Temperature-Dependent Plasmon Frequency and Linewidth in a Semimetal

E. T. Jensen,[a] R. E. Palmer, and W. Allison
Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

J. F. Annett
Physics Department, The Pennsylvania State University, 104 Davey Laboratory, University Park, Pennsylvania 16802
(Received 11 July 1990)

High-resolution electron-energy-loss spectroscopy of the surface of graphite reveals a discrete loss feature attributed to the excitation of a π-band plasmon polarized with $\mathbf{E} \parallel \mathbf{c}$. The frequency of the plasmon is found to be strongly temperature dependent. This arises from the contribution of thermally generated carriers to the plasma frequency, as confirmed by explicit calculations using the graphite band structure. From the observed temperature dependence of the plasmon width, we also obtain quantitative details of the plasmon decay channel, which is found to be dominated by the low-frequency electron-hole pair excitations characteristic of a semimetal. Similar effects are expected in other semimetals.

PACS numbers: 73.20.Mf, 71.45.Gm, 79.20.Kz

High-resolution electron-energy-loss spectroscopy (HREELS) has recently been used to make several important observations of new phenomena in the surface-plasmon properties of metals.[1-4] Deviations from the jellium model due to band-structure effects have been an important theme of these studies. In this Letter we demonstrate two novel effects in the plasmon spectrum of graphite. These effects are consequences of the unusual semimetallic band structure and are quite different from plasmons in metals. The first effect is that in semimetals the energies of low-energy plasmons may be very strongly temperature dependent. We have observed the energy of the π-band $\mathbf{E} \parallel \mathbf{c}$ plasmon in graphite, first identified by Boyle and Nozieres,[5] increase by a factor of 2 as the temperature is changed from 150 to 400 K. Second, the linewidth of the plasmon is also strongly temperature dependent. We show that this is a consequence of the low-energy continuum of electron-hole pair excitations which exists in semimetals,[6] and which causes strong plasmon damping at all temperatures and wave vectors. In contrast, plasmons in conventional metals only have significant decay into electron-hole pairs if their wave vector exceeds a certain critical value.[2,7] These temperature dependences of frequency and linewidth have not been observed in previous studies of plasmons in graphite or other semimetals, nor have they been predicted theoretically, even though they are straightforward consequences of the semimetallic band structure. We have confirmed our interpretations of the temperature dependences of both the graphite plasmon energy and the linewidth by theoretical calculations, which are in quantitative agreement with our data.

HREELS spectra were obtained using a spectrometer based on conventional single-pass hemispherical dispersing elements, housed in a diffusion and ion pumped UHV chamber with a base pressure of $<2\times10^{-10}$ mbar. The samples used were of highly oriented pyrolytic graphite (HOPG).[8] The crystals were cleaved in air with tape, mounted in a cryogenic sample holder similar to one previously described,[9] and cleaned in UHV by resistive heating to 1100 K. The sample temperature was measured with a Rh-Fe four-wire resistance sensor in good thermal contact with the sample surface. The HREELS spectra obtained below room temperature were recorded as the sample holder slowly warmed up after cooling with liquid N_2; data taken at temperatures above 300 K were obtained while the sample slowly cooled down after resistive heating.

Figure 1 shows a series of HREELS spectra obtained over a range of sample temperatures (152–384 K) with an incident beam energy of 55 eV and in the specular direction. A discrete loss peak is observed at each temperature, superimposed on an intense sloping "background" caused by electron-hole pair excitations.[6] Previous HREELS studies of graphite at lower electron impact energy have observed only a shoulder in the loss spectrum at room temperature.[10] The loss peak in Fig. 1 can clearly be seen moving out to higher frequency in the loss spectrum as the sample temperature is raised; at 310 K its frequency is 53 meV. In previous HREELS measurements we have characterized both the phonon spectrum of graphite[11] and the electron-hole pair continuum,[6] and neither of these can explain the discrete loss feature in Fig. 1. Transmission HREELS data from bulk graphite at (presumably) room temperature[12] show two loss features assigned to plasmon modes, at 45 and 128 meV, and comparison with optical reflectivity measurements leads to the conclusion that these are polarized with $\mathbf{E}$ parallel and perpendicular to the c axis, respectively.[13] Thus we identify the temperature-dependent loss peak in Fig. 1 with the plasmon mode polarized with $\mathbf{E} \parallel \mathbf{c}$. The small shift in frequency between our data and the transmission HREELS results may arise from the difficulty of accurately subtracting the loss

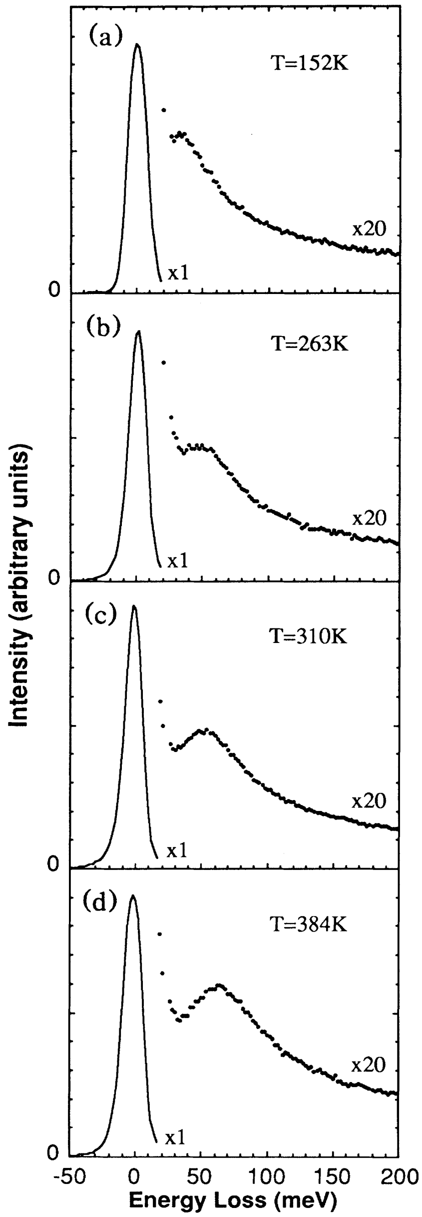

FIG. 1. HREELS spectra of graphite obtained at a series of sample temperatures. The incident beam energy is 55 eV in each case, and the spectra were all recorded in the specular scattering direction ($\theta_i = \theta_f = 60°$). The discrete loss feature, assigned to a π-band plasmon, shifts upwards in frequency as the temperature is raised.

background in Ref. 12.

In Fig. 2 we plot the frequency of the plasmon mode as a function of sample temperature. The frequency we plot is extracted from experimental loss spectra, of which those shown in Fig. 1 are examples, by subtracting a background given by the loss spectrum obtained at 20 K,[14] where no discrete loss peak is visible, and fitting the loss feature thus obtained with the dipole scattering

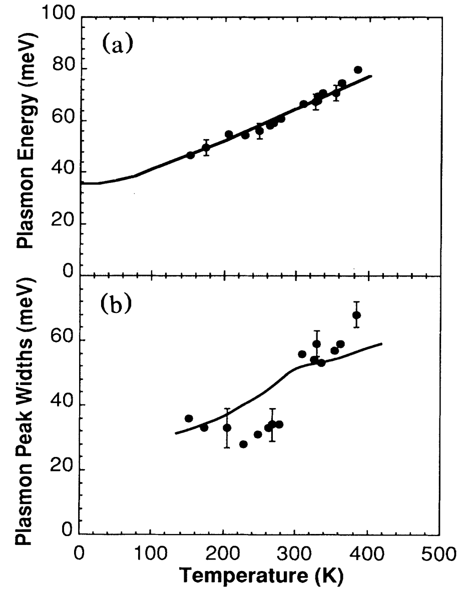

FIG. 2. (a) Experimentally derived plasmon frequency ω_p in graphite, after background subtraction, as a function of temperature (points). The solid line shows the plasmon frequencies calculated from the graphite band structure, using $\varepsilon^0 = 1.25$. (b) The experimentally observed (points) and calculated (solid line) plasmon linewidths as a function of sample temperature, showing the marked increase in peak width as the temperature is increased.

HREELS loss function[6,15] using a Drude dielectric function for the plasmon. The plasmon frequency plotted in Fig. 2(a) is seen to rise distinctly and monotonically with temperature. Indeed, the plasmon frequency changes by a factor of 2 on raising the temperature from 150 to 400 K. This effect has not been observed previously in any of the previous measurements of this plasmon.[12,13,16] Previous calculations[17,18] of the plasmon frequency neglected the substantial effects of finite temperature demonstrated in Figs. 1 and 2.

At the qualitative level, a consideration of the band structure of graphite is helpful in forming a physical picture that can account for the observed temperature dependence. Graphite has a layer structure, and sp^2 hybridization of the carbon $2p$ orbitals leads to two sets of bands (σ and π). To first approximation the π and π^* bands meet at the K point in the Brillouin zone, through which the Fermi level passes, leading to a very small density of states at the Fermi level, $n(E_F)$. The density of states $n(E)$ rises rapidly both above and below E_F, yielding the familiar semimetallic behavior of graphite.[18] The plasmon frequency is small (40–100 meV) because of the smallness of $n(E_F)$. Thermal excitation of electrons from the valence band and into the conduction band is expected to radically alter the population of carriers (electrons and holes) involved in the π-band plasma resonance. This thermal population of electrons in the conduction band is directly evident in the energy-loss spectrum, as a temperature-dependent energy-gain wing corresponding to the annihilation of electron-hole pairs generated thermally at high temperature.[19] Thus, at higher temperature, we expect the density of carriers to rise and with it the plasma frequency, qualitatively accounting for the effect so graphically illustrated in Figs. 1 and 2(a). Thermal excitation of carriers is, of course, well known in doped semiconductors, and in those materials this effect can also lead to temperature-dependent dielectric properties.[20]

In order to test this explanation of the observed temperature-dependent plasmon energy quantitatively, we have carried out calculations of the graphite plasmon frequencies (for $\mathbf{E} \parallel \mathbf{c}$) as a function of temperature, as also shown in Fig. 2(a). The plasmon occurs at a frequency ω_p where the c-axis dielectric function $\varepsilon(\omega)$ vanishes. In the random-phase approximation (RPA) the c-axis dielectric function can be written as

$$\varepsilon(\omega) = \varepsilon^0 - \Omega_p^2/\omega^2 , \tag{1}$$

where ε^0 is the contribution from interband transitions and $-\Omega_p^2/\omega^2$ is the contribution from intraband transitions.[18] It is straightforward to show that at finite temperatures Ω_p^2 is given by

$$\Omega_p^2 = -\frac{e^2}{\hbar \pi^2}\int_{-\infty}^{\infty} dE \frac{df(E)}{dE}\left(\int d^2k \frac{v_i v_j}{|\mathbf{v}|}\right). \tag{2}$$

Here $\mathbf{v}$ is the band velocity, and the wave-vector integral is over the constant-energy surface with energy E. In this equation, temperature dependence arises both because of the width of the Fermi distribution $f(E)$ [i.e., $f(E)$ is an explicit function of kT] and because $f(E)$ depends upon the chemical potential which also varies with temperature, results which can be physically interpreted in terms of a thermal population of carriers involved in the plasma resonance. The theoretical curve in Fig. 2(a) was calculated by numerical evaluation of Ω_p from the integral in Eq. (2). We used the Slonczewski-Weiss-McClure parametrization of the band structure near the Fermi surface[8] with the *ab initio* parameter values obtained by Tatar and Rabii.[18] As a check, the low-temperature limit of our results agrees with the zero-temperature value obtained by Tatar and Rabii.[18] Assuming that the $\mathbf{E} \parallel \mathbf{c}$ interband dielectric function is a real constant, ε^0, over the frequency and temperature ranges of interest, the calculated plasmon frequency follows from Eq. (1).[21] Values of ε^0 present in the literature vary widely,[13,22] so we treat it as a free parameter. The full theory curve in Fig. 2(a) was obtained by taking $\varepsilon^0 = 1.25$, which gives excellent agreement both in the temperature dependence and in the absolute values of the plasmon energy.

In Fig. 2(b) we plot the width of the plasmon as a function of temperature. The width is seen to rise monotonically as the temperature increases. In principle, contributions to the damping of the plasmon could arise from various mechanisms, such as phonon scattering and electron-hole pair excitation. Theoretically, the width can be derived from the imaginary part of the dielectric function, and Fig. 2(b) shows the width calculated by introducing into Eq. (1) a term corresponding to the imaginary part of the interband dielectric function:

$$\varepsilon(\omega) = \varepsilon^0 + 4\pi i \sigma(\omega)/\omega - \Omega_p^2/\omega^2 . \tag{3}$$

The interband optical conductivity $\sigma(\omega)$ is calculated from the graphite band structure using standard formulas.[23] The EELS loss function, $\mathrm{Im}[-1/\varepsilon(\omega)]$, calculated from Eq. (3) shows the plasmon peak at ω_p superimposed upon a background continuum due to interband electron-hole pair excitations, which we have discussed elsewhere.[6] The plasmon-peak width derived from Eq. (3) is plotted in Fig. 2(b), and agrees well with the experimental values. This leads us to the conclusion that the plasmon lifetime is dominated by decay into interband electron-hole pair excitations. In a normal metal the decay of a plasmon into electron-hole pair excitations is severely limited by energy-momentum conservation laws, and plasmons may only decay through this channel if their wave vector exceeds a certain critical value.[2,7] Here, because of the semimetallic band structure, electron-hole pair excitations are allowed at all energies, even at small wave vectors. The plasmon decay channel in semimetals, such as graphite, is thus qualitatively different from that in conventional metals.

Finally, we have calculated the plasmon frequency as a function of doping the graphite with impurities which move the position of the Fermi level. We find that as the Fermi level is either increased or decreased away from the minimum in the density of states $n(E)$ the plasmon frequency increases and its temperature dependence becomes weaker. This fact has some important implications. First, the experimental results in Fig. 2 are inconsistent with calculations for doped graphite, confirming that our results represent intrinsic undoped graphite and impurities are not a significant factor. Second, it implies that the temperature dependence of the plasma frequency in a metal, where $n(E_F)$ is large, will be a tiny fraction of the $T=0$ value, whereas in other semimetallic materials, where $n(E_F)$ is low, e.g., As, Sb, and Bi,[24] the effect is expected to be much more significant. The plasmon mode recently observed in Sb films on GaAs(110) (Ref. 25) seems like an excellent candidate where such behavior might be observed. In the case of graphite, one can test the theoretical prediction by deliberately adsorbing dopants (e.g., alkali metals) on the surface to act as charge donors, and experiments on K/graphite are currently in progress.

In conclusion, we have demonstrated by experimental measurements and theoretical calculations that in a typical semimetal, graphite, low-energy plasmons may be strongly temperature dependent. The plasmon frequency is temperature dependent because of carriers thermally excited from the valence to the conduction band. The plasmon linewidth is dominated by decay into electron-hole pair excitations, a decay channel forbidden in conventional metals except at large plasmon wave vectors. Finally, it is interesting to note that the band structure of the flux-phase model[26] of high-temperature superconductors is remarkably similar to that of graphite near the Fermi level, and one may speculate as to whether similar temperature-dependent plasmon effects may be evident.

We are most grateful to Toby Duffield, Sergei Esipov, and Milton Cole for helpful discussions. This research was supported by the Royal Society. E.T.J. thanks the Cambridge Commonwealth Trust and the University of Victoria for support through a scholarship.

---

[a]Present address: Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, Canada M5S 1A1.

[1]K.-D. Tsuei, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. **63**, 2256 (1989).

[2]S. Suto, K.-D. Tsuei, E. W. Plummer, and E. Burstein, Phys. Rev. Lett. **63**, 2590 (1989).

[3]K.-D. Tsuei, E. W. Plummer, A. Liebsch, K. Kempa, and P. Bakshi, Phys. Rev. Lett. **64**, 44 (1990).

[4]M. Rocca and U. Valbusa, Phys. Rev. Lett. **64**, 2398 (1990).

[5]W. S. Boyle and P. Nozieres, Phys. Rev. **111**, 782 (1958).

[6]R. E. Palmer, J. F. Annett, and R. F. Willis, Phys. Rev. Lett. **58**, 2490 (1987); J. F. Annett, R. E. Palmer, and R. F. Willis, Phys. Rev. B **37**, 2408 (1988).

[7]D. Pines, *Elementary Excitations in Solids* (Benjamin/Cummings, Reading, MA, 1963), Chap. 3.

[8]M. S. Dresselhaus and G. Dresselhaus, Adv. Phys. **30**, 139 (1981).

[9]R. E. Palmer, P. V. Head, and R. F. Willis, Rev. Sci. Instrum. **58**, 1118 (1987).

[10]C. Oshima, T. Aizawa, R. Souda, Y. Ishizawa, and Y. Sumiyoshi, Solid State Commun. **65**, 1601 (1988).

[11]J. L. Wilkes, R. E. Palmer, and R. F. Willis, J. Electron Spectrosc. Relat. Phenom. **44**, 355 (1987).

[12]J. Geiger, H. Katterwe, and B. Schroder, Z. Phys. **241**, 45 (1971).

[13]H. Venghaus, Phys. Status Solidi (b) **81**, 221 (1977).

[14]E. T. Jensen, Ph.D. thesis, University of Cambridge, 1990 (unpublished). This procedure for subtracting the background omits the weak temperature dependence in the intensity of the loss continuum, which scales with $n_\nu+1$, where $n_\nu=1/[\exp(h\nu/kT)-1]$. However, this factor tends to be compensated by an observed broadening of the quasielastic peak width at low temperature, and we estimate uncertainties in the extracted plasma frequencies of only around ± 3 meV.

[15]J. E. Demuth, B. N. J. Persson, F. Holtzberg, and C. V. Chandrasekhar, Phys. Rev. Lett. **64**, 603 (1990); B. N. J. Persson and J. E. Demuth, Phys. Rev. B **42**, 8057 (1990).

[16]Y. Sato, J. Phys. Soc. Jpn. **24**, 489 (1968).

[17]A *pressure* dependence of the plasmon frequency was predicted by K. Nakao, J. Phys. Soc. Jpn. **47**, 208 (1979).

[18]R. C. Tatar and S. Rabii, Phys. Rev. B **25**, 4126 (1982).

[19]R. E. Palmer, Ph.D. thesis, University of Cambridge, 1986 (unpublished).

[20]M. Cardona, Phys. Chem. Solids **17**, 336 (1960); Phys. Rev. **121**, 752 (1961); W. E. Bron, S. Mehta, J. Kuhl, and M. Klingenstein, Phys. Rev. B **39**, 12642 (1989); J. A. Stroscio and W. Ho, Phys. Rev. Lett. **54**, 1573 (1985); J. A. Stroscio and W. Ho, Phys. Rev. B **36**, 9736 (1987). None of these measurements directly observed a plasmon loss peak, but indirectly inferred temperature-dependent, plasmon effects.

[21]This result only strictly holds in the limit of infinite plasmon lifetime τ. The values of ω_p presented in Fig. 2 account for the finite values of τ, which are obtained from the spectra using a Drude dielectric function.

[22]R. Klucker, M. Skibowski, and W. Steinmann, Phys. Status Solidi (b) **65**, 703 (1974).

[23]L. G. Johnson and G. Dresselhaus, Phys. Rev. B **7**, 2275 (1973).

[24]X. Gonze, J.-P. Michenaud, and J.-P. Vigneron, Phys. Rev. B **41**, 11827 (1990).

[25]C. Mariani, M. G. Betti, and U. del Pennino, Phys. Rev. B **40**, 8095 (1989); G. Annovi, M. G. Betti, U. del Pennino, and C. Mariani, Phys. Rev. B **41**, 11978 (1990).

[26]M. J. Rice, Y. R. Wang, and E. J. Mele, Phys. Rev. B **40**, 5304 (1989).