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Reflection electron energy loss spectrum of single layer graphene measured on a graphite substrate



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ABSTRACT

Reflection electron energy loss spectra (REELS) have been measured on a highly oriented pyrolytic graphite (HOPG) sample. Two spectra were measured for different energies, 1600 eV, being more sensitive to the bulk and 500 eV being more sensitive to the surface. The energy loss distributions for a single surface and bulk excitation were extracted from the two spectra using a simple decomposition procedure. These single scattering loss distributions correspond to electron trajectories with significantly different penetration depths and agree with energy loss spectra measured on free standing single layer graphene and multilayer graphene (i.e. graphite). This result implies that for a layered electron gas (LEG) material, the number of layers which responds in a correlated fashion to an external perturbation is determined by the depth range penetrated by the external perturbation, and not by the number of layers actually present in the specimen.

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In spite of the fact that the in-plane electrical conductivity of graphite is several orders of magnitude larger than along the *c*-axis, implying that charge transport is essentially two-dimensional (the conductivity along the *c*-axis is negligible for most purposes), plasmonic excitations in graphite are three-dimensional [1]. This fact is attributable to the strong correlation of the π -electrons along the *c*-axis. Indeed, Shung [2], by taking into account the fact that the π -electrons of adjacent layers prefer to move in phase and are thereby correlated, extended the earlier two-dimensional models of Wallace [3] and Slonczewski and Weiss [4] to a genuine three-dimensional model. Shung's approach nowadays in many instances is instrumental for understanding the dielectric response of freestanding single- and multilayered graphene [1,5,6], as well as other layered electron gas materials (LEG).

For example, electron energy loss measurements on multilayered graphene performed in the transmission electron microscope [1] exhibit a strong shift of the so-called ($\pi + \sigma$)-plasmon resonance from about 15 eV (single layer graphene) to ~25 eV (multilayer graphene essentially equivalent to graphite) [1]. The fact that the (π - π)-interaction which is responsible for the weak van der Waals interlayer bonding (being the *raison d'être* for the exfoliation technique) manifests itself by such a large shift in the plasmon resonance energy is remarkable. These

authors observed that the measured value of the resonance energy even serves to identify the number of layers in a freestanding multilayered graphene sample measured in transmission. Their data are quantitatively reproduced by model calculations based on Shung's theory [5].

One of the merits of Shung's approach is the fact that it can be used to (numerically) convert the dielectric response of a three-dimensional layered electron gas material, such as graphite, into its two-dimensional counterpart, such as a single layer of graphene. Reed et al. [6] proved this by applying Shung's LEG-theory to the experimental data of Ref. [1] for graphite and comparing the result with the graphene data of the same authors, providing a justification for the analysis of their X-ray scattering data for single layer graphene which were in fact measured on a macroscopic graphite sample.

In the present work, we highlight another aspect of the dielectric response of an LEG material to an external perturbation. By analysing two reflection electron energy loss spectra measured on graphite for two different primary energies where the relative contribution of surface and bulk scattering is sufficiently different (500 eV, more surface sensitive and 1600 eV, being more sensitive to the bulk) and using a simple deconvolution scheme [10,11], the surface and the bulk part of the dielectric response are extracted from these data. The surface component obtained in this way agrees with the single-layer graphene data of Ref. [1], while the bulk component matches the data of these authors for graphite as well as earlier measurements of the optical data of graphite [8,9]. This can only be explained by the variation of the surface sensitivity with energy if it is assumed in addition that the correlation in the response of the π -subsystem is in fact not governed by the number of layers present in the sample, but rather by the number of layers which

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are penetrated by the beam. Note that this is a stronger statement than following from the works cited above. Most importantly, it suggests that the number of layers of an LEG material that responds in a correlated fashion to an external perturbation can be tuned by varying the primary energy of the beam.

Reflection electron energy loss spectra (REELS) were measured in a UHV-system (base pressure 2×10^{-10} mbar) equipped with a hemispherical analyser operated at a pass energy of 20 eV. The full polar angle of acceptance of the analyser was set to 24° in order to minimize diffraction effects in the loss spectra. The polar angle of incidence and detection were equal and amounted to 60° , but the plane of incidence was tilted with respect to the plane of detection by 35° . The sample was a commercial highly oriented pyrolytic graphite (HOPG) sample which was “cleaned” by exfoliation immediately before insertion into the system and was not heated prior to measurement. The Auger spectrum of the sample exhibited a single graphitic C-KLL peak. Reproducibility of the measurements was verified by varying the measurement position on the sample and also by repeating the measurements on a freshly (ex-situ) exfoliated sample.

Fig. 1a shows the REELS measured for a primary energy of 500 eV (more surface sensitive, blue) and 1600 eV (more bulk sensitive, red) after elimination of the elastic peak. The loss features were divided by the area of the elastic peak and the width of the energy channel to give the loss distribution in absolute units of reciprocal eV [12]. Both spectra are very similar, exhibiting a plasmon resonance at 6 eV which is commonly referred to as π -plasmon, although it is in fact a hybrid plasmon since screening by the σ -subsystem lowers its resonance energy from 10 eV, as expected on the basis of the π -electron density, to the observed value of about 6 eV [9]. The $(\pi + \sigma)$ -plasmon at ~ 25 eV is somewhat broader on the low energy side for the more surface sensitive measurement while for the more bulk sensitive measurement it seems somewhat broader on the high energy side, but this is difficult to distinguish due to the overlap with the multiple scattering region.

Deconvolution of multiple scattering can be effected by applying the following procedure to the measured spectra $y_1(T)$ and $y_2(T)$ [10]:

$$y_{1,2}^*(T) = y_{1,2}(T) - \int_0^T y_{1,2}(T-T') y_{1,2}^*(T') dT', \quad (1)$$

where the resulting spectra $y_1^*(T)$ and $y_2^*(T)$ are referred to in the literature as the Tougaard–Chorkendorff “effective” cross section for inelastic scattering [7]. However, these quantities, which are shown in Fig. 1b, are not cross sections, but rather a linear combination of the surface scattering loss distribution, the bulk scattering loss distribution and the convolution of the two (neglecting vanishingly small contributions of higher order) [10]. The relative intensity of these contributions is not only governed by the value of the inelastic mean free path, but also by the probability for experiencing a surface excitation as well as elastic scattering and therefore depends i.e. on the selected geometric configuration, the energy, etc. Since the surface scattering zone is very shallow, being of the order of the elastic mean free path, surface crossing proceeds without significant deflections and therefore plural surface scattering is governed by Poisson statistics. The average number of surface excitations is inversely proportional to the time the probing electron spends in the surface scattering zone, giving an energy dependence of the form: $\langle n_s(E) \rangle \propto 1/\sqrt{E}$ [10]. Therefore, the contribution of surface excitations in the spectra measured at 500 and 1600 eV differs approximately by a factor of two, which should lead to sufficiently distinct differences between the spectra y_1^* and y_2^* , allowing one to separate these contributions using the algorithm in Ref. [10].

Indeed, after elimination of multiple scattering, the data in Fig. 1b now exhibit a clear difference, the low energy side of the $(\pi + \sigma)$ -plasmon being more accentuated in the surface sensitive data exhibiting a

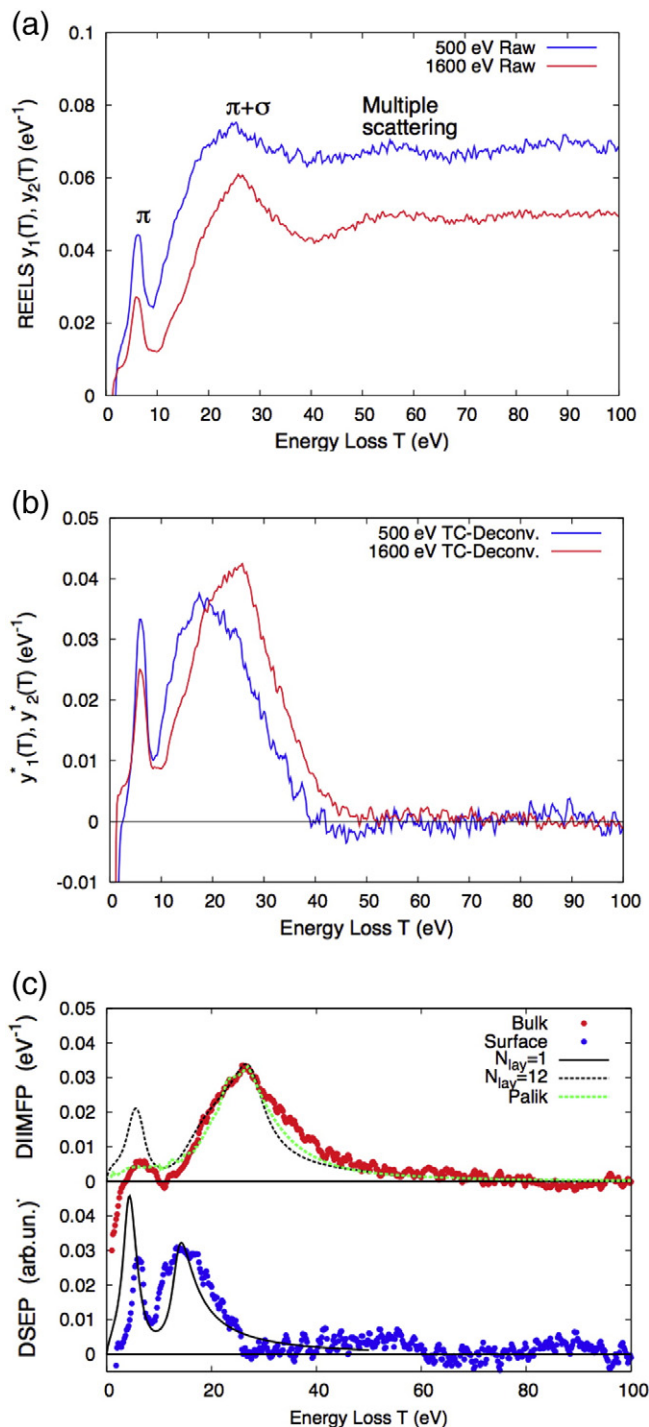


Fig. 1. (a) REELS spectra of HOPG for two primary energies 500 eV (more surface sensitive, blue) and 1600 eV (more bulk sensitive, red) after subtracting the elastic peak, and dividing the resulting spectrum by the area of the elastic peak and the channel width, giving the loss spectrum in absolute units of reciprocal eV; (b) The spectra shown in (a) after they were subjected to the Tougaard–Chorkendorff deconvolution algorithm [7]; (c) Decomposition into surface (blue) and bulk (red) components. The black curves are results of model calculations [5] based on Shung’s LEG-theory. The dashed green curve is the energy loss function of graphite measured by optical means [8,9]. The latter as well as the black curves were scaled by a multiplicative constant to match our data.

shoulder at ~ 15 eV, while the bulk sensitive data on the other hand show a broader tail at the high energy side of the $(\pi + \sigma)$ -plasmon.

The relative intensities of the three terms making up the spectra in Fig. 1b can be estimated by e.g. Monte Carlo calculations for the partial

intensities for electron reflection. Then the bulk ($w_b(T)$) and surface ($w_s(T)$) components can be established via [10]:

$$w_{b,s}(T) = u_{10}^{b,s} y_1^*(T) + u_{01}^{b,s} y_2^*(T) + u_{11}^{b,s} y_1^*(T) \otimes y_2^*(T), \quad (2)$$

where the symbol “ \otimes ” denotes a convolution and the coefficients $u_{k,l}^{b,s}$ depend on the relative intensities of surface and bulk scattering and are different for the reconstruction of the surface and bulk components [10]. The first order reduced partial intensities for volume scattering are always close to unity as indeed found for the present case: $\gamma_1(500 \text{ eV}) = 1.04$, $\gamma_1(1600 \text{ eV}) = 1.12$, while the relative contribution of surface scattering differs by a factor of 1.73. Using these values for calculation of the deconvolution coefficients (see Eqs. (22) and (26) in the appendix of Ref. [10]), the surface and bulk components presented in Fig. 1c are obtained.

The bulk component, shown by the red data points is the normalised differential inelastic inverse mean free path (DIIMFP), which is obtained in absolute units. The differential surface excitation probability (DSEP) shown in the lower panel by the blue data points is given in relative units by this procedure [11–13].

The black curves are model calculations based on Ref. [5] which reproduce the energy loss spectra of Ref. [1] for free standing single layer graphene as well as for a sample consisting of 12 graphene layers measured with the transmission electron microscope. Agreement with the present assessment is reasonable, except for the π -plasmon resonance. In additional simulations on the basis of the model in Ref. [5] (not shown) the π -plasmon resonance energy increases from $\sim 4.5 \text{ eV}$ to $\sim 6.5 \text{ eV}$ when changing the energy from 100 keV to 500 eV, implying that the difference in the π -plasmon energy seen in Fig. 1c is a consequence of the primary energy dependence. The agreement between our data and the multilayer graphene results (i.e. bulk graphite) as well as with the earlier optical data for graphite [8,9] is also quite convincing, again with exception of the π -plasmon region. The important point is, however, that according to Ref [1], it is the resonance energy of the $(\pi + \sigma)$ -plasmon which corresponds to the number of layers seen in the transmission electron microscope. Multiple scattering dominates the raw REELS spectra (see Fig. 1a), whereas it is absent in the high-energy transmission measurements since there the mean free path lengths exceed the electron trajectory lengths travelled in the specimen. The agreement between the different approaches in Fig. 1c shows that both elimination of multiple scattering as well as decomposition into surface and bulk components are successfully accomplished by the deconvolution algorithm summarized by Eqs. (1) and (2).

In conclusion, the present analysis of energy loss measurements on a macroscopic graphite specimen yields decomposition into loss spectra of 2D (graphene) and 3D (graphite) carbon allotropes. The fact that this was done without invoking any property concerning the electronic structure or electronic correlation of LEG-materials, just by the deconvolution procedure of Eqs. (1) and (2), deserves to be discussed. Although the present results agree with those in Refs. [1,6], it should be emphasized that they

were obtained in a significantly different way: in Ref. [1] the measurements were actually performed on freestanding multilayer graphene by electron transmission, while in Ref. [6], the theoretical relationship between the 2D and the 3D dielectric responses of layered electron gas materials was invoked in the analysis.

The basic idea of the decomposition into bulk and surface components is to measure and analyse two spectra for which the *average* penetration depth of the primary electrons is changed so that the difference in the relative contribution of surface and bulk components in the two spectra allows one to decompose them. A variation in the surface sensitivity can be achieved either by changing the primary energy of the beam giving rise to a change in the electron inelastic mean free path as well as the surface excitation probability, or, alternatively, by varying the incidence or emission angle [12]. In both cases, electron trajectories with *any arbitrary* pathlength contribute to the spectrum, but the *distribution* of pathlengths as well as the *relative probability* for surface and bulk excitations is different. This allows one to decompose the spectra into surface and bulk components. This leads to the 2D- and 3D-dielectric responses exhibiting a significantly different energy distribution characterized by the shift of the $(\pi + \sigma)$ -plasmon, which is a signature of the number of layers which respond to the external perturbation in a correlated fashion. This can only be understood if it is assumed that electron trajectories with different penetration depths give rise to electronic correlations in the material over a depth range governed by the actual number of layers penetrated by individual electrons rather than by the number of layers present in the specimen.

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