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## High-energy angle-resolved secondary-electron emission spectroscopy of highly oriented pyrolytic graphite

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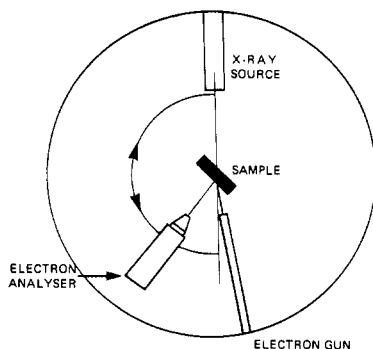
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**Abstract.** The angle-resolved secondary-electron emission (ARSEE) spectra of highly oriented pyrolytic graphite have been measured in the 7–70 eV electron kinetic energy range. A peak observed at  $\approx 59$  eV with  $k_{\parallel} = 1.35\text{--}1.65 \text{ \AA}^{-1}$  was tentatively explained within a semiempirical approach based on a free electron parabola with an inner potential of  $-16.2$  eV (relative to the vacuum level) which crosses the M point at 59 eV. From the crossing of the free electron parabola with the zone centre peaks at 16 eV and 28.5 eV were independently described. These results suggest that the empty density of states for large kinetic energies are well described by a free electron parabola. In the energy range below 30 eV good agreement was obtained with previously published ARSEE experiments. XPS and AES measurements were performed to verify that the 59 eV peak did not originate from an impurity level. After argon ion bombardment the fine structure observed in the ARSEE spectra of HOPG was completely removed.

### 1. Introduction

Secondary-electron emission (SEE) spectroscopy has previously been used to map the empty states of single-crystal graphite [1–5] and of highly oriented pyrolytic graphite (HOPG) (6–11). Very good agreement was obtained with band structure calculation of single-crystal graphite extending 25 eV above the Fermi level (12–13). In the 0–30 eV electron kinetic energy range highly dispersive structure were observed in the angle-resolved SEE (ARSEE) spectra along the  $\Gamma$ –M and  $\Gamma$ –K symmetry line of single-crystal graphite. For HOPG an azimuthal average of the dispersion line occurs due to the random distribution in the  $a$  direction. In angle-integrated measurements electron collection occurs mainly in  $K$ -space regions with high density of states.

In this work we extended the energy range for which ARSEE of HOPG has previously been measured up to 70 eV. This was motivated by observations of a peak at 63 eV in the Auger spectrum of HOPG both by ourselves [14] and others [15–17]. This peak could not be associated with impurities by high sensitivity AES and XPS measurements. In our ARSEE measurements a peak at  $\approx 59$  eV was observed at emission polar angles between  $15^{\circ}$  and  $25^{\circ}$ . This peak was tentatively explained based on a semiempirical approach assuming that the empty states at high energies can be described by a free electron parabola with an inner potential of  $-16.2$  eV (related to the vacuum level), which crosses the M point ( $k_{\parallel} = 1.48 \text{ \AA}^{-1}$ ) at 59 eV, corresponding to the energy position and  $k_{\parallel}$  of the



**Figure 1.** Schematic picture of the system where ARSEE measurements were performed.

peak observed in our ARSEE measurements at 59 eV. It was found that lower-energy peaks at 16 eV and 28.5 eV with  $k_{\parallel} = 0$  were also described by the same parabola.

## 2. Experimental details

Prior to insertion into the UHV system the HOPG ( $10 \times 10 \text{ mm}^2$ ) was freshly cleaved by the standard peeling technique. The amorphous carbon was produced as a thin film by electron beam evaporation onto Si(100) with a thickness of about 400 Å.

Two spectrometers were employed; one for AES and the other for XPS and ARSEE. The former had a base pressure of  $1 \times 10^{-9}$  Torr, and the later  $5 \times 10^{-10}$  Torr. Both systems were equipped with argon ion guns.

The Auger measurements were performed with a Varian CMA equipped with a coaxial electron gun. The primary current was  $1 \mu\text{A}$  and the electron energy  $E_p = 2400 \text{ eV}$ . A 2 V peak-to-peak modulation was used and the spectra were recorded in the  $d(EN(E))/dE$  versus  $E$  mode.

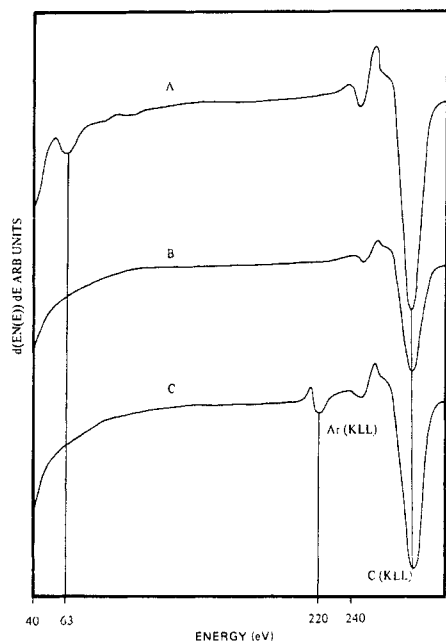
The XPS and ARSEE measurements were performed in a custom designed Vacuum Science Workshops multitechnique angle-resolved electron spectrometer. The XPS measurements employed Al  $K\alpha$  (1486.6 eV) radiation. The ARSEE experiments were carried out using an electron beam energy,  $E_p = 200 \text{ eV}$ , as primary excitation at a fixed angle of incidence  $\theta_i = 45^\circ$  with respect to the surface normal ( $c$  axis). The electron detection was performed using a hemispherical energy analyzer mounted on a goniometer which provided rotation in the plane defined by the electron beam and the normal to the surface sample. The energy resolution of the analyzer was  $\approx 0.5 \text{ eV}$  (250 eV pass energy) and the angular resolution was  $2^\circ$ . The same electron analyzer was used in the XPS measurements. A schematic diagram of the sample position, the x-ray source, electron gun and energy analyzer (EA) is shown in figure 1.

The XPS and ARSEE experiments were performed both before and after *in situ* sample heating at 950 K for 2 h, and similar results were obtained in both cases.

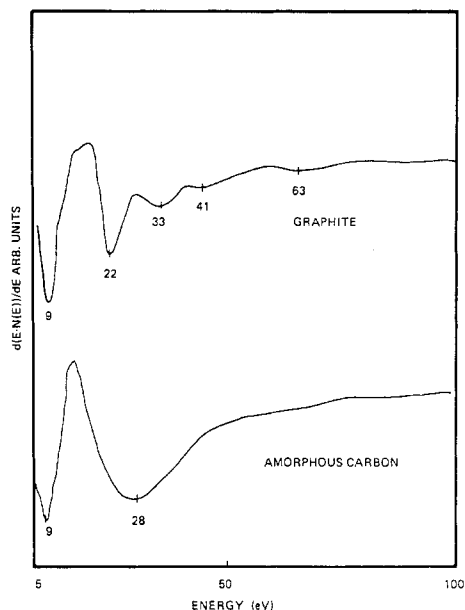
## 3. Results

### 3.1. Auger measurements

The Auger spectra, recorded in the  $d(EN(E))/dE$  vs  $E$  mode, were measured for the as-cleaved HOPG, amorphous carbon (electron beam evaporated) and  $\text{Ar}^+$  ion beam irradiated HOPG cleaved surface ( $6.4 \times 10^{14} \text{ Ar}^+$  ions  $\text{cm}^{-2}$ , 1.5 keV). The spectra in the



**Figure 2.** Auger spectra in the 40–300 eV range. A: HOPG; B: amorphous carbon; C: HOPG after  $6.4 \times 10^{14}$  Ar<sup>+</sup> ions cm<sup>-2</sup> irradiation at 1.5 keV.



**Figure 3.** SEE spectrum in the 5–100 eV as measured with the CMA in the  $d(EN(E))/dE$  mode, for graphite and amorphous carbon.

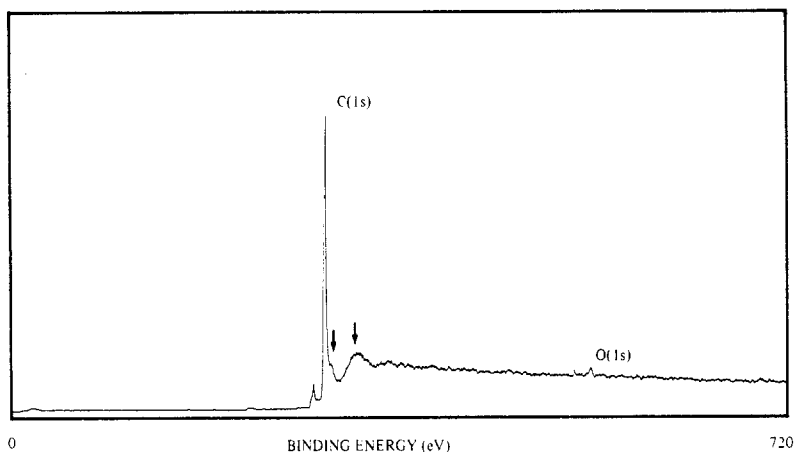
40–300 eV range are shown in figures 2 (A, B, C respectively). As is evident from these figures the C(KLL) Auger line shape is characteristic of the different carbon allotropes (i.e. graphite and amorphous carbon) [15]. For HOPG an additional peak is observed at 63 eV. After Ar<sup>+</sup> irradiation (figure 2, C) this peak disappears. The  $d(EN(E))/dE$  versus  $E$  spectra recorded in the 5–100 eV range for HOPG and amorphous carbon are shown in figure 3. The corresponding spectrum of HOPG after Ar<sup>+</sup> irradiation (not shown) was very similar to that measured for amorphous carbon. As seen from figure 3 the low energy spectrum of HOPG shows distinctive features at 9, 22, 33, 41 and 63 eV whereas for amorphous carbon (or the Ar<sup>+</sup> irradiated HOPG) only the 9 eV peak, together with a broad peak centred at 28 eV are observed. To assess the possibility that the 63 eV peak originates from an impurity the higher energy range (up to 1500 eV) of the Auger spectrum was measured but no high-energy peaks were observed.

### 3.2. XPS measurements

The XP spectrum of the as-cleaved HOPG sample was measured in the 0–720 eV binding energy range. The spectrum is shown in figure 4. Two loss peaks characteristic to graphite were clearly observed at 7 eV and 23 eV to the higher binding energy side of the C(1s) peak (7 eV:  $\pi$ -plasmon, 23 eV: composite bulk plasmon). A small O(1s) peak was also present. The XPS measurements were repeated at higher sensitivity and at grazing angle (to increase the surface sensitivity); however, no peaks additional to that of carbon and the small trace of oxygen were detected.

### 3.3. Angle-resolved secondary-electron emission measurements

The distribution of emitted electrons was measured as function of polar angle in the 7–70 eV electron kinetic range. In figure 5 the ARSEE spectra for different polar emission



**Figure 4.** XP spectrum of HOPG in the 0–720 eV binding energy range. (The arrows refer to the 7 eV and 23 eV plasmon losses.)

**Table 1.** Summary of peak position and  $k_{\parallel}$  as function of emission angle measured in ARSEE experiments. The peak positions were determined as maxima in the  $N(E)$  and  $E$  curves shown in figure 5.

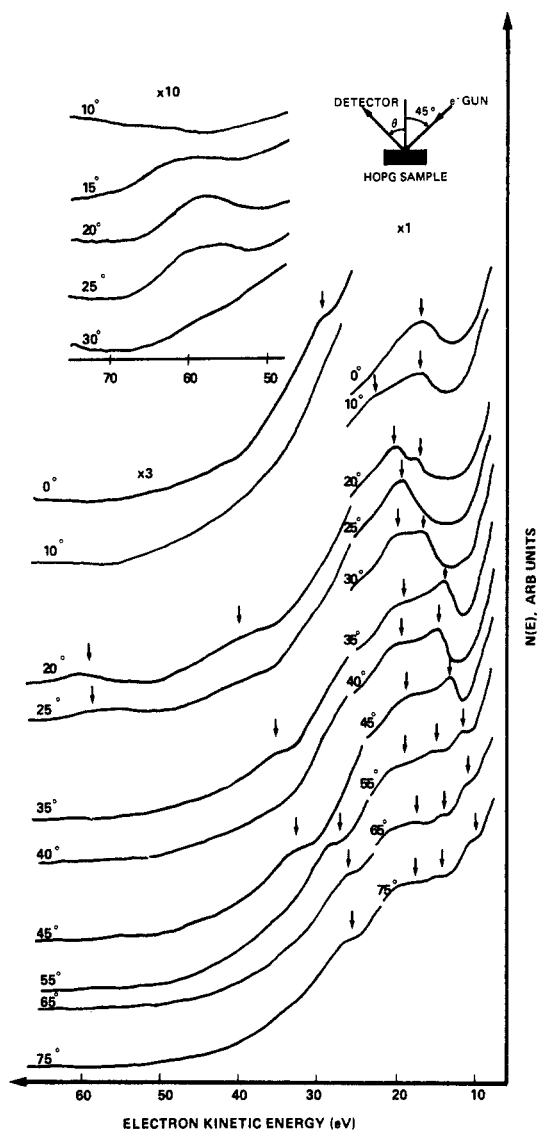
$\theta_e$ (deg)	Peak positions (eV)	$K_{\parallel}$ ( $\text{\AA}^{-1}$ )
0	16.0, 28.5	0, 0
10	17.0, 22.6	0.36, 0.42
20	17.0, 19.8, 40.4, 59.4	0.72, 0.78, 1.11, 1.35
25	18.0, 58.4	0.94, 1.65
30	16.6, 18.9	1.04, 1.11
35	13.5, 19.0, 34.9	1.08, 1.28, 1.73
40	14.4, 19.0	1.25, 1.43
45	12.6, 19.0, 32.2	1.28, 1.58, 2.06
55	10.8, 14.2, 18.1, 27.9	1.38, 1.58, 1.79, 2.22
65	10.2, 13.8, 17.0, 26.0	1.49, 1.72, 1.91, 2.36
75	9.8, 11.6, 17.4, 26.0	1.55, 1.68, 2.06, 2.52

angles are shown. Although superimposed on a large background, well defined peaks appear in the ARSEE spectra which show a strong angular dependence. In particular, a peak at 59 eV is present in the narrow polar angle range between 15° and 25°. In table 1 the peaks marked in the ARSEE spectra of figure 5 are summarized.

After argon ion bombardment of the HOPG surface no fine structure was observed in the ARSEE spectra. In particular, the 59 eV peak was not observed at any emission angle. The irradiation dose was  $1 \times 10^{15}$   $\text{Ar}^+$  ions  $\text{cm}^{-2}$  and the ion energy 1.5 keV.

#### 4. Discussion

Here we attempt to identify the origin of the peak observed at 63 eV in the Auger spectrum (and that at 59 eV in the ARSEE spectrum) of HOPG. However, before embarking on this we first consider the possibility that an impurity could be responsible for this peak. This was rejected on the following grounds:



**Figure 5.** Angle-resolved secondary-electron emission spectra of HOPG in the 7–70 eV electron kinetic range. The arrows show the position of the different peaks in the spectra (maxima in the  $N(E)$  and  $E$  curves).

(i) The low-energy spectrum was calibrated with the Cu(MNN) and Al(LVV) Auger peaks at 61 eV and 67 eV respectively. Based on this calibration the Auger (minimum) peak position was determined as 63 eV, which could not be associated with any impurity. However, since handbook kinetic energy values (particularly for Auger transition involving valence electrons), may be influenced by the chemical environment, the higher energy range was examined for accompanying Auger transitions involving core levels. No such transitions were observed (within the sensitivity of our Auger measurements).

(ii) The XP spectrum of the HOPG sample (figure 4) shows the only impurity to be a small O(1s) trace, even at the highest sensitivity. Each time the peeling procedure was repeated similar results were obtained.

(iii) Instrumental artifacts could not be responsible for the 63 eV peak (nor the

lower energy peaks shown in figure 3) because, following  $\text{Ar}^+$  irradiation (and without changing the sample position), a spectrum without this peak and similar to that measured for amorphous carbon (figure 2, C) was obtained. These results also were reproducible after each peeling procedure.

(iv) The ARSEE spectra also confirm that the 59 eV peak is not due to an impurity, since an Auger peak originating from an impurity would be expected to show an isotropic angular distribution and not the strong emission angle dependence actually observed.

Based on the above considerations we conclude that the lower-energy structure observed in the Auger spectrum is intrinsic to the secondary electron emission spectrum of HOPG.

To gain further insight into the nature of the 63 eV 'Auger' peak we examined the secondary-electron emission spectrum up to 70 eV, extending the 0–40 eV energy range previously studied. The SEE measurements were performed first with the CMA as an analyzer, and are shown in figure 3. The peaks at 22 eV and 33 eV are in good agreement with previous SEE measurements in the 0–40 eV range performed with a CMA [8, 9]. These peaks were previously found to be independent of the primary energy,  $E_p$ , of the exciting electrons (above 50 eV) and were associated with the unoccupied density of states above the vacuum level [7]. Based on band structure calculation they were shown to correspond to the critical point behaviour of bands at zone boundaries [7].

Since the 63 eV peak cannot be associated with a carbon or impurity Auger transition, it would seem likely that its origin is similar to that of the lower-energy peaks, i.e. secondary electrons that, previous to propagation into the analyzer, occupied empty states in the crystal field above the vacuum level.

The peaks observed at 63 eV and at 59 eV in the Auger and ARSEE spectra respectively are considered to have similar origins. The difference in their energy position is attributed to the different measurement modes and conventions of where the peak position is determined. The 63 eV value is measured at the minimum of the  $d(EN(E))/dE$  versus  $E$  mode whereas the 59 eV value is measured at the maximum of the  $N(E)$  versus  $E$  distribution. Nevertheless although these absolute energy values differ the relative energy positions of different peaks in each of these modes are expected to be the same.

In the lower (7–30 eV) energy range our ARSEE spectra are in good agreement with these previously reported [1–7]. There, the  $E(k_{\parallel})$  dispersion lines (where  $k_{\parallel} = (2mE/\hbar^2)^{1/2} \sin \theta_e$ ), were found to correspond to empty states above the vacuum level as calculated for single-crystal graphite [12, 13]. The justification for using band structure calculations for single-crystal graphite to interpret HOPG results lies in the following argument: For energies above  $\approx 5$  eV, for single-crystal graphite, the experimental and calculated dispersion lines  $E(k_{\parallel})$  along the  $\Gamma$ –K direction were found to be similar to those along the  $\Gamma$ –M line [1–5]. All azimuths are thus essentially equivalent, so that effectively makes no difference that in the HOPG case an azimuthal distribution of coverages occurs. Most of the features observed in the ARSEE spectra in the higher energy range were interpreted in terms of such two-dimensional analysis. Three-dimensional effects were found to be important only in the lower energy range ( $< 5$  eV) in which some peaks were associated with the interlayer electronic structure.

The prominent features in the ARSEE spectra measured in our experiments are as follows. At normal emission (which samples the energy states at the  $\Gamma$  symmetry point), peaks at 16.0 eV and 28.5 eV are observed. The peak at 16.0 eV shows a slight dispersion with polar angle, in agreement with band structure calculations. This feature was correlated with a flat  $\sigma$ -band. The 28.5 eV peak shows a clear dispersion to lower energies, and was correlated with a  $\pi$ -band. In the higher energy range a peak is observed for  $\theta_e = 20^\circ$  at 40.4 eV. For  $\theta_e = 45^\circ$  a peak is observed at 32.2 eV decreasing in energy to 26.0 eV

at  $\theta_e = 75^\circ$ . A further peak at  $\approx 59$  eV is observed in the narrow polar angle range  $15^\circ$ – $25^\circ$  (but not at lower or higher angles).

Table 1 summarises the energy position of these peaks, together with the calculated  $k_{\parallel}$ , as function of emission angle.

As in the earlier work, it would be appropriate to compare the present results with band structure calculations. Since, however, these extend only up to  $\approx 25$  eV above the vacuum level a comparison with our higher-energy ARSEE results is not possible (one early band structure calculation [7] does extend up to 55 eV above  $E_F$ ; however in the region of current interest above 25 eV its bands are in disagreement both with later calculation [12] and experiment [6], so it has not been employed.

As a general principle, though, secondary electrons can be promoted to the empty levels above  $E_F$ , whereafter those above  $E_v$  can decay into the vacuum. Their contribution to the emission current will be proportional to the density of states at each energy. Thus in general any such ARSEE derived feature could be expected to correspond to regions in the Brillouin zone with high density of states (particularly at zone boundaries where the slope of the  $E$  versus  $k$  curves is at a minimum) [24, 25].

Now, it has been proposed that the important final states in the photoemission of solids, above  $\approx 20$  eV, can be described well by a free electron parabola with an inner potential correction [18–21]. It is suggested that when secondary electrons are located on this parabola, and particularly at zone boundaries, they are likely to be emitted into the vacuum and appear as prominent structure in ARSEE spectra.

An important parameter to be established is the inner potential,  $U$ , of this parabola. For this work, its value was empirically determined so that it crosses the M point ( $1.48 \text{ \AA}^{-1}$ ) at an energy of 59 eV, as this peak has a  $k_{\parallel}$  value in the  $1.35$ – $1.65 \text{ \AA}^{-1}$  range (table 1). The inner potential so calculated was  $-16.2$  eV relative to the vacuum level ( $-11.2$  eV relative to  $E_F$ ). This free electron parabola was drawn in the Brillouin zone and taking  $\varphi = 4.6$  eV for the work function, it starts from  $-16.2$  eV relative to the vacuum level at the  $\Gamma$  point, in the  $\Gamma M$  direction it crosses the high-symmetry points at  $-7.84$  eV (M point),  $17.22$  eV ( $\Gamma$  point),  $59$  eV (M point), etc.; while in the  $\Gamma K$  direction it crosses the high symmetry points at  $-5.04$  eV (K point),  $28.42$  eV ( $\Gamma$  point) and  $84.19$  eV (K point), etc.

The above value of  $16.2$  eV for the inner potential is comparable to the value of  $19$  eV derived by early workers to describe multiple-scattering resonance effects in low-energy electron diffraction studies of single-crystal graphite (22), and of  $14.5 \pm 1.0$  eV derived from final state effects as studied by synchrotron-radiation-excited angle-resolved PES of single-crystal graphite [23].

As this free electron parabola crosses the  $\Gamma$  point at  $17.22$  eV and  $28.42$  eV it could also be anticipated that peaks might be observed at these energies in the ARSEE spectrum at normal emission. Such peaks were indeed observed at  $16$  eV and  $28.5$  eV in very good agreement with the anticipated values.

Following argon irradiation the fine structure in the ARSEE spectra disappears. This suggests that the high-energy electronic structure is strongly dependent on crystallinity. Secondary-electron emission measurements as function of irradiation dose showed that already for doses as low as  $5 \times 10^{13} \text{ Ar}^+$  ions  $\text{cm}^{-2}$  (2 keV ion energy) the SEE spectrum is modified [14]. This result suggests that SEE spectroscopy can be used as an indicator of the degree of crystal damage.

Finally, in relation to the SEE spectrum measured with the CMA, since the  $63$  eV has been identified with that at  $59$  eV in the ARSEE spectrum, so also should the  $33$  eV peak correspond to that at  $28.5$  eV. Likewise, although their energy difference is somewhat



greater, it is suggested that the 22 eV measured with the CMA and the 16 eV ARSEE peaks also have the same origin. This additional discrepancy is likely due to the dispersion of this peak, as observed in the ARSEE spectrum, where it moves from 16 eV for normal emission to  $\approx 19$  eV for  $k = 1.5 \text{ \AA}^{-1}$ . Hence the larger collection angle of the CMA would result in an average of these relative values.

## 5. Conclusion

ARSEE spectra of HOPG were measured in the 7–70 eV range. A peak previously observed at 63 eV in the Auger spectrum of HOPG was identified as a true secondary-electron emission intrinsic to HOPG. After  $\text{Ar}^+$  irradiation ( $6.4 \times 10^{14} \text{ Ar}^+ \text{ ions cm}^{-2}$ ) the SEE spectrum becomes very similar to that of amorphous carbon. In the ARSEE spectrum this peak was observed at 59 eV in the  $15^\circ$ – $25^\circ$  emission angle range (corresponding to  $k_{\parallel} = (1.35\text{--}1.65) \text{ \AA}^{-1}$ ). The origin of this peak was interpreted on the basis of a free electron parabola with an inner potential of  $-16.2$  eV (relative to the vacuum level) which crosses the M point ( $k_{\parallel} = 1.48 \text{ \AA}^{-1}$ ) at 59 eV. The same parabola gives the energy position of other peaks observed in the ARSEE spectra. It is therefore concluded that the high-energy electronic structure of HOPG at zone boundaries is described qualitatively quite well by this free electron parabola.

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