Loss Structure in the Electron-Energy-Loss Excitation Continuum of a Semimetal

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We have observed a new type of feature in electron-energy-loss spectra, which is not related to a particular discrete loss channel, although it is a peak which exhibits dispersion. Calculations show that this feature is due to the kinematical nature of the dipole scattering probability function and the unusual form of the surface response function generated by the semimetallic band structure of graphite. The peculiarly intense continuum of electron-hole pair excitations allows the loss structure to be observed.

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It has recently been shown that electron-energy-loss spectroscopy (EELS) can be used to probe the surface response function $g(\mathbf{q}_\parallel,\omega)$ of a metal,[1,2] semiconductor,[3,4] or thin metal film.[4,5] Contributions to the imaginary part of the surface response function, Img, in a metal produce a continuum tail of electron-hole pair[2] and phonon[6] excitations, as well as Stoner excitations in a ferromagnet.[7,8] Specifically, the probability (in dipole scattering theory) that an incident electron is scattered from state $\mathbf{k}$ to $\mathbf{k}'$ is the product of two terms:

$$P(\mathbf{k},\mathbf{k}') = A(\mathbf{k},\mathbf{k}')\mathrm{Im}g(\mathbf{q}_\parallel,\omega), \quad (1)$$

where $A(\mathbf{k},\mathbf{k}')$ is a kinematic factor and $g(\mathbf{q}_\parallel,\omega)$ is the surface response function in terms of wave vector $\mathbf{q}_\parallel$ and energy $\hbar\omega$ of the excitations.[1,9] In the case of a semimetal, such as graphite, the intensity of the excitation continuum is about 2 orders of magnitude greater (in comparison with the elastic-peak intensity) than for metals or crystals with a band gap (see below). As a consequence, we are able to observe that the above interrelation between the kinematic factor and the surface response function in the overall scattering probability acts to generate a dispersing "ghost" loss peak which is not due to any particular discrete loss channel but is a consequence of the intrinsic kinematics of the electron-energy-loss probability function. Moreover, the increased intensity of the loss continuum makes it possible for us to identify particular characteristics with the electronic band structure of semimetallic graphite.

The EELS spectra were obtained with a conventional single-pass hemispherical spectrometer system. The analyzer and specimen can be independently rotated in the scattering plane, and data were taken both in the specular direction and away from specular in both directions. The samples used were of highly ordered pyrolitic graphite (HOPG)[10]; thus the experiment averages over all directions parallel to the surface in the Brillouin zone, though the band structure is close to cylindrically symmetric in the energy range we have studied.[11,12] The crystals were cleaved in air with tape and cleaned by heating to 1300 K in UHV, which removed contaminant peaks initially evident in the EELS spectrum.

Figure 1 shows the EELS spectrum obtained in the specular reflection position at an incident energy of 9 eV and a nominal incident angle[13] of 60°—note that the magnification factor is only 20, i.e., the loss continuum is highly intense compared with other materials.[2-8] The inset in Fig. 1 shows schematically the proposed origin of the continuum[14]—electron-hole pair excitations are represented in terms of the Π-symmetry energy bands in graphite near the Fermi level. The Fermi level intersects the Π bands at the symmetry point K on the vertical edge of the hexagonal Brillouin zone.[11,12] The density of states is zero at E_F but rises sharply both above and below E_F in semimetallic graphite. Thus, we can excite vertical transitions from zero energy upwards, as sketched in Fig. 1 (inset). These are the transitions which occur when there is no parallel momentum transfer, i.e., when $\mathbf{q}_\parallel = 0$, as is approximately the case for small energy excitations in the specular direction. Such transitions are not possible, however, in semiconductors, insulators, or metals; viz., in the two former cases, the band gap prevents the electron-hole pair con-

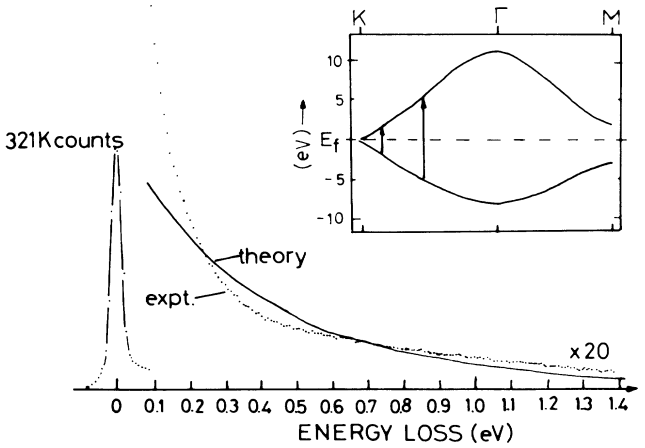

FIG. 1. EELS spectrum in specular direction ($\Delta\theta = 0°$). Incident energy $E_i = 9$ eV; incident angle $\theta_i \simeq 60°$. Inset: Π bands of graphite (Ref. 11) showing interband (optical) transitions about Fermi energy, E_F.

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tinuum from extending down to zero energy, while in the metallic case the only low-energy excitations allowed are nonvertical intraband transitions requiring finite $\mathbf{q}_\parallel$.

To confirm the origin of the intense loss continuum of Fig. 1 we have calculated the spectrum given by Eq. (1) (at each energy loss the absolute loss intensity peaks sharply on specular, demonstrating that the scattering mechanism is long-range dipole scattering[2]). The kinematical factor $A(\mathbf{k},\mathbf{k}')$ has a simple analytic form (see below). We calculate the surface response function using the random-phase approximation (RPA) which gives[15,16]

$$\mathrm{Im}g(\mathbf{q}_\parallel,\omega)=\frac{2\pi^2}{q_\parallel A}\sum_{\mathbf{k},\mathbf{k}'}(n_{\mathbf{k}}-n_{\mathbf{k}'})\,|\langle\mathbf{k}'|\phi|\mathbf{k}\rangle|^2\delta(\epsilon_{\mathbf{k}'}-\epsilon_{\mathbf{k}}-\hbar\omega), \tag{2}$$

where $|\mathbf{k}\rangle$ are the electronic eigenstates of the substrate with energies $\epsilon_{\mathbf{k}}$ and occupation numbers $n_{\mathbf{k}}$. A is the surface area and ϕ is the potential induced in the solid by a periodic external field. We approximate the states $|\mathbf{k}\rangle$ of the graphite Π bands with a tight-binding[17] model which gives a good description of the band structure in the vicinity of the Fermi level, including the 0.8-eV splitting of the degenerate bands at the K point due to interlayer interactions.[11,12,18] In previous work[15] the RPA expression of Eq. (2) has been used to calculate the electron-hole pair response of a jellium surface; ours is the first such calculation for a realistic band structure. A verification of the accuracy of the calculated response function is found in the function's $q\rightarrow 0$ (optical) limit where it agrees well in both form and magnitude with that derived from experimental optical data via the relation

$$g(0,\omega)=[\epsilon(\omega)-1]/[\epsilon(\omega)+1], \tag{3}$$

where $\epsilon=(\epsilon_1\epsilon_3)^{1/2}$ with ϵ_1 and ϵ_3 the optical dielectric constants (from Daniels *et al.*[19]) perpendicular and parallel to the c axis. $\mathrm{Im}g(0,\omega)$ obtained from either the present theory or these optical data is about 2 orders of magnitude larger than for a typical metal,[2,16] thus explaining the anomalously large continuum intensity. The full line of Fig. 1 represents the calculated EELS spectrum (integrated over the detector aperture). Because both the crystal reflectivity and the analyzer detection efficiency are unknown, the theoretical intensity has to be normalized arbitrarily. The calculation confirms that vertical (optical-type) electronic transitions can account for the continuum distribution which is observed.[14]

The spectrum 10° off specular towards the surface normal, Fig. 2, reveals an interesting change in the shape of the loss continuum. The intensity is now seen to rise again beyond about 0.6 eV. The inset in Fig. 2 illustrates what is going on. When we are off specular, $\mathbf{q}_\parallel\neq 0$ at small energy loss and the allowed transitions in $\mathbf{k}$ space are no longer nearly vertical. For a given $\mathbf{q}_\parallel$ this can be represented by our shifting the bands above E_F rigidly by $\mathbf{q}_\parallel$ and then looking for vertical transitions. It can be seen that a finite energy (E_c) is now required before transitions can take place. The actual energy E_c is given by $E_c=cq_\parallel$, where c is the minimum slope of the Π bands at the K point.[19] This implies that the surface response function $\mathrm{Im}g(\mathbf{q}_\parallel,\omega)$ will be zero if $\omega<cq_\parallel$.

Our calculated response function exhibits this behavior: Its contribution (together with the relevant kinematic factor) to the EELS spectrum is shown by curve A, Fig. 2, and produces the observed rise in intensity in the higher energy-loss region. The reason why the experimental intensity does not go to zero in the cutoff region below 0.3 eV is, we propose, because of diffuse elastic scattering prior to energy loss. A double-scattering event, in which the electron is first elastically scattered towards the analyzer and then inelastically scattered, will produce a weaker emulation of the specular spectrum (i.e., Fig. 1) superimposed on the off-specular spectrum. Thus, in Fig. 2, we add curve B, the specular spectrum of Fig. 1 scaled according to the ratio of the elastic peak heights, to the calculated single-scattering curve A (the latter is normalized arbitrarily because of the undetermined angular dependence of the analyzer detection efficiency). The result is the solid line ($A+B$, Fig. 2) which correctly reproduces the behavior of the experimental spectrum. Thus the observed shape of the

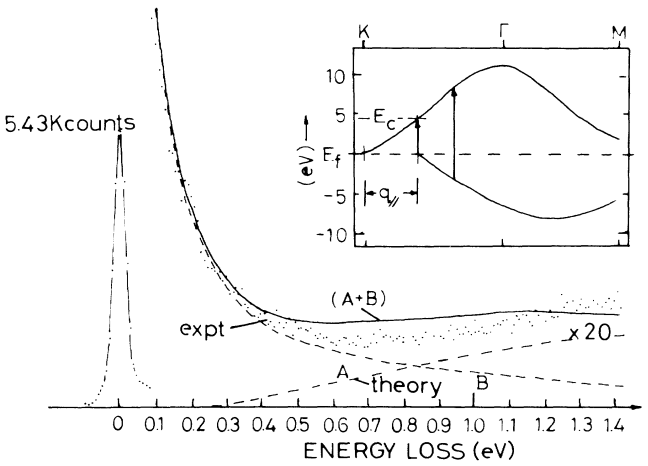

FIG. 2. EELS spectrum 10° off specular towards surface normal ($\Delta\theta=-10°$). $E_i=9$ eV; $\theta_i\simeq 60°$. Curve A is the calculated single-scattering loss function and curve B the contribution from diffuse elastic scattering followed by energy loss (see text). Inset: Π bands of graphite, showing finite-$\mathbf{q}_\parallel$ transitions of minimum energy E_c, represented by shifting of the bands relative to each other.

spectrum is due to the cutoff effect for nonzero $\mathbf{q}_\parallel$ transfer arising from the detailed shape of the graphite Π bands, together with double-scattering events involving diffuse elastic scattering.

The EELS spectrum taken 10° off specular in the other direction, i.e., towards the surface [Fig. 3(a)] shows another effect, i.e., a rise followed by a decrease in the background intensity to produce a strong loss peak centered around 0.7 eV. This structure disperses upwards in energy with increasing angle away from specular (see below), behaving like a dispersing feature arising from interband transitions between discrete energy band states. However, this peak does not correspond to a particular loss channel. Rather its origin is to be found in the combined effect of the response function $\mathrm{Im}g(\mathbf{q}_\parallel,\omega)$ and the kinematic factor in the scattering probability function [Eq. (1)]. The rise in intensity above $\simeq 0.3$ eV loss energy can be accounted for by the band-structure cutoff effect at finite $\mathbf{q}_\parallel$, Fig. 2, and this is demonstrated by the dashed theoretical curve for $\mathrm{Im}g(\mathbf{q}_\parallel,\omega)$ shown in Fig. 3. The kinematic factor has the form[1]

$$A(\mathbf{k},\mathbf{k}') = \frac{2}{(ea_0\pi)^2}\frac{1}{\cos\theta_i}\frac{k'}{k}\frac{q_\parallel}{(q_\parallel^2+q_\perp^2)^2}. \tag{4}$$

We note especially that A is zero at $q_\parallel=0$, provided $q_\perp\neq 0$, causing the scattering probability to vanish. At any particular angle away from specular towards the surface, the kinematic condition $q_\parallel=0$ (i.e., $\mathbf{k}'_\parallel=\mathbf{k}_\parallel$) is satisfied at one particular energy loss. The curve for $A(\mathbf{k},\mathbf{k}')$ in Fig. 3(a) shows that the zero in the kinematic factor 10° off specular towards the surface occurs at 1.1 eV. (On specular, $q_\parallel=0$ at zero energy loss, but $q_\perp=0$ there also, and so the kinematic factor does not have such a node.) To get the scattering probability which corresponds to what the experiment actually measures we multiply together the kinematic factor and the response function and integrate over the finite collection angle of the analyzer (2.5°). The integration smears the kinematic node zero near 1.1 eV into a dip, as the calculated total scattering probability [full line of Fig. 3(a)] shows. Thus the observed loss peak near 0.7 eV arises from the band-structure cutoff which reduces the intensity at lower energies together with the kinematic factor node which reduces the intensity above it. The peak is, in this sense, "kinematically induced"—it would not be seen but for the kinematic factor.[20] A dip in intensity due to the zero of the kinematical factor will always be observed in dipole electron scattering if Img is sufficiently intense to allow measurements to be made near the energy loss where the kinematic factor vanishes. Observation of the type of peak seen in Fig. 3(a) depends also upon Img being small for small energy losses; in the case of a semimetal, this arises from the band-structure–induced cutoff effect discussed above in connection with Fig. 2.[21]

As an illustration of the dispersion of the loss features observed in Fig. 3(a), Fig. 3(b) shows the energy of the kinematically induced minimum as a function of angle away from specular towards the surface.[22] Considering experimental uncertainties in determination of the absolute electron beam energy and the precise angle of incidence, the deviations from the theory's predictions are satisfactorily small.[23] The key point is that the dispersion behavior of the observed peak and of the minima in Fig. 3(a) does occur and is predicted by the model

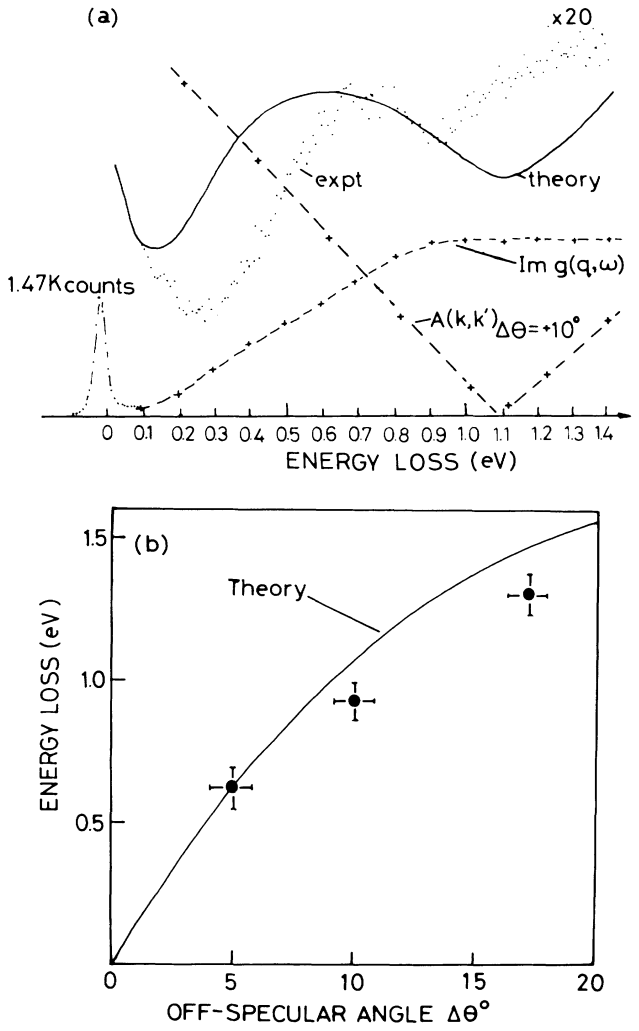

FIG. 3. (a) EELS spectrum 10° off specular towards the surface ($\Delta\theta=+10°$) ($E_i=9$ eV; $\theta_i\simeq 60°$), showing a peak in the loss spectrum at 0.6 to 0.7 eV due to the effect of the kinematic factor $A(\mathbf{k},\mathbf{k}')$ at $=+10°$, and the surface response function $\mathrm{Im}g(\mathbf{q}_\parallel,\omega)$, combined to give the scattering-probability curve (full curve, theory), which also includes the low-energy double-scattering tail on the elastic peak (see discussion of Fig. 2 in text). (b) Energy of the "kinematic dip" [observed at 0.9–1 eV in (a)] as a function of angle ($\Delta\theta$) away from the specular direction towards the surface. Full line, theory; filled circles, experimental points.

presented here.

In conclusion, we have shown that the EELS spectrum of a semimetal (in this case graphite) is hallmarked by a big increase in the probability for exciting electronic excitations at low energy, as compared with a metal or semiconductor. Both the shape of the band structure near the Fermi level and the kinematic factor in the loss probability (whose effect is exposed only because of the intensity of the excitations observed) produce distinctive structure in the EELS spectra away from specular. This structure has been reproduced by a theoretical calculation which derives the surface response function $\mathrm{Im}g(\mathbf{q}_{\parallel},\omega)$ from the Bloch functions of graphite near the Fermi level and is validated by optical data. For a finite parallel momentum transfer, these excitations vanish below a critical frequency. A dispersive loss peak is seen which we have shown to originate in the combination of the kinematic factor and the surface response function in the dipole scattering probability function. The observations also serve to confirm the essential correctness of the surface-response-function dipole scattering theory.

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[21]At higher energy losses than shown in Fig. 3(a) the continuum is found to fall again, thus generating a second ghost peak. The theory predicts that this will happen as the kinematic factor decays again.

[22]We compare the kinematically induced minimum position rather than the peak maximum because of the influence of the diffuse scattering background at lower energies on the peak profile.

[23]If the incident angle is taken as 67° rather than 65° the theory curve passes through all the experimental points.