

# Assessing the anisotropic response in the out-of-equilibrium electron dynamics of black phosphorus

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## Introduction

The discovery of graphene has shown that 2D materials may exhibit a great variety of interesting physical and chemical properties that are unknown in the conventional 3D form [1]. Nowadays several 2D systems have been successfully produced, and they manifest insulating (h-BN [2]) and semiconducting behaviors (transition metal dichalcogenides TMDCs [3]). The study of black phosphorus (BP), the stable allotrope of phosphorus, has experienced a *renaissance* upon its exfoliation to the 2D limit [4], named “phosphorene”.

Many of the transport properties of BP fall in between the one of graphene and TMDCs [5]. On top of those, BP has two unique characteristics; tunability of the band-gap [6], highly anisotropic optical and electrical response [7]. The former has been subject of a previous time- and angle- resolved photoelectron spectroscopy (tr-ARPES) study of our group, in which we have shown that an intense optical excitation can reduce the BP band-gap [8]. The latter is the focus of the present experiment, in which we explore the anisotropic response in the out-of-equilibrium electron dynamics of BP.

## Anisotropic properties of BP

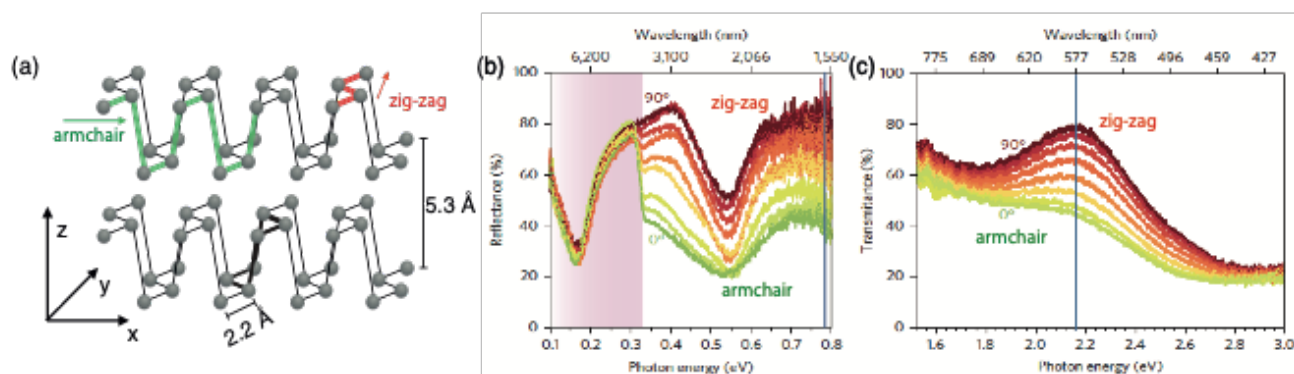
The electrical conductivity and the thermopower of BP strongly

vary with the in-plane directions [7]. The optical properties show, as well, a large dependence on the relative orientation of the light polarization with respect to the crystal lattice, and this reflects into difference in the absorption coefficient [9] and in the photoluminescence yield [10]. The anisotropy originates from the highly anisotropic crystal structure; in contrast to graphene and TMDCs that are flat, BP is puckered due to the local  $sp^3$  hybridization of the  $p$  orbitals. Figure 1(a) shows the crystal structure; the honeycomb lattice is distorted into two strongly inequivalent directions; armchair and zig-zag. Along the two directions, different effective masses and different orbital projections are responsible for the anisotropy in the electronic and optical properties [11].

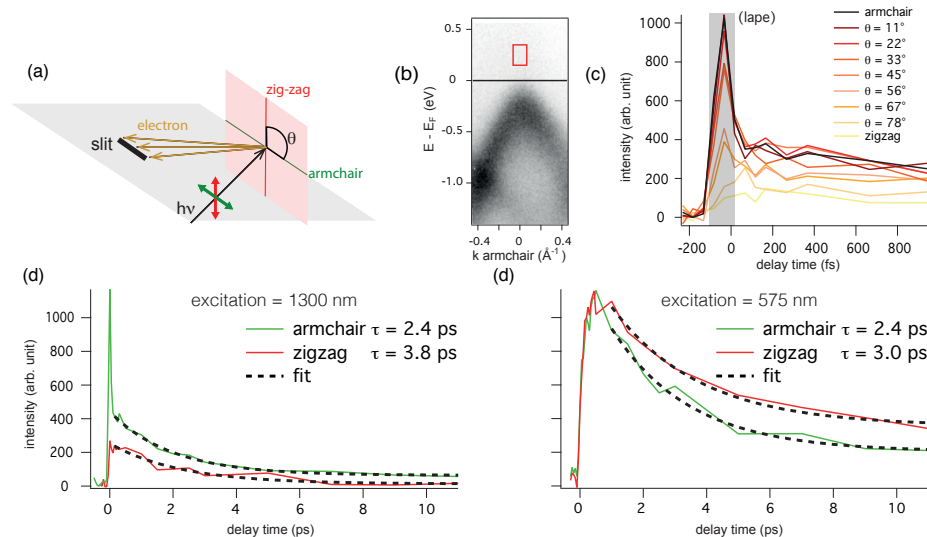
Figure 2(b) and (c) show the change in reflectance (b) and transmittance (c) as a function of wavelength and as a function of the polarization direction, which varies from armchair ( $0^\circ$ ) to zig-zag ( $90^\circ$ ) (adapted from Ref. [11]). These experimental results represent the starting point of our experiment at ARTEMIS, aimed at assessing the possibly different ultrafast electron dynamics of BP.

## Experimental results

The experimental geometry is strictly imposed by the necessity



**Figure 1:** (a) Crystal structure of BP. The armchair and the zig-zag direction are indicated. (b) Reflectance and transmittance (c) of BP for different wavelengths as a function of the orientation of the light polarization. Adapted from Ref. [11]



**Figure 2:** (a) Experimental geometry. (b) Band dispersion of BP measured along the armchair direction at the G point of the 2<sup>nd</sup> BZ. (c) Electron dynamics at the bottom of CB, in the region indicated in panel (b) by a red rectangle. The color of the curves encodes the evolution of the pump polarization direction from armchair to zig-zag. (d) Comparison between the dynamics for an optical excitation centered at 1300 nm. The characteristic decay times are indicated. (e) The same comparison, but for an optical excitation centered at 575 nm.

to satisfy simultaneously two conditions. First, the interesting region of the band structure of BP is located at the zone center of the Brillouin zone (BZ),  $\Gamma$  point. Second, we need to avoid an out-of-plane component when varying the light polarization. The latter, in fact, hampers a direct comparison between the response of the zig-zag and armchair direction. Moreover, an out-of-plane component of the electric field is responsible for the well-known laser assisted photoelectric effect (LAPE), which would dominate the ultrafast electron dynamics during and immediately after the optical excitation [12].

Figure 2 (a) shows the geometry adopted in our experiment.

The analyzer slit is horizontal and together with the light direction defines the scattering plane (grey plane). The BP crystal is aligned with the armchair (zig-zag) direction along the horizontal (vertical) axis. The sample surface (pink plane) is at normal incidence; in this condition the out-of-plane component of the electric field is ideally equal to zero, and by varying the angle  $\theta$  of the light polarization from linear horizontal ( $0^\circ$ ) to linear vertical ( $90^\circ$ ) we excite BP along the armchair and zig-zag directions. The probe photon energy is set equal to 24 eV, in such a way that the  $\Gamma$  point of the second BZ lies in the angular region accessible to the electron analyzer.

Figure 2 (b) shows the band structure of BP measured along the armchair direction. We resolve clearly the parabolic valence band, whose maximum is at the 2<sup>nd</sup>  $\Gamma$  point (which is set as zero of the momentum axis). The red rectangle indicates the bottom of the conduction band (CB), which in our experiment is transiently populated by the optical excitation.

Figure 2 (c) compares the dynamics for a pump wavelength centered at 1300 nm, for different pump polarizations as indicated by the colors. The first result, which is somewhat expected from Fig. 1 (b), is that due to the different reflectance, the absorbed fluence varies with the light polarization, and the total number of charges in CB varies as well. It is important here to point out that the fast dynamics, within the grey area, might be affected by a residual LAPE effect, due to a small misalignment of the sample surface.

A second noticeable result is shown in Fig. 2 (d), where we compare the electron dynamics over a wider temporal range for the two extreme cases of polarization parallel to the armchair (green) and to the zig-zag (red) directions. In these experiments, we have compensated for the different reflectance, in order to excite the crystal with a comparable absorbed fluence, of 0.55 mJ/cm<sup>2</sup>. A fit to the electron dynamics, which neglects the fast LAPE process, gives two different characteristic decay times:  $t = 2.4$  ps and  $t = 3.8$  ps, for the optical excitation along the armchair and the zig-zag directions, respectively.

In order to reduce the spurious effect induced by the LAPE, we have repeated the experiment with an optical excitation centered at 575 nm. In fact, the intensity of LAPE effect scales non-linearly with the wavelength, and at 575 nm it is strongly

suppressed [13]. Moreover, the optical excitation is tuned in the region, indicated by a green line in Fig. 1 (c), where the linear dichroism of BP is the largest [11]. Figure 2 (e) shows the same comparison of panel (d), but for the optical excitation at 575 nm. Also in this case, a fit to the electron dynamics results in faster relaxation dynamics when the optical excitation is parallel to the armchair direction.

## Conclusions

We have experimentally observed a small but non-negligible difference in the dynamics of the electrons optically excited in the bottom of the conduction band, when the light polarization is varied from the armchair to the zig-zag direction. This finding is suggestive that different scattering mechanisms might be available for electrons excited in states with different orbital projections. A better description of this process requires the support of *ab-initio* calculations accounting for the dichroism in the optical excitation.

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