

Interlayer conduction band states in graphite-sulfur composites

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We present experimental evidence for the existence of interlayer states formed in graphite-sulfur (C-S) composites. We have studied occupied and unoccupied p bands of the C-S composites by means of soft x-ray absorption and emission spectroscopy. New spectral features in the C $1s$ absorption are interpreted as contributions arising from the interaction of sulfur s states with graphite interlayer states. The equivalence of C $K\alpha$ x-ray emission spectra of C-S and graphite lets us conclude that the interlayer states are entirely located above the Fermi level.

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Carbon-based materials have attracted great attention during the last years because they are considered promising candidates for high-temperature superconductors.¹⁻⁴ This was enhanced by the recent discovery of superconductivity (at 117 K) in hole-doped $C_{60}/CHBr_3$ (Ref. 5) and in graphite-sulfur (C-S) composites at 32–37 K) as shown in Refs. 6–8. A superconducting phase is present at 0.55 K (Ref. 9), at 20 K (Ref. 10), and above room temperature (Ref. 11) as reported for carbon nanotubes, which are graphite sheets folded into a cylindrical shape. The recently discovered superconductor MgB_2 ($T_c = 39$ K; see Ref. 12) is electronically and crystallographically similar to graphite.

The origin of superconductivity in C-S composites is not yet clear. It is known that the reaction temperature during the C-S preparation is too low in order to destroy the layered graphite structure. X-ray structural analysis measurements⁶ suggest a small decrease in distance between the graphite planes in S-doped graphite samples. This fact does not support a possible presence of the intercalation effect. The difference in electronegativity of carbon (2.54) and sulfur (2.58) appears to be too small to possibly amount to significant charge transfer in C-S composites, although evidence for the donor nature of sulfur in diamond has been reported.¹³ On the other hand, it has been shown¹⁴ that topological defects in graphite can be responsible for the formation of curved, fullerene-like carbon fragments, leading to an enhancement in the density of states as well as to p -wave superconductivity. A theoretical analysis¹⁵ suggests that sulfur atoms adsorbed along the boundaries of graphite fragments can trigger a curvature of the graphene plane.

The intention of our study is verification of changes in the band structure of graphite caused by the carbon-sulfur interaction. In the present work we present x-ray emission and absorption spectra of the C-S composite and compare the results to spectra of pure graphite.

Soft x-ray emission and absorption measurements were performed at Beamline 8.0.1 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.¹⁶ The emitted radiation was measured using a Rowland-circle-type spectrometer with spherical gratings and a multichannel two-dimensional detector. The instrumental resolution at the C $1s$

is about 0.2 eV. The excitation energy for the nonresonantly excited carbon $K\alpha$ emission was 320 eV.

A sample of highly oriented pyrolytic graphite (HOPG) was ground to powder and pressed into a pellet. The C-S composite samples were prepared by letting sulfur vapor react with the graphite powder. Graphite pellet and sulfur powder were placed into a sealed quartz tube under Ar atmosphere, annealed at 400 °C for 1 h and then cooled to room temperature with a rate of 4 °C per hour. During this procedure the mass was monitored and the mass of the graphite pellet increased by 5.6% as a result of the sulfur adsorption. The presence of superconductivity⁶⁻⁸ in the C-S samples was verified by magnetic susceptibility measurements using a superconducting quantum interference device (SQUID) magnetometer MPMS5.

Figure 1 shows nonresonant C $K\alpha$ soft x-ray emission spectra (XES) of C-S composite and corresponding reference samples (HOPG and sulfur). The radiative carbon $2p \rightarrow 1s$ transition probes the occupied density of C $2p$ states. The nonresonant C $K\alpha$ emission spectra are practically identical

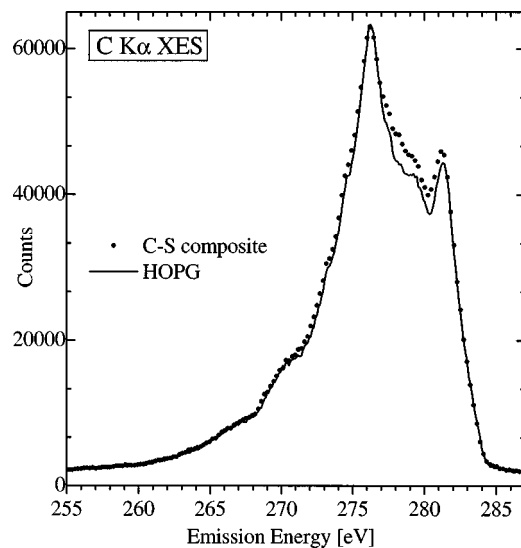


FIG. 1. Nonresonant carbon $K\alpha$ emission spectra of C-S composite and HOPG.

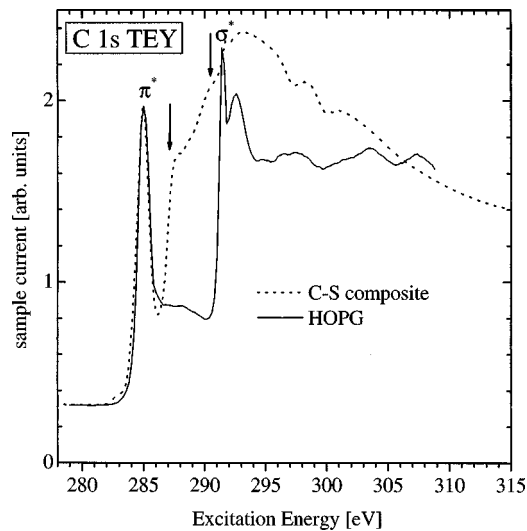


FIG. 2. C 1s soft x-ray absorption spectra of C-S composite and graphite. The spectra are measured in the total electron yield (TEY) mode.

for C-S composite and pure graphite, indicating the same density of the occupied C 2p states for both materials. Figure 2 displays C 1s absorption spectra measured for HOPG and C-S. According to Refs. 17–19, the first feature of C 1s absorption of HOPG (the π^* resonance) around 285 eV is associated with the conduction π states around the M and L points of the Brillouin zone (BZ). The second prominent feature is the σ^* peak at 291.5 eV, which is due to the dispersionless σ states at the Γ point of the BZ. The electronic states that correspond to both features have been identified by previous polarization dependent near-edge x-ray absorption fine structure measurements.²⁰ The main difference between the C 1s absorption spectra of C-S composite and graphite is the broad spectral weight situated at 287–290.5 eV (labeled by arrows in Fig. 2). Taking into account a binding energy of 284.5 eV for HOPG,²¹ we estimated these states to be situated 2.5–6.0 eV above the Fermi level. Band structure calculations have revealed that such electronic states can originate from states in the interior of the Brillouin

zone that have neither σ nor π symmetry,²² but display free-electron character in the direction parallel to the layers. We conclusively interpret the main difference between the C-S and HOPG absorption spectra as due to interlayer conduction band states of C-S. A similar interlayer band located 4 eV above the Fermi level of lithium-intercalated graphite has been verified by inverse photoemission measurements.²³ At the same time, the similarity of C $K\alpha$ emission between HOPG and C-S (Fig. 1) indicates that the lower edge of the interlayer band is situated above the Fermi level and cannot be probed by soft x-ray emission spectra, which probe the occupied states.

It is important to note that such interlayer states are proposed to exist in pure graphite.^{24,25} The contribution of these states to the total density of states is small, and they are difficult to detect in C 1s total electron yield (TEY) of HOPG. Our results indicate that when the S atoms are incorporated into graphite forming C-S composite, their outermost s states interact with the graphite interlayer states, attributing more spectral weight and hence detectable via C 1s TEY spectra.

To conclude, we have studied the occupied and unoccupied bands of C-S composite and graphite using carbon K emission and absorption spectra. The differences found in carbon K absorption spectra are attributed to strong dispersion normal to the basal plane as a result of interaction of sulfur s states with graphite interlayer states. We consider this important experimental evidence for the existence of interlayer states. In layered compounds all states up to about 10 eV above the Fermi level are usually considered to be two-dimensional.

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