained at $\mathbf{G} + \mathbf{q}$ where $\mathbf{G} = Q_z \times (111)$ and $Q_z=1$ (top, left), $z=2$ (top, right), $z=3$ (bottom), while \mathbf{q} lies in-plane and we give its modulus along the $(1\ -1\ 0)$ direction in reduced length units for each spectra. For both top panel the energy resolution is 3 meV. For the bottom panel we compare an energy resolution set-up of 3 meV (left), with calculation normalized to the mode at about 50 meV, with energy resolution set-up of 1.5 meV (right), with calculation normalized to the lowest energy mode.

in agreement to Ref. 20. As a consequence the 11 meV excitations is not due to a longitudinal plasmon, but most likely to impurities.

A possible origin of the impurity mode would be the presence of lithium in the preparation of the samples by liquid-solid synthesis method [9]. This hypothesis is supported by a strong XPS signal for the lithium ion at the K-edge (results not shown). However, this measurements are not confirmed by nuclear microprobe analysis.

A further possibility would be the presence of a $P6_3/mmc$ phase in the sample coexisting with the most stable $R\bar{3}m$ one. However the attempt to describe the c-axis phonon dispersion in terms of a similar $P6_3/mmc$ phase is also unsatisfactory since the dispersion of the low energy modes is hardly distinguishable from the dispersion $R\bar{3}m$ of the phase. Still it is possible that the avoided crossing is generated by the presence of vacancies or other similar defects.

An anomaly at a similar energy is also observed in another set of data which consists in constant Q 2D-phonon density of states, with a propagation vector \mathbf{q} lying in the plane perpendicular to the (1 1 1) direction and corresponding to the a^*b^* plane. For this IXS experiment, the choice of $\mathbf{G} = Q_z \times (1,1,1)$, with $Q_z \neq 0$ resulted in a significant contribution from transverse modes. In this respect what is measured is a 2-dimensional density of states obtained averaging over all the structure factors having modulus of the IXS exchanged momentum $|\mathbf{G} + \mathbf{q}|$, where $|\mathbf{q}|$ is in the plane as reported in Fig.2 and 6. Even if the measurement is not equivalent to a phonon dispersion calculation, as both longitudinal and transverse modes are measured, the low energy modes are fairly well reproduced, except for an extra intensity measured at about 10 to 13 meV for all Q_z , in particular for the spectra with q from 0.3 to 0.4, (see arrows in Fig.6) in agreement to what we found along the c-axis.

In a recent paper on a comparable sample of CaC_6 [8], using IXS only, Upton and co-workers incorrectly assigned the flat band at ~ 11 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. Note that the region close to zone center, below $q = 0.15$, is difficult to measure using IXS due to the large elastic peak at zero energy generated by disorder. This is not the case in INS scattering data and only by using this experimental technique the avoided crossing behav-

ior of the higher-longitudinal and lower-optical mode can be revealed.

We note that for the first time, using the in-plane configuration with IXS, we found good agreement between the data and the simulation in the 50 meV energy region. This is particularly important as vibrations propagating in-plane in this energy window are supposed to be among the ones contributing to electron-phonon mechanism [4, 24].

IV. CONCLUSIONS

In conclusion, we show that low energy phonon structure of the superconducting graphite intercalated compound CaC_6 , show clear anomalies, in disagreement with DFT calculations assuming the perfect crystal structure. In particular we observe an anti-crossing of the acoustic longitudinal mode with an additional longitudinal flat mode. Calculation of the electron susceptibility suggests that this mode can not be attribute to a plasmon excitation, so we infer it is most likely due to defect, impurity or vacancies. On the other hand, we found good overall agreement between the data and the simulation. In particular, in the 50 meV energy region where the C_z vibrations propagating in-plane in this energy window are supposed to provide the largest contribution to electron-phonon mechanism.

Acknowledgments

M. D., M. C., G. L. and F. M. enjoyed fruitful discussion with A. C. Walters, C. A. Howard, M. Ellerby, T.E. Weller, M.P.M Dean and S.S. Saxena. We acknowledge M. Krisch for useful discussion and D. Gambetti for technical help. Calculations were performed at the IDRIS supercomputing center (project 081202). S. Y. Z., J. G. were supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We acknowledge the support from University of California, Berkeley, through France Berkeley Fund Grant, for reciprocal visit of the Berkley and Paris team, to perform experiment, data analysis and discussion. This work was supported by ESRF through Experiment No. HS-3189 and by LLB through Experiment No. 8170.

[1] T. Enoki, M. Suzuki, and M. Endo, *Graphite intercalation compounds and applications* (Oxford University Press, Oxford, New York, 2003).
 [2] E. Weller, M. Ellerby, S. S. Saxena, R. P. Smith, and N. T. Skipper, *Nat. Phys.* **1**, 3 (2005).
 [3] N. Emery, C. Hérod, M. d'Astuto, V. Garcia, C. Bellin, J. F. Maréché, P. Lagrange, and G. Loupiau, *Physical Review Letters* **95**, 087003 (2005).

[4] M. Calandra and F. Mauri, *Physical Review Letters* **95**, 237002 (2005).
 [5] J. S. Kim, L. Boeri, R. K. Kremer, and F. S. Razavi, *Phys. Rev. B* **74**, 214513 (2006).
 [6] A. Sanna, G. Profeta, A. Floris, A. Marini, E. K. U. Gross, and S. Massidda, *Phys. Rev. B* **75**, 020511 (2007).
 [7] I. I. Mazin, L. Boeri, O. Dolgov, A. Golubov, G. Bachelet, M. Giantomassi, and O.K.Andersen, *Proceedings of the*

- M2S Conference in Dresden (2006).
- [8] M. H. Upton, A. C. Walters, C. A. Howard, K. C. Rahnejat, M. Ellerby, J. P. Hill, D. F. McMorrow, A. Alatas, B. M. Leu, and W. Ku, *Physical Review B (Condensed Matter and Materials Physics)* **76**, 220501 (2007).
- [9] S. Pruvost, C. Hérold, A. Hérold, and P. Lagrange, *Eur. J. Inorg. Chem.* p. 1661 (2004).
- [10] E. Burkel, *Inelastic scattering of x-rays with very high energy resolution*, vol. 125 of *Springer tracts in modern physics* (Springer, Berlin, Heidelberg, 1991).
- [11] N. Emery, C. Hérold, and P. Lagrange, *J. Solid State Chem.* **178**, 2947 (2005).
- [12] R. Verbeni, F. Sette, M. H. Krisch, U. Bergmann, B. Gorges, C. Halcoussis, K. Martel, C. Masciovecchio, J. Ribois, G. Ruocco, et al., *J. Synchrotron Radiation* **3**, 62 (1996).
- [13] C. Masciovecchio, U. Bergmann, M. Krisch, G. Ruocco, F. Sette, and R. Verbeni, *Nucl. Instr. and Meth. B* **111**, 181 (1996).
- [14] M. d'Astuto, M. Calandra, S. Reich, A. Shukla, M. Lazzeri, F. Mauri, J. Karpinski, N. D. Zhigadlo, A. Bossak, and M. Krisch, *Physical Review B (Condensed Matter and Materials Physics)* **75**, 174508 (2007).
- [15] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., *Journal of Physics: Condensed Matter* **21**, 395502 (19pp) (2009), URL <http://www.quantum-espresso.org>.
- [16] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- [17] J.P.Perdew, K.Burke, and M.Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [18] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- [19] M. Calandra and F. Mauri, *Physical Review B* **74**, 094507 (2006).
- [20] V. M. Silkin, A. Balassis, P. M. Echenique, and E. V. Chulkov, *Physical Review B* **80**, 054521 (2009).
- [21] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, *Comput. Phys. Commun.* **178**, 685 (2008).
- [22] I. Souza, N. Marzari, and D. Vanderbilt, *Phys. Rev. B* **65**, 035109 (2002).
- [23] N. Marzari and D. Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997).
- [24] K. Sugawara, T. Sato, and T. Takahashi, *Nat. Phys.* **5**, 40 (2008).