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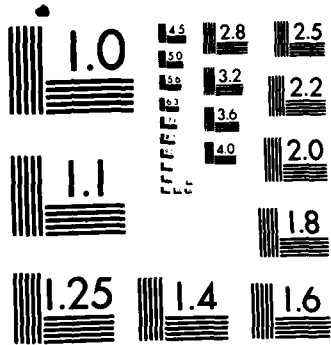
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DYNAMIC CORE-HOLE SCREENING EFFECTS IN THE C(KVV)
AUGER LINESHAPE OF GRAPHITE

By

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DYNAMIC CORE-HOLE SCREENING EFFECTS IN THE
C(KVV) AUGER LINESHAPE OF GRAPHITE

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ABSTRACT

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 the shakedown contribution considerably improves agreement in the threshold region between the experimental lineshape and a simple one-electron model.

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Auger lineshapes 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) lineshape of graphite.

Figure 1a shows the C(KVV) lineshape from amorphous graphite after careful data reduction. An extensive discussion of the sample preparation, data acquisition, and data manipulation is presented elsewhere [2]. The experimental lineshape is compared to a model consisting of the self-fold of the empirically determined graphite one-electron density of states (DOS) modulated by symmetry-determined, atomic Auger matrix elements [2]. Significant differences between the lineshapes 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 maximum are 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(1s) hole creation in graphite and that this can produce Auger intensity of the proper lineshape and energy.

The existence of a core-excitonic state in graphite has been established using Electron Energy Loss Spectroscopy (EELS) [3]. 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 but the lineshapes resulting from excitation by electrons (which can give rise to resonant pumping as seen in the EELS results [3]) 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 [4]. 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 process whose lifetime widths are 0.06 and 0.0002 eV, respectively [5].

X-ray Photoemission Spectroscopy (XPS) data involving the C(1s) excitation [6] reveals a Doniach-Sunjic [7] lineshape indicating significant valence electron-hole pair formation during core hole creation. This distorted lineshape is suggested to arise from shakeup of valence electrons into an excitonic level just above the Fermi level [6]. 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 [6]. 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 assuming 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 lineshape. 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 lineshape consists of a convolution of the delta function at the threshold energy (two final-state holes in the excitonic

level) and a convolution of the delta function with the total DOS (one final-state hole in the valence band and one in the excitonic level). The former contribution will be shown to be sufficiently small so as to be ignored.

Inclusion of the latter contribution with the one-electron model is shown in Fig. 1b 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,

$$A(v/c) = 2 B_A n_{v/c}^{\circ} \{ P_{ksp} \delta_p^* \sigma_s + P_{kpp} (\delta_p^* \sigma_p + \delta_p^* \pi_p) \} \quad (1)$$

where P_{ksp} and P_{kpp} are the Auger matrix elements, $n_{v/c}^{\circ}$ is the initial occupancy of the valence/core excitonic level, B_A is the Auger branching ratio, σ_s , σ_p , and π_p are the occupied partial DOS, δ_p indicates the excitonic state having p symmetry and located at the Auger threshold (284.6 eV), and "*" 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 (± 0.5 eV). From Fig. 1b, the relative intensity of the shakedown contribution compared to the total C(KVV) intensity is about 7%. The total C(KVV) intensity is estimated to be $\sim 15 e^2$ [2] while the parameters of eq. 1 yield an estimated intensity of $10 n_{v/c}^{\circ} B_A e^2$. Therefore, relative to the total intensity, the effective electron occupancy of the valence/core excitonic state is given by,

$$n_{v/c}^{\circ} B_A = 0.11. \quad (2)$$

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,

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

where $\tau_{v/c}$ ($\omega_{v/c}$) and τ_c (ω_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(1s) lineshape [6]. Modeling the undistorted core-level lineshape 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 compare 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., $n_{v/c}^0$) giving an Auger branching ratio of 0.22. The core-hole lifetime width is 0.06 eV [5] requiring, from eq. 3, a valence/core lifetime width of 0.21 eV. Although this is twice the width estimated in ref. 5, 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.

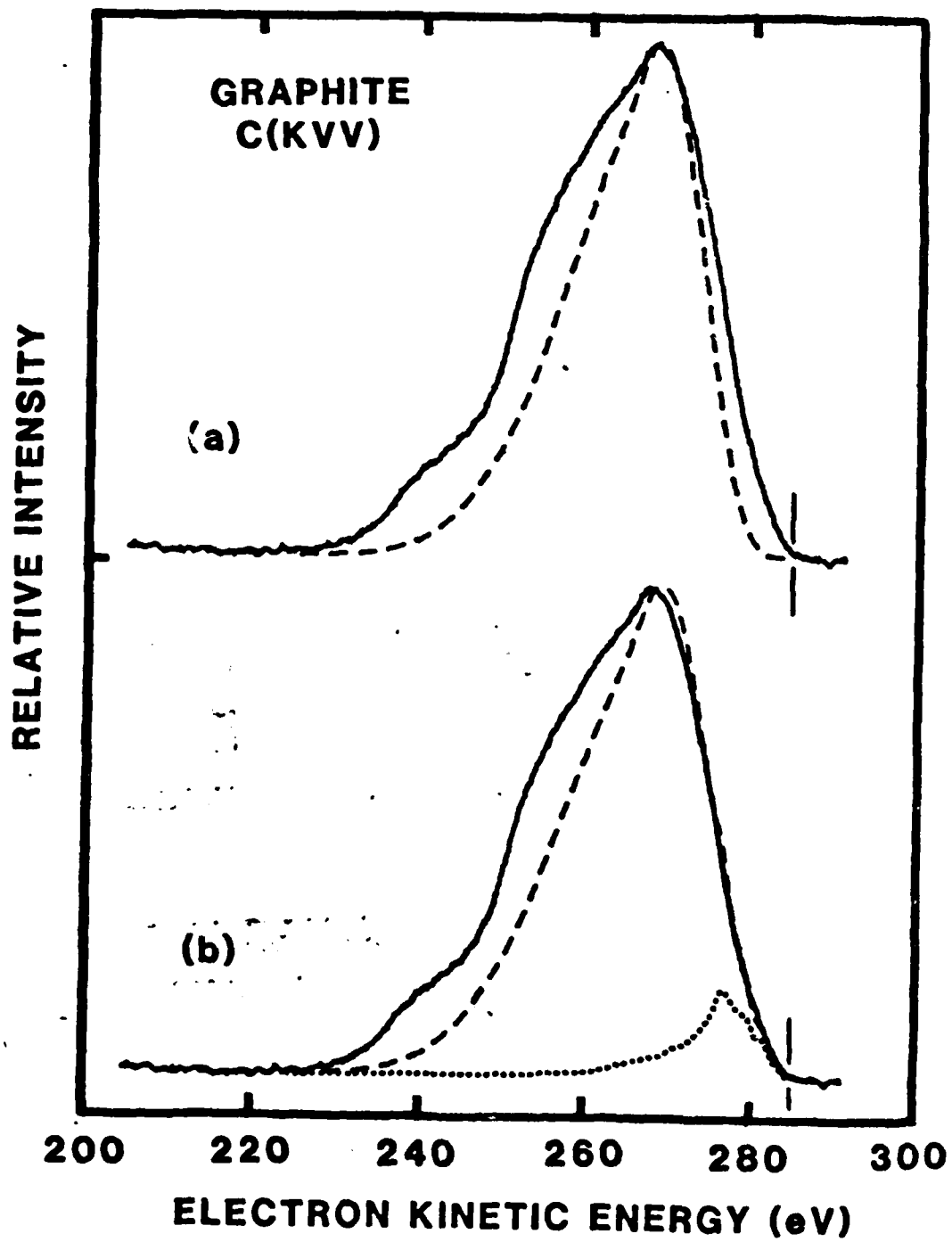
Since the Auger yield for carbon is near unity [5], and the core hole and valence/core exciton lifetimes are comparable, the valence/core exciton is expected to participate in the Auger process but not in the slower XES process. This fact makes it possible to distinguish the valence/core contribution to the Auger lineshape as the difference between the model (which was determined in part from XES data) and the experimental lineshape in Fig. 1a.

The experimental Auger spectrum has no detectable sharp feature near threshold indicating that the probability of a two-hole final state in the valence/core excitonic level is

low. An effective occupancy of 0.11 electrons in this level would give an intensity ratio of only 2% between the Auger feature resulting from both holes compared to one hole 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 [8] and they show the expected linear and quadratic variation.

Alternate mechanisms could produce Auger intensity near the threshold region. Such a feature in the $L_{23}VV$ lineshape for Ti and V has been attributed to initial-final state nonorthogonality [9] and negative hole-hole correlation [10]. For graphite these effects can be ruled out since our DOS were determined empirically (if present, nonorthogonality is already included in our model lineshape) 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 lineshape [2].

In summary, evidence has been presented for the presence of a shakedown contribution near the threshold energy in the $C(KVV)$ Auger lineshape 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 lineshape from such states will occur in a broad range of materials.



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FIGURE CAPTIONS

- Fig. 1 (a) A comparison of the loss-deconvoluted experimental Auger lineshape [2] for POCO graphite (solid) with a model lineshape (dashed) calculated as the self-convolution of an empirical DOS. The threshold level at 284.6 eV (the C(1s) binding energy) is indicated by the vertical line.
- (b) A comparison of the experimental lineshape (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 electrons.

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