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Lifetime and screening of the C 1*s* photoemission in graphite

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High-resolution soft-x-ray photoemission spectra of the C 1*s* line of graphite have been analyzed to determine the various contributions to the linewidth and line shape. The natural lifetime width Γ is 210 meV, much larger than those of small molecules (for which $\Gamma \simeq 110$ meV), or that calculated for the isolated carbon atom (for which $\Gamma = 56$ meV). The phonon width is no larger than 50 meV. The general trend toward an enhanced Auger decay rate from the isolated atom to the small molecule and solid is indicative of significant contributions from interatomic Auger processes. However, the large increase in width from molecules to solids must be due to another phenomenon, perhaps to the formation of the excitonic final state in the solids. Our line-shape analysis confirms that the line has an asymmetry like that associated with metallic screening, which had been earlier related to the excitonic final state in graphite, but the singularity index is significantly smaller than that obtained in the previous analysis.

I. INTRODUCTION

The line shape of core-excitation spectra is the result of a number of distinct processes, reflecting properties of both the atom and its environment. The decay of the core hole contributes a Lorentzian natural width which, for the inner electrons, is generally dominated by Auger or Coster-Kronig processes. When these decay processes involve valence electrons, the Auger rate may well be sensitive to the chemical environment of the atom. Vibrational broadening contributes a temperature-dependent width. In metals, core-hole screening contributes a distinct line asymmetry, reflecting the excitation spectrum of the conduction electrons. Extrinsic energy losses of the outgoing electron, due to the excitation of plasmons and interband transitions, add a tail on the high–binding-energy side. Additional complications may arise from unresolved chemically shifted components. Although the physical processes which determine the line shape are of considerable interest, they have not been accessible in the majority of experimental data because of poorly defined or excessively large instrumental resolution which precluded detailed analysis of the line shape.

We present a soft-x-ray photoelectron spectroscopy (SXPS) study of the carbon 1*s* core level in graphite, carried out using synchrotron radiation with an overall resolution so much better than the natural linewidth that the observed width is dominated by the intrinsic core-hole decay mechanism. The most interesting result is that the natural width Γ, 210 meV full width at half maximum (FWHM), is approximately four times larger than theoretical calculations for the isolated carbon atom in the s^2p^2 configuration.[1] This result demonstrates a large enhancement of the Auger decay rate, suggesting that in graphite this decay mechanism is strongly enhanced by interatomic decay processes. A comparison with C 1*s* natural linewidths of small molecules shows, however, that interatomic Auger processes alone cannot explain the observed lifetime. There is a systematic increase in the natural linewidth from the isolated atom to the small molecule and the solid, which is not simply a function of the number of electrons in carbon bonds in the initial state. This observation is tentatively related to the excitonic core-hole screening in the solid. The C 1*s* line shape is distinctly asymmetric and may be successfully fit with the Doniach-Šunjić (DS) function, confirming that there is some enhanced metal-like screening of the C 1*s* core hole in the semimetal graphite. The value of the singularity index α is, however, significantly smaller than that of a previous determination.[2]

II. EXPERIMENT

The photoemission experiment was performed on the AT&T Bell Laboratories "Dragon" high-resolution soft-x-ray beamline,[3] located at the National Synchrotron Light Source, Brookhaven National Laboratory (Upton, NY). The Dragon was operated at 320-eV photon energy, with the energy resolution set at 85 meV FWHM. A Vacuum Science Workshop 150-mm hemispherical analyzer with multianode detection was used to measure the energy distribution curve of the photoelectrons. It was operated at 5-eV pass energy resulting in an energy resolution of 90 meV FWHM. The total instrumental bandwidth is then approximately 125 meV FWHM. The sample, a piece of highly oriented pyrolytic graphite

(HOPG), was cleaved in the spectrometer chamber with a vacuum of 2×10^{-10} torr. The data shown here were taken at 300 K.

III. RESULTS AND ANALYSIS

The SXPS spectrum of the C 1s in graphite is shown in Fig. 1. The experimental curve has been fitted with a model function containing three contributions: (1) the convolution of a Doniach-Šunjić function with a Gaussian for the line itself; (2) an energy-loss tail with a functional form discussed below; and (3) a linear background. The choice of a meaningful formulation for the loss function is one of the most critical aspects of the fitting procedure, because it directly affects the other fitting parameters, especially the singularity index α.

This loss function is equivalent to the *angle*-integrated transmission electron-energy loss of electrons with energy comparable to the photoelectron kinetic energy of the photoemission line. In our case, this energy is ~30 eV (320-eV photon energy minus ~290 eV C 1s binding energy), so that a direct measurement of the energy-loss function is unfeasible. Although a large number of electron-energy-loss studies, both in transmission and in reflection geometries, have been previously performed for graphite, none of them provide the required information. Transmission studies[4,5] are not *angle*-integrated, reflection experiments[6,7] have different kinematic factors, and the high-resolution studies are also not *angle*-integrated. However, the electron-energy-loss data available in the literature,[4–7] and the optical properties of graphite,[8] suggest that one can simulate the *angle*-integrated loss function, $y(x)$, within the first 4 eV by the following expressions:

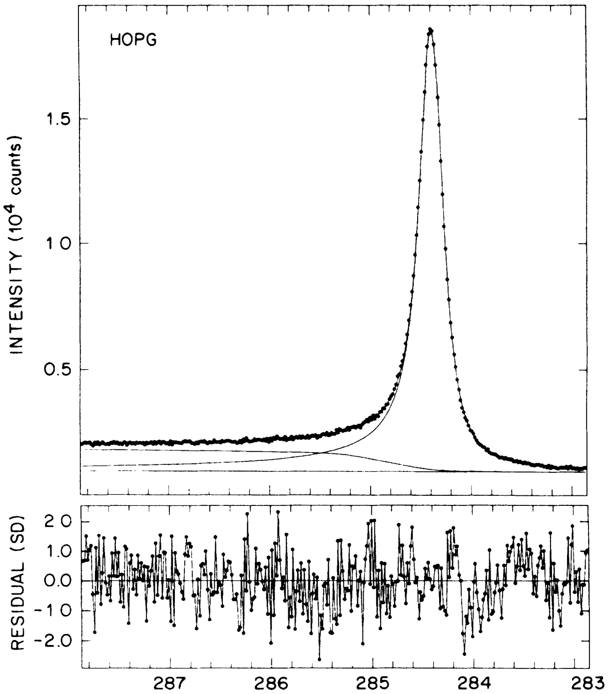

FIG. 1. C 1s SXPS spectrum of HOPG graphite taken with 320-eV photons (dots), and the best fit (solid line) obtained by adding a Gaussian-broadened Doniach-Šunjić function, an energy-loss background described in the text, and a linear background. The individual line shape, the energy-loss background, and the linear background are also shown as solid lines. The residuals from the curve fitting (in units standard deviations) are displayed in the bottom panel of the figure. The other parameters obtained from this fit, which gives the best χ of 0.926, are $x_0=0.80$, $\Gamma_G=129$ meV, $\Gamma=212$ meV, and $\alpha=0.074$.

$$y=\begin{cases} y_0x/x_0, & \text{for } 0\le x\le x_0 \qquad \text{(1a)}\\ y_0, & \text{for } x_0\le x<4\,, \qquad \text{(1b)}\end{cases}$$

where x is the loss energy and x_0 and y_0 are the two parameters determining the linearly increasing and the constant regions of the loss function. The background itself is obtained by convolving the Gaussian-broadened DS line with the loss function defined by Eqs. (1). In the fitting procedure x_0 and y_0 were free adjustable parameters. The best fit is shown in Fig. 1, where the line shape, the loss-function background, and the linear background are also displayed. The residuals of the fit are shown in the bottom of Fig. 1.

In Table I we report the values of the Gaussian and Lorentzian widths, Γ_G and Γ, and of the singularity index α, obtained when the loss-function parameter x_0 is constrained to fixed values. The statistical χ values are also shown. This analysis provides a means of checking the extent to which the various parameters of the model function depend on the details of the loss function. A number of significant conclusions emerge from this tabulation.

Independent of the choice of x_0, the Gaussian width is always 129 ± 5 meV FWHM. This value is only slightly larger than our best estimate of the instrumental broadening, which is assumed to be Gaussian. We therefore conclude that the combined effects of inhomogeneous broadening due to static disorder, and phonon broadening due to the excitation of acoustic low-energy phonons is much smaller than the observed Gaussian width, i.e., less than 50 meV. Such weak phonon broadening is consistent with the finding that the linewidth in the spectrum taken at 300 K is identical

TABLE I. Best values for Γ, Γ_G, and α for different x_0. The χ values are also reported.

x_0 (eV)	Γ_G (meV)	Γ (meV)	α	χ
0.00	129	214	0.0491	0.939
0.25	131	214	0.0512	0.945
0.50	132	212	0.0616	0.951
0.75	129	212	0.0724	0.927
1.00	127	211	0.0803	0.944
1.25	124	211	0.0869	1.004
1.50	126	208	0.0939	1.099
1.75	128	204	0.0992	1.223
2.00	133	198	0.1039	1.363

within ±10 meV to that taken at 90 K. We also looked for broadening by the excitation of optical phonons, which would give rise to a second peak shifted ~200 meV toward higher binding energy, by fitting the spectra with two peaks instead of one. Negligible intensity was found for the second line, ruling out broadening by this mechanism.

Table I further shows that the Lorentzian width, Γ, is also largely insensitive to the choice of x_0. This is not unexpected since the shape of the low-binding-energy side of the photoemission peak is largely determined by the combined effects of the Gaussian and Lorentzian widths. Moreover, it is insensitive of the energy-loss tail, and only weakly dependent on the singularity index. On the low-energy side the background is also typically well behaved. Consequently the low-binding-energy side of the spectrum provides a strong constraint on both the Lorentzian and Gaussian widths. The Lorentzian linewidth, which represents the C 1*s* core-hole lifetime in graphite, is determined within a precision of ~5%, i.e., $\Gamma=210\pm10$ meV.

Unlike the Gaussian and Lorentzian linewidths, the singularity index α does depend significantly on the shape of the loss-function background, increasing as x_0 increases. In Fig. 2 we show this correlation by plotting α as a function of x_0. The corresponding χ values are also displayed. For $x_0 \leq 1$ eV the values of χ remain below unity, implying that the corresponding fits are all compatible with the statistical uncertainty of the data points so that an optimal value of x_0 cannot be identified within that range. It is gratifying that values of x_0 in this range are consistent with the expected shape of the loss function.[3-6]

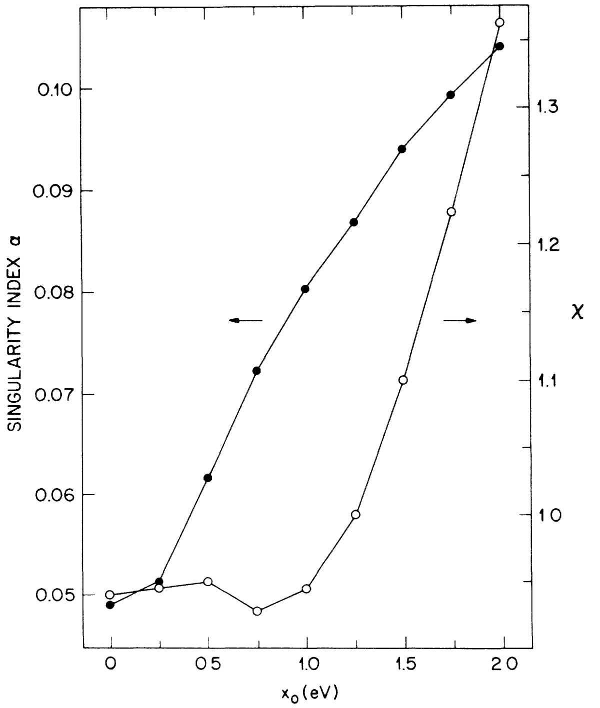

FIG. 2. Dependence of α (solid circles) and χ (open circles) on the energy-loss function parameter x_0 defined in Eq. (1) (see Table I). The lines are drawn as a guide to the eye.

The corresponding values of α lie in the range 0.065 ± 0.015. This value of the singularity index is significantly smaller than that reported in the earlier study using Al $K\alpha$ radiation and substantially larger instrumental broadening: α was found to be 0.14.[2] Possible reasons for this difference may arise from the omission of the inelastic loss tail in the model function used in that work, and from the different shape and intensity of the background signal due to the different kinetic energy of the photoelectrons in the two experiments.[9] Although the present result indicates that metal-like screening in the semimetal graphite is not as large as previously believed, the nonzero value of α confirms that the electronic screening process of the C 1*s* core hole is greatly enhanced relative to that possible in the ground state of this solid where the density of states at the Fermi level is very small.[2] In fact, the smaller value of α is in better agreement with the previously proposed excitonic screening model.[2]

IV. DISCUSSION

In many respects the most interesting result is the large natural width of the carbon 1*s* core hole in graphite. It is well known that the decay of the C 1*s* core hole is almost entirely a result of *KLL* Auger processes, and that the Auger rate is primarily determined by the electrons in those orbitals that have the greatest overlap with the core-hole wave function. If the *L* electrons were corelike, the natural width of the C 1*s* line would be an atomic property and would be insensitive to the chemical environment of the atom. However, since the *L* electrons are valence electrons, chemical perturbations of the core-hole lifetime are not unexpected. Theoretical calculations for the KL_1L_1, $KL_1L_{2,3}$, and $KL_{2,3}L_{2,3}$ Auger rates in isolated atoms[1] give a natural width for the carbon atom in the s^2p^2 electronic configuration of only 56 meV; the value for the sp^3 configuration is 47 meV. The value measured for the C 1*s* core hole in graphite is approximately four times larger than either of these theoretical widths. The reliability of these atomic calculations was verified earlier experimentally for the isolated Ne atom, where the measured 1*s* core-hole linewidth was found to be $\Gamma=270$ meV,[10,11] which compares favorably with the calculated value of 240 meV.[1] The theoretical values should then be reliable to within 20%.

Using the calculated Auger rates of the three decay channels of the carbon atom, $a=23.5$ meV for a KL_1L_1 process, $b=5.6$ meV for a $KL_1L_{2,3}$, and $c=10.1$ meV for a $KL_{2,3}L_{2,3}$, we can write an expression for the Auger decay rate *r* of carbon atoms with different 2*p*-orbitals occupancies:

$$r=a+2bn_p+cn_p(n_p-1)/2 \,, \tag{2}$$

where n_p is the occupation of the 2*p* orbitals of an atom in the $s^2p^{n_p}$ configuration, and *a*, *b*, and *c* are defined as above. Effect of changes in the radial part of the 2*p* wave function with occupancy are neglected. The widths for

TABLE II. Total Auger rates for different $s^2p^{n_p}$ configurations of the carbon atom, calculated using Eq. (2).

n_p	r (meV)
1	34.7
2	56.1
3	87.4
4	128.9
5	180.5
6	242.2

various values of n_p are given in Table II.

We note that an Auger decay rate comparable to the measured natural width in graphite would require between 7 and 8 L electrons to be available for the decay. It is tempting, therefore, to assign this large number of electrons to those coming from the three doubly occupied in-plane covalent σ orbitals and the out-of-plane half-filled π-like orbital of graphite. This interpretation would also explain the photoabsorption measurements in diamond, where the lifetime of the core exciton was found to be 240±20 meV,[12,13] a value comparable to that of the core hole in graphite.

This interpretation of the enhanced Auger decay rate as due solely to the contribution of the bonding electrons surrounding the excited atom in the initial state is, however, difficult to reconcile with recent C 1*s* lifetime measurements of molecular systems that have a similar bonding configuration and the same orbital hybridization of graphite. The C 1*s* lifetimes in C_2H_4 and C_6H_6 molecules for the 1*s*-to-π transition are found to be only 110 meV,[14,15] a value between that of graphite and the isolated carbon atom. Similarly, a lifetime of 140 meV has been derived for the C 1*s* x-ray photoelectron spectroscopy (XPS) line of gas-phase CH_4.[10] Comparable values have also been obtained from the C K-edge photoabsorption and emission spectra of many other carbon-containing molecules such as CH_4, C_2H_2, C_2H_6, CO, CO_2, and carbon fluoride molecules.[10,11,14] Summarizing these observations, it appears that the C 1*s* core-hole lifetime is ~60 meV for the isolated atom, and typically has values of ~120 meV in molecular structures and ~220 meV in solids.

This intriguing systematic trend indicates that the simple calculation relating the interatomic Auger decay to the initial-state *sp*-bond occupancy does not suffice to explain the observed C 1*s* natural widths in carbon-containing systems. It is possible that the mechanism responsible for the extra broadening in solids is related to excitonic states which increase the effective occupation of the 2*p* orbitals of the core-excited carbon atom in solids, compared to molecules with similar local bonding configuration. Excitonlike states localized on the core hole, typically formed in core excitations, can in fact be occupied in solids by valence electrons near the Fermi level. In molecules, although new excitonic states may be available, often their energy position is not sufficiently low, compared to the other valence electron states, to become occupied. Another possible mechanism contributing to the lifetime decrease in solids can be related to the screening of the two valence holes in the Auger final state. The better screening in solids compared to molecules, decreasing the Coulomb repulsion, allows the two valence holes to get closer to each other, thus increasing the overlap with the core hole in the initial state, and, consequently, the Auger decay rate.

V. CONCLUSIONS

In conclusion, we have accurately measured the line shape of the C 1*s* core hole in graphite, demonstrating that the core-hole lifetime is substantially shorter than in the isolated atom. We point out a systematic decrease in the carbon 1*s* core-hole lifetime from the isolated atom to small molecules and pure solids that is not simply related to the local chemical environment of the core-excited carbon atom. The enhanced natural linewidth of the C 1*s* hole in graphite is related to an interatomic Auger process utilizing the valence electrons of neighboring atoms. This simple approach, however, yields comparable widths for small molecules which have *sp*-bond occupancies comparable to those of graphite in the initial state. We consequently suggest that the difference in lifetime between locally similar molecular and solid systems is related to the excitonic final state in the solids. It would be of particular interest to confirm these suggestions with observations on other atomic species. A satisfactory understanding of these effects on the core-hole decay rate will require more detailed theoretical calculations. These measurements and their analysis demonstrates the importance of measuring core-electron line shapes with high instrumental resolution.

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