A new technique for the sp²/sp³ characterisation of carbon materials

J. T. Titantah and D. Lamoen

TSM, Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

We present a technique to determine the sp³/sp² ratio of carbon materials which is based on the electron energy-loss spectroscopy and which uses the theoretical spectrum of graphite obtained from ab initio electronic structure calculations. The method relies on the separation of the π∗ and σ∗ components of the carbon K-edge of graphite. This π∗ spectrum is adopted and assumed to be transferable to other carbon systems given an appropriate parametrisation of the broadening. The method is applied on a series of Monte-Carlo generated amorphous carbon structures and is shown to be stable over a wide range of the energy windows for which spectral integration is performed. The results are found to be in good agreement with the sp³ ratio obtained from a microscopic scheme which uses the π−orbital axis vector (POAV1) analysis. The technique was also applied on a series of experimental spectra of amorphous carbon and was found to be in good agreement with the results obtained from a functional fitting approach.

One of the parameters that determine the hardness of amorphous carbon is the fraction of sp³ bonded carbon atoms. This fraction can be determined by making use of the X-ray photoelectron spectroscopy (XPS) [1], the plasmon energy technique [2,3], the near-edge X-ray absorption spectroscopy (NEXAFS) [4] and the high-energy electron energy-loss spectroscopy (HEELS) [5,6,7,8].

The high-energy EEL spectrum of an amorphous carbon is made of a π∗ part whose onset is at about 284 eV and a σ∗ component whose onset is about 5-7 eV from that of the π∗ component. The HEELS sp³/sp² characterisation technique is based on the ability to isolate the π∗ features and subsequently its cross-section from the entire spectrum. All the isolation methods that are often used are limited by the assumption that the π∗ and the σ∗ bands are well separated in energy such that their cross-sections can be independently deduced by spectral integrations over fixed energy windows. But it is well known that plural inelastic scattering such as core-loss excitation plus additional plasmon losses modifies the edge intensities by spreading oscillator strengths to higher energies [9]. The π∗ band can spread to energies as high as 30 eV beyond the edge onset thereby overlapping with the σ∗ band. Density functional theory (DFT) calculations on graphite and amorphous carbon, which will be presented elsewhere [9], reveal that the π∗ band is exceptionally broad, extending even to energies beyond 30 eV. Therefore, a sp³/sp² ratio characterisation that ignores these finite π∗ intensities (of the HEELS or NEXAFS) at higher energies is not entirely consistent. In this letter we present a new technique for the characterisation of the sp³/sp² ratio in (amorphous) carbon systems which is based on the π∗/σ∗ separation of the calculated energy-loss near-edge structure (ELNES) of graphite. We show that this consistent treatment of the π∗ and the σ∗ spectra can lead to sp³ proportions that are independent of the choice of the size of the integration energy window in sharp contrast with other techniques [10].

DFT calculations are performed using the all-electron Full-Potential-Linearised-Augmented-Plane-Wave (FLAPW) code WIEN2k [10]. The exchange and correlation energy is treated using the local density approximation [11]. Muffin-tin radii (RMT) are fixed at 1.3 atomic units (a.u.) for graphite and 1.25 a.u. for amorphous carbon, while RMT×Kmax values of 5.5 and 5.0 are used for graphite and amorphous carbon, respectively; Kmax being the plane wave cut-off. Up to 1000 k-points are used to sample the full Brillouin zone of graphite (72 in the irreducible Brillouin zone (IBZ)) while 20 (4 in the IBZ) are used for the amorphous carbon. The core-hole effect is introduced in the ELNES of graphite via the so-called excited-core method (in a supercell approach). The π∗ component of the ELNES of graphite is obtained using the expressions of ref. [12] for the differential cross-section which was recently implemented on hexagonal boron nitride [13] and on
nanotubes \[14\].

In order to obtain insight into the local structure of amorphous carbon, we generate amorphous carbon systems by means of classical Monte Carlo (MC) simulations based on the Tersoff empirical potential \[15\] for carbon \[16\]. We generated amorphous carbon structures at densities of 2.0, 2.6, 3.0 and 3.6 g/cm\(^3\) by quenching hot gaseous carbon from 8000K down to 300K. This was done via a continuous space, periodic boundary condition (PBC), constant volume, constant temperature and constant number of atoms classical Metropolis Monte Carlo procedure on cubic cells made of 64 atoms. The ELNES spectra (without core-hole) were computed for the four generated carbon systems. The average (over all atoms) ELNES spectra of each of the systems were calculated. On Figure 1 we show the ELNES spectra of the four generated carbon systems.

![Figure 1: Total ELNES (in the sudden approximation) of four MC-generated carbon structures of varying densities of 2.00-3.60 g/cm\(^3\).](image)

The application of this technique to all three-coordinated atoms of our MC-generated structures provides a more precise approach to characterise the sp\(^3\) fraction because it accounts for the non-planarity of the three-coordinated atoms. However, not all four-coordinated atoms are having the ideal sp\(^3\) local bonding structure as follows from the local geometry and our calculations of the core-loss ELNES spectra of the generated structures. We can easily account for the distortion-induced sp\(^2\) character in such four-coordinated atoms by analysing the \(\pi^*\) components for every non ideal tetrahedral four-coordinated atom as explained in ref. \[2\]. The sp\(^3\) fraction obtained by this approach is consistently higher than that obtained by using the coordination number method for low and intermediate densities (see Table I). For high densities the two methods yield the same results.

The technique of the sp\(^3\)/sp\(^2\) characterisation presented here is based on the assumption that the ELNES of any carbon atom can be decomposed into two independent parts. One of these ELNES components (the \(\pi^*\) component) is sought by performing first-principles calculations on graphite for which the two components are well defined. To some extent, the method is comparable to the experimental work of ref. \[21\]. The sp\(^3\)/sp\(^2\) quantification procedure is described as follows

- We identify the energy position \(E_{\pi}\) of the main \(\pi^*\) peak from the spectrum of the uncharacterised sample and rescale the intensity to have a value of one at this peak. We denote this new spectrum as \(I(E)\) where \(E\) is the energy loss.
- We consider a normalised smoothening function \(g(\sigma, E)\) (which could be a Gaussian or a Lorentzian) of full width at half maximum \(\sigma\).
- We define an energy scale shift parameter \(s\) by which the unbroadened calculated graphite \(\pi^*\) spectrum should be shifted to align the maximum of its main \(\pi^*\) peak to that of the unknown sample. After the spectral shift the \(\pi^*\) spectrum is scaled to one at \(E_{\pi}\).
Using this new shifted graphite \( \pi^* \) spectrum which is convolved with \( g(s, \sigma, E) \), denoted as \( \Pi(s, \sigma, E) \), we define the function

\[
F(s, \sigma) = \int_{E_{\text{min}}}^{E_{\text{max}}} (I(E) - \Pi(s, \sigma, E))^2 dE
\]  

(1)

where \( E_{\text{min}} \) is the edge-onset. In Eq.(1) it is implied that the spectrum of the amorphous carbon is entirely of \( \pi^* \) character up to the main \( \pi^* \) peak.

F is minimised for \( s \) and \( \sigma \). The minimal values of \( s \) and \( \sigma \) are used for \( \Pi(s, \sigma, E) \) to deduce the \( \pi^* \) spectrum which best fits the lower energy part of the unknown spectrum. This shifted and convolved \( \pi^* \) spectrum is assumed to be that of the unknown amorphous carbon system.

An energy window \( \Delta E \) whose lower limit is fixed at the edge onset is chosen and the integrals \( I_\pi(\Delta E) = \int_{E_{\text{min}}}^{E_{\text{min}}+\Delta E} \Pi(s, \sigma, E)dE \) and \( I_{\text{Total}}(\Delta E) = \int_{E_{\text{min}}}^{E_{\text{min}}+\Delta E} I(E)dE \) are evaluated.

The ratios, for various \( \Delta E \), \( R(\Delta E) = I_\pi(\Delta E)/I_{\text{Total}}(\Delta E) \) are calculated.

The ratio \( R_0(\Delta E) \) for a well characterised sample, whose \( sp^2 \) fraction is \( x_0 \) is known, is also calculated and the \( sp^2 \) fraction in the unknown amorphous carbon sample is deduced as

\[
x(\Delta E) = \frac{R(\Delta E)}{R_0(\Delta E)} x_0
\]  

(2)

and the \( sp^3 \) fraction is \( 1 - x \).

To test and validate this method, we applied this technique to the ELNES spectra of the four generated amorphous carbon systems described above. The ratio \( R(\Delta E) \) for each system is plotted as a function of \( \Delta E \) on Figure 2. From this figure it is seen that for each energy window \( R \) decreases monotonically as the density increases. It is also seen that for the wide range of \( \Delta E \) considered (15 eV < \( \Delta E \) < 55 eV) all the curves showing the variation of \( R \) with \( \Delta E \) seem to be parallel to each other. This suggests that if one of the spectra was a reference spectrum then the ratio of \( sp^2 \) carbon in each spectrum with respect to this reference will be fairly constant over this wide energy range. This demonstrates that the method should yield \( sp^2 \) or \( sp^3 \) fractions that are independent of the choice of the energy window in contrast to other techniques. In those techniques the \( sp^3 \) fraction depends crucially on both the width and position of the energy window.

To determine the \( sp^3 \) fraction, we take one of the Monte-Carlo generated amorphous carbon structures as a reference. Because the \( sp^3 \) fraction determined by the POAV1 analysis coincides with that obtained by the nearest neighbour counting method for high densities (see Table I), the structure having a density of 3.6 g/cm\(^3\) with an \( sp^3 \) fraction of 90% is considered as the reference. The resulting fractions for the other three systems are shown on Figure 3. The \( sp^3 \) fraction is clearly seen to be independent of the size of the energy window. The largest variation recorded did not exceed 6%. The values obtained, reproduced in Table II were in very good agreement with those obtained from a POAV1-based analysis. These results are given as intervals because of the standard deviations on the POAV1-corrected \( sp^3 \) fractions recorded on the entire systems of the three-coordinated atoms. In the table we also report the proportion of 4-coordinated atoms in each of the systems.
Figure 3: The sp$^3$ percentage for the four generated carbon structures. The $\rho = 3.6g/cm^3$ sample made of 10.3% sp$^2$ atoms (according to the POAV1 approximation) is used as the reference system.

Table I: The sp$^3$ percentages of the four generated amorphous carbon systems. The 3.6 g/cm$^3$ system is considered as reference and its sp$^2$ ratio (0.103) according to the POAV1 is adopted.

| density | new method | coordination number | POAV1 |
|---------|------------|---------------------|-------|
| 2.00    | 32-38      | 16                  | 28-32 |
| 2.60    | 39-40      | 20                  | 35-37 |
| 3.60    | 56-58      | 55                  | 54-56 |
| 3.60    | 90         | 90                  | 90    |

Table II compares the sp$^3$ percentages of the five amorphous carbon samples with results obtained using the functional fitting method.

| Sample | new method | Fitting technique |
|--------|------------|-------------------|
| I      | 58-68      | 67-68             |
| II     | 60-63      | 61                |
| III    | 56-57      | 56                |
| IV     | 54-55      | 51-53             |
| V      | 52-55      | 53                |

Table II: The sp$^3$ percentages of the five amorphous carbon samples. The 3.6 g/cm$^3$ system is considered as reference and its sp$^2$ ratio (0.103) according to the POAV1 is adopted. Apart from sample I, all samples show excellently stable results within the 30 eV window.

Figure 4: The sp$^3$ percentage for the five amorphous carbon samples.

Table II compares the sp$^3$ percentages of the five amorphous carbon samples with results obtained using the functional fitting method.

The use of this technique is not restricted to computer generated samples (in contrast to the POAV1 analysis) but can also be applied to experimental spectra. On Figure 4 and in Table II we show the sp$^3$ fractions of five spectra obtained from ref. [22]. In this table we also listed the values obtained in [22] using a functional fitting method with three Gaussians. Remark the good agreement with the functional fitting technique. Sample I showed the strongest dependence on $\Delta E$, but for the large energy window range of 15 eV - 45 eV the variation did not exceed 10% for this sample.

In summary, we have developed a method to quantify the sp$^3$ fraction of carbon materials based on the theoretical separation of the $\pi^*$ and $\sigma^*$ components of the carbon 1s electron energy-loss spectra. The $\pi^*$ spectrum of graphite is adopted and assumed to be transferable to other carbon systems given an appropriate parametrisation of the broadening. This has enabled the isolation of the $\pi^*$ spectrum of the carbon systems and a subsequent characterisation of their sp$^3$ contents. We have applied the method to a series of Monte-Carlo generated amorphous carbon structures and shown that the method...
gives stable results over a wide range of the energy window used for spectral integration and that the sp$^3$ fractions obtained using this method agree with values resulting from an exhaustive analysis of the distortion-induced hybridisation of every carbon atom by means of the $\pi$-orbital axis vector (POAV1) technique. The method has also been applied to five experimental amorphous carbon spectra and found to be in good agreement with the results obtained from a more traditional functional fitting technique.

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