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Tunable quantum interference in bilayer graphene in double-resonant Raman scattering

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ABSTRACT

The line shape of the double-resonant 2D Raman mode in bilayer graphene is often considered to be characteristic for a certain laser excitation energy. Here, in a joint experimental and theoretical study, we analyze the dependence of the double-resonant Raman scattering processes in bilayer graphene on the electronic broadening parameter γ. We demonstrate that the ratio between symmetric and anti-symmetric scattering processes sensitively depends on the lifetime of the electronic states, explaining the experimentally observed variation of the complex 2D-mode line shape.

1. Introduction

Establishing the concept of double-resonant Raman scattering by Thomsen and Reich in 2000 [1] has led to a fundamental understanding of inelastic phonon scattering processes in graphene and related graphitic carbons [2–5]. It enabled a unified description of the complete Raman spectrum of these materials, explaining anomalous peak shifts with laser excitation energy and the occurence of various Raman modes in graphene, few-layer graphene, graphite, and carbon nanotubes [6–13].

The 2D mode is one of the most discussed peaks in the Raman spectrum of graphene and related graphitic carbons. In single-layer, graphene the 2D mode can empirically be fitted by a single Lorentzian line shape with a slight asymmetry towards the high-frequency side [14,15]. In bilayer graphene this mode splits up into four different components with different relative intensities and frequencies as a function of the laser excitation energy. The origin of these four components and their relation to the underlying double-resonant Raman scattering processes has been discussed by various authors in the past [9,16–18] and only recently a consistent interpretation of the complex 2D-mode line shape has been presented [19].

The consideration of interference effects is an integral part for the understanding of Raman spectra from graphene sheets. Only internal quantum interference between different Raman scattering processes explains the narrow line widths of the 2D band or the absence of phonons with $\mathbf{q} = \mathbf{K}$ in the Raman spectrum of graphene [4]. The influence of the line width broadening has been elucidated for single-layer graphene, influencing the intensity of the D mode and consequently the D/G intensity ratios as demonstrated by Bruna et al. [20] and Fröhlicher et al. [21].

Here, we present a joint experimental and theoretical analysis of the 2D-mode line shape in bilayer graphene as a function of the electronic broadening γ in the double-resonance process. We demonstrate that the electronic broadening determines the interference of different scattering paths resulting in different intensity ratios of the Raman peaks related to symmetric and anti-symmetric scattering processes. We support our theoretical findings by experiments in which the electronic broadening is tuned as a function of defect densities and as a function of the electron-phonon coupling.

2. Experimental and calculation details

Freestanding bilayer graphene samples were prepared by micro-mechanical exfoliation from natural graphite crystals onto prepatterned SiO_2/Si substrates with an oxide thickness of 100 nm. Holes in the substrate were fabricated by reactive ion etching (RIE), exhibiting a diameter of 3 μm and depth of approximately 8 μm.

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Defective bilayer graphene samples were prepared by swift heavy ion irradiation (Xe^{26+}, 91 MeV) [22,23] at normal incidence using different ion fluxes [12].

Raman measurements were carried out with a Horiba HR 800 spectrometer, equipped with solid-state and gas lasers. Raman spectra were recorded in back-scattering geometry under standard ambient conditions using a 1800 lines/mm grating and an 100 × objective, yielding a spectral resolution of approximately 1 cm^{-1}. The laser excitation energies were between 1.96 eV and 2.81 eV and the laser power was kept below 0.5 mW during all measurements in order to avoid laser-induced modification of the graphene samples [24,25].

The calculation of the double-resonant Raman scattering cross-section was done as proposed in Refs. [1,7], and [19]. We used the *GW*-corrected electronic bandstructure and TO phonon dispersions for bilayer graphene from Ref. [19], which were both calculated using the Quantum Espresso DFT Code [19,26]. For simplicity, we assumed all matrix elements to be constant and restricted the integration to the one-dimensional $\Gamma - K - M$ high-symmetry direction. This approach is justified as the main contributions in the double-resonance process stem from the high-symmetry lines [7,10,12].

3. Results and discussion

Each double-resonant intervalley scattering process P_{mi}^{lj} in bilayer graphene can be described by four indices that refer to the band indices of the initial electron m and the excited electron l, as well as the band indices of the scattered electron j and the scattered hole i. Two representative examples of these scattering processes are shown in Fig. 1. For symmetric processes, electrons and holes are scattered between bands with the same index, *i.e.*, $m = i$ and $l = j$, whereas the band indices are changing during anti-symmetric scattering processes, *i.e.*, $m \neq i$ and $l \neq j$. Furthermore, the scattering processes split up into so-called 'inner' and 'outer' processes according to the resonant phonon wave vectors in the double-resonance process [7]. As demonstrated before [19], the complex 2D-mode line shape can be understood as composed of contributions from symmetric scattering processes P_{11}^{44} and P_{22}^{33} on the low- and high-frequency side, respectively, and contributions from degenerate anti-symmetric scattering processes (P_{12}^{43}, P_{21}^{34}) in the centre (compare Fig. 1). Except for the highest-frequency peak (P_{22}^{33}-out in Fig. 1), all contributions to the 2D mode stem predominantly from inner processes, *i.e.* phonons with wave vector between Γ and K [19,27]

Although the assignment between the scattering processes and the different spectral features in the 2D-mode line shape has been discussed before [9,17–19,28–31], the origin of their different relative intensities and their distinctive variations as a function of the laser excitation energy remained unclear. It is however an important aspect of the 2D-mode in bilayer graphene as can be seen in Fig. 2. The relative intensities of single contributions drastically change as a function of the laser excitation energy. In this context, we want to show that the electronic broadening γ plays a decisive role. The electronic broadening, which reflects the inverse lifetime of the electronic states, is usually approximated as given by Ref. [7] and is composed of three different contributions

$$\gamma = \gamma^{e-ph} + \gamma^{D} + \gamma^{e-e}. \tag{1}$$

Here, γ^{e-ph} reflects the intrinsic contribution from electron-phonon scattering, which can be further separated into the contribution from Γ and K point phonons [7,14]. γ^{D} refers to the electron-defect scattering rate and γ^{e-e} represents the contribution to γ from scattering between charge carriers. In principle, all three contributions can be manipulated experimentally. For instance, γ^{e-ph} depends on the laser excitation energy ε_L [7], as well as on temperature [32,33]. Naturally, γ^{D} depends on the amount and type of defects and is also influenced by the laser energy [7,21]. Finally,

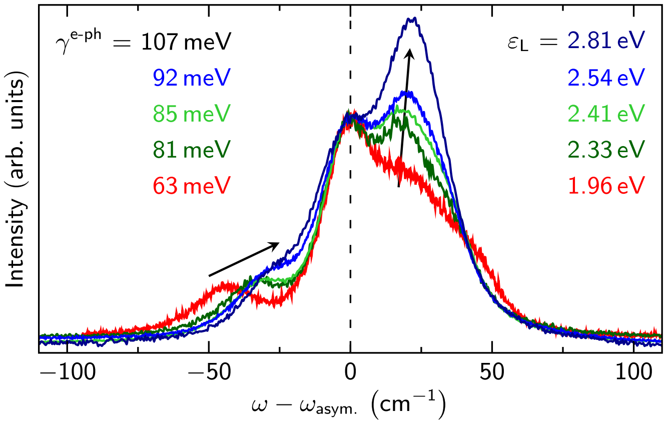

Fig. 2. Laser-energy dependence of the 2D-mode line shape in freestanding bilayer graphene. All spectra are frequency- and intensity-normalized to the contribution from anti-symmetric scattering processes. γ^{e-ph} is calculated according to Ref. [7]. Raman spectra for ε_L = 1.96 eV, 2.33 eV, 2.41 eV, and 2.54 eV are taken from Ref. [19].

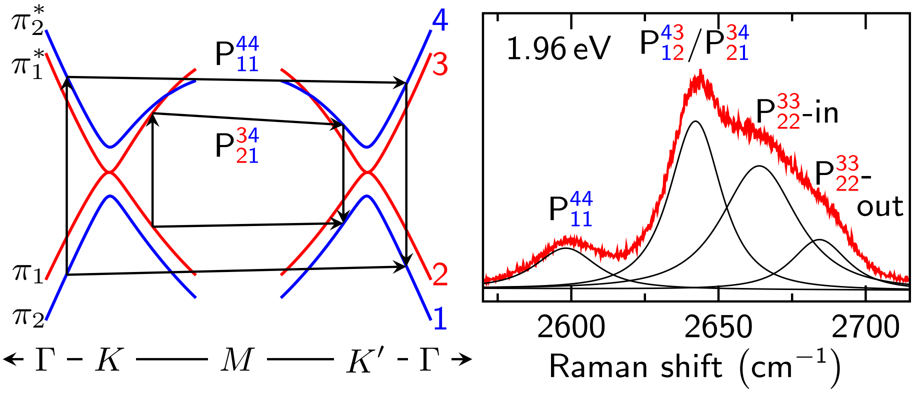

Fig. 1. Left: Illustration of the different intervalley double-resonant Raman scattering processes P_{mi}^{lj} in the electronic bandstructure of bilayer graphene. The indices m, i and l, j number the valence and conduction bands, respectively. For symmetric scattering processes equals $m = i$ and $l = j$. For anti-symmetric processes is $m \neq i$ and $l \neq j$. Right: Representative Raman spectrum of freestanding bilayer graphene at 1.96 eV laser energy. The assignment between the scattering processes and the different spectral contributions is indicated. All contributions stem from inner processes except for the highest-frequency peak, indicated with P_{22}^{33}-out.