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Surface and bulk components in angle-resolved core-level photoemission spectroscopy of graphite

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Angle-resolved x-ray photoelectron spectroscopy of the C 1s line of highly oriented pyrolytic graphite reveals two components separated by 194 ± 6 meV, with markedly different asymmetry parameters and natural linewidth. Analysis of the intensity of these peaks as a function of angle demonstrates that the higher binding-energy peak is associated with the outermost graphite layer(s). The conflicting core-level photoemission data from graphite in the literature are addressed in light of these measurements.

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Despite the deceptive simplicity of the electronic and geometric structures of graphite, there is a remarkable lack of consistency in the literature regarding core-level photoemission from the (0001) surface of this material. Controversy exists over the presence^{1–6} or otherwise^{7–9} of a surface core-level component to the C 1s line, the magnitude of the surface-bulk core-level splitting (when such surface and bulk components are observed), and the potential influence of defects on the C 1s line shape.¹⁰ It is important to resolve these inconsistencies if core-level photoemission is to be applied successfully to the detailed characterization of novel graphitic materials, particularly graphene, carbon nanotubes, and related few-layer structures.

One of the first reports of the C 1s line shape of graphite (0001) was by van Attekum and Wertheim⁷ from measurements on a highly oriented pyrolytic graphite (HOPG) substrate. A significant asymmetry in the line shape was observed, which was explained in terms of a single core-level component characterized by an asymmetry parameter (or singularity index), α , of 0.14. This magnitude of asymmetry was much larger than could be explained by the density of states near the graphite Fermi level and was attributed to the formation of an excitonic final state. High-resolution synchrotron-radiation excited soft x-ray photoemission spectroscopy (SXPS) studies of graphite by Sette *et al.*⁸ and Prince *et al.*⁹ revealed a single C 1s component with an asymmetry parameter substantially smaller than previously reported ($\alpha \sim 0.05$ – 0.1).⁷ SXPS of the graphite C 1s line of HOPG by Balasubramanian *et al.*¹ showed two components, attributed to surface and bulk states, with a difference in energy of 120 meV and with both surface and core lines possessing a small asymmetry parameter (0.048 ± 0.006) and narrow Lorentzian width (160 ± 10 meV). The absence of two components to the core lines in the previous SXPS studies^{8,9} was attributed to the photon energies chosen for excitation resulting in suppression of the bulk component, suggesting that they can be regarded as high-resolution studies of just the surface component of the C 1s line. Further evidence for surface and bulk components to the C 1s line was provided by Takata *et al.*⁶ They observed a shift in binding energy between the C 1s line from HOPG in normal-emission spectra obtained at a photon energy of 340 eV (where the surface component dominates) and that measured with 870 eV photons (where the bulk component dominates). The magnitude of the shift observed was consistent with the surface-bulk core-level splitting observed by Balasubrama-

nian *et al.*¹ A very recent SXPS study by Lizzit *et al.*² also showed surface and bulk components similar to those observed by Balasubramanian *et al.*¹ for the C 1s line of HOPG. However, for Kish graphite and graphite grown by annealing SiC, only a *single* C 1s component was seen,² which is of similar binding energy and asymmetry parameter to the main line found for HOPG. Through comparison of the C 1s lines from the three different types of graphite, the minor component in the C 1s line from HOPG (at lower binding energy) was attributed to an unspecified type of defect which, from the variation of intensity with emission angle, did not appear to be related simply to emission from the bulk.

Recent laboratory-based angle-resolved x-ray photoelectron spectroscopy (ARXPS) studies reported in the literature offer a diversity of results similar to the SXPS studies described above. Smith *et al.*³ found surface and core-level components separated by 470 meV in ARXPS from HOPG, a value much larger than that theoretically predicted,⁵ or observed in SXPS measurements.^{1,2} In their high-resolution ARXPS study Speranza and Minati⁴ came to the conclusion that surface and bulk core-level components were both present but that the surface-bulk splitting varied with emission angle due to instrumental effects. Speranza and Minati⁴ also found a natural (Lorentzian) linewidth for both surface and bulk components much smaller than that reported by the (higher resolution) SXPS studies described above. Moreover, it was found that the surface component had a larger asymmetry parameter than the bulk, much larger than that for the surface component deduced from SXPS data.^{2,8,9} Finally, Yang and Sacher¹⁰ argued that the C 1s line of graphite is inherently symmetric and that asymmetries arise from the presence of surface defects.

In this Brief Report we present a careful high-resolution ARXPS study performed at emission angles between 0° and 70° , which addresses the inconsistencies in the literature described above. By careful analysis of the data we show that the C 1s line of HOPG consists of both surface and bulk components: the line shape of the surface component is found to be consistent with that observed in SXPS studies, a constant (to within experimental error) surface-bulk energy splitting is observed, and the variation of the relative intensity of surface and bulk components is consistent with measurements of the inelastic mean-free path (IMFP) of electrons of the appropriate kinetic energy in graphite.^{11,12} Some of the origins of the spread in results so far reported in the literature are discussed.

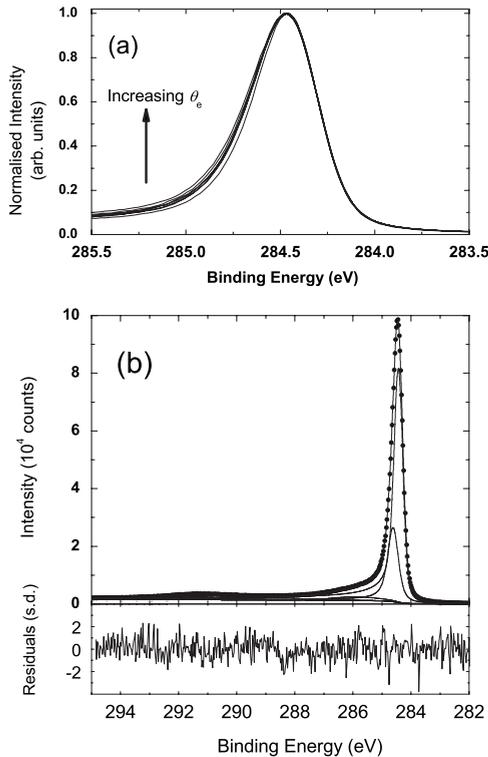


FIG. 1. (a) C 1s core-level spectra obtained from graphite (0001) as a function of emission angle. A clear increase in peak width to higher binding energy is apparent with increasing emission angle associated with the presence of a surface core-level component. The spectra have been normalized to peak height. (b) A typical fit to a full C 1s spectrum (emission angle 20°) with residuals shown in units of standard deviation of the data. The experimental data are presented as points, with the fit and components thereof as solid lines.

Measurements were performed using a Scienta ESCA300 x-ray photoelectron spectrometer at the National Centre for Electron Spectroscopy and Surface Analysis (NCESS), Daresbury, U.K. Spectra were obtained with monochromated Al K_α radiation (1486.6 eV) at a resolution of 294 ± 5 meV, as determined from the Gaussian broadening of the Fermi edge of a silver calibration sample measured at room temperature. The linearity of the spectrometer energy scale was calibrated with the Ag sample, and measurements on the calibration sample as a function of emission angle showed no energy shift. HOPG, (ZYH, Advanced Ceramics) was prepared by cleaving either with tape or with a razor blade and was immediately inserted into ultrahigh vacuum (UHV). The sample was then heated to $>600^\circ\text{C}$ in a preparation chamber for at least 1 h to remove any adsorbed material and, after allowing it to cool, transferred under UHV to the analysis chamber. The presence of contamination was checked for by XPS at grazing (70°) emission. Measurements presented here were performed with x-ray exposures of less than one hour (typically 40 min), and the sample was then recleaned due to the observation of low levels of contamination [an O 1s line at ~ 533.5 eV and a shoulder to the C 1s line at ~ 286.6 eV associated with C-OH and/or -C-O-C- (Ref. 13)] after exposure of the sample to the x-ray beam for extended periods ($\sim 1\%$ contamination, determined from O 1s:C 1s

ratio, was observed after ~ 8 h exposure). No contamination was observed when the sample was held in the chamber for a similar time without x-ray exposure. As a result of the short acquisition time, contamination levels for the data used in this Brief Report were always below experimentally detectable limits.

Figure 1(a) shows the C 1s line of HOPG measured at normal emission and at 10° intervals for emission angles between 20° and 70° . A clear increase in linewidth to the high binding-energy side can be observed, consistent with previous ARXPS studies,^{3,4} indicating the presence of a low kinetic-energy component on the line associated with the surface of the sample. No difference in line shape could be observed for spectra taken at the same emission angle for samples cleaved by the two techniques outlined above, providing evidence that surface defects¹⁰ may not be the origin of the observed behavior. Figure 1(b) shows a typical fit to the data using two Doniach-Šunjić lines convolved with a Gaussian broadening for the main peak and two broad weak components associated with bulk and surface π plasmons. A small defect-related peak at a binding energy of ~ 1.5 eV with respect to the bulk C 1s component is also included, which becomes slightly more significant with increasing emission angle, although it never represents more than 3% of the main peak area. The background is modeled by the Shirley approach, and the Gaussian width of both Doniach-Šunjić components is fixed at the instrumental resolution of 294 meV—allowing this parameter to vary during the fit yielded values within 5 meV. The quality of the fit can be seen from the fit residuals, which show the expected statistical variation from Poisson noise and show no systematic variation. The reduced χ^2 of all fits is close to 1, and the Abbé factors are between 0.4 and 0.8, further attesting to the appropriateness of the fitting model employed.

Fit parameters are reported in Table I and show that the analysis reveals a constant surface-bulk core-level energy shift (SCLS) to within experimental error, with an average value of 194 ± 6 meV, which is somewhat larger than the 120 meV reported by Balasubramanian *et al.*¹ and the theoretical values of Simunek and Vackar.⁵ However, the asymmetry parameter of the surface component, 0.05 ± 0.01 , is consistent with that measured for the surface component in high-resolution SXPS studies.^{1,2,8} Possible reasons for the difference in surface-bulk core-level energy shift are discussed below. The magnitude of the surface-bulk core-level splitting is much smaller than the shift predicted for defect-related states in graphite⁵ (>400 meV) lending further support for the assertion that the C 1s line shape is not determined by defects such as vacancies and surface steps. Indeed, the density of steps and surface defects on our samples, examined by *ex situ* atomic force microscopy (AFM) and scanning tunneling microscopy (STM) measurements (not shown), is so low that it is difficult to quantify. Such a low surface defect density—typical in cleaved pyrolytic graphite—further contradicts the model put forward by Yang and Sacher¹⁰ in which the increased high binding-energy width of the C 1s line would require surface defect densities significantly greater than 10%.

It is apparent from the data in Table I that the surface and bulk C 1s components have differing values for the asymme-

TABLE I. Fit parameters and weighted average obtained from ARXPS data; see text for details.

Emission angle	0°	20°	30°	40°	50°	60°	70°	Weighted average	
Bulk component	Lorentzian width (meV)	98 ± 2	100 ± 5	97 ± 1	94 ± 2	94 ± 1	92 ± 2	90 ± 4	95 ± 3
	Asymmetry index (α)	0.08 ± 0.02	0.093 ± 0.006	0.09 ± 0.01	0.10 ± 0.01	0.101 ± 0.008	0.11 ± 0.01	0.12 ± 0.02	0.10 ± 0.01
Surface component	Lorentzian width (meV)	220 ± 30	221 ± 3	234 ± 7	228 ± 6	230 ± 6	237 ± 3	243 ± 8	231 ± 8
	Asymmetry index (α)	0.05 ± 0.01	0.047 ± 0.008	0.045 ± 0.005	0.06 ± 0.02	0.05 ± 0.01	0.055 ± 0.005	0.08 ± 0.04	0.05 ± 0.01
Common SCLS (meV)	Gaussian width (meV)	294 ± 5	294 ^a	294					
		200 ± 10	192 ± 5	191 ± 8	193 ± 8	194 ± 8	196 ± 3	187 ± 12	194 ± 6

^aParameter fixed during fit.

try parameter with that for the surface component (0.05 ± 0.01) significantly smaller than that for the bulk (0.10 ± 0.01). Moreover, we find that the natural (Lorentzian) linewidth of the bulk component is very narrow, 95 ± 3 meV, compared with the surface, 231 ± 8 meV (the latter is again consistent with SXPS measurements).^{1,2,8} The value for the Lorentzian linewidth of the bulk C 1s component is similar to that used by Speranza and Minati⁴ and that observed in small gas-phase molecules¹⁴ and in diamond,¹⁵ therefore the difference in bulk and surface linewidths may explain the apparent discrepancy between the lifetime broadening measured in SXPS and that which might be expected from comparison with closely related systems.^{8,9} The changes in linewidth and asymmetry parameter between bulk and surface are significant and point to notable differences between the response to the core hole at the surface and in the bulk of graphite. In metals one typically finds a *larger* value for the asymmetry parameter at the surface compared with the bulk,¹⁶ which has been related to an increase in atomiclike character for the screening response of surface atoms due to their lower coordination. The strong intralayer and weak interlayer bonding in graphite has the result that surface atoms are not significantly more “atomiclike” than those in the bulk; hence, one would not expect the same behavior as observed in metals. The *reduction* in asymmetry parameter observed at the graphite surface may instead be related to reduced screening and electronic density of states near the Fermi level at the surface, in comparison with the bulk, which also contributes to the surface core-level shift observed.

The origin of higher binding-energy core-level component as the outermost layer of the graphite(0001) surface can be confirmed by considering the intensity of core and surface components as a function of emission angle (measured with respect to the sample normal). The integrated intensity of the surface-related C 1s peak is shown in Fig. 2(a) and is seen to be independent of angle, to within experimental error. The

intensity of the bulk component varies strongly with emission angle [Fig. 2(b)], but the variation is nonmonotonic, possibly reflecting diffraction effects¹⁷ and/or the microscopic roughness visible on the surface at optical length scales. Assuming emission from discrete graphene layers of *c*-axis spacing d (3.355 Å), the ratio of surface-to-bulk core-level intensity can be expressed as³

$$\frac{I_s}{I_b} = e^{d/\lambda \cos \theta} - 1,$$

where θ is the emission angle, λ is the inelastic mean-free path of the photoelectrons, I_s is the intensity of the surface component to the C 1s line, and I_b is the intensity of the bulk

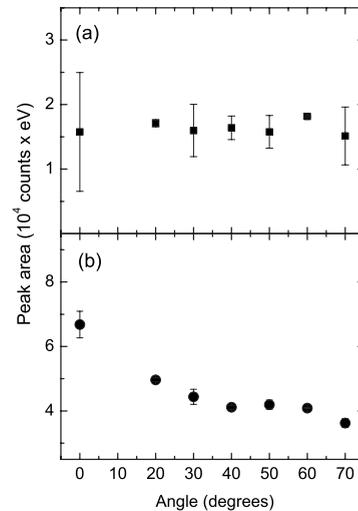


FIG. 2. (a) Integrated area of the surface C 1s fit component as a function of emission angle. Fits are made to raw (non-normalized) data. The lack of variation of component area as a function of emission angle is clear. (b) Variation of the integrated intensity of the bulk component of the C 1s line as a function of emission angle. A nonmonotonic decrease is observed.

component. Due to the nonmonotonic variation of the bulk signal values for the IMFP of the C 1s photoelectrons vary between ~ 13 and 26 Å, with the mean value of 16 ± 5 Å in good agreement with the measurements of IMFP in carbon by Steinhardt *et al.*¹¹ and Zemek *et al.*¹²

In their analysis of a smaller ARXPS data set Speranza and Minati⁴ drew somewhat different conclusions about the nature of the surface and bulk components, finding a surface core-level shift which varied with emission angle, and that the asymmetry parameter of the surface component was much larger than that reported for the bulk (0.18 vs ~ 0.12). However, Speranza and Minati⁴ found a common natural linewidth of 95 meV, in close agreement with the value reported here for the bulk component, for *both* surface and bulk components, which is much narrower than the typical natural linewidth reported in (surface sensitive) SXPS studies.^{1,2,8,9} We find that fits constrained in this way result in a large surface asymmetry parameter as the fit tries to compensate for the artificially narrow surface natural linewidth, leading to poor values for both reduced χ^2 and Abbé factor (the systematic deviations quantified by a poor Abbé factor can be seen in the fit residuals of Speranza and Minati⁴). Such artificially constrained fits also lead to a variable surface core-level shift and surface-to-bulk intensity ratios which imply an electron inelastic mean-free path more than three times that measured for carbon materials.^{11,12}

Balasubramanian *et al.*¹ explained the lack of a bulk C 1s component in some SXPS studies of graphite in terms of the final state of the bulk photoelectron. However, this hypothesis does not explain the observations of Lizzit *et al.*² of a low-energy C 1s component only for HOPG and not for other graphite types nor the angular dependence of the low binding-energy component. The anomalous behavior of the low binding-energy C 1s component in the data of Lizzit *et al.*² (i.e., vanishing with increasing emission angle far faster than might be expected from a bulk component) may be explained by diffraction effects, the strength of which are dependent on the incidence angle of the photon beam.¹⁷ A strong forward focusing of photoelectron intensity occurs along specific crystallographic directions of graphite¹⁷ but is most pronounced for normal emission. Thus, one would expect

the weak bulk peak in the SXPS data to disappear much more rapidly than expected from escape depth calculations. The absence of a bulk component in other forms of graphite might be explained by the well-known difference in the quality of *c*-axis stacking between different forms of graphite. For example, HOPG samples have been demonstrated to show two-dimensional electronic phenomena such as the quantum Hall effect, which cannot be observed in graphites with better *c*-axis order such as Kish graphite.¹⁸ We therefore propose that it is the weaker *c*-axis coupling in HOPG which gives rise to a resolvable surface component (and therefore is, in a way, defect related). Given that a 6% expansion in the graphite interlayer spacing is theoretically predicted to produce a 60 meV increase in surface core-level shift⁵ differences in the degree of *c*-axis disorder, and hence expansion, between graphite types may explain why the surface core-level shift reported here differs from that of SXPS studies^{1,2,8} by an amount greater than experimental error. Further careful high-resolution ARXPS studies on different graphite types, perhaps using synchrotron-radiation excitation, are required to resolve this issue.

In conclusion, by careful analysis of ARXPS measurements the existence of bulk and surface-related components in the C 1s core line of graphite is demonstrated. The surface component is observed to have a constant integrated area as a function of emission angle, smaller asymmetry index than the bulk but a larger natural linewidth (95 ± 3 meV against 231 ± 8 meV) which may arise from the differing electronic environments of bulk and surface and/or levels of surface and bulk disorder. A constant surface-bulk core-level splitting of 194 ± 6 meV is found to be independent of emission angle, consistent with theoretical predictions⁵ but larger than that found in SXPS studies of HOPG. It is suggested that this difference in energy splitting, and the reported absence of split surface and bulk components in other graphite types,² is associated with the varying degree of *c*-axis disorder among graphites produced by differing routes.

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