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Core-level photoemission from graphite

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Core-level photoemission spectra of graphite have been measured at very high resolution. The C 1*s* level is found to have a lifetime width with an upper limit of $165 \pm 15\,\mathrm{meV}$, which is considerably narrower than previously reported. The width is still substantially larger than that observed for carbon ionic states in small molecules. We argue that the additional broadening in the solid state is not due to a surface core-level shift or initial-state band formation, but may be due to unresolved final-state phonon broadening.

I. INTRODUCTION

Graphite is one of the simplest elemental solids and one of the easiest to prepare for experiments in ultrahigh vacuum. Being a semimetal, its electronic properties fall between those of the much larger classes of metals and semiconductors, and so it is an interesting solid on which to test theories of line shapes in photoemission. The C 1*s* line shape has been studied previously by van Attekum and Wertheim[1] who first showed that the line shape was asymmetric, indicating metallic screening of the core hole. They fitted their data with a Doniach-Sunjic line shape and obtained values for the asymmetry parameter α. Later Sette *et al.*[2] reported a Lorentzian linewidth of 210 meV and confirmed the asymmetric line shape. A particular problem in extracting quantitative information is the method of fitting the background, and this was discussed extensively by these authors. The problem stems from inelastic losses, which create a background that is related to but not the same as the optical loss function. This value for the linewidth is much larger than the photoemission linewidths of small molecules in the gas phase, typically 85–90 meV,[3] and begs the question why the width is so different.

The linewidth reported by Sette *et al.* was analyzed in terms of three contributions: the intrinsic lifetime contribution the phonon contribution due to the Franck-Condon nature of the transition and the resolution. They also considered the possibility that there is a surface core-level-shifted component. Because each layer is bound only by van der Waals forces to the next, it is expected that the surface layer is in a chemical environment that is nearly equal to that of the bulk, and is not influenced by the vacuum. Thus the initial-state surface core-level shift due to chemical effects is expected to be zero. However, in the final state, the core hole may be screened by both intralayer and interlayer processes, and the surface core-level shift may be nonzero if the screening of the hole has a significant component due to polarization of adjacent layers. This is because in the bulk there are two adjacent layers, whereas at the surface there is only one. In this study we examine this possibility by varying the kinetic energy of the outgoing electrons to change the surface sensitivity of the photoemission signal.

II. EXPERIMENT

The samples were natural crystals from Bavaria, Germany, measuring about $2 \times 3\ \mathrm{mm}^2$, and were fixed to a substrate with epoxy resin, inserted from air, and cleaved in UHV. During the measurements the pressure was below 3×10^{-10} mbar. The spectra were measured at the VUV beam line of the synchrotron radiation facility Elettra, Trieste, using the 700 lines per mm grating. The analyzer was a VSW 150 mm mean radius hemispherical electron energy analyzer. Light was incident normally on the sample while electrons were emitted at an angle of 55° with respect to the normal, and all spectra were taken at room temperature. The low-energy electron diffraction pattern was checked and was sharp with a low background.

The resolution of the electron energy analyzer was determined by photoemission from Ne 2*p* using a He lamp some time before these experiments, and gave a value of 50 meV (Table I). A resonance lamp rather than synchrotron radiation was used to eliminate any uncertainty due to the resolution of the photons. The kinetic energy of the electrons in the present experiment, and therefore the retard ratio of the analyzer, are much higher but the resolution is expected to be similar as it is determined primarily by the slit size and pass energy. In any case, it is not expected that the resolution will *improve* at high kinetic energy; possible sources of error will degrade the resolution. If the actual analyzer resolution is

TABLE I. Best-fit results and estimated contributions to the resolution. Doniach-Sunjic line shape, linear background. Γ_l and Γ_g are the fitted Lorentzian and Gaussian linewidths, respectively. All parameters were left free.

Photon energy (eV)	320	421	500
Γ_l (meV)	178±8	152	162±14
Γ_g (meV)	50	165	245
Asymmetry parameter α	0.07–0.10	0.08	0.085
Resolution of monochromator (meV)	60	93	160
Resolution of analyzer (meV)	50	50	50
Bandwidth of C 1*s* (see discussion) (meV)	17	17	17
Total experimental Gaussian contribution (meV)	80	107	168

worse than estimated due to some error, the natural linewidth determined will be narrower, i.e., the measured value becomes an upper bound. However, we have done the best we can to eliminate sources of error.

The resolution of the monochromator was determined by gas-phase photoabsorption at the nitrogen *K* edge (401 eV) shortly after the experiment. The value of 90 meV was only slightly larger than the calculated value for this grating and slit setting. At other energies the calculated curve was used to estimate the photon energy resolution (Table I). The fitting algorithms and the formula for the line shape are given in Ref. 4.

III. RESULTS

Spectra were measured at 320, 421, and 500 eV nominal photon energies, in order to vary the kinetic energies of the photoelectrons, and therefore the surface sensitivity (Fig. 1). The goal was to test for the presence of a surface core-level-shifted peak. All spectra showed a pronounced asymmetry as in previous studies. The full widths at half maximum at kinetic energies of 31.5, 133.7, and 213.7 eV were 200±5, 290±5, and 369±5 meV, respectively, which is consistent with increased broadening due to changing photon energy resolution. We therefore conclude that, with the available resolution, it is not possible to detect a surface peak. It was not possible to vary the surface sensitivity in another commonly used mode, by varying the angle of emission, due to the geometry of our experimental setup.

The total width of the best resolved peak at 320 eV photon energy is 200 meV, and so immediately indicates that the value of the Lorentzian width previously reported, 210 meV,[2] is too large. The data were fitted in several stages, and in the first stage a search was made for a possible surface component. One series of fits assumed a surface core-level-shifted component, with an energetic difference between the peaks that was fixed while all other fit parameters were varied, particularly the Gaussian and Lorentzian widths. The fit always converged with negligible intensity for one of the peaks, supporting the conclusion that the surface core-level shift is 0±20 meV. The results are summarized in Table I together with the estimated total resolution.

The value of the Gaussian component of the broadening for the best fit at 320 eV photon energy was slightly smaller than the calculated resolution. This may indicate that the experimental broadening is not purely Gaussian, but has a Lorentzian-like component. The spectra were therefore fitted with fixed, larger values of the Gaussian width and gave only slightly worse values of χ^2. We therefore consider these the most reasonable values (Table II).

IV. DISCUSSION AND CONCLUSIONS

In this analysis we have found a value of the Lorentzian linewidth by imposing a value for the Gaussian linewidth

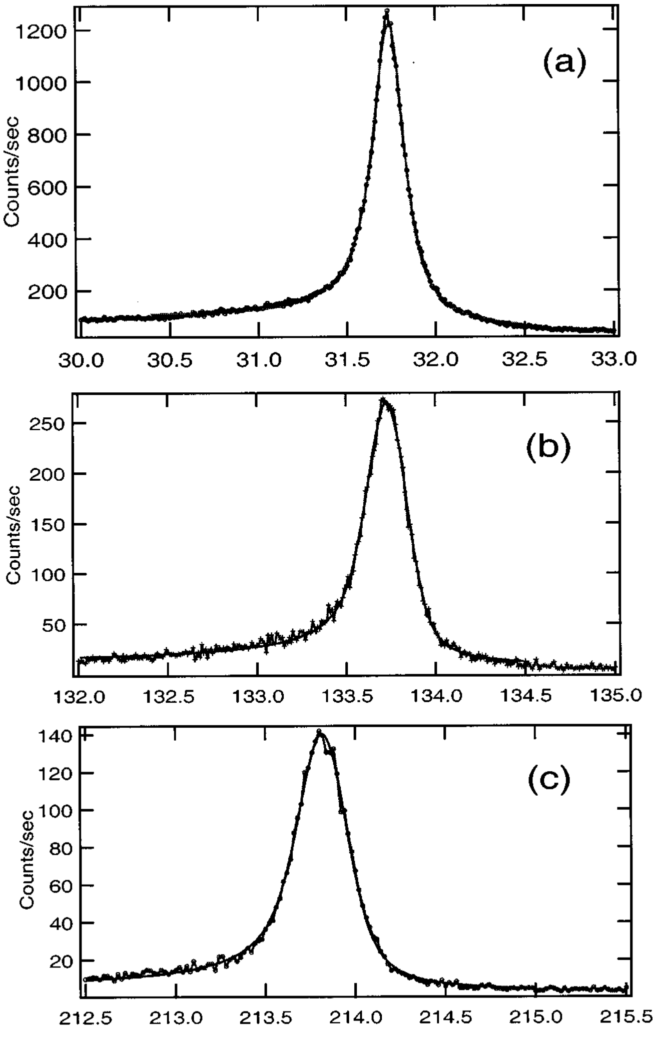

FIG. 1. C 1*s* photoemission spectra at (a) 320, (b) 421, and (c) 500 eV nominal photon energy. Dotted lines, data; solid lines, fit.

TABLE II. Most reasonable fit values (photon energy=320 eV) obtained by fixing Γ_g.

Γ_g (meV)	Γ_l (meV)	α
80	178±8	0.052
100	164±6	0.056

TABLE III. Lifetime widths of carbon 1*s* holes.

State	Width	Reference
Graphite	165±15	present work
Graphite	210	2
Diamond	110	7
C_{60}	110±40	8
C_{60}	171	10
C_2H_4	85±15	5
C_2H_2	90±10	6

contribution corresponding to the estimated resolution. The values of the Gaussian broadening can, however, be considered only as lower limits, as the final-state phonon contribution to the broadening, which is usually approximated as a Gaussian or Poisson distribution, is not known. The final-state phonon broadening is due to the Franck-Condon nature of the transition; Sette *et al.*[2] eliminated possible phonon contributions due to initial-state broadening, as their spectra did not change between liquid-nitrogen and room temperatures. In a molecule, the vibrational final states can be calculated from a Franck-Condon analysis; in the solid the vibrations become phonon bands, and the intensity distribution can be calculated from a vibrational analysis. This point has been discussed by Ma *et al.* (Ref. 9 and references therein) and a large distortion of the bonding geometry (10–40 % in the case of diamond) is expected. The equivalent-core model can be used to estimate the nature of the broadening. An ionized carbon atom becomes equivalent to a nitrogen atom impurity in a graphite sheet, and is screened by the valence charge density. The nitrogen atom is expected to adopt sp^3 hybridization in the final state, giving rise to strong bending vibrations, but we are unable to quantify the bandwidth.

Some broadening may be due to the formation of electron bands within the solid by the C 1*s* electrons. For a core level this broadening will be small, but we can estimate the magnitude by comparison with free molecules. Recently, the core-hole splittings of the carbon atoms in ethene and ethyne were investigated by Kempgens *et al.*[5] and found to be 105 ±10 meV for ethyne. In ethene the bond length is longer and the splitting was estimated to be 20–30 meV.[6] The bond length in ethene (1.337 Å) is slightly shorter than in graphite (1.421 Å). Within a simple tight-binding model, the bandwidth is expected to be proportional to the square root of the coordination number and to decrease exponentially with bond length. Only the bonds to the three nearest neighbors within a sheet of graphite are significant, as the interlayer spacing is much larger. From the gas-phase data we estimate a broadening of about 17 meV. This is small but significant, and in a first approximation will contribute to the Gaussian width.

With an estimated Gaussian width of 80–100 meV at 320 eV, the Lorentzian width is considerably smaller than previously reported, and our best estimate is 165±15 meV. This is still considerably larger than for gas-phase molecules such as ethene (Table III), where core holes might be expected to have a very similar lifetime to those in graphite, as the bonding is also sp^2. It is also larger than the estimated value for another allotrope of carbon, namely, diamond (Table III). This value is an estimate, like that for C_{60},[8] but the direct measurement[10] gives a value of 171 meV, similar to the present value. In this case the C_{60} was in the form of a thin film measured at 270 K and the Gaussian component was 256 meV, representing resolution and phonon contributions.

What then is the cause of this extra broadening in the solid state with respect to the gas phase? We have eliminated as major causes other possible effects such as a core-level-shifted component or initial-state band formation. The solid state band structure does not seem to provide extra or faster decay channels in graphite. In the ionic state, the core hole is screened more efficiently by the conduction band than by the valence band in a free molecule. However, this is a minor effect whose lifetime contribution should be similar to the difference between the lifetimes of ionic states and neutral core-excited bound states in molecules, i.e., a few tens of meV.

We suggest the decreased lifetime is apparent and not real, and that phonon broadening in the final state gives rise to a non-Gaussian line-shape contribution. This interpretation casts doubt on the significance of the asymmetry parameter in the Doniach-Sunjic fits; the asymmetry may not be all due to electronic excitations at the Fermi edge, but may be due in part to vibrational broadening. In any case the value of α we obtain, 0.056±0.05, is in good agreement with the published value of 0.065±0.015.

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