

Observation of a surface chemical shift in carbon 1s core-level photoemission from highly oriented pyrolytic graphite

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Contributions to the line shape of high-resolution Al $K\alpha$ x-ray excited carbon 1s photoemission of highly oriented pyrolytic graphite are described and compared with previous work. A two-component system is used to model experimental results obtained from two photoelectron takeoff angles. The splitting between the two components is 0.47 ± 0.02 eV, with a variation in the intensity ratio consistent with that expected for the two takeoff angles. The photoemission lines are found to have a lifetime broadening Γ_L of 0.128 ± 0.006 eV full width at half maximum (FWHM), an asymmetry α of 0.125 ± 0.002 , and additional broadening over that of the instrumental resolution of 0.28 ± 0.04 eV FWHM.

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I. INTRODUCTION

High-resolution measurements of core-level photoemission lines have revealed shifts in binding energy between the bulk and surface atomic environments of elemental metals,¹ and more recently in highly oriented pyrolytic graphite (HOPG).² In this work we report on the results obtained by x-ray photoelectron spectroscopy (XPS) on HOPG, which show surface and bulk contributions to the carbon 1s line shape.

There have been a limited number of high-resolution studies of the carbon 1s photoemission line of graphite.²⁻⁵

In an early study van Attekum and Wertheim³ (PvA) measured the carbon 1s photoelectron line of Advanced Ceramics ZYB highly ordered pyrolytic graphite (HOPG) using monochromated Al $K\alpha$ radiation. The resolution of the Hewlett-Packard (HP) 5950 instrument used in that work was not quoted, but at the same time,⁶ the instrumental contribution was determined to be a skewed Gaussian with width 0.6-eV full width at half maximum (FWHM). Rather surprisingly, given the low density of states at the Fermi energy E_F in graphite, they found the carbon 1s core-level line shape to be significantly asymmetric. After allowing for the resolution of the instrument and making no allowance for a background of inelastically scattered electrons, they were able to fit a single-component Doniach-Sunjić (DS) line⁷ to the spectrum over a 5-eV range. The only parameter given from the fit is the asymmetry, given as $\alpha = 0.14 \pm 0.01$. The large value of α is ascribed to the effects of the formation of an exciton close to E_F in the final state.

Sette *et al.*⁴ (FS) measured the carbon 1s line of HOPG using synchrotron radiation of 320 eV with a total (Gaussian) instrumental resolution quoted as approximately 125-meV FWHM. After allowing for instrumental resolution and a parameterized background of inelastically scattered electrons, they were able to fit a single-component DS line to the experimental data. The lifetime broadening of the DS line was determined to be $\Gamma_L = 0.212 \pm 0.010$ eV (FWHM), with an asymmetry $\alpha = 0.065 \pm 0.015$. Slightly differing values of Γ_L and α were determined depending on the choice of parameters used to model the inelastic background, but little effect

was seen on the total line broadening due to Gaussian components, which was consistently $\Gamma_G = 0.129$ eV (FWHM). They concluded that other Gaussian contributions to the line shape, which might arise from phonon broadening and inhomogeneous contributions from static disorder were less than 0.050-eV FWHM.

A recent study on natural graphite, also employing synchrotron radiation, was carried out by Prince *et al.*⁵ (KP). The lifetime broadening obtained was determined to be $\Gamma_L = 0.165 \pm 0.015$ eV (FWHM) and the asymmetry was determined to lie in the range $\alpha = 0.056 \pm 0.05$. In a search for a contribution from a surface-shifted peak, they varied the photon energy from 320 to 500 eV to increase the electron attenuation length, and thus depth of sample studied. KP argued that the increase in the carbon 1s linewidth observed in these experiments was consistent with the energy dependence of the resolution of the monochromator and concluded that there was no surface-shifted component, as attempts to model the data using two components showed a second, shifted contribution of negligible intensity. The geometry of their experiment made it impossible to check for a surface component by increasing surface sensitivity by varying the photoelectron emission angle.

Most recently, Balasubramanian, Andersen, and Walldén² (TB) observed a surface-shifted peak in the photoemission spectrum of HOPG with the use of synchrotron radiation. The photon energy was varied between 300 and 350 eV with a total experimental energy resolution of about 0.050 eV. A second peak, identical in shape to the major component and seen at a binding energy 0.12 eV lower, was attributed to a contribution from a subsurface layer. They obtained results for the core hole lifetime of $\Gamma_L = 0.160 \pm 0.010$ eV (FWHM) with an asymmetry $\alpha = 0.048 \pm 0.006$. TB observed variations in the intensity of the subsurface feature with the energy of the exciting radiation, which they were able to correlate with the availability of final states in the band structure for photoelectrons excited from the bulk material. The geometry of this work was fixed at emission normal to the surface, and variation of angle to acquire a spectrum with an enhanced surface contribution was not investigated.

In the work presented here we demonstrate the presence of surface and bulk contributions to the core-level photo-

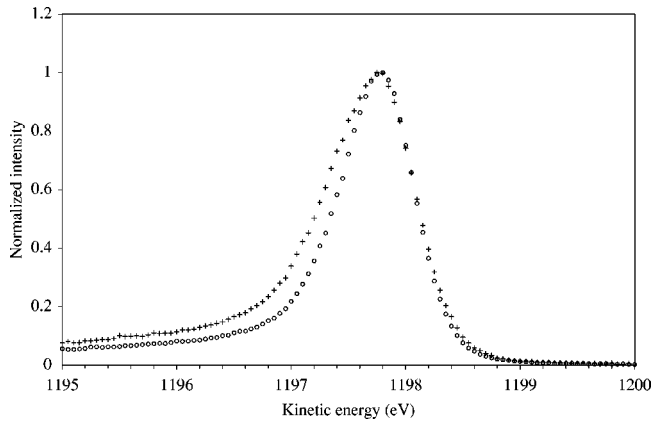


FIG. 1. Comparative plot of spectra of XPS acquired at 90° (open circles) and 10° (crosses) takeoff angles, measured relative to the graphite surface plane. Data were normalized to peak maximum height after an energy-independent background subtraction. A small shift due to x-ray dispersion was included in the 10° dataset.

emission line shape of HOPG. This has been achieved by measuring spectra at takeoff angles of 90° and 10° relative to the specimen surface to vary the relative intensity of a possible surface-shifted component and by the use of a monochromated Al $K\alpha$ x-ray source, the high photon energy of which results in a large electron escape depth and hence a large relative contribution from the bulk at normal emission compared to that obtained in the synchrotron studies of FS, KP, and TB.

II. EXPERIMENT

Measurements were made on a specimen of Advanced Ceramics ZYA grade HOPG, cleaved in vacuum in a pressure less than 10^{-6} mbar and immediately transferred to the UHV of the measurement chamber. Any oxygen contamination was below detectable limits at either emission angle.

The photoemission studies were carried out with a 150 mm mean radius hemispherical analyzer with multichannel detection using monochromated Al $K\alpha$ exciting radiation at 1486.6 eV. Carbon $1s$ photoelectron spectra were acquired using a pass energy of 22 eV over the kinetic-energy range 1180–1216 eV with a channel width of 0.05 eV. The contribution to the total instrumental broadening from the monochromated Al $K\alpha$ source was estimated to be 0.42-eV FWHM from measurement of the Fermi edge of silver.

Spectra were acquired at two takeoff angles; normal emission and 10° emission relative to the specimen surface. The sample rotation produced a small relative shift of approximately 0.08 eV in the energy scales of the measurements at the two angles, arising from the dispersion of x rays in the focus from the monochromator. This was taken into account in the analysis.

III. RESULTS

The two carbon $1s$ spectra acquired at 90° and 10° emissions relative to the surface are shown in Fig. 1. The spectra have been normalized to the same peak height and corrected for the small shift in energy scales due to the slight change in

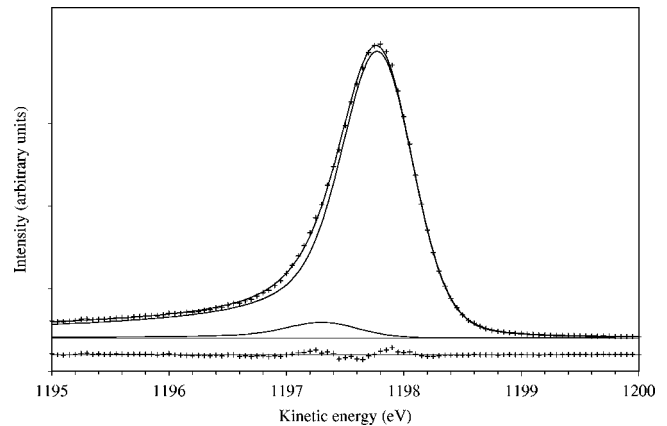


FIG. 2. Plot of XP spectrum of HOPG acquired at 90° takeoff angle (crosses) compared with the model used (described in the text). The two components of the model are shown under the envelope of the model sum total. The background used is not shown. Residuals (difference between experimental value and model value) are shown beneath the main plot.

x-ray energy for the two measurements.

It is apparent from Fig. 1 that the spectrum obtained at low takeoff angles is broader than that obtained at normal emission. The difference in linewidth of the spectra obtained at the two takeoff angles suggests that there are two components present in the spectrum, namely, a bulk peak and a surface peak, occurring at slightly different kinetic energies and with relative intensities which change markedly between the two takeoff angles. Inspection of the peaks indicates an increase in intensity on the low-kinetic-energy side of the spectrum using a low takeoff angle. This suggests a surface component at a higher binding energy than the bulk component, in agreement with the findings of TB.

To check the hypothesis that the spectra included surface and bulk components and in order to identify these components, the spectra were modeled using two DS lines convoluted with Gaussian distributions to represent instrumental and other effects. A background of inelastically scattered electrons was included by Shirley's specifications,⁸ along with a small energy-independent background.

To produce a consistent explanation of the results, the spectra obtained at the two takeoff angles were fitted simultaneously. Each spectrum was modeled by two components, with the parameters for lifetime, asymmetry, Gaussian broadening, and line positions varied but constrained to take the same values in the fit to each spectrum. The intensities of the two components and the inelastic and constant backgrounds were allowed to vary freely in the fitting procedure. Two optimization tools were used and gave similar results. The fits obtained to the two sets of data are shown in Figs. 2 and 3 and the parameters obtained from the fitting procedure are summarized in Table I.

IV. DISCUSSION

We note that whereas the experiments of PvA, FS, KP, and this work were conducted on cleaved specimens those of TB were carried out on specimens cleaned by heating. We do

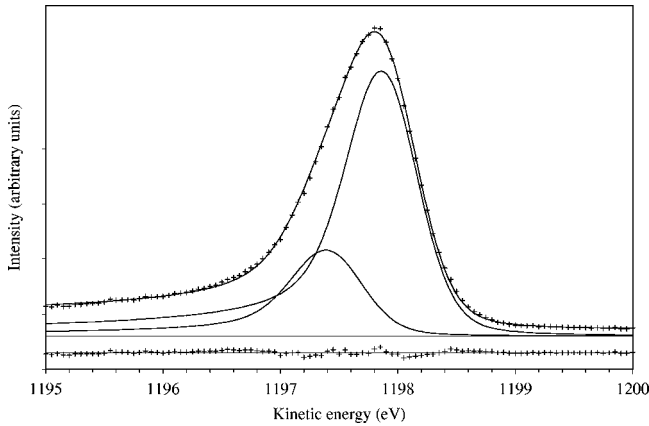


FIG. 3. Plot of XP spectrum of HOPG acquired at 10° takeoff angle (crosses) compared with the model used (described in the text). The two components of the model are shown under the envelope of the model sum total. The background used is not shown. Residuals (difference between experimental value and model value) are shown beneath the main plot.

not think that this difference can account for the differences in the results obtained in these studies but it should be noted.

The most notable difference between our results (Table II) and those of TB, the only other work to show a surface core-level shifted component to the C $1s$ photoemission line of graphite, is our finding of a larger shift of 0.46 eV as compared to the value of 0.12 eV of TB. The main experimental differences between the two studies are the fixed geometry and the higher resolution of the low-energy photon source employed by TB and the variable geometry and lower resolution of the high-energy Al K_α source employed in our work. These differences mean that our results sample a considerably greater depth of material than those of TB, the difference in the kinetic energies of the C $1s$ lines excited in the two studies giving rise to expected attenuation lengths⁹ of ~ 2.5 nm for 1200-eV photoelectrons and ~ 0.25 nm for

~ 30 -eV photoelectrons. Consequently, in our work the bulk component makes the dominant contribution to the spectrum whereas in TB's work the surface peak dominates. The relative intensity of the bulk peak observed by TB follows the exponential photocurrent attenuation expected for suitable estimates of inelastic mean free path¹⁰ (IMFP) or effective attenuation length⁹ for the photon energies used in their experiments. We have examined the sensitivity of our determination of the component separation to the values of other parameters used in the fitting procedure; and while we find that the total Gaussian broadening, the asymmetry and the Lorentzian contributions are not completely independent parameters, none of these parameters interact at all significantly with the value determined for the surface to bulk shift. Furthermore, the value found for the surface to bulk shift is strongly influenced by the constraint that the spectra obtained at the two takeoff angles are fitted simultaneously. We conclude that there is a significant difference between our results and those of TB for the surface to bulk shift.

TB conclude that KP were unable to resolve a bulk component in their experiments due to the absence of appropriate final states in the band structure when using a photon energy which gave a sufficiently resolved spectrum. Since FS used a photon energy similar to KP, we conclude that the results of both these groups are effectively high resolution studies of the surface component alone. We were unable to improve the quality of simultaneous fits to our two sets of data by constraining the parameters describing the surface component to values determined by FS, KP, or TB, and our results are not consistent with the surface-bulk splitting determined by the latter authors. Since we found a significant interdependence of the values for the asymmetry parameters of the bulk and surface components in our data in less constrained fits, we have restricted this parameter and the Lorentzian and total Gaussian parameters to a common value for each component. There is no *a priori* reason why these parameters

TABLE I. C $1s$ line-shape parameters determined from simultaneous fit to experimental data at two emission angles.

| Fitted parameters | | 90° spectrum | 10° spectrum |
|-------------------------|--|---------------------|---------------------|
| Surface component | Lorentzian lifetime (Γ_L , eV, FWHM) | 0.128 ± 0.006^a | 0.128 ± 0.006^a |
| | Asymmetry index α | 0.125 ± 0.002^a | 0.125 ± 0.002^a |
| | Gaussian broadening (Γ_G , eV, FWHM) | 0.616 ± 0.008^a | 0.616 ± 0.008^a |
| | Fractional intensity I_s | 0.052 ± 0.006^b | 0.246 ± 0.007^b |
| Bulk component | Lorentzian lifetime (Γ_L , eV, FWHM) | 0.128 ± 0.006^a | 0.128 ± 0.006^a |
| | Asymmetry index (α) | 0.125 ± 0.002^a | 0.125 ± 0.002^a |
| | Gaussian broadening (Γ_G , eV, FWHM) | 0.616 ± 0.008^a | 0.616 ± 0.008^a |
| | Fractional intensity I_b | 0.948 ± 0.006^b | 0.754 ± 0.007^b |
| Surface-bulk shift (eV) | | 0.47 ± 0.02^c | 0.47 ± 0.02^c |

^aLifetime, asymmetry, and broadening; each common to both peaks and both spectra.

^bIntensities freely variable within and between spectra.

^cShift is variable between peaks but common to both spectra.

TABLE II. Comparison of C $1s$ line-shape parameters determined by other workers with those determined in this work.

| | | PvA | FS | KP ^c | TB ^c | This work |
|--|-------------------------|------|-------|-----------------|-----------------|-----------|
| Surface or single component ^a | Γ_L^b | | 0.212 | 0.165 | 0.160 | 0.128 |
| | α | 0.14 | 0.074 | 0.056 | 0.048 | 0.125 |
| | Total Γ_G^b | | 0.129 | 0.08–0.1 | ~0.065 | 0.616 |
| | Instrument Γ_G^b | ~0.6 | 0.125 | ~0.08 | ~0.05 | 0.55 |
| Bulk component | Γ_L^b | | | | 0.160 | 0.128 |
| | α | | | | 0.048 | 0.125 |
| | Total Γ_G^b | | | | ~0.065 | 0.616 |
| | Instrument Γ_G^b | | | | ~0.05 | 0.55 |
| Surface-bulk shift (eV) | | | | | 0.120 | 0.47 |

^aIf only one line is used in a model, the results are given under “surface component.”

^b Γ_L and Γ_G values are FWHM in eV.

^cValues for KP and TB are best estimates given in those papers. Values of Γ_G are not directly comparable due to the large variation seen with photon energy in synchrotron work; values quoted are those from a “best estimate” determination.

should have a common value. We found that adding a third identical component in our fitting procedure did not greatly improve the quality of simultaneous fits to the two datasets. From this we infer that it is the line shape rather than the number of components that is most important. Within the constraint that the two components have the same line shape, we found little interdependence of the results for the Lorentzian and Gaussian contributions, and neither parameter was significantly dependent on the value found for the common asymmetry.

The lifetime broadening determined from the analysis of our results is slightly lower than that obtained in the studies using synchrotron radiation (Table II) but is larger than that obtained for methane in the gas phase.¹¹ Schlögl and Boehm¹² have indicated that C $1s$ binding energies and line-widths vary for different graphite specimens as a result of differences in crystalline perfection. This observation could account for the differences in the Lorentzian contribution found by FS, KP, TB, and ourselves.

We have noted that in unconstrained fits the values found for the asymmetry parameters of the two lines are strongly coupled and also depend weakly on the strength of the Shirley-type background. The tendency in simultaneous unconstrained fits to the two datasets is for the asymmetry of the surface component to increase and that of the bulk component to decrease. This may just be a reflection of the fact that the surface peak, as the lower-energy component, is more sensitive to inadequacies in the treatment of the background of scattered electrons. It is interesting that even after allowing for the uncertainty of the fitting procedure we find a significantly higher value of the asymmetry parameter than found in any of the studies using synchrotron radiation. Our results for α are similar to the early results of PvA who also used Al $K\alpha$ x-ray excitation. Given the low density of states at the Fermi energy in graphite, PvA attributed the large value of α to the formation of excitons. It is possible that in the studies using synchrotron radiation that the restriction in

the density of excited states accessible with low-energy photons reduces the probability of exciton formation.

In our results the total Gaussian broadening of the observed line shapes is increased from that expected from the monochromator and analyzer by an additional contribution of 0.28-eV FWHM. As discussed by FS and KP, it is unlikely that this contribution arises from phonon broadening; and KP also conclude that contributions from C $1s$ band-structure formation is negligibly small. Given the larger escape depths in our experiments it is possible that this additional broadening arises from crystal imperfections from lower layers. ZYA HOPG is produced as a neutron or x-ray monochromator component, requiring good basal plane alignment throughout its structure with few defects. Theoretical values¹³ for the graphite lattice are a density of 2.265 g/m and a layer spacing of 3.3539 ± 0.0001 Å. The Advanced Ceramics specifications for ZYA are a density of 2.255–2.265 g cm⁻³ and a layer spacing of 3.355–3.359 Å with a mosaic spread—FWHM of the distribution of off- c -axis alignment about a mean—of $0.4 \pm 0.1^\circ$, indicating a very high degree of layer ordering.¹⁴ The density of graphite is known to decrease markedly with the introduction of defects into the structure,¹³ so the implication of the stated values is of a very well crystallized material. Photoelectrons at about 1200 eV would be subject to practically complete attenuation within 10 nm in graphite. Poorly ordered HOPG is composed of crystallites of 1 μ m width and about 10 nm thickness; well-ordered HOPG is comprised of crystallites approximately 50 μ m wide and 500 nm thick.¹⁵ Thus, with respect to traversal along the c axis, all photoelectrons originate in single crystals. Additionally, the effects of sample preparation, such as random structural disorder caused by the tape-cleaving method, should manifest at least equally in the surface layer in comparison with underlying layers. The works of FS, KP, and TB show no appreciable statistical broadening above that contributed by the instrument used, so we believe no additional statistical broadening should be seen for lower layers.

This view is supported by the similarity of the experimental data of PvA to our own results; a mechanical-cleaving method would be expected to produce somewhat more random results. This in turn would give a varying statistical broadening effect which is not, in fact, seen.

The relative intensities of the surface, I_s , and bulk, I_b , contributions to the carbon 1s line shape is expected⁹ to vary as

$$\frac{I_s}{I_b} = e^{|d/\lambda \sin \theta|} - 1, \quad (1)$$

where d is the thickness of the surface layer, λ the IMFP, and θ the takeoff angle measured relative to the surface plane. Taking the effective depth of the surface layer to be one-half of the interplanar spacing and using the estimated electron IMFP of 2.79 nm in glassy carbon¹⁰ equation (1) yields expected values of I_s and I_b of 0.043 and 0.959, respectively, at normal emission and 0.237 and 0.763, respectively, at 10° takeoff angle. These values are in reasonably good agreement with the experimental results given in Table I. Perfect agreement would not be expected as the approach ignores the effects of elastic scattering, and the estimated IMFP may not be accurate for the surface layers of HOPG. Nevertheless, the agreement lends support to the identification of the two components as originating from surface and bulk contributions to the spectra.

The main difference between our experiments and those of TB is the order of magnitude increase in effective electron attenuation lengths, ~ 2.5 nm in our experiments compared with ~ 0.25 nm in those of TB. Given the low value of the IMFP and thus sampling depth in their experiments, it is possible that TB were essentially measuring the difference in binding energy of C 1s levels from the surface layer and the first subsurface layer. We have examined the effect of simultaneously fitting the spectra obtained at 10° and 90° takeoff angles to three peaks with the parameters of the first two “surface” peaks constrained to the values found by TB. Good fits to the spectra could be obtained with the principal result being that the separation of the bulk peak from the average position of the surface peaks increased to 0.5 eV and the relative intensity of the surface components was very sensitive to the precise details of the peak fit parameters.

It is well known that there are two contributions to the difference in core-level binding energies between two atomic environments.¹⁶ One arises from differences in the atomic valence charge in the initial states, and the second from differences in the electron screening of the core hole in the final state. Unfortunately, the classic way of separating these two contributions by combining measurement of core-level shifts and Auger shifts in the Auger parameter^{16–19} is not available for carbon since the electronic structure of this element is too shallow to allow Auger transitions that only involve core levels. In this circumstance, the final-state contribution cannot be assessed and we restrict the analysis of the surface to bulk shift to a consideration of the initial-state effect employing a frequently used potential model.^{18,20,21} The potential in the core of an atom is represented^{18,21} by

$$V = kq, \quad (2)$$

where q is the negative of the number of valence electrons, which is 4 for C, and k is given to an accurate approximation by

$$k = a + bN + dq, \quad (3)$$

with N defined as the negative of the number of core holes. The values of a , b , and d for C have been determined as 32.90, 6.77, and 5.05 eV, respectively.²¹ The difference in binding energy between two atomic sites can be expanded as a Taylor series in the derivatives of the potential with respect to the number of core holes.²¹ Keeping terms up to the first derivative we arrive at an expression for the difference in binding energy of the surface and bulk C environments in terms of the charges on the surface and bulk atoms, q_s and q_b , of

$$\begin{aligned} \Delta E_b = & a(q_s - q_b) + bN(q_s - q_b) \\ & + d(q_s^2 - q_b^2) - 0.5b(q_s - q_b). \end{aligned} \quad (4)$$

Assuming the bulk carbon atoms to have a full complement of valence electrons, the value obtained for ΔE_b of 0.46 eV yields a loss of ~ 0.14 electron by a surface carbon atom. Using the results of TB and assuming the splitting of 0.12 eV corresponds to a difference between the first and second layers equation (4) predicts a difference in local charge in the initial state of ~ 0.04 electrons between the two layers.

These estimates of the difference in electron population of surface C atoms are larger than those estimated from core-level shifts for K adsorbed on graphite by Bennich *et al.*²²

V. CONCLUSIONS

We have resolved the surface to bulk core-level shift in graphite in photoelectron experiments using a high-resolution monochromated Al $K\alpha$ x-ray photoelectron spectrometer together with angular rotation of the specimen. The value obtained for this shift in our bulk-sensitive experiments is 0.46 eV, which is nearly four times greater than that obtained by Balasubramanian, Andersen, and Walldén² in surface-sensitive measurements excited by photons in the range 300–350 eV. We believe the differences between our result and that of Balasubramanian, Andersen, and Walldén,² and the differences between the various other data reported for HOPG, arise from a combination of factors including sampling depths, availability of final states, and the specific nature of the HOPG specimens used. This last factor, in particular, is known to have potentially significant effects¹² and requires further investigation.

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