PHYSICAL REVIEW B, VOLUME 64, 205420

Surface-bulk core-level splitting in graphite

T. Balasubramanian,[1] J. N. Andersen,[2] and L. Walldén[3]
[1]*MAX-Lab, Lund University, Lund S-22100, Sweden*
[2]*Department of Synchrotron Radiation Research, Lund University, Lund S-22100, Sweden*
[3]*Physics Department, Chalmers University of Technology, Göteborg S-41296, Sweden*

(Received 21 May 2001; published 6 November 2001)

Photoemission from highly oriented pyrolytic graphite reveals two C 1*s* components separated in binding energy by 120 meV. The high binding-energy component is ascribed to atoms in the outermost atomic layer and the other to deeper layers. The interpretation is based on the low relative intensity observed for the low binding-energy line at photon energies chosen such that excitation beneath the surface layer is suppressed by a bulk band gap at the energy of the final state. The surface emission line, which dominates, is slightly asymmetric and has a Lorentzian width of 160 meV (full width at half maximum).

DOI: 10.1103/PhysRevB.64.205420 PACS number(s): 79.60.Bm

Recent advances in synchrotron light sources and development of high-resolution beam lines has stimulated interest in long-standing questions concerning the shape and width of core-level photoemission lines. Graphite is of interest in this respect. While metals typically show asymmetric emission lines due to a multitude of low-energy excitations as the hole is created,[1] the asymmetry is less pronounced for the 1*s* level in graphite, which is expected for a semimetal with a near vanishing density of electrons at the Fermi level. The line was, however, found to be unexpectedly wide (210 meV Lorentzian width) when compared to the C 1*s* spectra recorded for small molecules (<100 meV).[2,3] A recent high-resolution study of graphite has narrowed the gap substantially. At $h\nu=320$ eV, Prince *et al.*[3] found a total width of 200 meV, and estimated the Lorentzian contribution to be 165 ± 15 meV. No line-shape details were resolved that could explain this still comparatively large width or allow the core-level binding-energy difference between surface and bulk to be measured. An upper limit of 20 meV was estimated for this difference.

Here we show that the C 1*s* photoemission line is a doublet. The relative intensity for the components varies rapidly as the photon energy is changed in the probed range, which is 10–60 eV above the excitation threshold. This variation, which can be understood with reference to the bulk band structure, allows us to explain the doublet in terms of a 120-meV-higher 1*s* binding energy for atoms in the surface layer. A likely reason why the doublet was not resolved by Prince *et al.* is that their measurement was made with sufficient resolution only at one photon energy, 320 eV. This energy turns out to be an unfortunate choice for resolving the doublet since one component is quite weak. Assuming that the widths are the same for the bulk and surface emission lines we obtain an upper limit on the Lorentzian width to be 160 ± 10 meV.

The experiments were performed at beamline I311 in the MAX synchrotron radiation laboratory at Lund University. The beamline is equipped with a modified SX-700 plane grating monochromator with a movable exit slit and a spherical refocusing mirror. The end station houses a Scienta 200 electron-energy analyzer. The spectra are obtained from a sample of highly oriented pyrolytic graphite. This consists of microcrystals that have a common *c* axis but are azimuthally disordered. For cleaning, the sample was heated to 1000 K. The light is *p* polarized and made incident at an angle of 55° with respect to the sample normal. In this geometry, the electron-energy analyzer accepts electrons emitted in directions near the surface normal. All measurements reported here were taken with the sample held at a temperature of around 100 K.

C 1*s* emission lines recorded at $h\nu=313$ eV and 328 eV are shown in Fig. 1. The total experimental energy resolution is about 50 meV. The doublet character is obvious at $h\nu=328$ eV but less so at 313 eV. We argue below that the component with lower binding energy is due to bulk atoms and the one with higher binding energy is due to the surface. The C 1*s* spectra shown in Fig. 1 and those measured at other photon energies were fitted using the Doniach-Sunjic line shape[4] convoluted with a Gaussian that accounts for other sources of broadening. The same parameters are used for both components of the doublet. The doublet is superposed on a background, which is nearly constant near the emission line for spectra taken at photon energies in the upper range of the probed range. A flat background is favorable for getting an accurate value of the asymmetry index. As the first step in the fitting procedure this index was determined to be $\alpha=0.048\pm0.006$ using spectra recorded at photon energies in the range 340–360 eV. The value for α agrees well with the two values, 0.052 and 0.056, obtained in Ref. 3. With this value for α all other spectra were fitted. We obtained a Lorentzian width of 160 ± 10 meV and a peak separation of 120 ± 3 meV. The Gaussian widths at $h\nu=313$ eV and 328 eV are 60 and 68 meV, respectively. It should be pointed out that even though the surface emission line is well reproduced by a Lorentzian of 160 meV full width at half maximum, this merely gives an upper limit to the lifetime width. One reason is that there are two different sites in graphite and the binding-energy difference between these is not resolved in our measurement. The bulk component is not sufficiently strong compared to the surface peak to allow an accurate determination of its width and line shape. Also for this line one expects a splitting due to layer-dependent binding energies for a few uppermost atomic layers that contribute significantly to the emission. Regarding

©2001 The American Physical Society

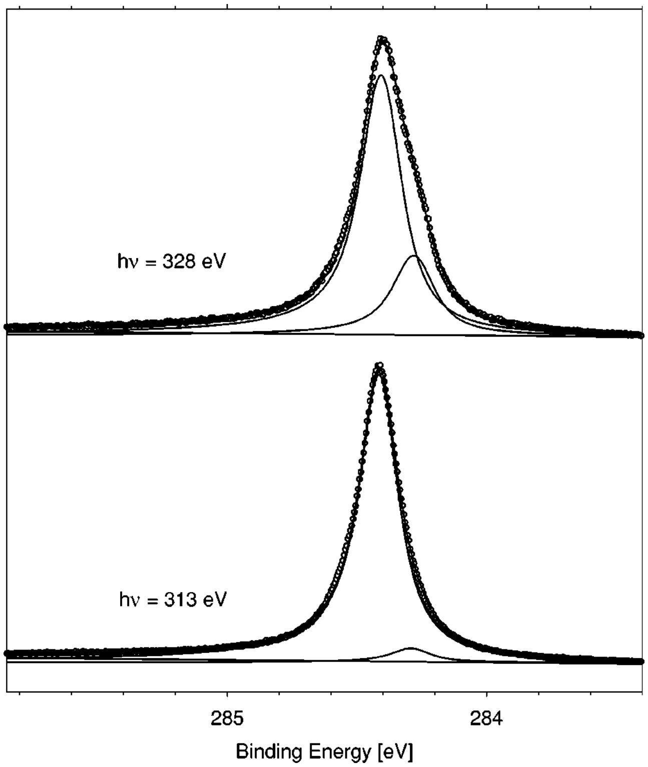

FIG. 1. C 1*s* photoelectron energy spectra (open circles) recorded along the surface normal of graphite at $h\nu = 313$ eV and 328 eV. The light is *p* polarized and the incidence angle is 55°. The sample temperature was held at around 100 K. The full drawn curves are obtained from a peak-fitting procedure used to determine the splitting of the doublet and emission line-shape characteristics.

the core-hole lifetime our result is that the Lorentzian width is less than 160 meV for the surface layer.

After noting a strong variation with photon energy of the relative intensity of the two 1*s* components, we recorded spectra between $h\nu = 300$ eV and 350 eV in steps of 1 eV. These spectra were obtained with slightly lower resolution than those used for a detailed line-shape analysis. Figure 2 shows a sample of the spectra from which the ratio between the intensity of the low and high binding-energy peaks, plotted in Fig. 3, is obtained. For this analysis the Lorentzian width, peak separation, and asymmetry index were set to 160 meV, 120 meV, and 0.048, respectively, while the Gaussian width was allowed to vary. As mentioned above the measurements reported by Prince *et al.*[3] were made with high resolution only at 320 eV. Since the intensity ratio is near a minimum at this photon energy, it is not surprising that the splitting of the C 1*s* level escaped notice.

In qualitative terms it is straightforward to explain the relative intensity variation shown in Fig. 3 if one component is due to atoms in the surface layer and the other is due to atoms in deeper layers. For bulk atoms to be represented in the spectra there must be bulk final states. Bulk emission will thus be suppressed at photon energies for which the final energy falls within a bulk band gap where only the lifetime tails of the states at the gap edges are available for the excited electrons. For estimates of this suppression one may describe the final state in the solid with a damped wave in-

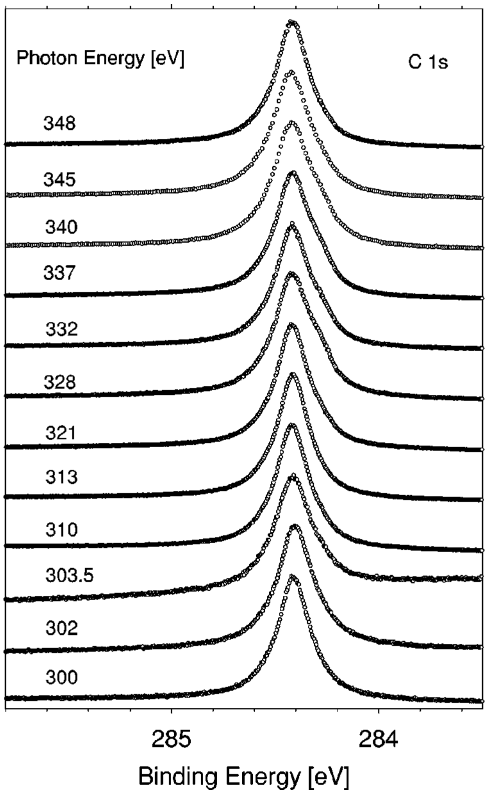

FIG. 2. C 1*s* spectra recorded along the surface normal of graphite at various photon energies. The temperature of the sample was held at around 100 K.

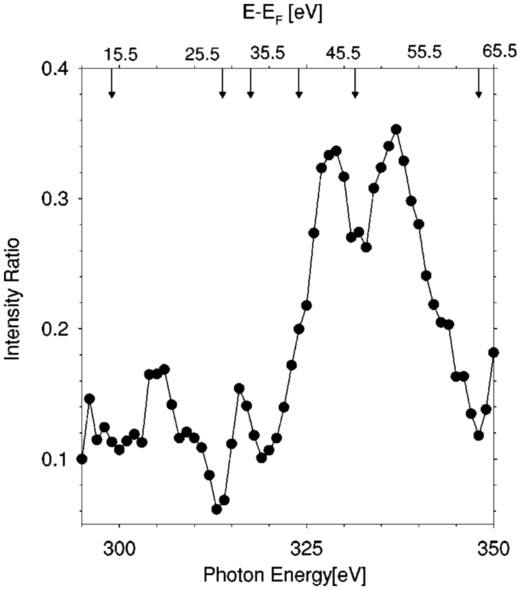

FIG. 3. The ratio between the intensities of the low and high binding-energy components of the C 1*s* doublet plotted versus photon energy (lower scale) and energy above E_F (upper scale). The filled circles are the experimental points and the lines are to guide the eye. The arrows indicate the energies above E_F at the midpoint of band gaps in graphite. These energies are obtained from TCS (Ref. 7) and electron-reflectivity (Ref. 8) data.

side the gap and a propagating one outside the gap adding in both cases a damping due to the limited lifetime in the final state.[5,6] The stronger damping inside the gap will enhance the surface sensitivity. For many solids the gaps are small and the lifetimes sufficiently short enough to effectively mask the gaps thereby making the intensity reduction modest. In graphite, however, there are a number of band gaps that are wide compared to the lifetime width of the states at the gap edges. Recently Strocov *et al.*[7] determined the energies of band extrema by using total current spectroscopy (TCS) for electron energies between 8 eV and 50 eV above the Fermi level. In TCS one measures the current accepted by the sample from an incident beam of electrons. Their results show that in the direction normal to the surface there are gaps between 11 eV and 18 eV and between 26 eV and 31 eV above the Fermi level. These are both well defined since the lifetime width at these energies is around 0.63 eV and 0.95 eV, respectively. At higher energy there is a narrow gap at 33 eV, another between 37 eV and 42 eV and yet another between 44 eV and 50 eV. These gaps appear more diffuse in the TCS spectra, which is partly due to shorter lifetimes and partly due to the angular spread of the electron beam. While the angular spread was not specified in Ref. 7, it is probably smaller than the 14° acceptance angle of our detector. At higher energies this difference in angles may be expected to have some influence on the energies obtained in the two experiments. All but one of the arrows in Fig. 3 indicate the midpoints of gaps determined by TCS. The exception is the arrow at 60 eV, which is outside the range probed by TCS. The position of this arrow is obtained from the electron reflectivity data of Lander and Morrison,[8] who measured the reflectivity at different incidence angles from low energies to 240 eV above E_F. Recently Ruocco *et al.*[9] reported reflectivity spectra at 34° incidence angle for kinetic energies in the range 90–500 eV. In this range a succession of Bragg peaks is observed, which fall at energies predicted by a simple kinematic expression. The two sets of data agree well when accounted for the different angles used. This gives credibility to the low-energy data, which in the energy range of our interest shows a reflectivity maximum at 60 eV for near-normal incidence. The good agreement between the energies at the minima observed for the intensity ratio and the position of bulk band gaps leaves little doubt about the assignment of the low-energy component to bulk atoms and the high energy component of the doublet to surface-layer atoms.

No strong structure caused by intrinsic excitation of vibrations is present in graphite C 1s spectra. This indicates a much weaker coupling between the core hole and phonons for graphite than for Be where prominent structures due to excitation of phonons was recently found experimentally.[10] One speculation is that the atom in its final state disturbs the surrounding lattice less for graphite than for Be. Within the $Z+1$ approximation for the final state[11] Be transforms to B, which means that another subshell becomes populated while nothing as dramatic happens as C transforms to N.

In conclusion we find that the C 1s photoemission line of graphite is a doublet, split by 120 meV, and ascribe this to a higher binding energy for atoms in the outermost layer than for atoms in deeper layers. The assignment is made via the observation of a strong photon-energy dependence for the relative intensity of the two components. One component, ascribed to the bulk, becomes weak at photon energies for which there is a lack of final states in the bulk. No vibrational fine structure is observed and the binding-energy difference between inequivalent carbon sites is not resolved.

We gratefully acknowledge the support of the MAX-lab staff and the financial support by the Swedish Natural Science Research Council.

---

[1] G.D. Mahan, Phys. Rev. **163**, 612 (1967); P. Nozières and C.T. DeDominics, *ibid.* **178**, 1097 (1969).

[2] F. Sette, G.K. Wertheim, Y. Ma, G. Meigs, S. Modesti, and C.T. Chen, Phys. Rev. B **41**, 9766 (1990).

[3] K.C. Prince, I. Ulrych, M. Peloi, B. Ressel, V. Cháb, C. Crotti, and C. Comicioli, Phys. Rev. B **62**, 6866 (2000).

[4] S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970).

[5] J. B. Pendry, *Low Energy Electron Diffraction* (Academic, London, 1974).

[6] P.J. Feibelman and D.E. Eastman, Phys. Rev. B **10**, 4932 (1974).

[7] V.N. Strocov, P. Blaha, H.I. Starnberg, M. Rohlfing, R. Claessen, J.-M. Debever, and J.-M. Themlin, Phys. Rev. B **61**, 4994 (2000).

[8] J. Lander and J. Morrison, J. Appl. Phys. **35**, 3593 (1964).

[9] A. Ruocco, M. Milani, S. Nannarone, and G. Stefani, Phys. Rev. B **59**, 13 359 (1999)

[10] J.N. Andersen, T. Balasubramanian, C.-O. Almbladh, L.I. Johansson, and R. Nyholm, Phys. Rev. Lett. **86**, 4398 (2001).

[11] N.D. Lang and A.R. Williams, Phys. Rev. B **16**, 2408 (1977).