

# Origin of the extended fine structure in the secondary-electron-emission spectrum of graphite

A. Hoffman

*Chemistry Department, Technion-Israel Institute of Technology, Haifa 32000, Israel  
and Solid State Institute, Technion-Israel Institute of Technology, Haifa 32000, Israel*

R. Brener

*Solid State Institute, Technion-Israel Institute of Technology, Haifa 32000, Israel*

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An extended fine structure (EFS) has been observed in the electron-excited secondary-electron-emission (SEE) spectrum of graphite. Measurements were performed in the 0–150-eV electron kinetic range as a function of primary-electron energy above and below the threshold for carbon core-level 1s ionization. For primary electron energies of 200, 500, and 1000 eV the spectra display a well-defined fine structure that does not depend strongly on the primary electron energy. However, a dependence of the spectrum on orientation of the sample with respect to the primary electron beam and the electron analyzer was found. The effect of structural disorder on the EFS-SEE spectrum of graphite was investigated by performing *in situ* measurements as a function of the 2-keV Ar-ion irradiation dose. It was found that the EFS-SEE is very sensitive to imperfections created by the ion beam for very low dose levels of ion irradiation. The sensitivity of the spectrum to short-range crystalline order was assessed by comparing the spectrum obtained for graphite to that of glassy carbon. It is concluded that the EFS-SEE of graphite originates from interband electronic excitation processes involving excitations of valence electrons by primary electrons and secondary electrons of sufficient energy into unoccupied electronic states of high density in the graphite crystal field. This conclusion is supported by comparison with other electron spectroscopic measurements of graphite.

## I. INTRODUCTION

Fine structures extending for several hundreds of eV above a particular electron excitation have been observed in different electron spectroscopies and the most well known are appearance-potential fine-structure (APFS),<sup>1</sup> elastically scattered electron fine-structure (ESEFS),<sup>2,3</sup> electron-energy-loss fine-structure (EELFS) (Refs. 4 and 5), and extended fine Auger structure (EXFAS) (Refs. 5–8). It is generally accepted that the physical mechanism responsible for the APFS, ESEFS, and EELFS is an EXAFS-like (extended x-ray-absorption fine-structure) process which can be described in terms of final-states interference effects mainly determined by short-range nearest neighbors to the site of primary ionization.<sup>9</sup> However, the interpretation of EXFAS data is still controversial. Although some arguments exist in favor of a long-range-order-sensitive diffraction process,<sup>10</sup> additional experimental results suggest that a combined mechanism including both EXAFS-like and diffraction effects should be taken into account.<sup>6</sup> Recently, an alternative process based on direct interband transitions has been suggested.<sup>8</sup> In this case, the prominent features in the EXFAS are associated with high density of unoccupied states at corresponding state energies. According to Crescenzi, Hitchcock, and Tyliczszak,<sup>6</sup> the secondary-electron-emission (SEE) spectrum of crystalline materials, like graphite, which do not have core levels and Auger lines in the low-kinetic-energy range (below ~270 eV) should still exhibit an extended fine structure (EFS) in this energy range due to diffraction of secondary electrons.

The SEE spectrum of graphite has been measured in the 0–70-eV kinetic-energy range and is found to consist of a fine structure superimposed on a large slowly varying band peaking at a few eV.<sup>11–16</sup> It has been generally agreed that the fine structure in the spectrum reflects features in the unoccupied density of electronic states at corresponding energies above the vacuum level.<sup>11–16</sup> Angle-resolved SEE measurements in the low-energy range were found to reflect the dispersion of high-energy unoccupied band states as calculated using a simple model in which a free-electron parabola modulated by the graphite crystal field and an inner potential of –16.2 eV was used.<sup>16</sup> It suggested that the electronic excitations which contribute to the fine structure in the low-energy range of the SEE spectrum consist of single-electron transitions induced by the primary electron beam or by secondary electrons of sufficient energy.<sup>17</sup>

Recently, we have demonstrated the appearance of an extended fine structure in the electron-excited secondary electron spectrum of graphite in the 0–150-eV electron kinetic-energy range.<sup>18</sup> However, the excitation mechanisms and the nature of the electronic processes involved in the production of this structure are unclear.

The aim of the present study is to investigate the origin and the mechanism of the electron excited EFS-SEE spectrum of graphite in the 50–150 eV electron-energy range. We assess the nature of the primary-electronic excitation that leads to a well-defined extended structure by measuring the dependence of the spectrum on primary-electron energy. The structural sensitivity of the spectrum was investigated by performing measurements as a function of low-energy Ar-ion bombardment of a cleaved

graphite surface. To assess the sensitivity of the spectrum to short-range order, the SEE spectrum of glassy carbon was measured.

## II. EXPERIMENT

The SEE measurements were performed in a Perkin-Elmer, PHI model 590A system using a cylindrical mirror analyzer (CMA) equipped with a coaxial electron gun. The SEE spectra were recorded in the first derivative  $d(E \times N(E))/dE$  mode. The spectrum in the 0–50-eV electron energy range was measured using a 2-V peak to peak modulation, whereas in the 50–150-eV range 6-V modulation was used. The Ar irradiation was performed *in situ* with a rastered ion beam at 2 keV. The measurements were performed using primary electron energies of 200-, 500-, and 1000-eV, primary beam current of 1  $\mu$ A and an incident electron-beam angle of 30° with respect to the sample normal. The angular sensitivity of the SEE spectrum was studied by changing the sample angle with respect to the incident primary electron beam. By changing the incident angle in a CMA the angular dependence of the SEE can be followed.<sup>19</sup> In the present work, no attempt was made to calculate the angular dependence of the SEE spectrum, but only to establish its sensitivity.

Prior to insertion into the ultrahigh vacuum chamber the graphite (HOPG, highly oriented pyrolytic graphite, supplied by Union Carbide) sample was cleaved in air by the standard scotch tape technique. The glassy carbon (GC, type V-25, supplied by Atomergic) sample surface is more complicated to prepare in order to obtain a well defined and reproducible surface at the microscopic level. No fresh surface may be produced by cleavage or other commonly used methods for producing well-defined structures, such as ion irradiation and subsequent annealing. Our strategy for preparing a well-defined GC surface, which would hopefully maintain its turbostratic structure, was to break the sample in air. After breaking, the sample surface morphology was found to be irregular when examined by scanning electron microscopy. No impurities were detected by Auger-electron spectroscopy and the SEE and *C* (KLL) Auger high-resolution line signatures were reproducible.

## III. RESULTS AND DISCUSSION

### A. Extended SEE spectrum

The SEE spectrum of cleaved HOPG excited by an electron-beam energy of 1000 eV at an incident angle of 30° and measured in the first derivative mode in the 0–220-eV electron kinetic-energy range using a modulation voltage of 6 V is shown in Fig. 1(b). In Figs. 1(a) and 1(c), the same spectrum is shown after numerical integration and as the negative of the second derivative:  $-d^2(EN)/dE^2$ , respectively. The SEE spectrum is presented in these three formats to show the relative intensity of the different peaks. The true energy position of the peaks occurs at maxima in the negative of the second derivative. The SEE spectra measured as a function of energy, angle, etc. will be presented below in first deriva-

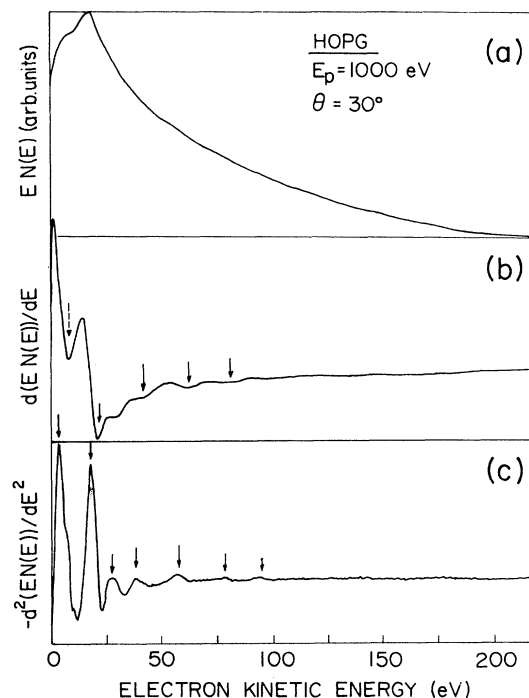


FIG. 1. Secondary-electron-emission spectrum of HOPG measured in the 0–220-eV range using a primary electron-beam energy of 1000 eV, (a)  $EN(E)$  mode, (b)  $dEN(E)/dE$  mode, measurement performed using 6-V peak to peak modulation, and (c)  $-d^2EN(E)/dE^2$  mode.

tive mode only. As observed from Fig. 1, the SEE spectrum is dominated by an intense low-energy peak and a number of lower intensity peaks at higher electron kinetic energies. The SEE structure of graphite up to an energy of 70 eV has been the subject of previous studies<sup>11,16,17</sup> and will not be discussed in the present work. At electron kinetic energies larger than 150 eV some structure was also observed. However, its intensity was very low and of similar amplitude to the noise of our measurements. The energy position of the peaks measured in the first and second derivative modes in the 50–150-eV kinetic-energy range are summarized in Table I.

### B. Dependence on primary electron energy

The dependence of the EFS-SEE spectrum on primary electron energy was performed in order to establish whether the higher-energy SEE structure is associated with (i) unscattered valence electrons (or holes) excited by the primary electron beam or secondary electrons of sufficient energy; or (ii) relaxation of C(1s) core ionization and Auger accompanied processes.

The SEE spectra of cleaved HOPG in the 50–150-eV range are shown in Fig. 2 for primary electron energies of 200, 500, and 1000 eV and an incident angle of 30°. The SEE spectra obtained using primary energies of 500 and 1000 eV are similar. However, for a primary energy of 200 eV, in addition to the SEE peaks, up to an electron

TABLE I. Summary of peaks observed in the extended secondary-electron-emission spectrum of HOPG in the 50–150-eV electron kinetic range. The peaks positions are shown in Figs. 1 and 2. Also, in this table are summarized peaks obtained by the free-electron parabola model calculation, by the CISS (Ref. 26) and reflectivity measurements,  $I_{00}$ , of HOPG (Ref. 27).

$d(EN)/dE$ (eV)	$-d^2(EN)/dE^2$ (eV)	Parabola (eV)	CISS (eV)	$I_{00}$ (eV)
61	57.5	59	53	60
80	78.50	84.50	65	76
100	96.50		68	
115	114	117.56	82	112
128				
144				150

energy of  $-130$  eV, a much more intense structure appears towards the higher-energy range. Further inspection of the spectrum indicates that the additional peaks, in the higher-energy range, are associated with plasmon losses to the primary backscattered beam.

These results show that, within the primary electron energies used in our measurements, the EFS-SEE spectrum is nearly independent of primary electron energies as low as 200 eV [below the binding energy of the C(1s)] at 284.5 eV. This indicates that core-level excitations and Auger-type deexcitation processes are not involved in the production of the EFS-SEE. Also, as the energy differences between the different peaks measured in the spectrum of graphite are not multiples of plasmon energies it is concluded that multiplasmon deexcitation processes are not responsible for the structure of the high-energy SEE peaks.

Based on these considerations, we conclude that the initial electronic process which results in the production of the EFS-SEE peaks involves only excitation of valence

electrons by primary electrons or secondary electrons of sufficient energy and Auger processes of the kind  $C(VVV)$ , where the primary excitation is localized in the valence band.

Not considering autoionization processes and final hole-hole interaction effects, the maximum electron kinetic energy of secondary electrons originating from Auger processes initiated by a valence-band hole is  $-20$  eV. Therefore,  $VVV$  Auger-type processes cannot account for the fine structure in the higher-energy range of the SEE spectrum.

Therefore, it is concluded that the structure in the SEE spectrum of graphite is determined by transitions from all possible initial electronic states to a particular final state. Considering that (i) electron impact ionization cross section above a certain primary electron threshold is a slowly varying function of electron impact energy; (ii) the width of the valence band for graphite is  $-20$  eV; and (iii) no rigid selection rules apply for electron impact ionization. Then, any structure in the SEE spectrum is expected to be mainly determined by final-state effects and not to be strongly dependent on electron-excitation energy. These conclusions are similar to those obtained from previous investigation of the lower-energy range of the SEE spectrum<sup>17</sup> and suggest that the EFS-SEE structure is dominated by final-state electronic effects, whereas initial-state effects are averaged out. The nature of the final states are further assessed in the next sections.

### C. Structural sensitivity

To establish whether the EFS-SEE in the high-energy range is associated with diffraction, band-structure, or EXAFS-like effects, the sensitivity of the spectrum on the electron-beam incident angle, reflecting the orientational dependence of the spectrum, and on the degree of crystal order were investigated. This was achieved by comparing the SEE spectrum of HOPG with that of GC and measuring the SEE spectrum of HOPG as a function of low-energy Ar-ion irradiation dose. By ion irradiation, a gradual amorphization of the HOPG structure is induced through the production of point defects. This process results, at saturation, in an amorphous  $sp^2$  bounded material.

If the extended structure of the SEE spectrum is associated with diffraction or band-structure effects, a depen-

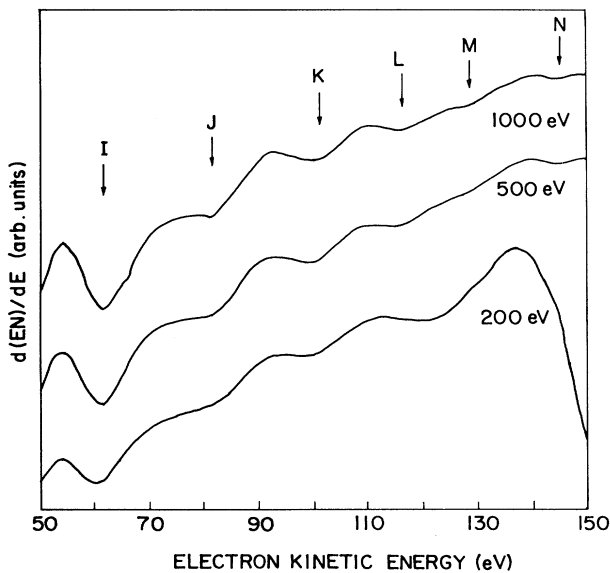


FIG. 2. Secondary-electron-emission spectrum of HOPG in the 50–150-eV range as a function of incident electron-beam energy.

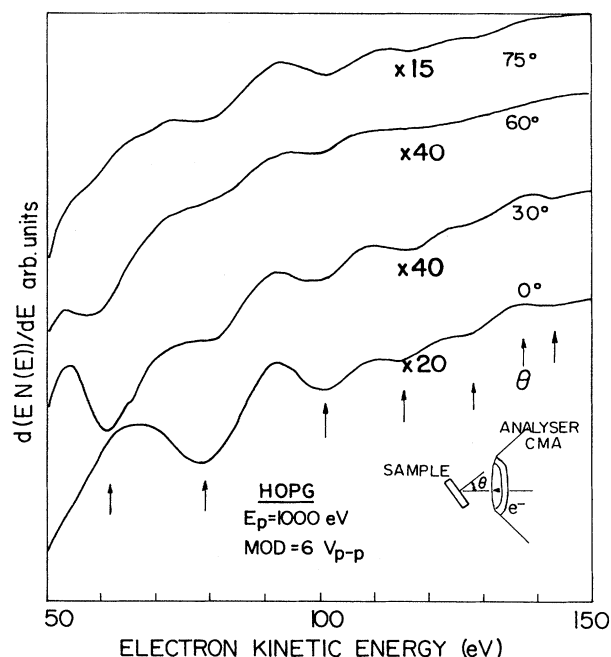


FIG. 3. Secondary-electron-emission spectrum of HOPG in the 50–150-eV range using various primary electron-beam incident angles.

dence on the electron-excitation angle may be expected. In Fig. 3, the SEE spectra in the 50–150-eV range measured for various electron incident angles are shown. The primary energy used in these experiments was 1000 eV. As seen from this figure the SEE spectrum is affected by the electron incidence angle used. A strong angular dependence was also observed in the lower-energy SEE range.<sup>16,20,21</sup> These results should rule out the locally sensitive and radially averaged EXAFS-like origin of EFS-SEE and should favor the diffraction or band-like mechanism.

If the high-energy range of the SEE spectrum is dominated by diffraction or band-structure effects, its structure would be expected to be sensitive to disorder induced by low-energy ion bombardment. The SEE spectra of HOPG measured after 2-keV Ar-ion irradiation are shown in Fig. 4 as a function of the irradiation dose. As observed from these figures very low levels of irradiation result in a gradual smearing of the SEE spectrum. An ion dose of about  $4 \times 10^{14}$  ions/cm<sup>2</sup> is sufficient to smear the entire structure of the SEE spectrum in the 50–150-eV range. Such an ion dose is sufficient to amorphize the near surface region (20–30 Å) of HOPG, thus providing a strong evidence that the EFS-SEE spectrum is strongly affected by crystal order.

To establish whether the EFS-SEES is associated either with diffraction or band-structure effects, the SEE spec-

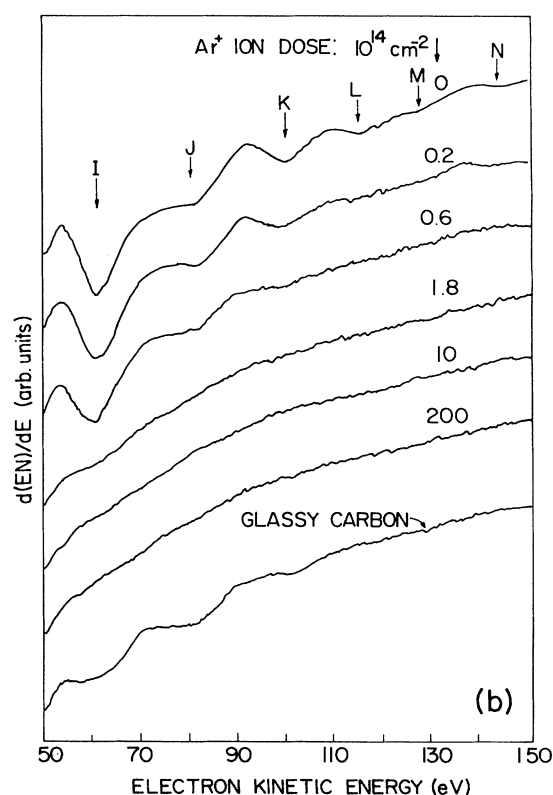
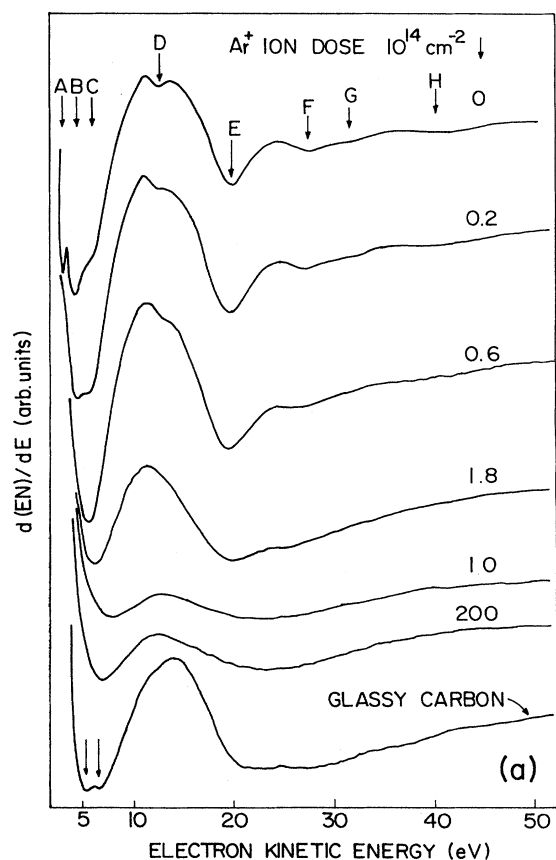


FIG. 4. Secondary-electron-emission spectrum of HOPG as function of 2-keV Ar-ion irradiation dose in the (a) 5–50-eV energy range and (b) 50–150-eV energy range. The last spectrum in both figures is that of glassy carbon (GC).

trum of GC was measured. Glassy carbon has a microscopic turbostratic structure<sup>22</sup> which comprises a network of  $sp^2$  bonded carbon atoms arranged in a hexagonal plane configuration of a few tens of nanometers in size with no correlation between these planes. Therefore, it is a disordered system with a short-range two-dimensional graphiticlike order. The absence of long-range order in GC has two effects. It does not allow for well-defined sharp diffraction patterns<sup>22,23</sup> and it causes a band structure similar to that of graphite, but without any fine details.<sup>24,25</sup> The EFS-SEE spectrum of GC is shown as the last curve in Figs. 4(a) and 4(b). In the low-kinetic-energy region the well-defined peaks observed for HOPG up to an energy of  $-40$  eV are smeared out almost completely for GC. However, in the higher-energy range, above  $-50$  eV, peaks of lower intensity and similar energies to HOPG are observed for GC. This comparison between HOPG and GC reflects the sensitivity of the SEE spectrum to the band structure in both low- and high-kinetic-energy range regions.

Equivalently, the comparison between the EFS-SEES of GC and HOPG suggests that the spectrum in the higher-energy range is more sensitive to short-range crystal order as compared to the lower range of the spectrum. This effect may be explained by considering the wavelength of the secondary electrons and the size of the nanocrystallites in GC. The larger the secondary-electron kinetic energy the shorter their wavelength, therefore, the smaller the volume they sample. Further studies are necessary to fully understand this effect.

#### D. Nature of the extended structure and comparison with other electron spectroscopies sensitive to high-energy excited-electronic states

Our experimental results strongly suggest that the EFS-SEE is associated with the band structure. To further support this conclusion, we compare the extended SEE structure with other electron spectroscopic techniques that reflect high-energy excited-electronic states of graphite. These techniques are core level electron-energy-loss spectroscopy (CEELS); constant initial-state spectroscopy (CISS) (Ref. 26), and electron reflectivity.<sup>27,28</sup> The comparison with C(1s) CEELS was performed *in situ* using our electron spectrometer, whereas the comparison with CISS and electron reflectivity was carried out using published results.<sup>26–28</sup> In the case of CEELS for primary electron energies much larger than the energy loss (so that the dipole approximation applies) the spectrum is expected to display an EXAFS-like structure at energies larger than  $-70$  eV above the C(1s) edge.<sup>4</sup> A comparison between the loss structure of the C(1s) CEELS using a primary energy of 1000 eV and the EFS-SEES was performed (not shown). This comparison revealed that up to  $-60$ -eV features appear in the SEE and EEL spectra at corresponding energies. This suggests that in this energy range both techniques reflect band-structure effects. However, at larger energies the EEL spectrum does not display any structure that may be associated with the extended structure mea-

sured in the SEE spectrum. As it is by now well established that the extended structure in EELS is associated with EXAFS-like states this provides further evidence that the extended SEE structure is not associated with EXAFS-like processes.

Peaks were observed in the CIS spectrum of graphite at 4, 45, 53, 65, 68, and 82 eV.<sup>26</sup> These measurements were performed using the C(2s) level as the initial state and photon energies in the 33–200-eV range. The CIS spectrum of HOPG was successfully explained by describing the propagation of the photoelectron in the crystal field using a multiple-scattering theory involving three carbon atoms.<sup>29</sup> As seen from Table I some of the peaks observed in our SEE spectrum appear at similar energies to those observed in the CIS C(2s) of HOPG. However, most of the peaks observed in our SEE measurements were not obtained in CIS. This is likely to be due to different experimental sensitivity and different selection rules for both spectroscopies. The comparison between the CISS and CEELS results, and the SEE spectrum in the 50–150-eV range strongly supports the notion that the EFS in the SEE spectrum is associated with band-structure effects. This is reinforced by a comparison with electron reflectivity measurements of HOPG as a function of electron kinetic energy.<sup>27</sup> Electron reflectivity measurements of HOPG in the 0–240-eV electron kinetic-energy range display peaks, in the electron range of interest to us, centered at about 60, 76, 112, and 150 eV. As the electron reflectivity spectrum was measured in the  $N(E)$  mode, the energy position of these peaks should be compared with those appearing in the  $-d^2N(E)/dE^2$  spectrum as summarized in Table I. The agreement between the energy position of the peaks measured in the SEE spectrum and electron reflectivity suggests that similar electronic processes are involved in both cases.

In an attempt to qualitatively describe the extended SEE spectrum of HOPG, we calculated the high-energy band structure of HOPG using a very similar model.<sup>16</sup> For the case of a crystalline material, the simplest model to describe high-energy electron states is a free-electron parabola modulated by the periodicity of the particular crystal field and an inner potential. Using a free-electron parabola with an inner potential of  $-16.2$  eV (with respect to the vacuum level) the main peaks in the SEE spectrum of HOPG up to 65 eV were explained.<sup>16</sup> In this model, the inner potential was established (as the only parameter) so that the parabola crosses the TM point at 59 eV measured in angular resolved SEE spectrum of HOPG. The same parabola, in the  $\Gamma K$  direction, crosses at higher energies with the K point at 84.5 eV. In the  $\Gamma M$  direction, the  $\Gamma$  point is crossed at 117.56 eV. These values are close to the 78.5 and 114 eV peaks measured in the SEE spectrum of HOPG. Based on this simple modulated parabola, with an inner potential, the experimental peaks at 57.4, 78.4, and 114 eV are explained. Considering that the free-electron parabola is the simplest possible model used to describe high-energy electron states this agreement is noteworthy. However, the 100, 128, and 144 eV peaks could not be described by this very simple approach.

## IV. CONCLUSIONS

In summary, in the present work, electron-excited extended fine structure in the SEE spectrum of HOPG was investigated. It is concluded that the fine structure originates from electronic processes involving excitation of

the valence electrons by primary electrons and secondary electrons of sufficient energy. Based on the sensitivity of the SEE spectrum to crystal order and its angular dependence, we conclude that the spectrum is dominated by band-structure effects. This conclusion is supported by a comparison with other electron spectroscopic measurements.

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