

# Anisotropy of Quasiparticle Lifetimes and the Role of Disorder for Ultrafast Electron Dynamics in Graphite

Gunnar Moos, Cornelius Gahl<sup>†</sup>, Roman Fasel\*, Martin Wolf<sup>†</sup> and Tobias Hertel

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

<sup>†</sup>*Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin, Germany*

*\*EMPA Dübendorf, Überlandstr. 129, 8600 Dübendorf, Switzerland*

(February 1, 2008)

Femtosecond time-resolved photoemission of photoexcited electrons in highly oriented pyrolytic graphite (HOPG) provides strong evidence for anisotropies of quasiparticle (QP) lifetimes. Indicative of such anisotropies is a pronounced anomaly in the energy dependence of QP lifetimes between 1.1 eV and 1.5 eV – the vicinity of a saddle point in the graphite bandstructure. This is supported by recent *ab initio* calculations and a comparison with experiments on defect-enriched HOPG which reveal that disorder, *e.g.* defects or phonons, increases electron energy relaxation rates.

Studies of the ultrafast dynamics of electronic excitations in solids have challenged experiment and theory for years. Advances in ultrafast laser technology and the latest theoretical developments allow us to investigate electron dynamics in growing detail and further our understanding of fundamental scattering processes in solids at the femtosecond time scale [1,2].

For an interacting 3D-electron gas the standard theory of *e-e* scattering – Landau’s theory of Fermi-Liquids – predicts a quadratic dependence of scattering rates on the quasiparticle (QP) energy ( $E - E_F$ ) [3]. In a periodic potential, however, the electronic states are modified with respect to those of a free electron gas and form Bloch states which may result in different QP lifetimes at the same energy if distinct *k*-states within the Brillouin zone are compared. Such anisotropies were indeed predicted by recent *ab initio* self-energy calculations for Al and Cu, which find strong variations of QP lifetimes for electrons in different bands [4,5]. Experimental verification of these predictions, however, remains truly challenging. Time-resolved photoemission from different copper surfaces has revealed some dependence of the measured electron dynamics on the crystallographic surface orientation, but the observed effects could not be clearly attributed to anisotropies of QP lifetimes [6]. Similar experiments on aluminum [7] have likewise not been able to identify band structure effects predicted theoretically [4].

Graphite, a semi-metal with layered structure, is expected to be an ideal candidate if band structure effects are to be observed experimentally. The strongly anisotropic band-structure of graphite is expected to furnish electron scattering processes with similar anisotropies, leading to anomalous QP lifetimes. The special topology of the graphite bandstructure has indeed

been used to explain apparent deviations of the electron dynamics observed on a ceasiated HOPG surface [8] from the standard predictions for a 3D-electron gas [9]. However, the experiments provided no evidence for anomalies that might be associated with anisotropic QP lifetimes. Furthermore, the overlap of the energy range probed experimentally in Ref. [8] and the range of validity of the approximations used in Ref. [9] is small and calls for more extended and more detailed theoretical as well as experimental work.

Here we present a time-resolved photoemission study of the electron dynamics in HOPG, with particular focus on its energy dependence and the influence of disorder on the relaxation rates. The most striking observation – a pronounced anomaly in the energy dependence of the electron dynamics between 1.1 eV and 1.5 eV – can be associated with electrons near a saddle point in the graphite band structure at the *M*-point of the Brillouin zone. This, and a comparison with experiments on defect enriched HOPG provide strong evidence for anisotropies of QP lifetimes in graphite which have also been predicted by a recent *ab initio* calculation [11].

The HOPG sample [13] was attached to a tantalum disk which could be temperature controlled from 25 K to 1200 K. It was mounted in an UHV chamber with a base pressure of  $2 \times 10^{-10}$  mbar. Experiments were performed at room temperature, unless mentioned otherwise. The HOPG sample was cleaved directly before being transferred into UHV and heated repetitively to 900 K. The defect enriched HOPG surface was produced by Ar-ion sputtering (0.5 keV, 7  $\mu$ A, 300 s).

Photoelectron spectra are obtained by means of the time-of-flight technique with an energy resolution of 10 meV. For time resolved pump-probe measurements a visible pump and frequency doubled probe pulse of typically 85 fs duration are focused on a spot of 50  $\mu$ m diameter on the sample. The photon energy of the probe pulse was chosen to exceed the work function of the sample ( $e\Phi = 4.50 \text{ eV} \pm 0.05 \text{ eV}$ ) by typically 0.15 eV in order to probe not only low energy electron but also hole dynamics. A more detailed description of the experiment can be found elsewhere [12].

We start our discussion with a brief overview of processes contributing to the dynamics of photoexcited carriers. After optical excitation the energy absorbed by the electrons is redistributed via electron-electron scattering

( $e-e$ ), electron-phonon scattering ( $e-ph$ ) and transport from the surface into the bulk. In graphite the transport of electrons out of the photoemission detection volume into the bulk is hampered due to the comparatively weak interlayer coupling and is further suppressed by frequent stacking faults in HOPG [14]. Therefore, the dynamics observed in the experiments are expected to be dominated by  $e-e$  and  $e-ph$  scattering processes with  $e-ph$  scattering becoming increasingly important closer to the Fermi level.

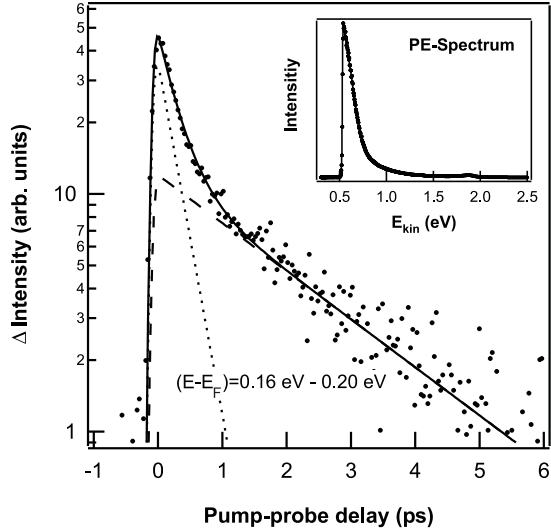


FIG. 1. Cross correlation trace: change of the photoemission intensity within a certain energy interval as a function of the pump-probe time-delay. The pump photon energy was 2.3 eV. The solid line is the fit to a bi-exponential decay. Fast and slow components are indicated by the dotted and dashed lines respectively. The inset shows a 2PPE-spectrum for simultaneous pump-probe excitation.

A typical photoelectron spectrum for simultaneous pump and probe excitation is shown in the inset of Fig. 1. The electron dynamics are obtained by plotting the change  $\Delta I$  of the photoemission intensity, resulting from excitation by the visible pump pulse, as a function of the pump-probe time-delay (see Fig. 1). These cross correlation traces (XCs) can clearly be characterized using a bi-exponential decay with a fast component decaying on the sub-picosecond time-scale and a slower component decaying on the ps time-scale.

A detailed analysis of photoelectron spectra obtained at different pump-probe time-delays shows that the electronic system approaches an internal equilibrium with a characteristic time constant of  $(250 \pm 50)$  fs. This is estimated using the deviation of photoelectron spectra from the best fit to a Fermi-Dirac distribution [15,17]. This process – referred to as internal thermalization – is associated with the initial fast decay seen in XC-traces and results in an increase of the electron gas temperature by 400 K. This is in reasonably good agreement with

the calculated temperature rise using the electronic heat capacity of graphite and the estimated laser power deposited within the optical penetration depth. The slow component of the XCs can be associated with thermalization of the electronic system with the lattice due to  $e-ph$  interaction [17–19].

In the following we focus on the initial fast decay, associated with the internal thermalization of the electronic system. The corresponding decay rates – as obtained from the fast component of the bi-exponential fit – are plotted in Fig. 2 as a function of the intermediate state energy as a function of the intermediate state energy  $(E - E_F) = E_{kin} + e\Phi - h\nu_{probe}$ . The data shown in Fig. 2 extend to energies  $\sim 0.15$  eV below  $E_F$ , and present, to the best of our knowledge, the first 2PPE measurements of electron *and* hole dynamics close to  $E_F$ . Note, that lifetimes of holes in the copper  $d$ -bands have been deduced indirectly from hot electron lifetimes by Petek and coworkers [16].

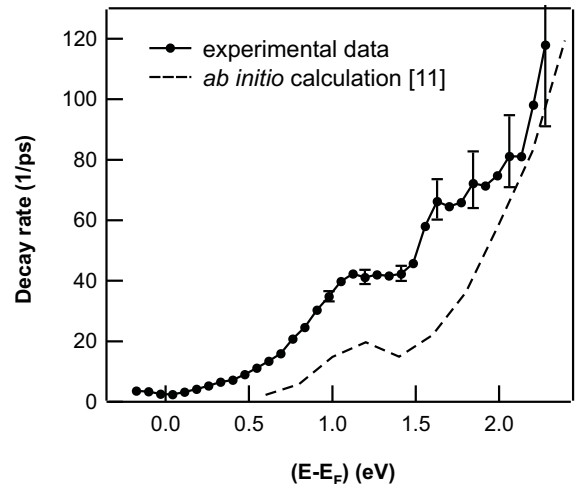


FIG. 2. Energy dependence of decay rates on the pristine HOPG surface. The anomaly near 1.5 eV is indicative of anisotropic QP lifetimes. This is supported by a recent *ab initio* calculation of QP relaxation rates for graphite which shows a similar anomaly in the same energy region [11].

Obviously the energy dependence of the decay rates cannot be described by a  $(E - E_F)^n$ -dependence with  $n = 2$  as expected for a Fermi Liquid or  $n = 1$  as previously predicted for a simplified bandstructure model of graphite [9]. The most striking deviation from a simple power law is the anomaly between 1.1 eV and 1.5 eV. In this energy range we observe a plateau-like region with no significant increase of the relaxation rates. The error bars in Fig. 2 reflect statistical errors obtained from the bi-exponential fit after averaging over 13 experimental runs. Systematic errors due to day-to-day variations are somewhat larger.

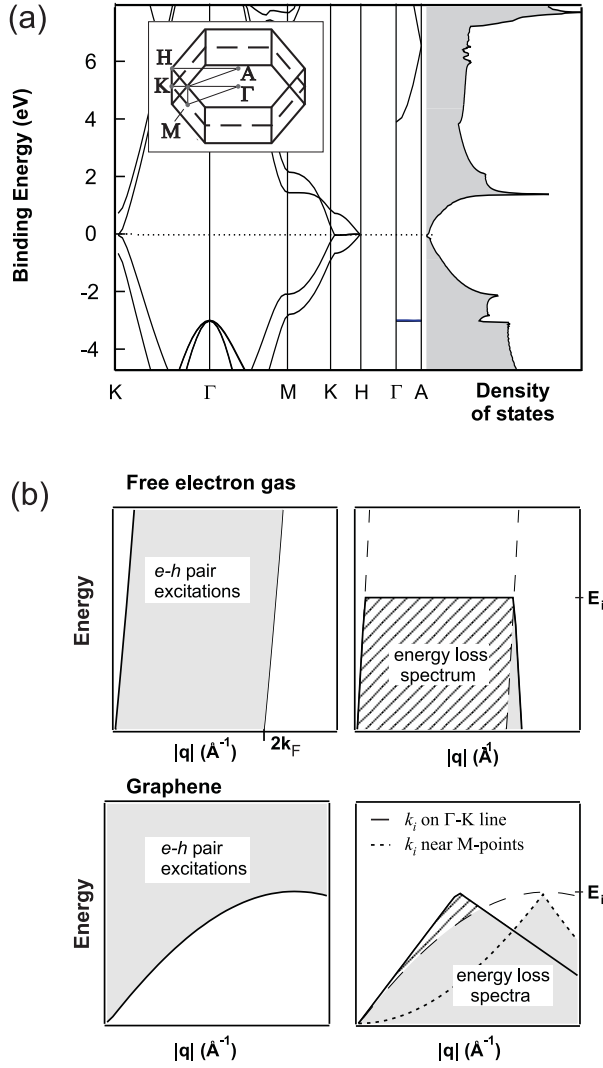


FIG. 3. (a) Graphite bandstructure along high symmetry lines and density of states. (b)  $e$ - $h$  pair spectrum for a free electron gas and a graphene sheet (left panels) as well as energy-loss *vs.* momentum-change for electrons decaying from an intermediate state with  $E_i = 1.5$  eV (right panels). The overlap of  $e$ - $h$  pair excitation- with energy loss-spectra is given by the hatched area.

The most obvious feature in the graphite bandstructure with which this plateau may be associated is a saddle point of the  $\pi^*$ -bands at the  $M$ -point of the graphite Brillouin zone (see Fig. 3a) and the resulting van Hove singularity at 1.5 eV in the DOS. Electrons excited to this region of the band-structure can only decay by a transfer of comparatively large momentum to secondary excitations ( $e$ - $h$  pairs), in contrast to electrons decaying from other iso-energetic regions of the bandstructure. This is illustrated schematically in the lower right panel of Fig. 3b) for a simplified band structure model of a graphene sheet [10]. The  $e$ - $h$  pair excitation spectrum of graphene on the other hand (lower left panel) has no overlap with the energy-loss and associated momentum-

change for electrons decaying from the vicinity of the  $M$ -point. In contrast, a much smaller mismatch exists for iso-energetic electrons along the  $\Gamma - K$  line. We speculate that this gives rise to strongly anisotropic QP lifetimes in graphite and ultimately leads to the observed anomaly in the decay rates. Note, that no comparable anisotropies exist for a free electron gas (upper panels in Fig 3b)) or for lower energy excitations in graphene.

Recent *ab initio* calculations of QP lifetimes in graphite by Spataru *et al.* [11] show a similar anomaly around 1.5 eV. The authors find pronounced anisotropies in the QP lifetimes with a distinct anomaly at 1.5 eV arising from electrons in the  $\pi^*$ -band around the  $M$ -point of the Brillouin zone. If averaged over the entire Brillouin zone – mimicking the averaging process in 2PPE due to scattering in the intermediate and final states – the calculated decay rates are reproduced by the dashed line in Fig. 2. The qualitative trends and features of both, experimental and theoretical decay rates are evidently the same.

The calculations by Spataru *et al.* strongly support, that the experimentally observed plateau around 1.5 eV is a direct consequence of anisotropic QP lifetimes in graphite. A quantitative comparison of theoretical and experimental results, however, appears to be difficult. This is most likely because theory does not account for finite temperatures, unavoidable lattice defects, and possible corrections from diffusive or ballistic transport of excited carriers out of the detection volume; effects which are expected to lead to higher decay rates as observed experimentally.

The influence of disorder, *e.g.* defects or phonons, on the electron dynamics is expected to depend strongly on anisotropies of QP lifetimes. This is best understood if one considers that lattice distortions break the translational symmetry of the crystal lattice and, thereby, lead to a coupling of different electronic states. If the states coupled in this manner have different lifetimes this should ultimately change the global electron dynamics. Matthiesens rule – which states that the rates of competing decay channels simply add up – would imply that the global dynamics is increasingly dominated by short-lived states once the coupling among states in the Brillouin zone is turned on.

To test this hypothesis we introduced lattice defects by Ar-ion sputtering. In Fig. 4 we plot the relaxation times of the electron population – the inverse of the rate – as a function of intermediate state energy. Qualitatively we find that the decay of the electronic population is accelerated significantly irrespective of the electron energy.

In agreement with the arguments presented above, these results provide further evidence for anisotropies in the QP lifetimes in graphite. Furthermore, they extend a recent study on the influence of defects on the electron dynamics in surface states [20] to the dynamics in bulk states.

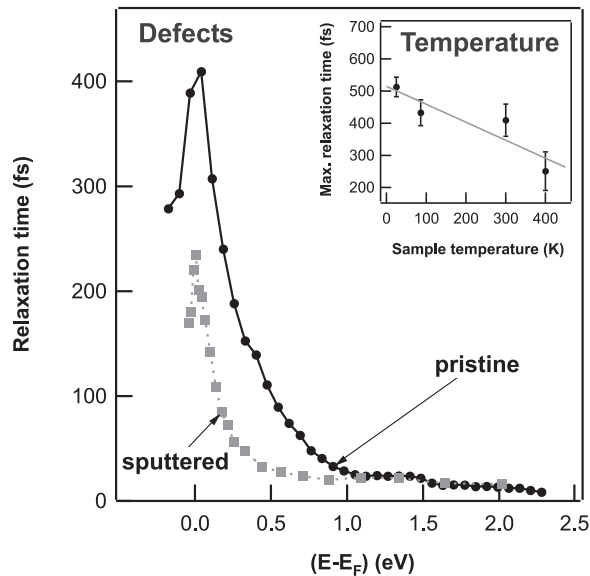


FIG. 4. Influence of defects and lattice temperature on the electron dynamics.

Alternatively, coupling between electronic states can be introduced by heating of the sample, *i.e.* by an increase of dynamic lattice distortions. This is most clearly illustrated by plotting the decay-time found at the peak of relaxation time curves like the one in Fig. 4, as a function of lattice temperature (see inset of Fig. 4). Very much like static defects, lattice vibrations can lead to a coupling of electronic states and reduce the measured relaxation times. We note, however, that the trend seen in Fig. 4 may be a superposition of different effects with additional contributions from the temperature dependence of  $e$ - $e$  scattering rates and enhanced inelastic  $e$ - $ph$  scattering.

These results may also shed new light on the apparent discrepancies between electron dynamics measured by different groups in graphite. Xu *et al.*, for example, have observed somewhat shorter relaxation times on a cesiated graphite surface [8] whose absolute values lie in-between our results for the pristine and the sputtered surface. Furthermore, as in our experiments on the defect enriched surface, neither Xu *et al.* nor Ertel *et al.* [21] find any evidence for a plateau around 1.5 eV. This may indicate that surface preparation and defect density plays a more important role for measurements of bulk electron dynamics than previously assumed.

In summary, we have investigated the electron dynamics in HOPG resulting from ultrafast optical excitation. The observed anomaly in the energy dependence of the electron dynamics can be linked to strongly anisotropic lifetimes of electrons excited to about 1.5 eV above the Fermi level. Electrons excited to a saddle point in the graphite bandstructure at the same energy are expected to be very long lived due to a mismatch of their energy loss spectrum and the  $e$ - $h$  pair excitations available

for scattering processes. Disorder is found to accelerate global electron dynamics, most likely due to the coupling of long- to short-lived states. This provides further evidence for the anisotropy of QP lifetimes, which have also been predicted by a recent *ab initio* calculation [11].

We thank W. Ekhardt and A. Rubio for helpful discussions and M. Bovet for kindly providing the graphite band structure. It is our pleasure to acknowledge G. Ertl for his continuing and generous support. R. F. acknowledges financial support by the Alexander von Humboldt foundation.

- 
- [1] H. Petek and S. Ogawa, Prog. Surf. Science **56**, 239 (1997).
  - [2] P. M. Echenique, J. M. Pitarke, E. V. Chulkov and A. Rubio, Chem. Phys. **251**, 1 (2000).
  - [3] D. Pines, P. Nozieres, The theory of Quantum Liquids, vol. I: Normal Fermi Liquids, Addison-Wesley, New York, 1989.
  - [4] W. D. Schöne, R. Keyling, M. Bandic and W. Ekardt, Phys. Rev. B **60**, 8616 (1999).
  - [5] I. Campillo, J. M. Pitarke, A. Rubio, E. Zarate and P. M. Echenique, Phys. Rev. Lett., **83**, 2230 (1999).
  - [6] S. Ogawa, H. Nagano and H. Petek, Phys. Rev. B **55**, 10869 (1997).
  - [7] M. Bauer, S. Pawlik and M. Aeschlimann, Proc. SPIE. **3272**, 201 (1998).
  - [8] S. Xu, J. Cao, C. C. Miller, D. A. Mantell, R. J. D. Miller and Y. Gao, Phys. Rev. Lett. **76**, 483 (1996).
  - [9] J. Gonzalez, F. Guinea and M. A. H. Vozmediano, Phys. Rev. Lett., **77**, 3589 (1996).
  - [10] P. R. Wallace, Phys. Rev. **71**, 622 (1947).
  - [11] C. D. Spataru, M. A. Cazalilla, A. Rubio, L. X. Benedict, P. M. Echenique and Steven G. Louie, Phys. Rev. Lett. *submitted*.
  - [12] E. Knoesel, A. Hotzel and M. Wolf, Phys. Rev. B **57**, 12812 (1998).
  - [13] Advanced Ceramics Corporation, graphite monochromator plate, ZYB grade,  $0.8 \pm 0.2$  mosaic spread.
  - [14] S. Ono, J. Phys. Soc. Japan **40**, 498 (1976).
  - [15] T. Hertel and G. Moos, Phys. Rev. Lett., **84**, 5002 (2000).
  - [16] H. Petek, H. Nagano, M. J. Weida, S. Ogawa, Chem. Phys., **251** 71 (2000).
  - [17] G. Moos, *et al.*, in preparation.
  - [18] T. Hertel and G. Moos, Chem. Phys. Lett., **320**, 359 (2000).
  - [19] K. Seibert, G. C. Cho, W. Kütt, H. Kurz, D. H. Reitze, J. I. Dadap, H. Ahn, M. C. Downer and A. M. Malvezzi, Phys. Rev. B **42**, 2842 (1990).
  - [20] M. Weinelt, C. Reuß, M. Kutschera, U. Thomann, I. L. Shumay, Th. Fauster, U. Höfer, F. Theilmann and A. Goldmann Appl. Phys. B, **68**, 377 (1999).
  - [21] K. Ertel, U. Kohl, J. Lehmann, M. Merschorf, W. Pfeiffer, A. Thon, S. Voll and G. Gerber, Appl. Phys. B **68**, 439 (1999).