Plasmon Dispersion and Damping at the Surface of a Semimetal

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We have investigated for the first time the dispersion and the momentum dependence of the damping of the surface plasmon of a semimetal, the low-energy π band plasmon of graphite, using high resolution electron energy loss spectroscopy. The measured dispersion is positive. In contrast to all previous studies on metals, the width of the plasmon loss decreases substantially with increasing parallel momentum and appears to collapse to a residual value beyond a critical momentum. These findings are explained in terms of the coupling to interband transitions in semimetallic graphite.

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In recent years considerable progress has been made in the understanding of the surface electronic excitation spectra of metal surfaces [1–4]. The dispersion of surface plasmons on metal surfaces has attracted great interest [1], both experimentally [1,2,4–10] and theoretically [2,3,11]. Moreover, an intriguing similarity has been identified between the dispersion of the surface plasmon as a function of the wave vector and the size dependence of the plasmon resonance frequencies in atomic clusters [12]. This relationship has recently been verified in the case of the simple metals [13], Ag [14] and Hg [15]. The surface plasmon dispersion of simple metals is now well understood in terms of a model, which, in the long wavelength limit, links the initial dispersion to the position of the centroid of induced charge associated with the plasmon field [3,11,16]. In contrast, there is still some controversy for noble metals, where deviations from this simple model are observed due to band structure effects. Here we present the first study of the plasmon dispersion at the surface of a semimetal. Using high resolution electron energy loss spectroscopy (HREELS) we have investigated the dispersion of the low-energy π band plasmon on graphite, a prototypical example of a semimetal whose band structure is well known [17–20] and which should therefore be a good model system for the examination of the interaction of the plasmon with interband transitions. The temperature dependence of the energy and linewidth of this plasmon were recently studied by Jensen *et al.* [21]. Furthermore, Li, Hock, and Palmer [22] and Hock *et al.* [23] have used K and O_2 adsorption on graphite to study the effect of charge transfer on the energy of this surface plasmon. In our measurements we find that the dispersion of the graphite plasmon is positive over the momentum range investigated. In contrast with all previous studies of surface plasmons, we also find that the plasmon width decreases with increasing parallel momentum $q_\parallel$, and collapses to a residual value beyond a critical wave vector $q_{\parallel c}$. We show that this behavior is a consequence of the low-energy continuum of electron-hole pair excitations characteristic of a semimetal, which dominates the plasmon damping up to a critical parallel momentum $q_{\parallel c}$.

The HREELS spectra presented in this Letter were obtained with a high resolution electron-energy loss spectrometer (LK 2000) mounted in an ultrahigh-vacuum (UHV) chamber with a base pressure of 5×10^{-10} mbar. The measurements were carried out with an incident electron energy of 50 eV and an incident angle of 60° with respect to the sample normal, while the scattering angle was varied in order to measure the dispersion. The samples used were highly oriented pyrolytic graphite (HOPG). The crystals were cleaved in air before mounting on a rotatable, variable temperature sample holder and cleaned regularly in UHV by electron bombardment heating to ~1100 K. Sample cleanliness was monitored using HREELS. All HREEL spectra were recorded at a sample temperature of 605 K, as at this elevated temperature the plasmon is shifted to higher energy and therefore is more clearly visible [21]. During these measurements the sample was radiatively heated using a W filament mounted behind the sample. The sample temperature was monitored by a Chromel-Alumel thermocouple mounted in close vicinity to the sample and was regulated to within 3 K by adjusting the filament current.

Figure 1(a) shows a series of HREEL spectra obtained for five different scattering angles. In all cases a discrete energy-loss feature is observed, superimposed on an intense sloping "background" caused by electron-hole excitations [24,25]. In line with previous studies [21] we attribute this discrete feature to the excitation of the π band plasmon polarized with $\mathbf{E}\|\mathbf{c}$. Since HREELS is a surface sensitive technique, what we are seeing is the π band plasmon at the surface of graphite. Because graphite is a layered material, the distinction between this "surface plasmon" and the corresponding "bulk plasmon" is blurred. The loss peak in Fig. 1(a) can be clearly seen to move to higher energy in the loss spectrum as the parallel momentum transfer $q_\parallel$ is increased. Furthermore, its width appears to decrease with increasing momentum

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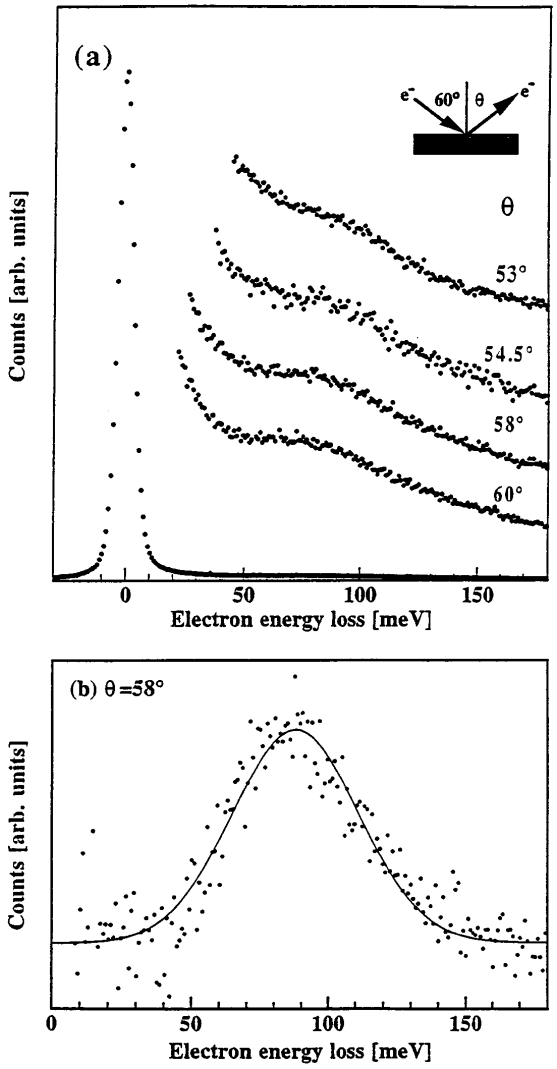

FIG. 1. (a) HREELS spectra of graphite obtained at different emission angles θ. The incident beam energy is 50 eV in each case, and all spectra were recorded with an incident angle of 60° with respect to the sample normal. During these measurements the sample temperature was 605 K. (b) Plasmon peak after background subtraction for an emission angle $\theta = 58°$. The solid line represents a Gaussian fit to the peak.

transfer $q_\parallel$. At $q_\parallel = 0$ the peak is positioned at ~86 meV and has a FWHM of ~65 meV.

In order to extract the position and the width of the plasmon mode from the experimental electron energy loss spectra [see Fig. 1(b) as an example] the background was interpolated into the region of the plasmon loss feature and subtracted. The function used for the interpolation of the background had the analytical form $f(x) = a(x - x_0) + b + c(x - x_0)^{-1} + d(x - x_0)^{-2} + e(x - x_0)^{-3}$, which gave the best fit to the shape of the background [26]. The loss feature thus obtained was fitted with a Gaussian [see Fig. 1(b)]. We also checked that the kinematic factor in the dipole scattering probability function [24,27] has a negligible effect on the plasmon energy and width so derived.

The energy of the plasmon mode as a function of parallel momentum transfer is shown in Fig. 2 for values of $q_\parallel$ from 0 to 0.4 Å^{-1}. In this momentum range the plasmon energy increases from ~86 to ~93 meV. Within the experimental error bars, the energy rises monotonically with increasing momentum transfer over this range, in particular, the initial dispersion seems to be weak, but positive. On closer inspection, the plasmon energy appears to level off at higher parallel momentum transfer.

Of particular interest in this study is the dependence of the linewidth of the graphite surface plasmon on the parallel momentum $q_\parallel$. In order to extract the linewidth of the surface plasmon, ΔE_P, the experimentally observed loss width, ΔE_{loss}, has to be corrected according to the formula

$$\Delta E_P = \sqrt{\Delta E_{\text{loss}}^2 - \Delta E_{\text{exp}}^2}\,, \tag{1}$$

where ΔE_{exp} is given by the transfer width of the spectrometer. ΔE_{exp} depends on the energy resolution of the spectrometer and its angular acceptance [1]. The latter term is connected to the slope of the plasmon dispersion and arises because the spectrometer samples a region in momentum space $\Delta q_\parallel$ due to its finite angular acceptance (under the conditions used in this experiment we estimate $\Delta q_\parallel = 0.06$ Å^{-1}). Since the plasmon dispersion is only ~6 meV over the whole momentum range investigated (0.4 Å^{-1}), the contribution due to the finite angular acceptance can be neglected compared to the energy resolution of the spectrometer of ~9 meV.

The $q_\parallel$ dependence of ΔE_P is shown in Fig. 3. We find that the width of the graphite surface plasmon decreases substantially as $q_\parallel$ increases, from a FWHM of ~65 meV at $q_\parallel = 0$ to ~32 meV for values of $q_\parallel \approx 0.28$ Å^{-1}, and appears to remain constant for higher $q_\parallel$. This behavior contrasts strongly to the behavior found on metals, which

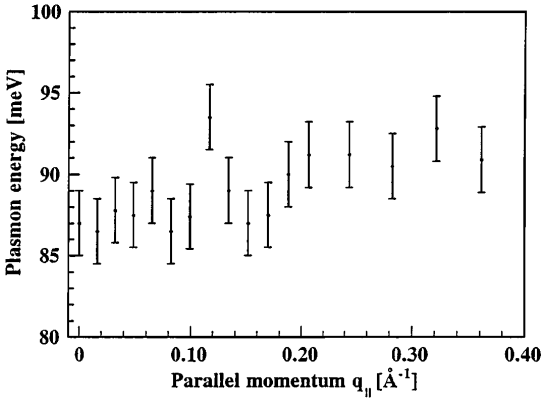

FIG. 2. Experimentally observed plasmon energy, derived after background subtraction, as a function of parallel momentum transfer $q_\parallel$. The sample temperature during these measurements was 605 K.

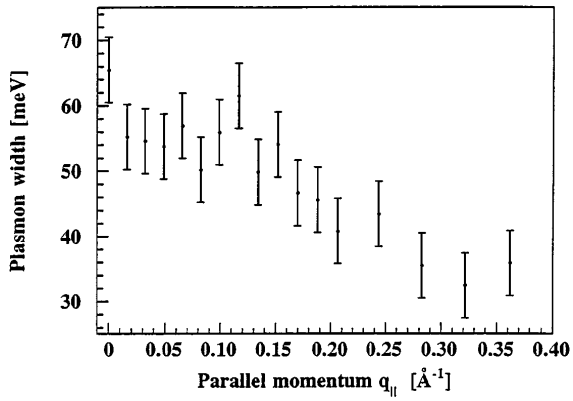

FIG. 3. Experimentally derived plasmon width (FWHM), as a function of parallel momentum transfer $q_\parallel$ at a sample of 605 K.

slow an increase of the surface plasmon width [1,2,8], which may be preceded by an initial small decrease in some cases [1,10].

We propose that the behavior observed for the graphite plasmon is a direct consequence of the semimetallic band structure of graphite. The origin of this effect can be seen most simply in terms of the two-dimensional single layer graphite band structure. The sp^2-hybridized carbon atoms form strong bonds within each layer, giving rise to the graphite σ bands. The remaining P_z orbitals point normal to the layer and overlap to form the π bands. For a single graphite layer the symmetry group leads to a degeneracy of the π bands at the corner of the hexagonal Brillouin zone (the K point) [17,18]. Near the K point the bands have a linear dispersion relation

$$\varepsilon(\mathbf{k}) = \pm p_0|\mathbf{k}|\,, \tag{2}$$

where $\mathbf{k}$ is the two-dimensional wave vector measured from the K point. The band slope parameter p_0 can be calculated from interatomic dipole matrix elements, yielding a value of $p_0 = 4.17$ eV Å [25]. The Fermi level intersects the π bands at the K point, leading to a very small density of states at the Fermi level and resulting in the semimetallic behavior of graphite. The density of states rises sharply both above and below E_F.

Because of this semimetallic band structure vertical interband electron-hole pair excitations are allowed at all energies, even at small wave vectors. Jensen *et al.* [21] showed that the plasmon lifetime is dominated by decay into these excitations [see Fig. 4(a)]. The behavior of this decay channel is thus qualitatively different from that in conventional metals, where plasmons can only decay through single electron-hole excitations if their wave vector exceeds a certain critical value [6,28]. For a finite parallel momentum transfer, $q_\parallel \neq 0$, the allowed transitions in $\mathbf{k}$ space are no longer vertical. For a given $q_\parallel$ this can be represented by shifting the bands below E_F rigidly by $q_\parallel$ and then looking for vertical transitions [Fig. 4(b)]. It is easy to see that transitions

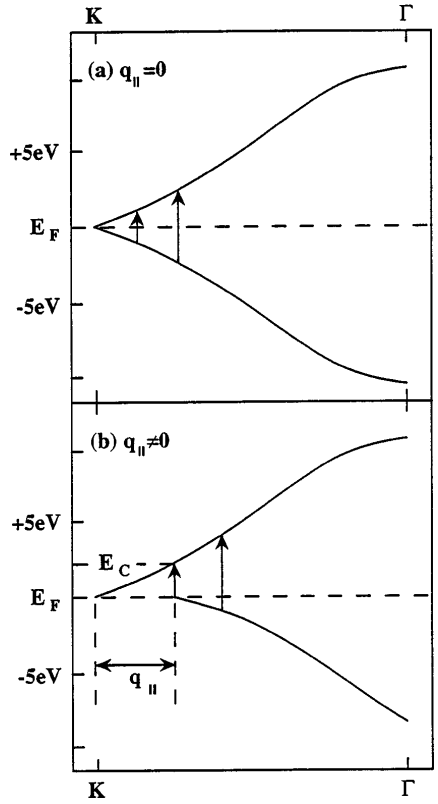

FIG. 4. Schematic diagram of the π bands of graphite showing interband transitions, for (a) $q_\parallel = 0$ and (b) finite parallel momentum $q_\parallel \neq 0$ and minimum energy E_c. In (b) the excitations are represented as vertical transitions between shifted bands.

can only occur if they exceed a critical energy $E_c = p_0 q_\parallel$, where p_0 is the minimal band slope parameter [25]. This simple cutoff condition is modified when the more complicated three-dimensional band structure, which allows for interlayer interactions, is included. Because of this interaction the π bands are split into four discrete bands of the K point [18]. The cutoff condition now becomes $E < E_c = p_0 q_\parallel - 2\gamma_1$ where $2\gamma_1 = 0.8$ eV corresponds to half the width of the π bands at the K point [25].

As the parallel momentum of the surface plasmon increases, the number of decay channels decreases, since only interband transitions above the critical energy E_c (which rises with increasing $q_\parallel$) are permitted. On this basis we expect the lifetime of the plasmon to increase, and therefore its linewidth to decrease, with increasing $q_\parallel$, in harmony with our observations (Fig. 3). From the cutoff condition we estimate a value of $q_{\parallel c} = 0.22$ Å^{-1}, above which the plasmon can no longer decay into interband electron-hole pair excitations. This value is broadly consistent with our experimental data (Fig. 3), where the width appears to "bottom out" beyond $q_\parallel \approx 0.28$ Å^{-1}. We believe that the residual damping of the plasmon at higher $q_\parallel$ arises from other mech-

anisms, such as phonon scattering and multiple electron excitations.

We believe that the observed dispersion of the plasmon can be accounted for by the same model. It is well known that interband transitions not only influence the width of the surface plasmon, but also its position. Examples of such an influence can be found in many metals, e.g., Ag, where the plasmon frequency is strongly shifted by the presence of the $d \rightarrow s$ transitions [29]. In graphite, at $q_{\parallel} = 0$, interband electron-hole pair excitations ranging from energy $E = 0$ to several eV exist, as described above. In contrast to Ag, where only one transition at a well defined energy exists, this whole band of interband transitions can influence the plasmon and shift its energy. It was shown by Venghaus [30] that the influence of these interband transitions leads to a redshift of the plasmon energy at $q_{\parallel} = 0$. For larger $q_{\parallel}$, as explained above, a lower cutoff energy E_c exists and interband transitions with energies below this critical energy E_c are not permitted. With increasing $q_{\parallel}$ (and therefore increasing E_c), the band of allowed interband transitions therefore shifts in energy further away from the plasmon energy resulting in a smaller influence on the plasmon energy. For very large $q_{\parallel}$, where this band will be energetically well separated from the plasmon excitation, the energy of the plasmon is therefore expected to converge to the value determined by the free carrier density and the static polarizability of the bound electrons. One therefore expects an initial positive dispersion of the plasmon which levels off for higher values of $q_{\parallel}$. This is consistent with our observations (Fig. 2).

In summary, we have, for the first time, measured the dispersion and the momentum dependence of the damping of the surface plasmon of a semimetal, the low-energy π band plasmon of graphite. We find that the dispersion is positive over the momentum range investigated. In contrast to metals, the width of the plasmon decreases with increasing $q_{\parallel}$ and appears to collapse to a residual value beyond a critical wave vector of $q_{\parallel} \approx 0.28$ Å^{-1}. We believe that both findings are results of the semimetallic band structure of graphite and can be explained in terms of the low-energy interband electron-hole pair excitations, which not only constitute the main damping channel for the plasmon at low $q_{\parallel}$, but are also responsible for the observed shift in plasmon energy.

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