COMMENTS AND ADDENDA

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Large anisotropy in the dynamic structure factor of graphite

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Inelastic x-ray scattering studies of single-crystal graphite with the direction of $\vec{k}$, the momentum transfer, parallel or perpendicular to the C axis reveal a significant qualitative difference in the $|k|$ dependence of the plasmon mode. The results along the A axis are similiar to and reveal the same anomalies as those previously reported for Li, Be, Al, and Si. The C-axis results, however, are in semiquantitative agreement with mean-field-theory predictions.

Recent inelastic x-ray scattering experiments have extensively probed the dynamic structure factor $S(k,\omega)$ of a wide variety of systems including Li, Be, Al, Si, and A-axis graphite.[1-3] These experiments have demonstrated that the evolution of the plasmon properties of those systems as a function of momentum transfer $\vec{k}$ seem to be similar when scaled according to electron-gas parameters. All those light elements deviate qualitatively from mean-field predictions in the region of momentum transfer $1 \leq k/k_F \leq 2$, where k_F is the Fermi momentum of the free-electron gas. The main source of the deviation was identified as arising from the persistence of a plasmonlike mode in that momentum-transfer region. The flat and somewhat negative dispersion of such a plasmonlike excitation was interpreted[2,4] as arising from incipient short-range order in the electron gas in those systems.

In this work we find that C-axis graphite does not display the anomalous plasmonlike excitation, but rather its spectrum agrees semiqualitatively with mean-field predictions. After presentation of the data, the reasons for the gross anisotropy in graphite will be discussed with particular emphasis on its implications for understanding plasmons in solid-state electron gases.

The measured scattered intensity $I(\vec{k}, \omega)$ for weak scattering of non-relativistic x rays is quite generally related to the inverse dielectric function $[\epsilon(\vec{k}, \omega)]^{-1}$, i.e.,[5]

$$I(\vec{k},\omega) = \left(\frac{d\sigma}{d\Omega}\right)_0 S(\vec{k}, \omega) , \tag{1}$$

$$S(\vec{k},\omega) = (k^2/4\pi e^2)\,\mathrm{Im}[1/\epsilon(\vec{k},\omega)]^{-1} . \tag{2}$$

Here $\vec{k}, \omega$ are the momentum and energy transfer involved in the scattering process, and $(d\sigma/d\Omega)_0$ is the Thomson cross section.

The experimental apparatus and procedure is as described previously.[1,2] The experiments are performed by first fixing the scattering angle θ and thus the momentum transfer $|k|$, where

$$|k| = 2k_1 \sin(\tfrac{1}{2}\theta) , \tag{3}$$

and k_1 is the momentum of the incident photon. The sample is then oriented with its C or A axis along the direction of momentum transfer. The spectrum of scattered x rays is then analyzed using a double-crystal Bragg spectrometer. The measured data are processed to remove the thermal diffuse peak, background, and $K\alpha_2$ component in the same manner as previously described.[1] The data were taken with the graphite crystal at helium temperature to minimize the large thermal diffuse scattering.

In Fig. 1, we give the results for $I(\vec{k}, \omega)$ for various values of the magnitude of k with $\vec{k}$ either parallel to the A axis [Fig. 1(a)] or to the C axis [Fig. 1(b)]. The difference between the two directions is immediately obvious. The difference is more clearly displayed in Fig. 2, where the C axis and A axis data for $k/k_F = 1.42$ ($k_F = 2.37$ Å^{-1})

are compared with each other and with the results of a random-phase-approximation (RPA) calculation, i.e., conventional random phase approximation using the Lindhard dielectric function with no band structure effects included. The data in all the figures are uncorrected for the essentially Lorenztian experimental resolution function (4.5-eV full width at half-maximum). The theoretical results have however been smeared with the experimental resolution function. Figure 2 shows the absence of the plasmonlike excitation for the C-axis results as well as the essential qualitative agreement for those results with the RPA calculation. It is clearly very tempting when looking at Fig. 2 to conclude, as was done in Ref. 2, that the A-axis data are comprised of an RPA-like piece (as found for the C axis) plus the additional plasmonlike excitation.

In Fig. 3 are plotted the A-axis and C-axis peak positions in units of the plasma frequency ($\hbar\omega_p$

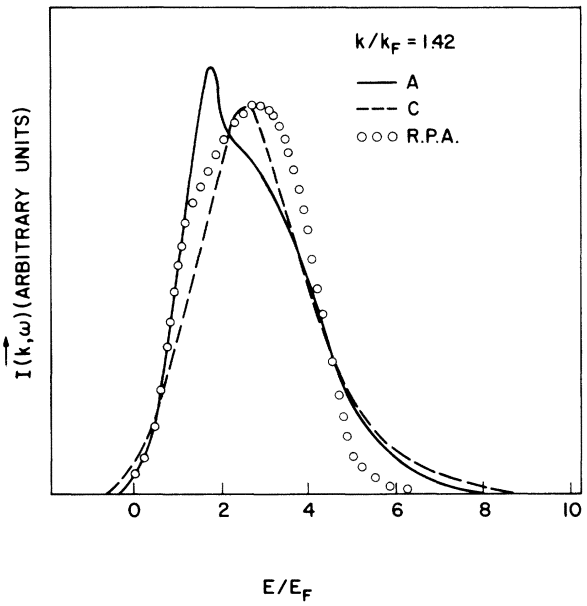

FIG. 2. For a momentum transfer to $|k/k_F| = 1.42$, the measured spectrum with k along the A axis (solid line) and k along the C axis (dashed line) are compared with each other and with RPA calculations (open circles).

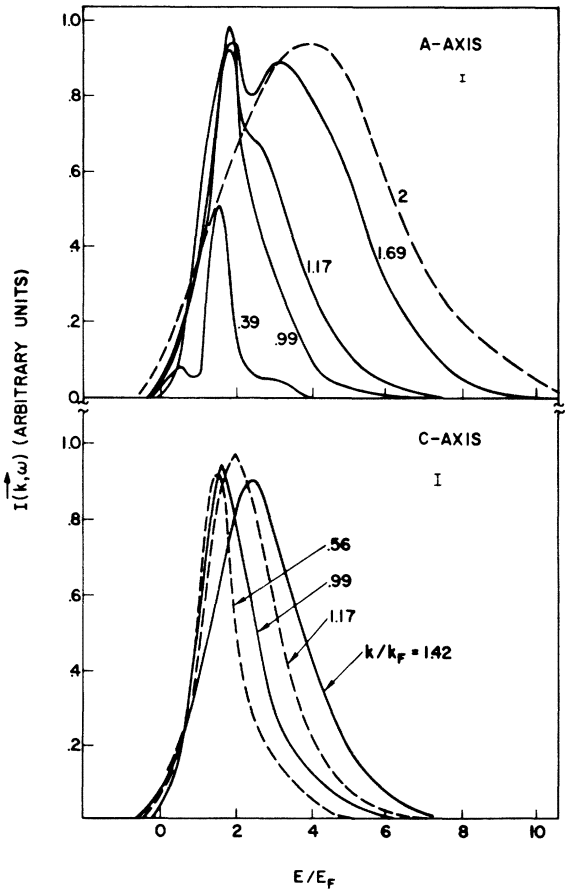

FIG. 1. Scattered intensity $I(\vec{k}, \omega)$ for various values of $|k/k_F|$ with $\vec{k}$ either parallel to the A axis or $\vec{k}$ parallel to the C axis. The intensity is arbitrary and the energy axis is in units of E/E_F.

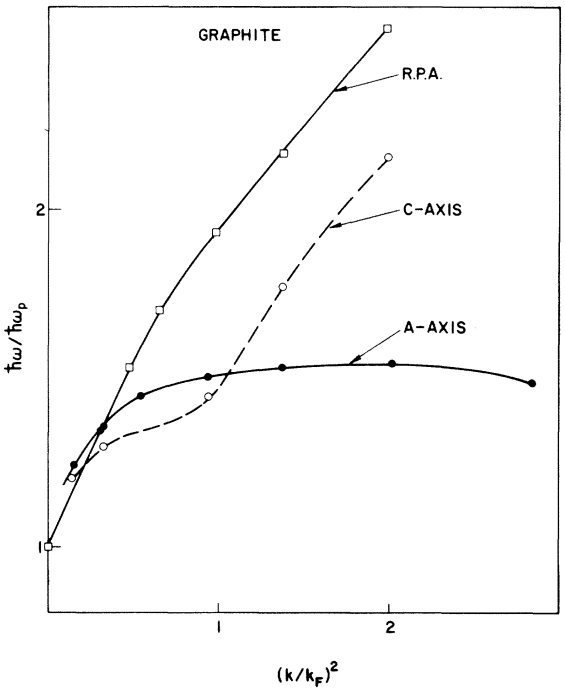

FIG. 3. Dispersion of the peak in $I(\vec{k}, \omega)$ as a function of $|k/k_F|^2$ with $\vec{k}$ along the A axis (solid circles) and with $\vec{k}$ along the C axis (open circles) as well as the results of an RPA calculation (open squares). The peak position is plotted in units of the free-electron plasma frequency.

= 25 eV) as a function of $(k/k_F)^2$. Also included for reference is a plot of the RPA results for the peak dispersion, where again those results were first smeared with the experimental resolution function before the peak position was determined. Due to the asymmetry of the RPA results, this smearing does lower the peak position slightly. Apart from the region $0.5 \leq k/k_F \leq 1.0$, the dispersion of the C-axis results are quite comparable to the RPA results. However, in the region $k/k_F > 1$, even though the two results are parallel to each other, there is a constant shift of about 10 eV between the two. This shift corresponds fairly closely to the value of the energy gap in graphite along the C direction.

A simple view would attribute the slight flattening and reduced value of the peak position along the C axis in graphite to band-structure effects while the significant deviations observed along the A axis would be attributed to a property of the electron gas. The latter view is strongly supported by the similarity of the experimental results for such disparate systems as Li, Be, Al, and Si with the A-axis graphite results,[2] when those results are scaled according to electron-gas parameters. A natural question to then ask is why the anomalous effect is not observed along the C axis in graphite.

The essential difference between the longitudinal properties of the electron gas along the C and A directions is that in the A direction the system is metallic and the electrons are strongly Coulomb coupled while along the C axis there is only weak coupling between the planes of carbon atoms which are separated by about 3.7 Å. The momentum k_c, characterizing the distance between carbon planes along the C axis, is 1.7 $Å^{-1}$ or $k_c/k_F = 0.75$.

In considering the C-axis properties, one should distinguish between two regimes $k/k_F < 0.75$ and $k/k_F > 0.75$. In the first regime one is considering the response of a collection of neutral but polarizable molecules. In order to understand why such a collection of neutral objects have a plasmonlike peak in their response at long wavelengths it is sufficient to think of them as a collection of harmonic oscillators. The long-wavelength dielectric function of such a system is

$$\epsilon(0,\omega) = 1 - \frac{4\pi ne^2/m}{\omega^2 - \omega_B^2 \pm i\omega/\tau} \ . \tag{4}$$

Here n is the density of oscillators, ω_B is their characteristic frequency (binding energy), and τ is a phenomenological relaxation time. For large τ and for $\omega_p = (4\pi ne^2/m) > \omega_B$, $S(0,\omega) \sim \mathrm{Im}[1/\epsilon(0,\omega)]$ has a peak at $\omega = \omega_p[1 + \frac{1}{2}(\omega_B/\omega_p)^2]$, i.e., close to the free-electron plasma frequency. In a solid like graphite $\omega_B \approx 10$ eV $\omega_p \approx 25$ eV. A simple expression like the one above predicts a plasmon shifted up by about 7%. More extensive band-structure calculations show[5] that a competing effect, the coupling to higher plasmon bonds, pushes down on the plasma frequency and that the resulting change is small.

In the second regime ($k > 0.7k_F$), we probe the system on a scale of distance such that there is little interference between the scattering from successive planes. Since the electrons in different planes are to first order not Coulomb coupled, one is simply considering the properties of a single plane of neutral carbon atoms. In a direction perpendicular to the planes, only single-particle-type excitations can be excited. These will, of course, be dependent upon the binding energy of the electrons in the C direction and on the recoil energy $(k^2/2m)$ transferred in the scattering. When $k > 0.7k_F$, $k^2/2m > 30$ eV, one would basically expect a single-particle Compton-like spectrum shifted by something of the order of the binding energy.[6]

The region around $k/k_F = 0.75$ should of course be the transition between the two types of responses and, as shown in Fig. 3, it is exactly in this region that the flattening occurs. The flattening along the C axis can then be qualitatively understood as resulting from the transition from excitations near 1.2 $\hbar\omega_p$ (due to plasmon dispersion) to single-particle-type excitations centered near the recoil energy.

The above explanation of the suppression of the abnormal peak along the C axis is qualitatively consistent with the view previously given that the extra peak is due to correlations between electrons which are strongly Coulomb coupled. Some recent calculations by Hansen *et al.*[7] seem to further substantiate the view that the anomalous behavior observed in a wide variety of systems is a property of the interacting electron gas. Their numerical calculations are for a classical one-component ion plasma immersed in a uniform positive background. The parameter analogous to r_s is the quantity $\Gamma \sim e^2 n^{1/3}/kT$, one over the number of particle in a Debye sphere. For large values of Γ, numerical simulation[8] shows that the plasma liquid condenses into a Coulomb solid where the plasmon (longitudinal-optic mode has negative dispersion) and is undamped for all k. For modest values of Γ, Hansen finds that the plasmon dispersion is supressed and that such excitations tend to persist well into the classical continuum. For increasing Γ, i.e., greater electron localization, the dispersion becomes significantly negative. The exact physical mechanism responsible for this effect is not easily discernible from their numerical calculation, though it is clearly a property of the plasma and not the background which is assumed rigid and spatially uni-

form. There have also been recent electron gas calculations reported[9] which go beyond RPA and which obtain semiquantitative agreement with the experimental results. We therefore believe that the qualitative arguments we have previously given are appropriate and hope at some future date that more physically interpretable calculations applicable to solid-state electron gases will be forthcoming.

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