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Excitonic Effects in Core-Hole Screening

P. M. Th. M. van Attekum and G. K. Wertheim
Bell Laboratories, Murray Hill, New Jersey 07974
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It is shown that the C 1*s* core-electron line shape of graphite in photoemission is determined by an excitonic state near the Fermi energy in the hole-state density of states.

The observation (see Fig. 1) that the carbon 1*s* photoemission line of graphite is strongly asymmetrical is difficult to understand from the point of view of many-body screening because the density of states at the Fermi energy (E_F) is very small compared with that of the simple metals. The additional fact that the *shape* of the line is well represented over a range of a few electron volts by the many-body power law only serves to deepen the puzzle since that shape is thought to be applicable only to the simple metals, i.e., those in which the density of states (DOS) remains constant near E_F. In graphite the DOS at E_F is very small and initially rises linearly in both directions. The resolution of this dilemma requires an extension of the usual treatment of the many-body screening formalism.

In the sophisticated treatment of the many-body phenomenon the behavior is studied only in the limit of small excitation energy.[1,2] The DOS, g, is assumed to be well behaved (i.e., no singularity) at E_F so that only $g(E_F)$ enters explicitly into the many-body line shapes. Using the approach due to Hopfield[3] it can be shown[4] that the joint density of states (JDOS) for electron-hole pair excitation plays a crucial role in determining the line shape. For a well-behaved DOS the JDOS rises linearly for small excitation energy. Such a linear rise translates directly into the many-body line shape

$$I(\omega) \propto [(\omega - \omega_0)/\xi]^{\alpha - 1}. \quad (1)$$

For simple metals it has been shown[5] that this behavior is realized over a range of $\sim E_F/4$, as one would expect on the basis of a calculated JDOS. In metals with highly structured DOS more detailed calculations using a JDOS obtained from the actual band structure are required.[4] For graphite this approach was tried with two forms of the band structure, those shown by Weinberger *et al.*[6] and by Dresselhaus, Dresselhaus, and Fischer.[7] The latter has more detailed structure in the vicinity of E_F. Neither one gives a line shape resembling that of graphite, largely because the JDOS is small and has strong positive curvature for small excitations.

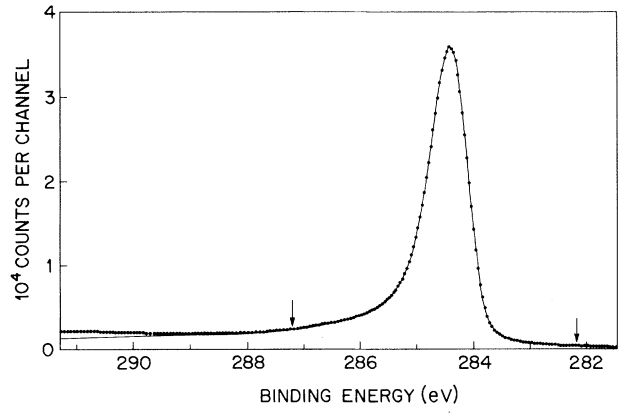

FIG. 1. X-ray photoemission spectrum of the C 1*s* electrons of highly oriented pyrolytic graphite. The solid line represents a least-squares fit to the data between the arrows (see text for details).

The data shown in Fig. 1 were taken with a HP 5950A spectrometer on a piece of vacuum cleaved graphite, highly oriented pyrolitic graphite (HOPG), grade ZYB, obtained from Union Carbide. Other forms of graphite give similar results. The data were fitted over a range from 282.2 to 287.2 eV with the power-law line shape, by use of the equation of Doniach and Sunjic,[8] and a closed-form expression for the instrumental resolution function. The resulting line is shown over full range of the data up to the 6-eV plas-

mon. The quality of the fit judged by the residuals was excellent, showing no systematic deviation on the high-energy side. The singularity index α is 0.14 ± 0.01.

Since the line shape of graphite is so well represented by the power law one is led to conclude that the JDOS must be proportional to the excitation energy, i.e.,

$$\int_0^{\epsilon} g(E_F - \epsilon + x) g(E_F + x) d\chi = g(E_F)^2 \epsilon. \quad (2)$$

While this equation is trivially satisfied by an energy-independent DOS, there are many other solutions for g which have the same property. In Fig. 2 we show a second class of DOS which satisfies Eq. (2). The linearly rising occupied DOS is a good representation of that of graphite. The exponential empty DOS has no counterpart in the *initial*-state band structure of graphite, but resembles the electron energy loss spectrum for $1s$-to-conduction-band excitations.[9]

For graphite the values of k_1 and k_2 are 0.04 state/eV^2 atom (Ref. 6) and 0.0058 state/eV atom.[10] (The decay constant of the exponential narrows to a δ function if k_2 goes to zero.) This discontinuous rise at E_F is not realizable in the real case because the hole-state DOS is broadened by the core-hole lifetime and band-structure effects. In order to test whether the sharp rise is important to the line shape calculated from the DOS we have broadened the DOS of Fig. 2 with a 1-eV (full width at half maximum) Gaussian[11] and then calculated the line shape by numerical means using the equation due to Hopfield[3]:

$$I(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} \exp(i\omega t) dt \left\{ \exp \int_0^{E_C} \alpha(\epsilon) [\exp(-i\epsilon t) - 1] \epsilon^{-1} d\epsilon \right\}, \quad (3)$$

$$\alpha(\epsilon) = (V^2/\epsilon) \int_0^{\epsilon} g(E_F - \epsilon + x) g(E_F + x) dx. \quad (4)$$

It was found empirically that the power-law line shape is retained provided that the Fermi level is lowered to keep it out of the high density-of-states region (see Fig. 3). The resulting shifted and broadened DOS closely resembles the energy-loss spectrum of Ref. 9. The agreement indicates that the excitonic state plays an important role in the screening of the core hole. We have, in effect, demonstrated the existence of this state entirely on the basis of the $1s$ core-electron line shape in photoemission. The line shape calculated for this DOS with the prescription of Eq. (3) provides a fit to the data which is indistinguishable from that shown in Fig. 1 in the vicinity of the peak. We conclude that the discontinuity at E_F is not essential to reproduce the

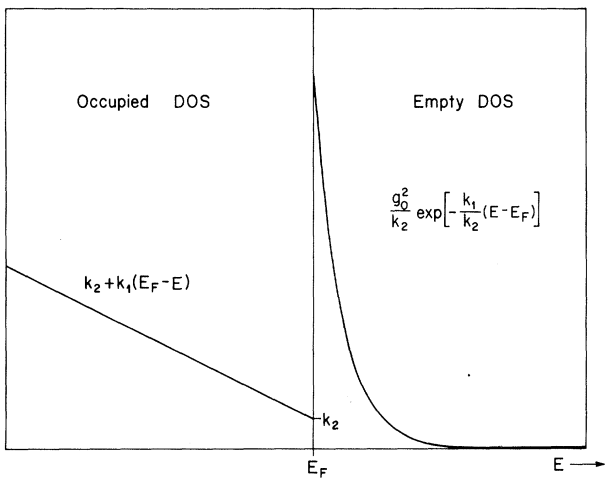

FIG. 2. A set of densities of states with discontinuity at E_F which rigorously results in a power-law line shape.

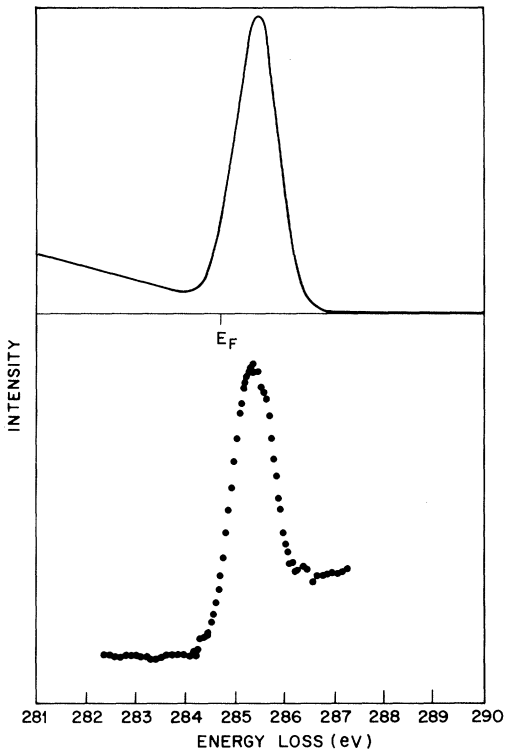

FIG. 3. Comparison between (top) the broadened and shifted DOS according to Fig. 2, and (bottom) the energy-loss data for graphite of Ref. 7.

power-law line shape when other broadening mechanisms are important.

The final question concerns the interpretation of the singularity index α in a case like graphite where the usual relationship to the Friedel phase shifts is not applicable. In terms of Eq. (4), α depends on the square of a matrix element V for transitions between the occupied and empty DOS, and on the JDOS. In order to discuss α for the case of graphite we must consider the free parameter in the model, the effective screening density of states, g_0. If we assume that the excitonic state is a one-electron state, i.e., $g_0^2/k_1 = 1$, then $g_0 = 0.2$ state/eV. This value is comparable to $g(E_F)$ in the simple metals and explains why the effective value of α in graphite is similar to that of Mg. (The transition matrix element is assumed to be similar in both cases.) The peak height of the exponential then is $g_0^2/k^2 = 6.7$ states/eV, but the experimental peak value is only ~ 1 state/eV because the DOS is greatly rounded by the core-hole lifetime and band-structure effects. The existence of an excitonic peak with large amplitude thus clearly emerges from the present analysis. It is clear, however, that other techniques, especially electron energy-loss spectroscopy, offer more direct methods for the detection of such excitonic states.

In summary, we have shown that the 1*s* core-electron line shape clearly requires the existence of an excitonic final state in graphite. The general conclusion is that the analysis of many-body screening effects in photoemission should always be based on a hole-state density of states. In metals the modification of the DOS in the final state is, however, expected to be much weaker than in graphite.

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