# Dynamic Core-Hole Screening Effects in the C-*KVV* Auger Line Shape of Graphite

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Evidence is presented for the presence of a "shakedown" satellite near threshold in the C-*KVV* Auger spectrum of graphite. Its origin is shown to be an electron in a relatively long-lived valence-core excitonic level (populated as a result of dynamic core-hole screening) which participates in the Auger decay. Modeling of the shakedown contribution considerably improves agreement in the threshold region between the experimental line shape and a simple one-electron model and represents the first report of Auger intensity resulting from this type of excitonic configuration.

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Auger line shapes are usually interpreted in the context of a two-step model involving the creation of a fully relaxed core-hole state followed by Auger decay from this state.[1] However, upon creation of a core hole, the dynamic screening response can lead to shakeup or shakeoff processes leaving locally excited core-hole states. Auger decay involving these states can result in intensity above or near the high-energy threshold giving rise to features known as "shakedown" satellites, their presence indicating a breakdown of the two-step model. Here we present evidence for a relatively long-lived valence-core excitonic state which produces shakedown structure in the C-*KVV* line shape of graphite.

Figure 1(a) shows the C-*KVV* line shape from amorphous graphite after careful data reduction which includes a subtraction of the secondary-electron background and loss deconvolution with use of an electron backscattering approximation for the loss function. An extensive discussion of the sample preparation and data acquisition and treatment is presented elsewhere.[2] The experimental line shape is compared to a model consisting of the self-fold of the empirically determined (obtained from x-ray emission and x-ray photoelectron results) graphite one-electron density of states (DOS) modulated by symmetry-determined, atomic Auger matrix elements.[2] Significant differences between the line shapes are apparent with the model missing intensity near threshold (284.6 eV) and in the region below the principal maximum ( ~ 265 eV). The differences in the region below the principal

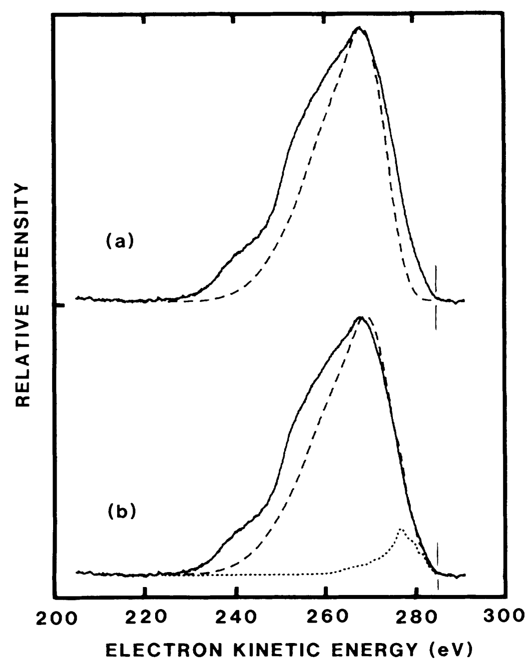


FIG. 1. (a) A comparison of the loss-deconvoluted experimental Auger line shape (Ref. 2) for machinable amorphous graphite (solid) with a model line shape (dashed) calculated as the self-convolution of an empirical DOS. The threshold level at 284.6 eV [the C(1*s*) binding energy] is indicated by the vertical line. (b) A comparison of the experimental line shape (solid) with the model (dashed) obtained above but now including the shakedown contribution (dotted) from the valence-core exciton level whose effective occupation is 0.11 electron.

maximum are shown to be due to final-state hole-hole interaction effects[3] discussed elsewhere[2] and are effectively independent of those near the threshold.

To establish that intensity near the threshold results from a shakedown mechanism, we will show that shakeup into a relatively long-lived state occurs simultaneously with the C(1$s$) hole creation in graphite and that this can produce Auger intensity of the proper line shape and energy.

The existence of a core-excitonic state in graphite has been established by electron-energy-loss spectroscopy (EELS).[4] It exists in the presence of the core hole and can be resonantly populated to reveal a sharp set of levels centered ~1.0 eV above the Fermi level (FWHM ~1.0 eV). Auger decay from this state could lead to intensity in the threshold region. However, the line shapes resulting from excitation by electrons (which can give rise to resonant pumping as seen in the EELS results[4]) and nonresonant photons (negligible resonant pumping) are identical.[2] The contrast between electron and nonresonant photon excitation is often used to identify the shakedown contributions in Auger spectroscopy.[5] With a measured lifetime-broadened width of ~1.0 eV, the core exciton apparently is too short-lived to participate significantly in the Auger or x-ray emission spectroscopy (XES) decay processes whose lifetime widths are 0.06 and 0.0002 eV, respectively.[6]

X-ray photoemission spectroscopy (XPS) data involving the C(1$s$) excitation[7] reveal a Doniach-Sunjic[8] line shape indicating significant valence electron-hole pair formation during core-hole creation. This distorted line shape is suggested to arise from shakeup of valence electrons into an excitonic level just above the Fermi level.[7] In contrast to the core exciton, this state contains two positive holes—one in the core level and one in the valence band—and an electron in an excitonic level.[7] We refer to this excited configuration as a valence-core excitonic state and we will show that it does contribute to the Auger process.

The shakedown intensity was modeled by the assumption that the valence-core exciton had $p$ symmetry and could be represented as a delta function at the Auger threshold energy. Its effective electron occupancy was then varied to obtain a "best fit" to the leading edge of the experimental line shape. The distribution of electrons excited from the valence band was assumed to be broad and featureless and to leave the shape of the DOS unchanged. With these assumptions, the shakedown contribution to the model line shape consists of a self-convolution of the delta function at the threshold energy (with both electrons involved in the transition originating in the excitonic level) and a convolution of the delta function with the total DOS (one of the transition electrons originating in the valence band and one in the excitonic level). The former contribution will be shown to be sufficiently small to be ignored.

Inclusion of the latter contribution with the one-electron model is shown in Fig. 1(b), where excellent agreement with the experimental spectrum in the threshold region is apparent. The function used for the total shakedown contribution, $A$(v-c), is given by

$$A(\text{v-c}) = 2B_A n^0_{\text{v-c}} [P_{ksp}\delta_p * \sigma_s + P_{kpp}(\delta_p * \sigma_p + \delta_p * \pi_p)], \tag{1}$$

where $P_{ksp}$ and $P_{kpp}$ are the Auger matrix elements, $n^0_{\text{v-c}}$ is the initial occupancy of the valence-core excitonic level, $B_A$ is the Auger branching ratio, $\sigma_s$, $\sigma_p$, and $\pi_p$ are the occupied partial DOS, $\delta_p$ indicates the excitonic state having $p$ symmetry and located at the Auger threshold (284.6 eV), and the asterisk denotes convolution.[2] Since the width of the DOS is broad, the model is not very sensitive to the precise position of the delta function ($\pm 0.5$ eV). From Fig. 1(b), the relative intensity of the shakedown contribution compared to the total C-$KVV$ intensity is about 7%. The total C-$KVV$ intensity is estimated[2] to be ~$15e^2$ while the parameters of Eq. (1) yield an estimated intensity of $10n^0_{\text{v-c}}B_A e^2$. Therefore, relative to the total intensity, the effective electron occupancy of the valence-core excitonic state is given by

$$n^0_{\text{v-c}} B_A = 0.11. \tag{2}$$

The branching ratio in Eqs. (1) and (2) takes into account the percentage of electrons in the valence-core excitonic state that decay by an Auger event and is determined from the relative lifetimes of these two processes by the expression

$$B_A = \tau_{\text{v-c}}/(\tau_{\text{v-c}} + \tau_c) = \omega_c/(\omega_c + \omega_{\text{v-c}}), \tag{3}$$

where $\tau_{\text{v-c}}$ ($\omega_{\text{v-c}}$) and $\tau_c$ ($\omega_c$) are the lifetimes (lifetime-broadened widths) for the valence-core excitonic state and the core-hole state, respectively.

The initial occupancy for the valence-core exciton can be estimated from the measured C(1$s$) line shape.[7] Modeling the undistorted core-level line shape by a Lorentzian based on the shape of the high-energy side of the experimental spectrum, we can subtract the model from the distorted spectrum and compared the resulting area with that of the total spectrum. This results in an estimated initial occupancy ratio of ~0.5 which represents the fraction of XPS events occurring in the presence of a valence-core exciton (i.e., $n^0_{\text{v-c}}$) giving an Auger branching ratio of 0.22. The core-hole lifetime width is 0.06 eV,[6] requiring, from Eq. (3), a valence-core lifetime width of 0.21 eV. Although this is twice the width estimated in Ref. 6, the agreement is sufficiently close (given the model dependence in both) to establish a connection between the two different measurements of the same excited state. The increase in lifetime of the valence-core excitonic state compared to the core exciton presumably is due to the enhanced local bonding resulting from the valence hole present in the former configuration.

Since the Auger yield for carbon is near unity,[6] and the core-hole and valence-core exciton lifetimes are comparable, the valence-core exciton is expected to participate in the Auger process but not in the slower XES process. This fact makes it possible to distinguish the valence-core contribution to the Auger line shape as the difference between the model (which was determined in part from XES data) and the experimental line shape in Fig. 1(a).

The experimental Auger spectrum has no detectable sharp feature near threshold indicating that the probability of both electrons involved in the Auger transition originating from the valence-core excitonic level is low. An effective occupancy of 0.11 electron in this level would give an intensity ratio of only 2% between the Auger feature resulting from both electrons originating in the valence-core excitonic level compared to only one in this state (which is itself only 7% of the normal Auger intensity). These two Auger final states are expected to have a quadratic and linear dependence on the valence-core exciton occupation, respectively. Both of these transitions are observed in donor intercalated graphite[9] and they show the expected linear and quadratic variation.

Alternate mechanisms could produce Auger intensity near the threshold region. Such a feature in the $L_{23}VV$ line shape for Ti and V has been attributed to nonorthogonality[10] of initial and final states and negative hole-hole corelation.[11] For graphite these effects can be ruled out since our DOS were determined empirically (if present, nonorthogonality is already included in our model line shape) and only positive values of $U$ have been observed.[2] Static initial-state screening, which could also produce intensity in this region, has been shown to have a negligible effect on our model line shape.[2]

In summary, evidence has been presented for the presence of a shakedown contribution near the threshold energy in the C-$KVV$ Auger line shape of graphite. On the basis of supporting evidence from EELS, XES, and XPS measurements, this shakedown structure is shown to result from dynamic core-hole screening involving valence electrons excited into an excitonic state in the presence of a core hole, i.e., a valence-core exciton. Although the nature of the excited core-hole state which results from dynamic core-hole screening will vary from material to material, we feel that contributions to the threshold region of the Auger line shape from such states will occur in a broad range of materials.

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