Angular Anomaly in the Dynamic Structure Factor of Graphite Close to Bragg Reflections

Collective excitations of valence electrons allow one to describe the physics of condensed matter systems in a compact way. The recent advance of inelastic X-ray scattering experiments using synchrotron light sources enables the investigation of collective excitations at large momentum transfers with high momentum and energy resolution and offers access to striking phenomena. At the same time, *ab initio* calculations allow us to analyze and predict experimental results and to unravel the underlying physics.

The present work is an example for a successful collaboration between theory and experiment: we have predicted, measured and explained an angular anomaly in the momentum-resolved dynamic structure factor $S(\mathbf{q},\omega)$ of graphite. Contrary to what one would expect naively, our calculations predicted drastic changes in the spectra upon very small variations in **q**, whenever the momentum transfer is close to specific reciprocal-lattice vectors **G** [1]. This effect has been clearly confirmed by our IXS measurements (Fig. 1). Unlike previous experiments [2], we did not consider momentum transfers exactly along the *c*-axis of graphite, but added a small in-plane component q_1=0.37 Å^{-1} that was kept constant, while the momentum along the *c*-axis q_3 was varied from 0.94 Å^{-1} to 2.84 Å^{-1}. Approaching the Bragg reflection at **G**=(002), the peak in the spectra is strongly shifted in energy and, most importantly, it abruptly disappears next to **G** ($q_3 = 2 \cdot 2\pi/c = 1.88$ Å^{-1}).

This striking behavior can be understood in terms of an interplay of anisotropy and crystal local field effects (LFE). The latter originate from the periodic modulation of the electron density in the crystal. Let us therefore first compare the excitation spectrum of electrons in a homogeneous electron gas (HEG) and in a solid. Figure 2 (left panel) shows the well known electron-hole excitations (shaded region) and plasmon excitations (red line) in the HEG. The energy of the plasmon increases quadratically with momentum **q** until it reaches the electron-hole continuum at q_c.

Assuming a weak periodic crystal potential, the excitation spectrum of a *solid* is given by folding back the free electron excitations into the first Brillouin zone (Fig. 2, right panel). Interband transitions to bands from higher Brillouin zones become possible and contribute to the damping of the plasmon at low momentum $q<q_c$ (1). Additionally, crystal local field effects become more and more important with increasing strength of the crystal potential. They couple excitations with momentum **q** and **q+G** from different Brillouin zones via internal Bragg scattering (**G** denotes a reciprocal lattice vector of the crystal). When this coupling is strong, the plasmon dispersion can develop several plasmon bands. In analogy to the electron bandstructure, an energy splitting at the Brillouin zone boundary at **q**=**G**/2 can occur (2) [3] or, most interestingly for the present work on

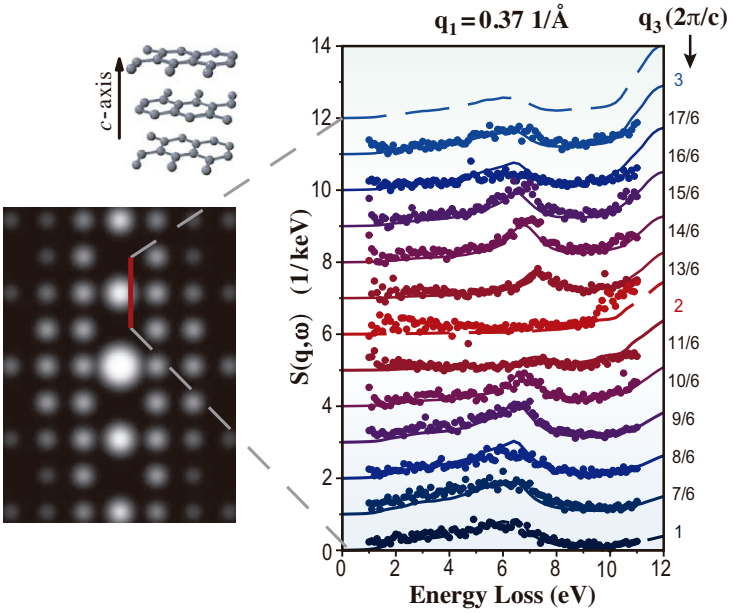

Fig. 1. The dynamic structure factor $S(q,\omega)$ of graphite was calculated (lines) and measured (dots) for different off-axis momentum transfers $q=(q_1,0,q_3)$ (given in reciprocal lattice units, compare with sketch of the diffraction pattern on the left). From [1].

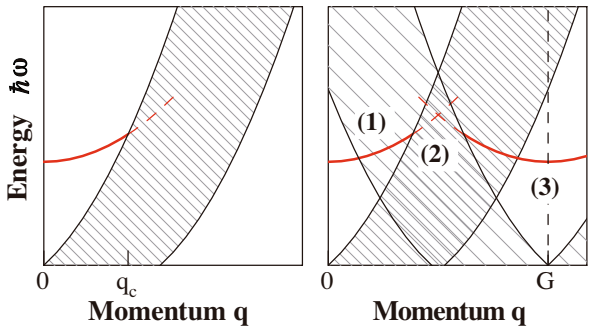

Fig. 2. Excitation spectrum of free electrons (left) and electrons in a weak periodic crystal potential (right). Hatched regions indicate electron-hole excitations, thick, red lines the plasmon dispersion (adapted from [3]).

graphite, the plasmon with small momentum $q<q_c$ may reappear in higher Brillouin zones (3) [4,5].

To illustrate this point, we artificially suppress the coupling via LFE in our *ab initio* calculations (Fig. 3, left panel). For small momentum-transfers q_3 along the *c*-axis (bottom), the spectra *without* LFE show a strong in-plane π-plasmon peak, which is shifted to lower energies with increasing q_3 due to the anisotropy of the system, and finally damped at large q_3 (top). If LFE are included (left panel), the plasmon excitation from the first Brillouin zone reappears at large momentum transfers (compare bold, red lines). Thus, in agreement with the plasmon band picture, we find a strong periodic dispersion at large q_3. Further analysis [1] of the coupling strength between excitations with momentum **q** and **q+G** shows that in graphite the coupling is particularly strong for **G**=(002), while it is forbidden for **G**=(001) by crystal symmetry. This explains the observed periodicity of the peak shift. But most importantly, the coupling depends on the angle between **q** and **q+G**. In particular, it vanishes completely if the two vectors are perpendicular, which is the reason for the completely flat spectrum at q_3=2 (bold, dashed line).

The presented effect might be observed in any solid that shows strong crystal local field effects, such as heterostructures or quasi-1D systems. Its identification has been possible due to a joint experimental and theoretical effort, which illustrates the power of such a combined approach.

The measurements were carried out at the Taiwan inelastic scattering beamline **BL12XU** in SPring-8.

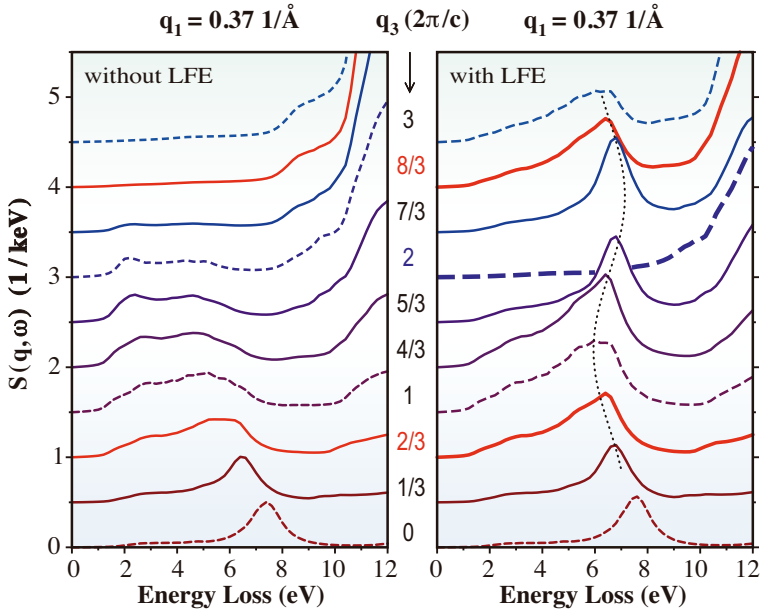

Fig. 3. *Ab initio* calculations of S(q,ω), without (left) or with (right) crystal local field effects (compare with Fig. 1).

R. Hambach[a,b], C. Giorgetti[a,b], N. Hiraoka[c] and Lucia Reining[a,b,*]

[a] Laboratoire des Solides Irradiés, Palaiseau, France
[b] European Theoretical Spectroscopy Facility (ETSF)
[c] National Synchrotron Radiation Research Center, Taiwan

*E-mail: lucia.reining@polytechnique.fr

References

[1] *R. Hambach, C. Giorgetti, N. Hiraoka, Y. Q. Cai, F. Sottile, A. G. Marinopoulos, F. Bechstedt and L. Reining: Phys. Rev. Lett.* ***101*** *(2008) 266406.*
[2] N. Hiraoka *et al.*: Phys. Rev. B **72** (20058) 075103.
[3] L.E. Oliveira and K. Sturm: Phys. Rev. B **22** (1980) 6283.
[4] Y.Q. Cai *et al.*: Phys. Rev. Lett. **97** (2006) 176402.
[5] K. Sturm *et al.*: Phys. Rev. Lett. **68** (1992) 228.