of remarkably reproducible thin potential wells and barriers, essentially rectangular and uniform to the order of a monolayer, can be created with molecular-beam epitaxy. The coupling behavior of the wells proves that synthetic superlattices can indeed be created. The molecular-beam-epitaxy technique for fabrication and the optical technique for energy-level determination should be applicable to additional configurations and compositions of interest for both basic and applied studies.

We wish to acknowledge L. Kopf for the determination of the Al content of the layers and for expert technical assistance. We thank C. H. Henry and M. B. Panish for helpful discussions.

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Direct Measurement of One-Dimensional Plasmon Dispersion and Damping

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(Received 12 March 1975)

Plasmons in the one-dimensional organic metal tetrathiafulvalene-tetracyanoquinodimethane were directly measured by high-energy inelastic electron scattering in thin crystalline films at 300°K. For plasmons propagating along the conducting b axis the plasmon energy decreases from 0.75 to 0.55 eV and the width increases linearly as the plasmon momentum increases. Plasmons at 45° to b have an energy of 0.6 eV and show no dispersion.

The organic charge-transfer salt tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) has been shown to have highly anisotropic electrical conductivity, and above 60°K has been characterized as a one-dimensional metal.[1] Since at high frequencies the room-temperature electronic behavior is certainly metallic in one dimension as established by the plasma edge reported in the normal-incidence reflectivity,[2-4] TTF-TCNQ provides an opportunity to study the elementary excitations of a one-dimensional electron gas. We report here the first known *direct* measurements of plasmon dispersion and damping in such a material. The experiment, performed at Princeton University, utilized high-energy inelastic-electron-scattering spectroscopy as the most sensitive and direct method to study dispersion and damping of plasma oscillations.

Epitaxial films of TTF-TCNQ (1000 Å thick) were grown on the (100) cleaved face of NaCl and had the same bioriented nature as previously observed.[5] That is, the film consisted of irregularly shaped regions (20 μm across) within each of which the conducting b axis of the crystals pointed along one of the two orthogonal [110] directions in the face of the salt substrate. Our sample thus was equivalent to two TTF-TCNQ crystals at right angles to each other (both having the

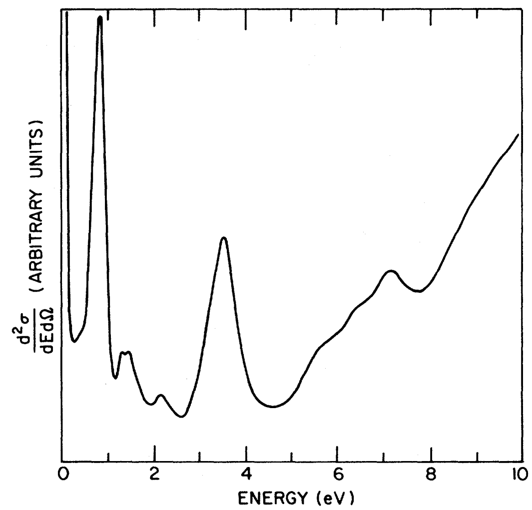

FIG. 1. Measured energy-loss spectrum of TTF-TCNQ from 0 to 10 eV at momentum transfer ~ 0.1 Å^{-1} along b axis.

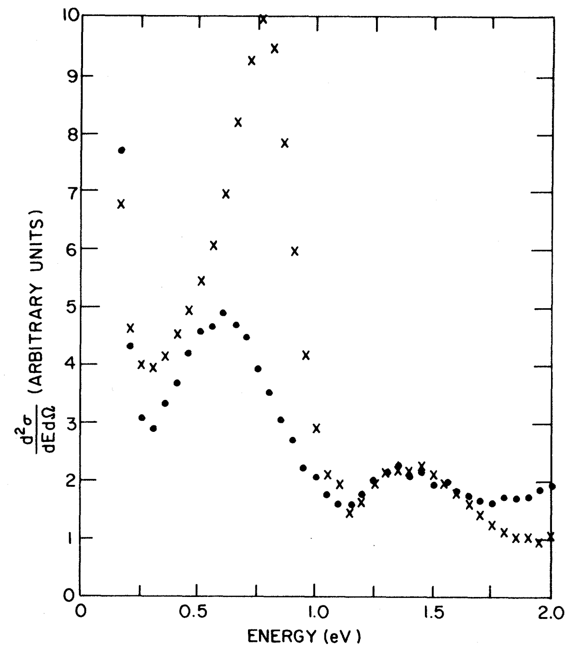

FIG. 2. Momentum-transfer dependence of plasmons along b normalized to peak at 1.4 eV; crosses, momentum transfer ~ 0.1 Å^{-1}, circles, momentum transfer ~ 0.7 Å^{-1}.

b axis in the plane of the film).

Energy-loss spectra were obtained for a 300-keV electron beam (5×10^{-9} A) focused on the sample to a 1-mm spot. The energy-loss resolution was 0.09 eV full width at half-maximum (FWHM) and the momentum-transfer resolution was 0.06 Å^{-1} FWHM. Measurements were made from 0.2 to 200 eV as a function of momentum transfer along several different directions in each sample. Typical results up to 10 eV for a small momentum transfer parallel to the b axis are shown in Fig. 1. The large peak at 0.75 eV is identified as a plasmon and structure at 1.4, 2.1, and 3.5 eV agrees with structure previously observed in optical experiments.[2,3,6] A study of the higher-energy excitations will be published later. Although electrons scattered with momentum transfer parallel to the b direction in one crystal could have been scattered in crystals whose b axis was perpendicular to the measured direction, we expect that in the region of the plasma energy these events will be negligible or at worst contribute a uniform background.[2,3] Moreover, potential complications due to multiple inelastic scattering and radiation damage were studied and found to be negligible.

That the peak in the energy-loss spectrum at 0.75 eV for small momentum transfer parallel to b is indeed a plasmon follows by a Kramers-Kronig analysis. The inelastic-electron-scattering cross section is $d^2\sigma/dE\,d\Omega \sim q^{-2}\,\mathrm{Im}(1/\epsilon)$, where q is the momentum transfer and ϵ is the longitudinal dielectric response function. In order to obtain $\mathrm{Im}(1/\epsilon)$ from the measured energy-loss spectra an extrapolated tail of the unscattered beam is subtracted from the data of Fig. 1 and the value of the peak at 3.5 eV arbitrarily set to that consistent with optical experiments.[6] From $\mathrm{Im}(1/\epsilon)$ one obtains $\mathrm{Re}(1/\epsilon)$ using a Kramers-Kronig integral over values of $\mathrm{Im}(1/\epsilon)$ from 0 to 200 eV. One finds that at 0.75 eV the real part of ϵ goes through zero while the imaginary part is small (~ 0.8), thus identifying a plasmon.

The dispersion and damping (width) of a plasmon propagating along the b axis can be directly seen in the raw-data example shown in Fig. 2. The low-momentum plasmon shifts to lower energy and broadens with increased momentum. Plasmons propagating at angles to the b axis were also measured and those with momentum at 45° to b are completely unambiguous since this angle is unique in our samples. The results for plasmon energy and damping for plasmons along b and at 45° to b are presented in Fig. 3. Plasmons were also measured at 22.5° to b and at small momenta their energy was intermediate between the plasmon energies at 0° and 45°. The straight line in Fig. 3(b) was determined by a linear least-squares fit to the data measured par-

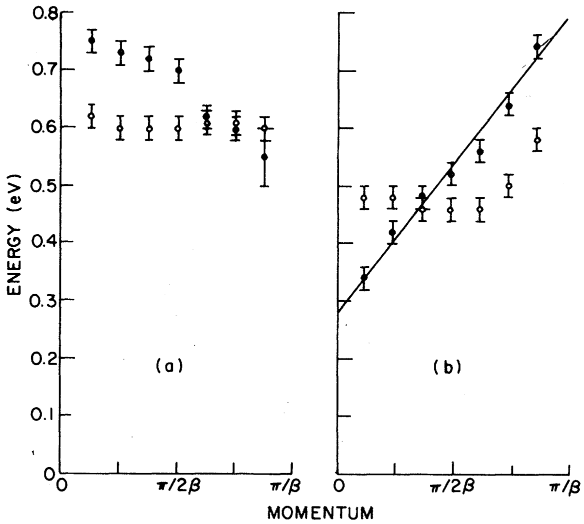

FIG. 3. Dispersion and damping of one-dimensional plasmons in TTF-TCNQ: (a) plasmon energy versus momentum, and (b) plasmon FWHM versus momentum. Closed circles, momentum along b direction, open circles, momentum at 45° to b. The first-Brillouin-zone boundary is at $q=\pi/\beta$, where β is the lattice constant along b (3.8 Å).

allel to b; the slope is 0.6 eV Å.

Williams and Bloch[7] have published a model calculation of the frequency- and wave-vector–dependent dielectric response of a quasi one-dimensional metal in the random-phase approximation. They predict that for low momenta the plasmon energy, E_p, will decrease as the angle of propagation with respect to the conducting b axis, θ, is increased, $E_p(\theta)=E_p(0)\cos\theta$. While we do observe this qualitative angular dependence, our measurements show less variation than a cosine dependence. We were unable to detect a significant plasmon peak when we measured an energy-loss spectrum for zero scattering angle (zero momentum transfer). This curious result may have been caused by our finite momentum resolution. If $E_p(\theta)$ predicted by Williams and Bloch is qualitatively correct then the distribution of plasmons sampled was smeared out in energy thus producing no single peak. However, the large dielectric constant below 0.75 eV causes additional energy losses due to Cherenkov radiation which occur only at small momentum transfer.[8] This Cherenkov continuum could obscure weaker plasma losses.

This first known observation of a negative dispersion for bulk plasmons is in qualitative agreement with the theory of Williams and Bloch.[7] The conducting electrons in TTF-TCNQ are generally regarded as forming a narrow tight-binding one-dimensional conduction band with considerable delocalization of charge density within the plane of the TCNQ anion as well.[3,9] This might be quite analogous to a one-dimensional tight-binding electron gas with the radius of the conducting strands being about 3 Å. For such a model slight negative dispersion is predicted and a degeneracy of plasmons in different directions midway to the zone boundary is found, in agreement with our results shown in Fig. 3(a).

The observed momentum dependence of the plasmon width, Fig. 3(b), is largely unexplained since no present theoretical treatment of plasmon damping agrees with experimental measurements. Hopefully, the one-dimensional tight-binding nature of plasmons in TTF-TCNQ will prove simpler to treat, particularly since a simple linear dependence on momentum is apparent from the data. Note that the increase in width divided by the plasmon energy as a function of q/k_F is of the same order of magnitude as in aluminum. Within the Williams and Bloch model Landau damping is not possible since the plasmon dispersion curve always lies above the single-particle excitation continuum.[7] Such a damping mechanism might be expected to cause a sudden increase in plasmon width for plasmons degenerate with single-particle excitations. Our data are inconclusive on this point since the plasmon width shows no discontinuity as a function of momentum along b suggesting that the same damping mechanism is operating throughout the Brillouin zone, while at 45°, the plasmon width does start to increase suddenly at about $q=3\pi/4\beta$.

Assuming the absence of Landau damping, if a higher nearby single-particle band did exist (for example, as sketched in Fig. 12 of Ref. 3) the plasma energy for momentum parallel to b should run along underneath it, consistent with the observed large negative dispersion. (For other directions in the zone, however, this may not be the case.) The difficulty is that we do not see such a higher band in our measured excitation spectrum. The peak at 1.4 eV is quite dispersionless, behaving like a highly localized intramolecular excitation. If the band does exist, the states giving rise to it must correspond to a small charge-density fluctuation having a small excitation probability. Moreover, lack of evidence for a higher band implies that the plasmon is not degenerate in energy with strong single-particle excitations and cannot couple to them via phonons. Thus the plasmon lifetime is not strictly related to the single-particle scattering time as had been conjectured.[2,3]

In considering other contributions to the plasmon width, there are several possibilities: Scattering by impurities and defects, interband and molecular transitions, electron-electron correlations, and scattering by phonons and intramolecular vibrations. Impurity and defect scattering can be ruled out as a major contributor since random disorder gives rise to a decrease in plasmon width with momentum[10] whereas we observe an increase. Interband and molecular transitions cannot contribute since it appears that the plasma energy is always below the threshold for such higher excitations; that is not the case in simple metals such as Na, Li, and Al. Electron-electron correlations, which allow the plasmon to decay into two electron-hole pairs has been considered by DuBois and Kivelson.[11] Their latest calculation indicates that this process is too weak to account for observed plasmon damping in simple metals; nevertheless it may be significant in a one-dimensional system. Note that in order for the plasmon to decay into two electron-hole pairs, energy conservation requires $E_p \leq 2W$, where W is the conduction-band width. Thus $W \geq 0.37$ eV which is consistent with previous estimates.[2,9] Phonons and intramolecular vibrations may play an important role in plasmon damping in this case since vibrations with nearly half the plasma energy exist.[3]

From the present study one can draw additional conclusions. Assuming the model of Williams and Bloch to be correct, we can put an upper limit on the bandwidth of the tight-binding conduction band simply as being the lowest plasma energy observed. Combining our two limits we have $0.37\text{ eV} \leq W \leq 0.55\text{ eV}$.

From our data we can obtain the $q=0$ plasmon lifetime, τ, by extrapolating the width $(\hbar/\tau)$ of the plasmon along b to zero momentum ($\tau = 2.4 \times 10^{-15}$ sec). This τ is consistent with optical data.[2,4] In the Drude model[2] (properly accounting for core polarizability) we may estimate the dc conductivity, σ, from our measured plasmon energy and lifetime, obtaining $\sigma \sim 600\ (\Omega\ \text{cm})^{-1}$ in surprising agreement with measured values.[1,2,4]

We have presented the dispersion and damping of one-dimensional plasmons in TTF-TCNQ. While a model calculation based on the random-phase approximation is seen to qualitatively explain some results there is no detailed agreement. It is hoped that the observed linear dependence of plasmon width on momentum transfer will lead to a better understanding of plasmon decay.

We are grateful to A. J. Heeger for useful discussions, as well as for graphs of unpublished data, to T. Witten for useful discussions, and to C. H. Griffiths for help in preparing the samples.

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