Surface plasmon observed for carbon nanotubes

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Electron energy loss spectroscopy and high-resolution images of carbon nanotubes, obtained using a 2 nm probe and energy resolution of 0.5 eV, revealed a 15 eV surface plasmon for tubes containing ≤ 12 cylindrical graphitic sheets. As the number of sheets increases further the 24 eV bulk plasmon quickly dominates the low-loss spectra. It is concluded that carbon nanotubes should be semimetallic, as is graphite. The first few graphitic sheets of nanotube structures act as if they are effectively decoupled electronically. As the radius of curvature increases then the interlayer structures approach the structure of graphite, as do the electronic properties. The present results do not exclude the possibility that the electronic structure of carbon nanotubes is the same as that of graphite, due to the operation of a conformal invariance principle.

I. INTRODUCTION

This paper presents parallel electron energy loss spectra (PEELS) results, obtained for individual carbon nanotubes, using nanoprobe techniques (1–2 nm diameter electron beam), energy resolution 0.5 eV, and collection times of 4–25 sec. The aim was to use a nanoprobe to compare PEELS spectra from different parts of a tube, in order to search for variations in sp^2/sp^3 bonding ratios as well as to look for orientation dependent plasmon and core-loss phenomena. It also seemed interesting to compare results for nanotubes with those for other varieties of graphitized carbons.

The most interesting result so far was the appearance of a 15 eV plasmon peak, which appeared only for tubes containing $\leq$ about 12 graphitelike layers. This peak did not shift significantly with tube size. Spectra obtained from larger tubes showed behavior similar to that described recently by Ajayan, Iijima, and Ichihashi[1] and Kuzuo, Terauchi, and Tanaka.[2] We also observed low-loss peaks at 6 eV of variable relative intensity; this peak was relatively very weak for amorphous tubes; it appears to be characteristic of graphitelike layers, as found for nanotubes and, of course, graphite itself.

This paper is restricted to discussion of the low-loss results. The experimental techniques are first described, including some details of the methods which may be used to disperse and support sooty carbons for high-resolution transmission electron microscopy (HRTEM). The results are then presented, followed by an interpretation of all the low-loss PEELS results, including those of the other authors referred to above.

II. EXPERIMENT

A. Specimen preparation

Plasma-deposited carbon specimens were made at the CSIRO Division of Coal and Energy Technology, Sydney. They were supplied to us by Dr. Louis S. K. Pang and were first studied by transmission electron microscopy[3] and high-resolution transmission electron microscopy.[4] The sooty carbon specimens contained a significant proportion of graphitized carbons, including nanotubes of the type discovered by Iijima[5] and studied already by many authors (see, e.g., Refs. 6 and 7). Whereas Iijima *et al.* appear to have obtained a very high yield of nanotubes, most other authors found nanotubes in association with a diverse variety of graphitized carbons. In this paper we will describe observations of nanotubes for the most part.

B. Electron microscopy

Specimen grids for electron microscopy were prepared using a variety of techniques designed to prevent extraneous carbon being included in the electron energy loss spectra; at the same time it was desirable to select nanotubes from the diverse range of graphitized carbons if possible.

The first experiments were made by simply placing clean, dry copper grids in contact with finely-ground sooty carbon. A useful number of nanotubes stuck to the grid bars, although it was necessary to search through a diverse variety of graphitized carbons to find them. In

order to increase the fraction of useful nanotubes sooty carbon was ground in an agate mortar and dispersed in a solvent, e.g., acetone or ethanol. After allowing the larger particles to settle, a drop of the suspension was allowed to dry onto copper grids covered with holey carbon films. This technique gave some selectivity for the tubes. Specimens dispersed in acetone proved useless for both HRTEM and PEELS studies due to contamination, which appeared when the specimens were exposed to the focused electron beam. This persisted, even after baking the specimen in the electron microscope at 80 °C for 2 h and then cooling to liquid nitrogen temperature.

Specimens dispersed in ethanol gave better results but most of the nanotubes having less than 10–15 graphitelike cylinders were transformed to amorphous carbon following an 80 °C outgassing treatment. However there was no contamination during observation and many tubes of larger diameter were available for study. The most important results, for the smallest tubes, were obtained for the dry mounted specimens.

Preliminary HRTEM/PEELS experiments were made using the JEOL 4000EX high-resolution instrument at the University of Melbourne. In this case the structural resolution was 0.17 nm; the beam diameter was typically 40 nm for PEELS data acquisition and the collection times were typically 1–2 min. A Gatan Parallel Detection Electron Spectrometer (Model 666) was used at 400 keV, with energy resolution 1.5 eV; the spectrometer was set at 0.5 eV per channel and the whole spectrum (low-loss plus core-loss) was recorded as one data set. All observations were made at about 25 °C. The HRTEM images were recorded on electron-image film.

Further experiments were made using the Hitachi HF-2000 field-emission electron microscope at I2M, EPFL Lausanne. Here the effective structure resolution was limited to about 0.25 nm by the objective lens spherical aberration coefficient C_s of 1.2 mm. A Gatan cooling/heating specimen holder and goniometer was used so that, if necessary, the specimen grids could be baked at 80 °C before observations were made at liquid nitrogen temperatures (actually −170 °C). This procedure ensured there were no problens with growth of beam-induced carbon contamination deposition on the specimens during observation. HRTEM images were recorded using a Gatan Slow-Scan TV camera and associated Digital Micrograph software.

PEELS data were again recorded using the Gatan Parallel Detection Electron Spectrometer (Model 666) and analyzed using the associated EL/P software. The electron beam diameter (nanoprobe) could be as small as 1 nm; however, in most cases it was approximately 2 nm. It was not possible to record simultaneously the HRTEM images with the nanoprobe, due to saturation of the TV camera. However, areas analyzed were indicated clearly in most cases by recording the HRTEM image with a somewhat defocused probe of about 10 nm diameter; the effective resolution of these images was much better than 0.34 nm, the 0002 spacing of graphite.

The measurement procedure was as follows: a suitable area was located and the HRTEM image digitized; the PEELS spectrometer was then fine-tuned and set

up to record low-loss (0–100 eV) and core-loss (260–350 eV) components using 0.05 eV/channel. Low-loss spectra were recorded in 4–8 sec whereas core-loss required typically 25–50 sec. Up to five spectra were recorded consecutively from the same area; this allowed reproducibility to be confirmed and made clear when beam-induced changes began to occur. The HRTEM image was then re-examined to check for beam-induced changes. Typically, transformation to a glassy state occurred after some time; which varied from one to several minutes, depending on the size, shape, beam current, probe size, etc.

As described above, growth of a carbon contamination layer was not a problem providing the precautions described above were taken. All of the spectra from this instrument were obtained at −170 °C.

III. RESULTS

Figure 1 gives a HRTEM image of part of a carbon nanotube consisting of 12 cylindrical graphitelike layers. The corresponding low-loss PEELS was obtained after focusing the electron beam onto seven layers, i.e., less than half of a nanotube (indicated by the black disk in Fig. 1). Note the plasmon peak at approximately 15 eV. This experiment was repeated for at least 12 such tubes, all with this same result; there was no evidence for shifting of the 15 eV peak with tube diameter, provided the number of layers was < 10–12.

Figures 2(a)–2(d) compare the PEELS results obtained from tubes containing 12, 17, 20, and 29 graphitelike layers, respectively; note that the plasmon peak centered at 22–24 eV is asymmetrical for tubes containing more than about 12 sheets. The 17 sheet tube showed clear evidence [Fig. 2(b)] for two overlapping plasmon peaks, at approximately 15 eV and 24 eV, as well as a 6 eV peak. Note that the zero-loss peaks have been subtracted from the spectra in Fig. 2, whereas Fig. 1 shows a raw spectrum. The photodiode counts are given in arbitrary units in Fig. 2 to allow a clear comparison of (a)–(f).

Figure 2(e) shows the PEELS result for an amorphous tube having about the same diameter as for the 12-sheet
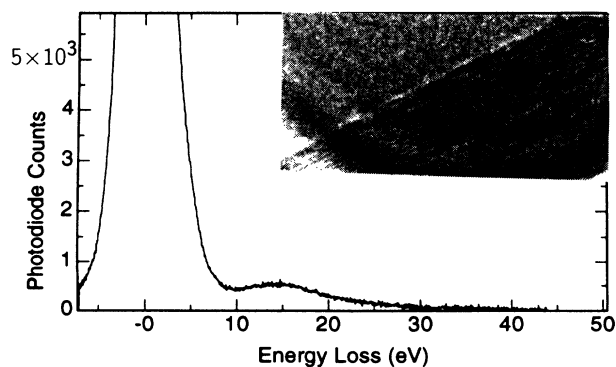

FIG. 1. HRTEM image of a carbon nanotube consisting of 12 graphitelike layers and low-loss PEELS spectrum from the area circled on the image. Note the 15 eV and 6 eV peaks.

tube (Fig. 1). Note that the plasmon peak is centered at approximately 20 eV; there is no 15 eV peak and the 6 eV peak almost disappeared. Finally, Fig. 2(f) shows PEELS for a graphite crystal viewed with the c-axis perpendicular to the incident electron probe. The corresponding lattice image showed at least 50 parallel fringes. The nanoprobe diameter was 2 nm, as was the case for all the PEELS results reported here. Note the plasmon peak centered at approximately 24 eV and also the smaller peak at approximately 6 eV. It is apparent that the 29 sheet tube [Fig. 2(d)] and the graphite crystal [Fig. 2(f)] gave virtually identical PEELS results for the low-loss region shown in Fig. 2. This was the case regardless of the position of the probe on this specimen.

PEELS spectra, obtained at about room temperature using the 400 keV instrument with 1.5–2 eV energy resolution, were comparable with Figs. 1(d) and 1(e) of Ajayan et al.[1] in that there was no resolution of the 15
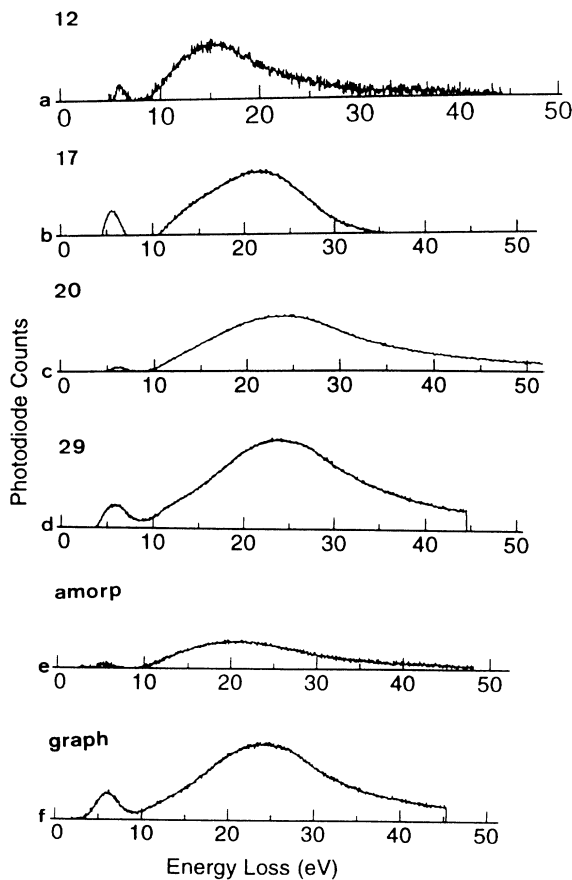

FIG. 2.   (a)–(d) PEELS spectra from nanotubes consisting of 12, 17, 20, and 29 graphitelike layers, respectively. The 17 and 20 sheet spectra show superposition of 15 eV and 24 eV peaks whereas the 29 layer tube shows only the 24 eV peak. (e) and (f) PEELS spectra from an amorphous tube of the same diameter as the 12 layer tube (cf. Fig. 1) and from a graphite slab containing 50 sheets lying parallel to the incident electron beam.

eV plasmon or of the 6 eV peak; only the 24 eV plasmon peak was observed.

IV. DISCUSSION

The most intriguing result above is the emergence of the 15 eV plasmon peak for very thin carbon nanotubes; the scattering efficiency of this peak relative to that of the well-known bulk plasmon at 24 eV is clearly dependent on the total number of graphitelike sheets of the tube. Thus the 15 eV plasmon was observed in pure form only if the number of graphitic layers was less than about 12. The bulk plasmon dominated as the tube included more sheets.

It would, in principle, be possible to scan the nanoprobe from the center to the edge of the smaller nanotubes. In practice we were unable to achieve this result; usually we recorded from a position similar to that indicated in Fig. 1. This limitation would be overcome if the HRTEM image and the PEELS spectra could be viewed simultaneously. As pointed out in the experimental section above, it was necessary to defocus the nanoprobe spot to record the image and then focus again to obtain the PEELS spectra. This procedure also required retuning of the PEELS spectrometer. Thus it was not possible to do a systematic set of experiments with the PEELS spectra recorded as the probe was scanned across the specimen.

It was possible to reposition the nanoprobe onto undamaged areas and obtain PEELS spectra from different areas of tubes containing more than about 25 sheets. However, in these cases the bulk-plasmon peak already overwhelmed the 15 eV plasmon and we did not observe any systematic variation of the spectra with probe position. Certainly future work may be directed to the consideration of the effect of probe position on the spectra. It is of considerable theoretical interest to explore the extent of localization of both surface and bulk plasmons and the question of optimization of momentum transfer to the surface modes. Similarly, the dispersion properties of surface-plasmon modes should be distinct from those of bulk plasmons and interband transitions. However, due to experimental difficulties, it was not possible to achieve such experiments.

Thus our main point remains that the changeover from the essentially pure 15 eV peak, interpreted below as due to excitation of surface plasmons, to the well-known 24 eV bulk-plasmon peak, occurs for tubes containing more than about 12 graphitic sheets.

Electron-energy-loss spectra (EELS) from individual carbon nanodiameter tubes have already been published by Kuzuo et al.[2] and Ajayan et al.[1] The first authors found two plasmon peaks; due to bulk π and $(\pi + \sigma)$ plasmons. The energy of the $(\pi + \sigma)$ plasmon varied, apparently, from 22.0 to 24.5 eV, which agrees roughly with the average bulk-plasmon energy (27 eV) of polycrystalline graphite.[8] A shoulder, interpreted as due to a single electron excitation, was observed at 13 eV, which was not observed in graphite. Plasmon peaks at 5.2 and 6.4 eV were also observed; these were interpreted as due to the π plasmons of two distinct types of nano-

tubes. It is important to note that in this case a relatively large beam spot was employed so that typically many nanotubes may have been sampled simultaneously.

Ajayan et al. gave a somewhat different picture; bulk-plasmon-loss peaks, presumably $(\pi + \sigma)$, were seen at about 27 eV in graphite. It was claimed that this plasmon peak undergoes a systematic shift, by up to about 9 eV for the thinnest tubes, towards lower energy as the tube diameter decreases. It was claimed that this peak shift may depend on the total number of graphite sheets which comprise the tube as well as the overall tube diameter. The lower-loss (π) plasmon (about 7 eV for graphite) was said to be weak and not well-defined for thin tubes.

It is important to note that Kuzuo et al. collected spectra using a 180 nm probe, which is many times the diameter of a single nanotube (3–15 nm typically). They used an effective energy resolution of 0.3 eV and collection times of about 1 min. On the other hand, Ajayan et al. used a smaller probe (8–20 nm diameter), relatively poor energy resolution of 2–3 eV, and collection times of about 2 min. In neither case was the probe diameter appropriate to isolate a single nanotube. In addition it is clear from the HRTEM images published by Ajayan et al. that the tubes studied by them appear to be coated with amorphous carbon, which would probably eliminate the possibility of observing a surface plasmon for the thinnest tubes. Kuzuo et al. studied only one relatively thick tube (31 nm diameter); their result is consistent with ours, they did not study very thin tubes so they did not find the 15 eV plasmon.

Consideration of all the EELS results, i.e., our Figs. 1 and 2 as well as Figs. 1 and 2 of Kuzuo et al. and Fig. 1 of Ajayan et al., leads us to the assertion that the low-loss EELS spectra of carbon nanotubes contain contributions from (1) a minor peak at 6 eV; (2) a 15 eV plasmon peak which is detectable only for thin tubes consisting of ≤ 12 graphitic sheets; (3) a 20 eV plasmon due to amorphous carbon which may be intrinsic in the case of coated tubes or extrinsic due to electron-beam-induced contamination, and (4) a 24 eV graphitic bulk plasmon in the case of thicker tubes. These different contributions have been clearly distinguished and observed in pure form in the present study. This was most obvious for the 15 eV plasmon which was only observed using a 2 nm nanoprobe and energy resolution of 0.5 eV. This peak was still contributing for tubes containing 20 graphitic sheets but for thicker tubes it becomes overwhelmed by the bulk-plasmon contribution. Thus the plasmon peak shift apparent for thinner tubes in the work of Ajayan et al. actually represents increasing relative contribution from the 15 eV peak as the tubes decrease in thickness. We emphasize once more that we could find no significant shifting of this peak; it always occurred at 15 eV for the thin tubes. In general a linear combination of all of the just-mentioned contributions will occur in experimental PEELS spectra obtained from carbon nanotubes. In order to see clearly the 15 eV plasmon it is necessary to eliminate carbon coating or contamination of the tubes and to confine the electron beam to a nanoprobe diameter 1–2 nm, as was achieved in the present work. In order to observe directly the relatively weak 6 eV peak,

an energy resolution of better than approximately 0.5 eV is necessary, as for the present work and that of Kuzuo et al.

The bulk plasmon $(\pi + \sigma)$ energy is centered at approximately 27 eV for polycrystalline graphite;[8] it is closer to 24 eV for graphite sheets oriented parallel to the incident electron beam, as was the case for our experiments. The thicker tubes, say > 12 sheets, gave (bulk)-plasmon energy 24 eV, which is consistent with the bulk-plasmon energy of graphite in this same orientation. Note that the amorphous tube bulk-plasmon energy was closer to 20 eV. Kuzuo et al. and Ajayan et al. obtained essentially these same results for thicker tubes.

Our first reaction, on observing a 15 eV plasmon for the thinnest tubes, was that this was simply a surface plasmon, bearing in mind the well-known relation between bulk- and surface-plasmon frequencies (see, e.g., Kittel[9]),

$$\omega_s^2 = (1/2)\omega_b^2. \tag{1}$$

Thus $(1/2)\sqrt{24} = 15.5$ eV. The bulk-plasmon frequency, given by

$$\omega_b = 4\pi n e^2 / \epsilon(\infty) m, \tag{2}$$

is just the frequency of the uniform collective oscillation of the electron gas against a background of fixed positive ions, where n is the number of charge carriers per unit volume, e is the charge of an electron, $\epsilon(\infty)$ is the high frequency dielectric constant, and m is the electron mass (see, e.g., Kittel[9]).

Graphite may be regarded as a semimetal[10] and has carrier density approximately 10^{18} cm^{-3}. Our observation that the thicker carbon nanotubes have essentially the same PEELS result as does crystalline graphite implies that the carrier electron density is essentially the same as for graphite; thus the larger nanotubes (presumably) are also essentially semimetals. It appears they are not metallic, either at room temperature or at $-170\,^\circ$C, as this would induce a carrier density of 10^{22} cm^{-3} and then shift the plasmon peak to much higher energy. Similarly, if the bonding were not graphitelike then one would expect the bulk plasmon to occur at much higher/lower energies. (This argument is probably oversimplified but it does raise an important point which needs to be settled.)

Although the 15 eV plasmon has the energy expected for a surface plasmon it is necessary to examine further the possibility that there may be a semimetal/semiconducting transition for the thinnest tubes, or at least a significant change in band gap. There are a number of theoretical results for carbon nanotubes on this point. These are reviewed briefly in the next paragraph, after which we will return to discuss the nature of the 15 eV plasmon.

Mintmire, Dunlap, and White[10] raised the question "are fullerene tubules metallic?" They analyzed theoretically tubules constructed from C_{10} rings added to the waist of a hemispherical C_{60} fullerene cap, with the tubule axis retaining D_{5h} symmetry. They predicted car-

rier density similar to that of metals, with zero band gap at room temperature. They further estimated that the mean field transition temperature from a Peierls-distorted (semiconducting) regime to a higher temperature metallic regime should be well below room temperature. They argued that the reason for the low conductivity of graphite (semimetal) is the low carrier density, approximately 10^{18} cm^{-3}, compared to typical metallic carrier densities of approximately 10^{22} cm^{-3}. From the tight-binding model, they calculated a carrier density, for an array of parallel-packed tubules,

$$n_e = 8\sqrt{3}m|V_0|a/(h/2\pi)^3 A, \qquad (3)$$

where a is the translation distance for each screw operation along the tube axis, $|V_0|$ is the mean inner potential (four times the band gap), and A is the cross-sectional area of the tubule. Assuming $A = 1$ nm^2, the carrier density may be estimated as approximately 10^{22} cm^{-3} to 10^{23} cm^{-3}. Assuming the carrier mobility along the tube axis is comparable to the high mobilities found for graphitic structures, they then predicted that the electronic conductivity parallel to the tube axis should be comparable to that of a good metal. They predicted further that tubules of increasing diameter should also have metallic conductivity at room temperature, although the carrier density should decrease due to increasing cross-sectional area A.

Perhaps the most complete treatment of the relationship between tubule structure and electronic properties so far is the paper of Hamada, Sawada, and Oshiyama.[11] These authors predicted that carbon nanotubes may exhibit sharp variation from metallic to semiconducting character with narrow or moderate band gaps, depending on the tube diameter and the specific degree of helicity of the C_6 hexagons in the tube structures. They discussed the physical origin of such remarkable changes by reference to the specific periodic boundary conditions imposed by tube structures having different helicities.

As pointed out by Iijima[5] there are many possible ways of cutting and joining a curved graphite sheet to make a nanotube and the number of possible structures increases further as successive sheets are added. Hamada et al. introduced an elegant representation in order to describe all possible structures. Thus each structure may be identified by its diameter and by the helicity of the carbon hexagons. Consider a single graphitic sheet; choose an origin (O) and a lattice point in the sheet. Next, roll the sheet so that the chosen lattice point is superimposed on the origin. The lattice points $A(n_1, n_2)$ each represent and describe uniquely a different tube structure. In order to maintain a one-to-one correspondence between the structure and the index it is necessary to restrict the parameter space to $n_1 \geq 2n_2 \geq 0$. Again, it is necessary to note that there are two ways of rolling the graphitic sheets, i.e., from the front to the back or vice versa; these operations may result in tubes which are chiral (mirror symmetric to each other). Hamada et al. neglected any differences between these two since the energy band structures are independent of chirality. (Note that this assumption may break down following

application of magnetic or electric fields.) Detailed discussion was given for $A(12, 0)$ and $A(13, 0)$ tubes, which gave band gaps of 0.008 eV and 0.697 eV, respectively. Hamada et al. then showed that a special class of tubes became metallic, in the case that the tube axis is perpendicular to a C-C bond. It was just one such case that was studied by Mintmire et al.[10] Following an analysis of the periodic boundary conditions imposed along the circumference of the tube structures, with reference to the band structure of graphite, Hamada et al. obtained the following general results for the band gaps of carbon nanotubes; a tubule $A(n_1, n_2)$ ($n_1 \geq 2n_2 \geq 0$) is (1) a metal for $n_1 - 2n_2 = 0$, (2) a narrow-gap semiconductor for $n_1 - 2n_2 = 3m$ ($m = 1, 2, \ldots$), and (3) a moderate-gap semiconductor otherwise.

The PEELS result above that the (bulk)-plasmon energy of thicker tubes is approximately 24 eV, the same as for graphite, implies immediately that the tubules are not metallic, but retain graphiticlike electronic conductivity, i.e., they are semimetals. This in turn implies that some assumptions made in Ref. 10 in applying Eq. (3) need to be reexamined. Neither Mintmire et al. nor Hamada et al. considered the possibility that nanotubes may be semimetals, rather than metallic.

If we assume that the 15 eV peak is indeed due to a surface plasmon, having frequency given by Eq. (1), then it has to be considered that the electronic density of states for the smallest tubules may also have a semimetallic nature. It must be accepted, however, that such a conclusion does not automatically follow from an analysis of the bulk-plasmon results for graphite and larger tubes.

Note that we found no evidence for a metal/semiconducting transition, or Peierls transition in the range room temperature down to $-170\,^{\circ}$C.

Scanning tunneling microscope images of carbon nanotubes, reported by Ge and Sattler,[12] have confirmed that the outer tube surface has helical structure, with chiral angle 5°. (The chiral angle refers to the smallest angle between the tube axis and the C-C bonds of the graphite net.) These authors went on to claim that their images contained evidence, in the form of a 1.6 nm periodicity, that the next to outer sheet had a helicity different from the outer sheet, claiming the second sheet was rotated 9° relative to the first, actually +5° and -4°. Note that such small helicity values require only small departures from the $n_1 - 2n_2 = 3m$ ($m = 1, 2, \ldots$) structures. Atomic modeling of tube structures, using crystal chemical arguments and imposing the condition that the interlayer spacing should be 0.34 nm, i.e., the same as for crystalline graphite, lead us to the conclusion that the nanotube structure should be of type (2) above, i.e., $n_1 - 2n_2 = 3m$ ($m = 1, 2, \ldots$). This structure has helicity zero.

It is clear that the relative alignment of successive tubes remains an outstanding structural problem. This is presently being studied in Melbourne by means of HRTEM; it requires two-dimensional images for both longitudinal and especially transverse cross sections.

Further interesting theoretical papers to which the reader may wish to refer are Lin and Shung[13] and Ajiki and Ando.[14] The first authors derive detailed results for

plasmon excitation in some tube geometries; however, they do not give specific numerical predictions which we could compare with our PEELS results. Note that Lin and Shung predicted that for plasmons having large angular momenta (L is conserved) the cylindrical symmetry leads to special boundary conditions for plasmon waves. Thus individual graphitic sheets behave as if decoupled and thus the plasmons are effectively those of individual graphiticlike cylinders. These authors did not point out, however, that in that case one would expect a surface plasmon peak at 15 eV rather than the well-known bulk-plasmon peak at about 24 eV. Again there is no theoretical prediction for the anticipated changeover from decoupled layers to more normal graphite type behavior as the number of layers and/or tube diameter increases.

Ajiki and Ando,[14] following Hamada et al., predicted that carbon nanotubes may change from metallic to semiconducting, depending on details of the structure; the band gap was predicted to be inversely proportional to the tube diameter. However, unfortunately, neither Lin and Shung nor Ajiki and Ando were as clear as Hamada et al. in their description of the possible tube structures, so it is not a straightforward matter to apply their theory to the PEELS results.

Consideration of the above discussion may prompt the reader to ask "to what extent are our observations unique compared to what 10–12 layers of graphite would show with the electron beam incident along the basal planes?" Our answer is simply that the (surface) plasmon obtained for effectively decoupled cylindrical graphitic sheets has the same frequency as that expected for surface plasmons of flat graphitic sheets. This result implies that graphitic sheets may possess the property of conformal invariance. Such a result would be quite interesting when one considers that this may be a consequence of the conformal mapping

$$iw = (L/2\pi)\log_e z \qquad (4)$$

which maps the entire z-plane of a strip of finite width L onto the surface of a cylinder (see Ref. 15 for a discussion of the role of conformal invariance in phase transitions). In simple terms, the periodic boundary conditions usually applied as an approximation for the case of translationally invariant crystals should apply exactly for the case of cylindrically symmetrical quasicrystals. The present results do not exclude the possibility that the electronic structure of carbon nanotubes is the same as that of graphite, due to the operation of a conformal invariance principle.

V. CONCLUSION

Finally, we assert that the 15 eV plasmon is probably due to a surface plasmon; we could find no evidence for a continuous shift of the 15 eV plasmon or of the 24 eV (bulk) plasmon characteristic of thicker tubes. It seems to us that the innermost 10–12 graphiticlike sheets are effectively decoupled so far as their electronic properties are concerned. This follows from a consideration of the atomic structures of the first few sheets. Thus, the first sheet contains 10 hexagons around its waist whereas the second sheet contains 20 such rings [assuming the $n_1 - 2n_2 = 3m$ ($m = 1, 2, \ldots$) structure]. As the number of sheets increases adjacent sheets assume more closely the structure of graphite. As pointed out above, full atomic details of the real tube structure(s) are not known and it is now imperative that this problem be solved so that further theoretical developments may make specific and quantitative predictions of the electronic and other physical properties, such as PEELS results.

The present results do not exclude the possibility that the electronic structure of carbon nanotubes is the same as that of graphite, due to the operation of a conformal invariance principle.

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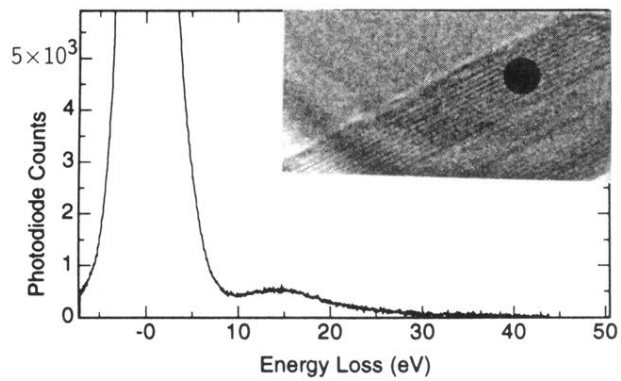
FIG. 1.   HRTEM image of a carbon nanotube consisting of 12 graphitelike layers and low-loss PEELS spectrum from the area circled on the image. Note the 15 eV and 6 eV peaks.