CARBON 85 (2015) 225–232

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

Symmetries and selection rules in the measurement of the phonon spectrum of graphene and related materials

Fernando de Juan [a,b,*], *Antonio Politano* [c], *Gennaro Chiarello* [c,d], *Herbert A. Fertig* [e]

[a] *Materials Science Division, Lawrence Berkeley National Laboratories, Berkeley, CA 94720, USA*
[b] *Department of Physics, University of California, Berkeley, CA 94720, USA*
[c] *Dipartimento di Fisica, Università degli Studi della Calabria, 87036 Rende (Cs), Italy*
[d] *Consorzio Nazionale Interuniversitario di Scienze Fisiche della Materia, via della Vasca Navale 84, 00146 Rome, Italy*
[e] *Department of Physics, Indiana University, Bloomington, IN 47405, USA*

ARTICLE INFO

Article history:
Received 23 July 2014
Accepted 26 December 2014
Available online 9 January 2015

ABSTRACT

When the phonon spectrum of a material is measured in a scattering experiment, selection rules preclude the observation of phonons that are odd under reflection by the scattering plane. Understanding these rules is crucial to correctly interpret experiments and to detect broken symmetries. Taking graphene as a case study, in this work we derive the complete set of selection rules for the honeycomb lattice, showing that some of them have been missed or misinterpreted in the literature. Focusing on the technique of high-resolution electron energy loss spectroscopy (HREELS), we calculate the scattering intensity for a simple force constant model to illustrate these rules. In addition, we present HREELS measurements of the phonon dispersion for graphene on Ru(0001) and find excellent agreement with the theory. We also illustrate the effect of different symmetry breaking scenarios in the selection rules and discuss previous experiments in light of our results. Finally we clarify why the shear horizontal label is not equivalent to odd parity, and how this can be misleading in the identification of selection rules.

1. Introduction

The investigation of surface phonons is an invaluable tool to study materials [1,2], as it provides a wealth of information on their structural [3], electronic [4], magnetic [5] or thermal properties [6], to name a few. Among many experimental probes, surface scattering experiments are particularly well suited to measure phonon spectra. As in any scattering setup, however, the mapping of the full phonon dispersion with these methods is sometimes limited by selection rules [1,7], which preclude the observation of certain phonon branches. The understanding of these rules is therefore crucial in the design and interpretation of these experiments.

The origin of selection rules is the presence of symmetries that enforce conservation laws. In surface scattering experiments, a selection rule applies when the scattering plane, defined by the momenta of the incident and scattered particles, coincides with a mirror plane of the surface. The selection rule states that phonons that are odd under this mirror reflection cannot be observed [7–10], and can be easily

* *Corresponding author at:* Materials Science Division, Lawrence Berkeley National Laboratories, Berkeley, CA 94720, USA.
E-mail address: ferdejuan@berkeley.edu (F. de Juan).

http://dx.doi.org/10.1016/j.carbon.2014.12.105
0008-6223/

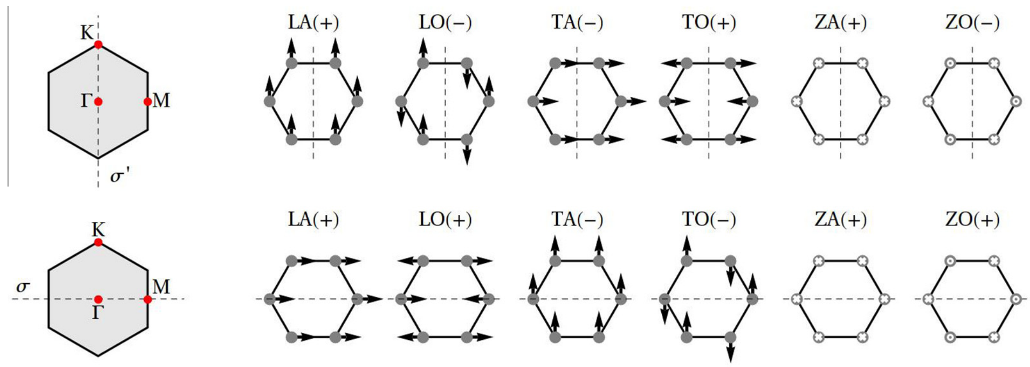

Fig. 1 – Honeycomb lattice phonon eigenvectors at the Γ point, with their polarization defined with respect to the ΓK (top) and ΓM (bottom) directions. Out of plane displacement is indicated by crosses (positive) and circles (negative). The mirror planes σ' (that leaves ΓK invariant) and σ (that leaves ΓM invariant) are represented as dashed lines. The parity of each phonon under the corresponding reflection is indicated in parenthesis. Phonons with odd (−) parity are not observed in HREELS. (A color version of this figure can be viewed online.)

understood as the conservation of parity under reflections: since incoming and scattered wavefunctions of the probe have even parity, the excitation of an odd parity phonon is forbidden, and the contribution to the cross section from this process is zero.

In experiments, the simplest geometry to measure phonon dispersions is planar scattering, with the scattering plane perpendicular to the surface. Since one is usually interested in the dispersion along high symmetry directions, the scattering plane is often a mirror plane and selection rules apply. Knowledge of these rules can thus be of great help to interpret the data, for example to assign symmetry labels to phonon branches or to detect broken symmetries. Moreover, this understanding can be used to devise more complicated non-planar scattering geometries [9–13] that are not affected by selection rules and allow one to observe the odd modes. [1]

To measure phonon dispersions, one of the most powerful experimental probes is high-resolution electron energy loss spectroscopy (HREELS). Among other advantages, this technique offers excellent energy and momentum resolution and allows one to map the full phonon spectrum. HREELS has been applied to many systems with great success, and is very useful in particular to measure the spectrum of epitaxial monolayers grown on a substrate, where inelastic neutron or X-ray scattering cannot be used. A well known example is the case of graphene monolayers, where the effect of different substrates on the phonon spectrum has been widely studied [14–27].

The case of HREELS studies of epitaxial graphene is of particular interest because, despite the many experiments reported, their interpretation in terms of selection rules has often been misleading. While most studies acknowledge the existence of a selection rule which forbids the observation of the shear horizontal mode, SH, (or transverse acoustic, TA) along the ΓM direction, other selection rules are sometimes misquoted and some have been completely missed. The purpose of this work is to provide a detailed study of the selection rules for surfaces with C_{6v} symmetry, taking the case of graphene as an example. Our main result is the full set of selection rules, summarized in Fig. 1: the modes TA and TO along the ΓM direction and the modes TA, ZO and LO along ΓK are all odd and thus should not be observed. Our results are worked out for HREELS for concreteness, but are equally applicable to any other planar scattering experiment.

In the rest of this work, we first discuss how selection rules appear in the computation of the HREELS scattering rate. We illustrate our results for this with a simplified phonon model, and we compare them with our experimental HREELS data for graphene on Ru(0001). Finally, we will discuss how symmetry breaking can render selection rules inactive, and interpret previous experiments in light of our results.

2. Selection rules in the HREELS intensity

The origin of the selection rule explained in the introduction can be seen more explicitly by considering the computation of the HREELS cross section [7,28] due to phonon excitations. The relevant kinematic regime for this process is known as impact scattering, where high-energy electrons interact with the short-range part of the atomic potential. The incoming electron with energy E_I and momentum $\mathbf{k}_I$ is scattered off a surface and is recovered with energy E_S and momentum $\mathbf{k}_S$. The excitation of a phonon of frequency ω and momentum $\mathbf{q}$ is detected in the loss spectrum as a resonance peak at $E_S = E_I \pm \omega$ and $\mathbf{k}_S = \mathbf{k}_I \pm \mathbf{q}$.

Because of the geometry of this problem it will be convenient to separate vectors into in-plane and out of plane components, $\mathbf{q} = (\vec{q}_\parallel, q_z)$, reserving the arrow notation $\vec{q}$ for two-dimensional vectors in the plane. For a given phonon of momentum $\vec{q}_\parallel$ in the Brillouin Zone (BZ) and eigenvector $\mathbf{u}^\alpha(q_\parallel)$, where α labels the different atoms in the unit cell,

[1] A selection rule for a particular high-symmetry line can be avoided altogether by choosing to measure q in a replica of this line that does not map onto itself under the corresponding reflection. This measurement usually requires two independent rotations of the sample and is far less common.