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X-RAY DIFFRACTION AND ELECTRON SPECTROSCOPY OF EPITAXIAL MOLECULAR C_{60} FILMS

by

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Films of the new carbon allotrope, molecular C_{60}, also known as Buckminsterfullerene, have been grown on Si(111) substrates by molecular beam epitaxy. The films have been characterized with x-ray two-theta diffraction, x-ray photoelectron spectroscopy, Auger electron spectroscopy, and electron energy-loss spectroscopy. The diffraction data from oriented films show that close-packed planes of C_{60} molecules are stacked parallel to the substrate surface, but that the correlation length for x-ray scattering is less than 200 Å. The electron spectroscopic data show that the C atoms of C_{60} are essentially sp^2-bonded, but there are significant differences with respect to graphite.

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X-ray Diffraction and Electron Spectroscopy of Epitaxial Molecular C_{60} Films

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ABSTRACT

Films of the new carbon allotrope, molecular C_{60}, also known as Buckminsterfullerene, have been grown on Si(111) substrates by molecular beam epitaxy. The films have been characterized with x-ray two-theta diffraction, x-ray photoelectron spectroscopy, Auger electron spectroscopy, and electron energy loss spectroscopy. The diffraction data from oriented films show that close-packed planes of C_{60} molecules are stacked parallel to the substrate surface, but that the correlation length for x-ray scattering is less than 200 Å. The electron spectroscopic data shows that the C atoms of C_{60} are essentially sp^2-bonded, but there are significant differences with respect to graphite.

I. INTRODUCTION

The recent discovery that all-carbon molecules containing 60 or more atoms can be made in relatively large quantities[1] has spurred a renewed interest in these systems, with particular emphasis on their molecular properties.[2-5] The solid-state properties of this new carbon allotrope are also being examined.[1,6-8] In particular, the electronic properties of C_{60} are thought to be somewhat graphitic in character, with the sp^2-bonded sheets curved into a sphere. In this investigation, we have compared the electron spectroscopic data of solid C_{60} to that of graphite in order to assess the similarities and differences of their electronic structures.

Most of the solid-state work done to date has been on material that was crystallized from solvents or sublimed onto a convenient surface under a relatively low vacuum. The samples are often exposed to the atmosphere for relatively long periods of time before or during analysis. Such material can contain solvent molecules or atmospheric contaminants in the large interstices within the C_{60} lattice, which may act like a sponge. It may also experience irreversible oxidation on long exposures to the atmosphere. The presence of impurities of any sort will strongly bias the data collected with surface sensitive electron spectroscopic techniques.

In an effort to examine the intrinsic structural and electronic properties of pure solid C_{60}, we have grown films of the new material under ultra-high vacuum conditions. We have chosen the Si(111) surface as the substrate because of its symmetry and small lattice mismatch with respect to the close-packed structure of C_{60}, as determined previously by Krätschmer *et al.*[1] Fig. 1 shows that a close-packed plane of C_{60} molecules has a registry with Si(111) corresponding to a $3\sqrt{3} \times 3\sqrt{3}$ R30° orientation with a lattice mismatch of only 0.8%. We have grown ten films to date, examined them using several tools for characterizing structural and electronic properties, and compared the results to those for graphite where appropriate.

II. EXPERIMENTAL PROCEDURE

The starting material for this investigation was produced by the Krätschmer-Huffman method, as described earlier.[1] The first films that were grown utilized the extract of the soot produced by this procedure without further purification. This material contained approximately 15% C_{70}. The later films were grown from material that had been purified to 0.05% by passing it through an alumina column, as described in ref. 5. The films were grown in an ultra-high vacuum chamber that had been used for the epitaxial growth of CuCl and other films.[9] The chamber is equipped with three Knudsen cells in a liquid nitrogen cooled shroud, a Low Energy Electron Diffraction (LEED) system that is also used for Retarding Field Auger (RFA) spectroscopy, a quartz crystal microbalance, and a leak valve for introducing controlled amounts of different gases.

About 15 mg of starting material was placed in a 2 cc quartz crucible, which in turn was inserted into a pyrolytic boron nitride crucible resistively heated by a coiled tantalum heating wire. The entire chamber was baked carefully so that the temperature of the crucible would not exceed 240°C. This step served to eliminate any high vapor pressure contaminants from the starting material. The base pressure of the system after bakeout was 5×10^{-9} torr. The Si(111) substrate was prepared by alternate cycles of flashing to 1100°C and annealing to 850°C until a sharp LEED pattern was obtained and the Auger spectra showed no detectable surface contamination. To eliminate any possible interference from the 7×7 reconstructed unit cell, the Si substrate was heated to 500°C and exposed to 10^{-5} torr of hydrogen gas for typically 2 minutes. After this treatment, the sample displayed a sharp (111) 1×1 LEED pattern.

To initiate the growth, the crucible was heated to about 300°C, as determined by a thermocouple in contact with the back of the crucible. The substrate was then positioned within the flux of material 1.5 cm from the face of the crucible for about one hour. In most cases, the substrate was at ambient temperature, essentially 25°C; we have also attempted to deposit at 120°C, but the C60 molecules did not appear to stick to the substrate at such high temperatures, so this approach was discontinued. During the initial stages of growth, the films were a deep translucent blue, but by the end of the growth cycle they were a semitransparent brown. After growth, the films were analyzed *in situ* with LEED and Auger: no LEED patterns were observed, and the Auger spectra revealed only carbon in the films. Profilometric measurements made after the films were taken out of the chamber showed that they were on the average 1500 Å thick, yielding a growth rate of approximately 25 Å/min for the above growth conditions.

The films were subjected to a large number of *ex-situ* analyses, including x-ray two-theta diffractometry, electron spectroscopic investigations, Scanning Tunneling Microscope analysis (STM), and conductivity measurements, of which only the first two will be discussed in detail. The conductivity measurements indicated that the films were considerably more resistive than the doped Si substrate. The STM images were indistinct and irreproducible, with only an occasional indication of arrays of spheres of about 10 Å in diameter.

The x-ray diffraction experiments were performed using a Norelco two-theta powder diffractometer with a Cu x-ray source. The Si substrate was slightly misoriented with respect to the detector, which greatly attenuated the features from the single crystal, but had little effect on the intensity of any diffraction peaks from the C_{60} overlayers because of the mosaic spread of the films. Since the films were thin and the scattering from carbon is weak, the scans had to be signal-averaged for 15 hours to obtain a reasonable signal-to-noise ratio. In general, samples were analyzed as soon after growth as possible to minimize contamination and oxidation of the films.

The electron spectroscopic measurements were performed in a Kratos XSAM system equipped with a 127 mm radius hemispherical analyzer. The system has a dual anode (Al/Mg) source for X-ray Photoelectron Spectroscopy (XPS), a 10 keV electron gun for scanning electron microscopy and Auger Electron Spectroscopy (AES), and a lower (2 keV) energy electron gun for Electron Energy Loss Spectroscopy (EELS). Samples that had been exposed to the atmosphere for days revealed significant contamination, so the later samples were transferred to the spectrometer immediately after they were grown. Such samples were essentially free of contamination. The XPS analyses included broad survey scans with both Al and Mg Kα sources to examine the chemical composition of the films and careful scans of both the C 1s and valence band regions to examine the lineshapes. The electron-excited C KLL Auger spectra were collected using the pulse-counting mode in order to maximize the spectral resolution and then differentiated numerically. The integral-mode EELS spectra were collected using a primary electron energy of 206 eV. The electron-energy analyzer was operated in constant-resolution mode for all these experiments, and the resolution of the spectra was better than 1 eV in all cases. The same types of spectra were also collected from a freshly cleaved highly oriented pyrolytic graphite (HOPG) sample for comparison.

III. RESULTS AND DISCUSSION

For films produced from the unpurified C_{60} material, the x-ray diffraction patterns, an example of which is given in Fig. 2, showed only two features from the films: peaks at two-theta values of 10.88 and approximately 21.5 degrees, which correspond to d-spacings of 8.125 Å and 4.13 Å, respectively. The positions of the diffraction peaks and the values of the associated d-spacings agree very well with those listed previously for the powder sample of C_{60} in ref. 1, which also reported several other diffraction peaks that indicated the C_{60} crystallites had a defected hexagonal close-packed structure. Films deposited from the purified C_{60} did not display the same level of order: the diffraction peaks were not as intense and there were more of them in the two-theta scans, which indicates a random orientation of the crystallites.

In the case of the oriented films grown during this study, the presence of only two diffraction peaks demonstrated that the C_{60} films were reasonably epitaxial, with close-packed planes of C_{60} molecules stacked parallel to the Si(111) surface. However, it was not possible with the instrumentation at hand to determine the stacking order of the planes perpendicular to the substrate, i.e., whether the crystal structure was hexagonal (ababab stacking) or cubic close packed (abcabc stacking). The latter type of structure has been observed consistently in diffraction data from macroscopic crystals grown from solution at UCLA. The diffraction peak at 10.88° is also quite broad, $\Delta(2\Theta) = 0.5°$ (FWHM), which corresponds to a coherence length for x-ray scattering in the film of only 190Å or so.[10] Thus, the stacking sequence of the close-packed planes may be irregular and/or interrupted by stacking faults. Impurities such as C_{70}

molecules may be necessary to stabilize an epitaxial film of the nearly spherical C_{60} molecules.

Electron spectroscopic data have been used extensively in studies of diamond and diamond-like carbon films, because the details of the C 1s XPS,[11] C KLL Auger,[12] and EELS[12] lineshapes are very sensitive to the hybridization of the C atoms and thus to the allotropic nature of the films. Therefore, a preliminary electron spectroscopic investigation of C_{60} has been carried out in order to provide a comparison with the major C sp^2-bonded allotrope, graphite.

The first sample to be examined had been exposed to air for four days before the spectroscopic measurements began. As shown in the upper portion of Fig. 3, a major oxygen contamination of the film was present, since the O 1s XPS peak was nearly as intense as the C 1s peak. This oxygen was not in the form of a lightly adsorbed species, such as water or molecular oxygen, since it could not be removed by heating the film in the vacuum chamber to 240°C, the temperature at which the films themselves begin to sublime. Thus, it appears as though at least the top few molecular layers of the film became irreversibly oxidized upon prolonged exposure to the atmosphere. The only way to remove the oxygen signal from the XPS spectra was to sputter the film. However, this treatment produced a film with a C 1s XPS signal that was very broad, which meant that the film was badly damaged by the ion bombardment. In contrast, a sample that was transferred through the air to the analysis chamber immediately after it was grown had no significant contamination, as shown by the middle spectrum of Fig. 3. The lower portion of Fig. 3 shows the XPS spectrum from a freshly cleaved HOPG sample for comparison.

The XPS spectra of the C 1s regions of both C_{60} and HOPG are shown in Fig. 4. The HOPG spectrum is in excellent agreement with that of Ref. 11. The binding energies of the C 1s peaks, referenced to the Fermi level of the spectrometer, are 284.9 eV and 284.7 eV for the C_{60} and HOPG, respectively. Both peaks have a FWHM of 1.7 eV, but the base of the high energy side of the HOPG peak is broader, which is consistent with the asymmetric XPS lineshape of a conductor. The C_{60} C 1s peak is more symmetric, as is usual for an insulator such as diamond.[11] However, both peaks have pronounced shoulders to the higher binding energy side, which is the signature of sp^2-hybridized carbon.[11] This broad energy-loss feature has been assigned to an interband transition involving the pi-states that is excited by some of the photoemitted electrons.[11] The differences between the C_{60} and HOPG loss features are subtle: the shoulder in the C_{60} spectrum is more intense and not as sharply peaked as the HOPG feature, which has a well-defined loss energy of 6.3 eV. Thus, the joint density of valence and conduction band states for C_{60} and for HOPG are definitely different, even though the XPS valence band spectra for the two materials are virtually identical.

The very broad features at an energy loss of 25-35 eV with respect to the C 1s lines in the spectra of Fig. 4 for the two forms of carbon are the result of plasmon excitations. For HOPG, the authors of Ref. 11 assigned two plasmons at 28.1 and 33.3 eV loss energy to their spectra, although one could just as easily assign a single loss feature at 30.5 eV. For C_{60}, the centroid of the plasmon feature is at a loss energy of about 29.2 eV and is significantly narrower than for HOPG. The smaller average energy for the plasmon loss of C_{60} is consistent with the facts that its density is lower than that of HOPG and the plasmon frequency is proportional to the square root of the valence electron density.[13]

The KLL Auger differential spectra of the two carbon allotropes also reveal significant differences, as shown in Fig. 5. The main negative portions of the spectra are essentially identical to each other, but the fine structure in the positive portions are quite distinct. The HOPG spectrum is very similar to that of Ref. 12, except that the features are sharper because the resolution of the spectrum in Fig. 5 is better. The Auger spectrum of C_{60} is actually similar to that for the amorphous carbon film shown in Ref. 12. Since the features in the C KLL Auger spectra arise primarily from peaks in the convolution of the valence band with itself,[12] they are very sensitive the the hybridization of the carbon atoms. The fact that the C_{60} Auger spectrum resembles that of amorphous carbon indicates that the hybridization of the carbon atoms in C_{60} is not strictly sp^2, but that the curvature of the molecular surface introduces some sp^3 character into the molecular orbitals.

The EELS spectra for the two allotropes are shown in Fig. 6. In the few-eV regime, EELS is essentially a convolution of the valence- and conduction-band states of the material investigated, and should be closely related to the energy loss features observed for the XPS peaks. In this case, the kinetic energy of the primary electrons is 206 eV instead of 1200 eV. The rise in intensity of the C_{60} EELS signal occurs at a larger energy loss than for the HOPG and with a somewhat smaller initial slope. In addition, the intensity of the loss signal from C_{60} goes to zero, whereas there is a nonzero minimum loss intensity for the HOPG spectrum. These facts are indications of a fully open bandgap for the C_{60}, as compared to HOPG, which has a relatively large bandgap except along one line in the Brillouin zone.[11] The energies of the plasmon loss features in the EELS spectra are consistent with the loss peaks observed for the C 1s XPS data.

IV. SUMMARY

Thin films of solid C_{60} have been grown on Si(111) substrates by sublimation in UHV. The films deposited from an unpurified source resulted in epitaxial layers consisting of close-packed planes of molecules stacked on top of one another, but the coherence length for x-ray scattering was less than 200Å. The electron spectroscopic data of these films show that the hybridization of the carbon is primarily sp^2, but with a significant admixture oı sp^3 hybridization. The photoemission lineshape and the EELS data reveal a fully open bandgap in solid C_{60}, which is consistent with preliminary conductivity measurements.

V. ACKNOWLEDGMENTS

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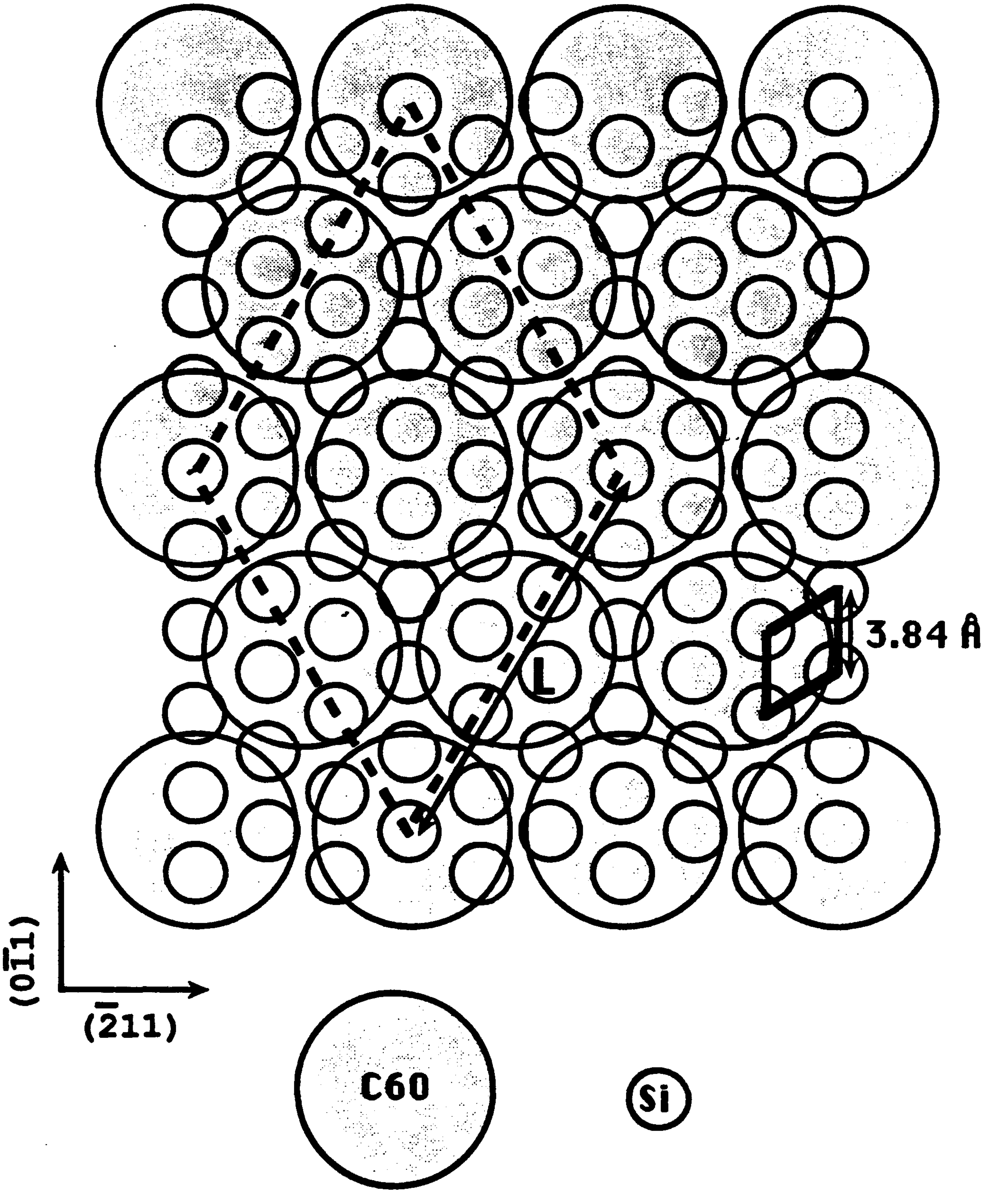
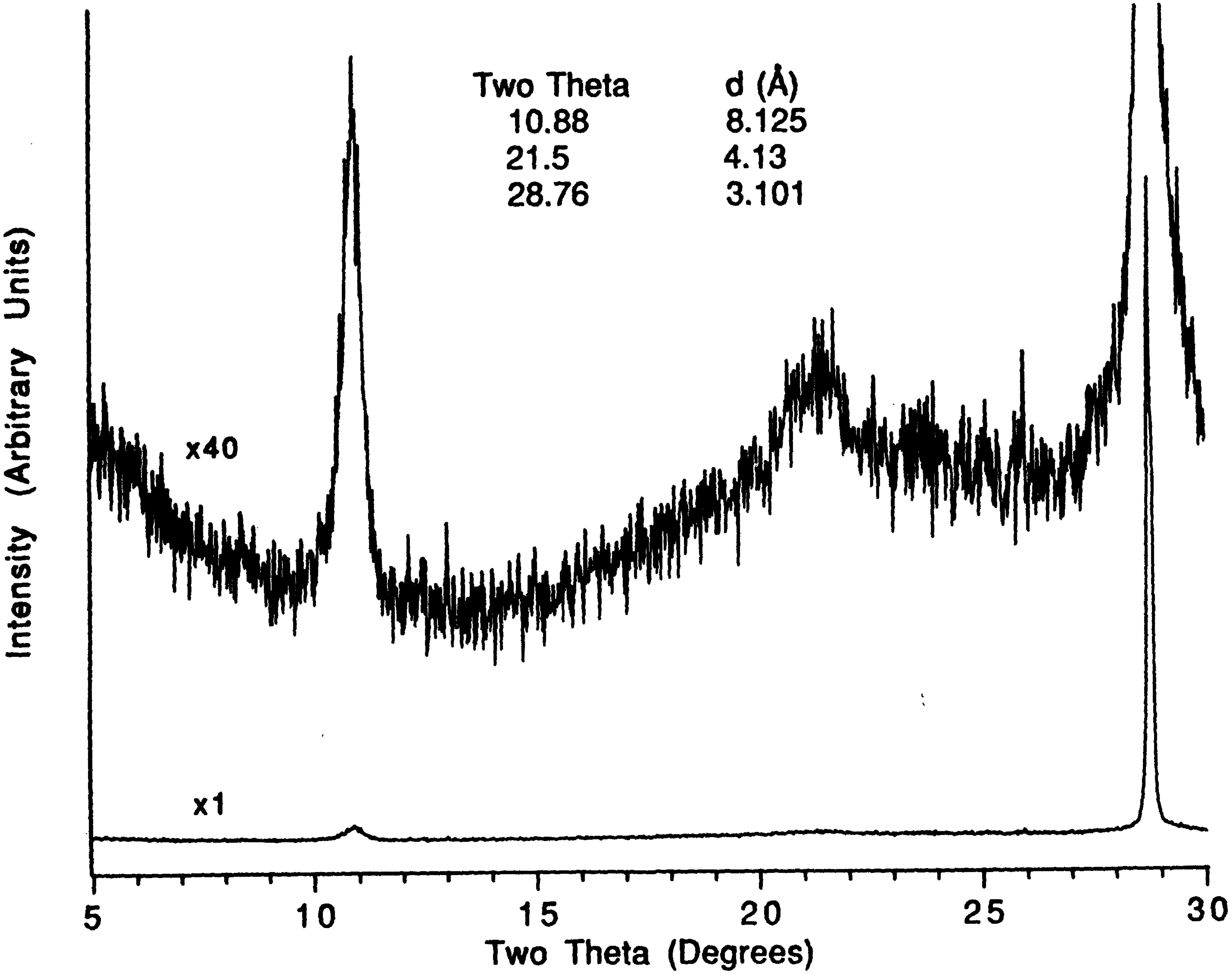
VII. FIGURE CAPTIONS

1. A schematic illustration of the lattice matching condition for a close-packed plane of C_{60} grown on an unreconstructed Si(111) surface.
2. The theta/two-theta diffraction pattern of a 1500Å film of C_{60} deposited from unpurified source material onto an ambient temperature Si(111) substrate. The two small peaks arise from the deposited C_{60} and correspond to reflections from the close-packed planes, whereas the large peak at a two-theta value of 28.76° is the Si (111) reflection.
3. XPS survey scans excited by Al Kα radiation: upper, a C_{60} film that had been exposed to atmosphere for four days prior to examination; middle, a C_{60} film that had been transferred to the spectrometer immediately after growth; and lower, a freshly cleaved HOPG surface. In the upper spectrum, a large O 1s peak is present at a binding energy of 528 eV, and the x-ray excited O KLL Auger peak is at 990 eV on the binding energy scale. No significant contamination can be observed in either the middle or lower spectra.
4. Al Kα XPS spectra of the C 1s regions of the C_{60} film and HOPG.
5. Electron-beam excited C KLL Auger spectra for upper, C_{60}, and lower, HOPG. The spectra were collected in pulse-counting mode and numerically differentiated to provide the best available resolution.
6. The EELS spectra, presented in integral mode, for C_{60} and HOPG. The primary electron beam energy was 206 eV, and the heights of the elastic peaks have been normalized to each other.



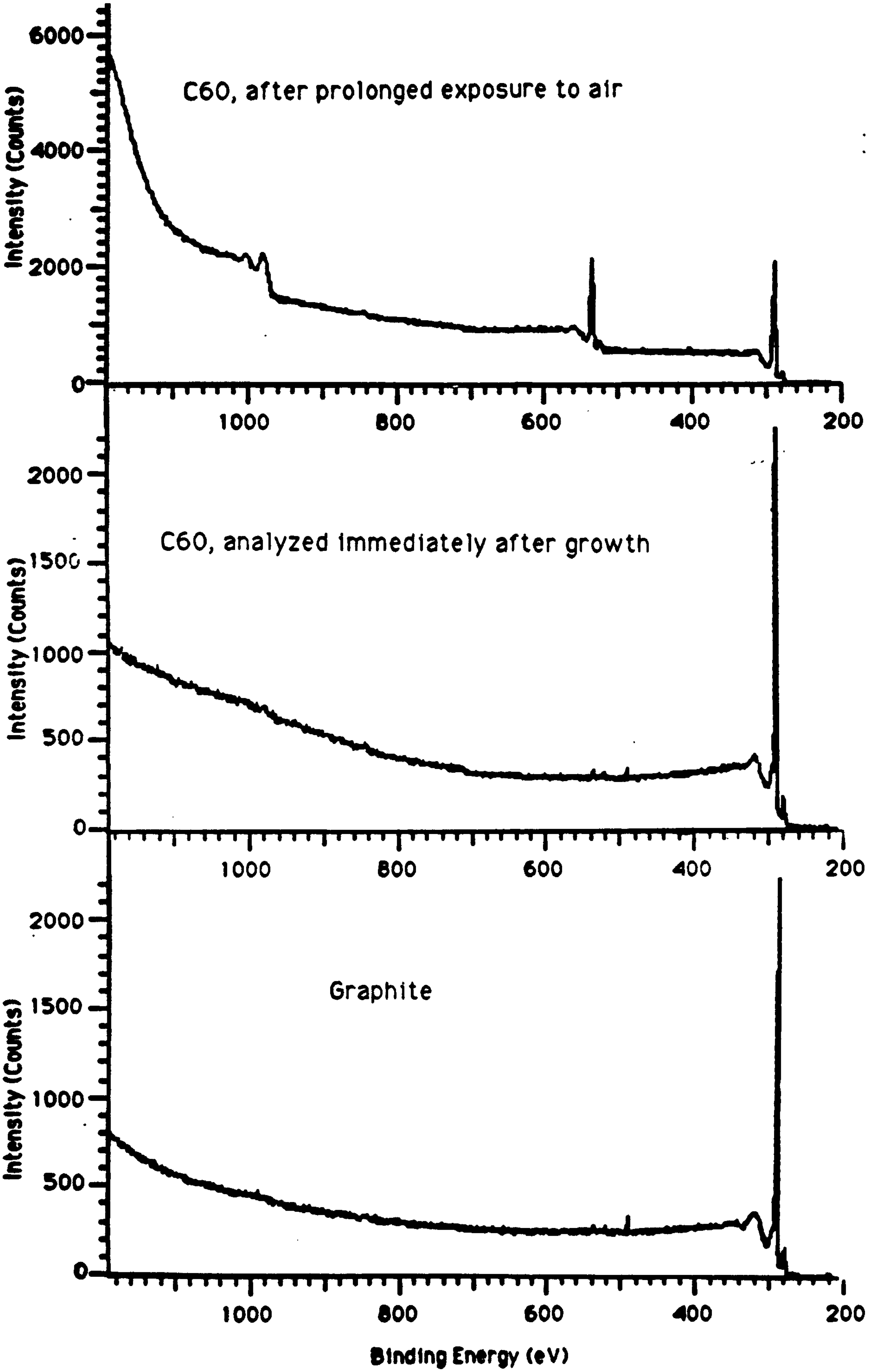
L = 19.95 Å for Si (111)
20.04 Å for C60 (from Ref. 1)

Fig. 1



Two Theta	d (Å)
10.88	8.125
21.5	4.13
28.76	3.101

Fig 2



C60, after prolonged exposure to air
C60, analyzed immediately after growth
Graphite
Intensity (Counts)
6000
4000
2000
0
2000
1500
1000
500
0
2000
1500
1000
500
0
1000
800
600
400
200
Binding Energy (eV)

Fig. 3

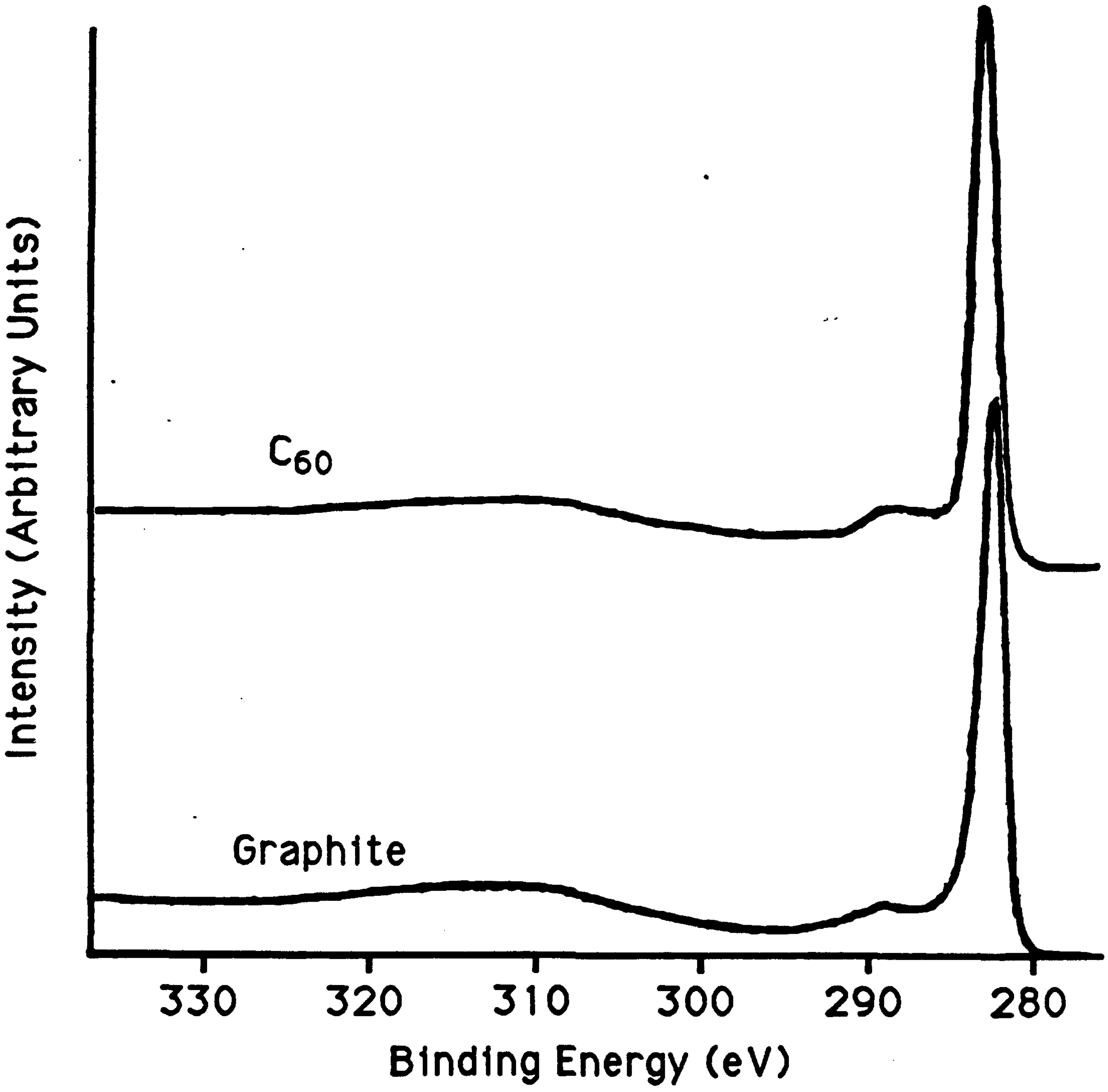
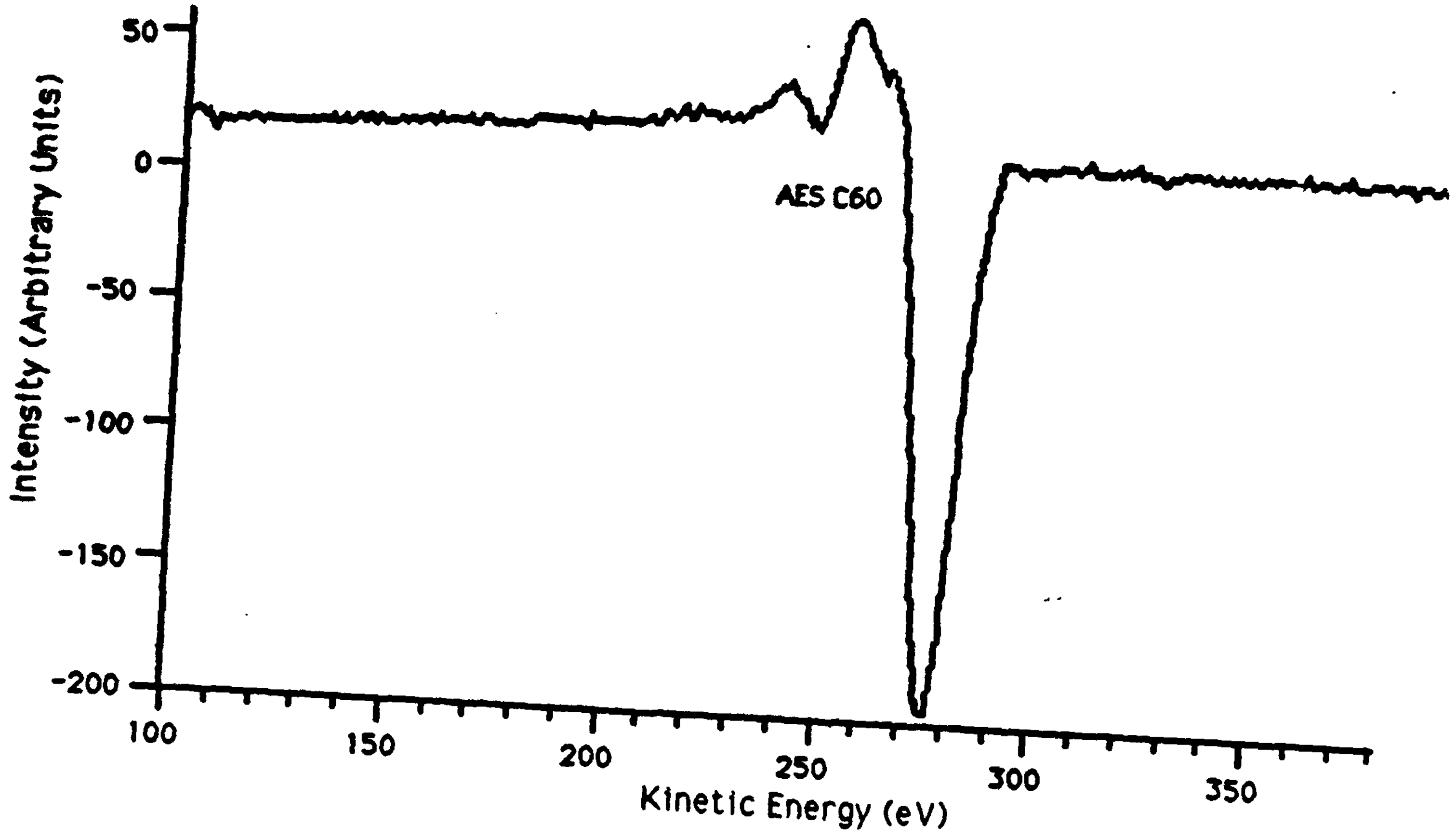
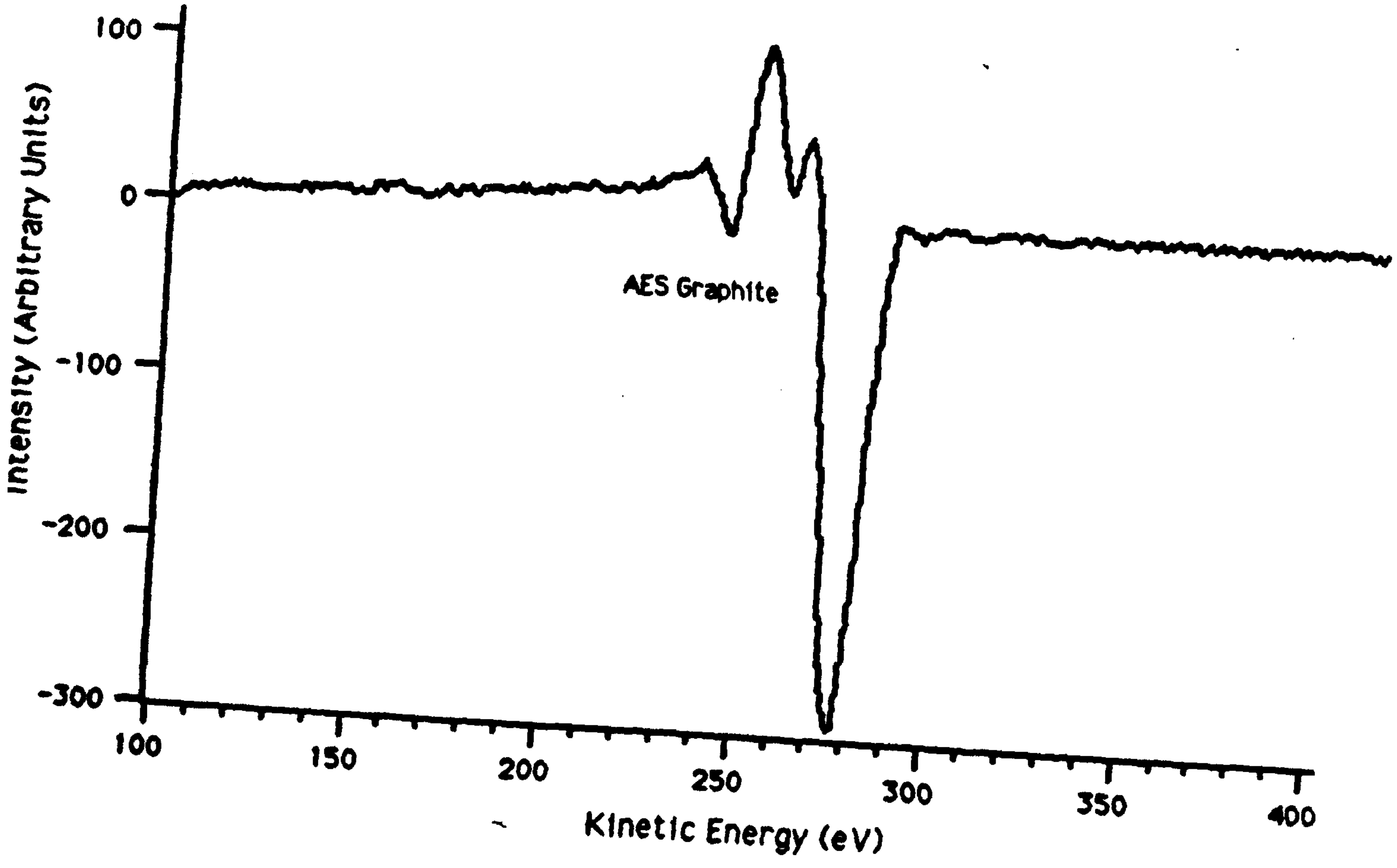

Intensity (Arbitrary Units)
C_{60}
Graphite
330
320
310
300
290
280
Binding Energy (eV)

Fig. 4



50
0
-50
-100
-150
-200
Intensity (Arbitrary Units)
AES C60
100
150
200
250
300
350
Kinetic Energy (eV)



100
0
-100
-200
-300
Intensity (Arbitrary Units)
AES Graphite
100
150
200
250
300
350
400
Kinetic Energy (eV)

Fig. 5

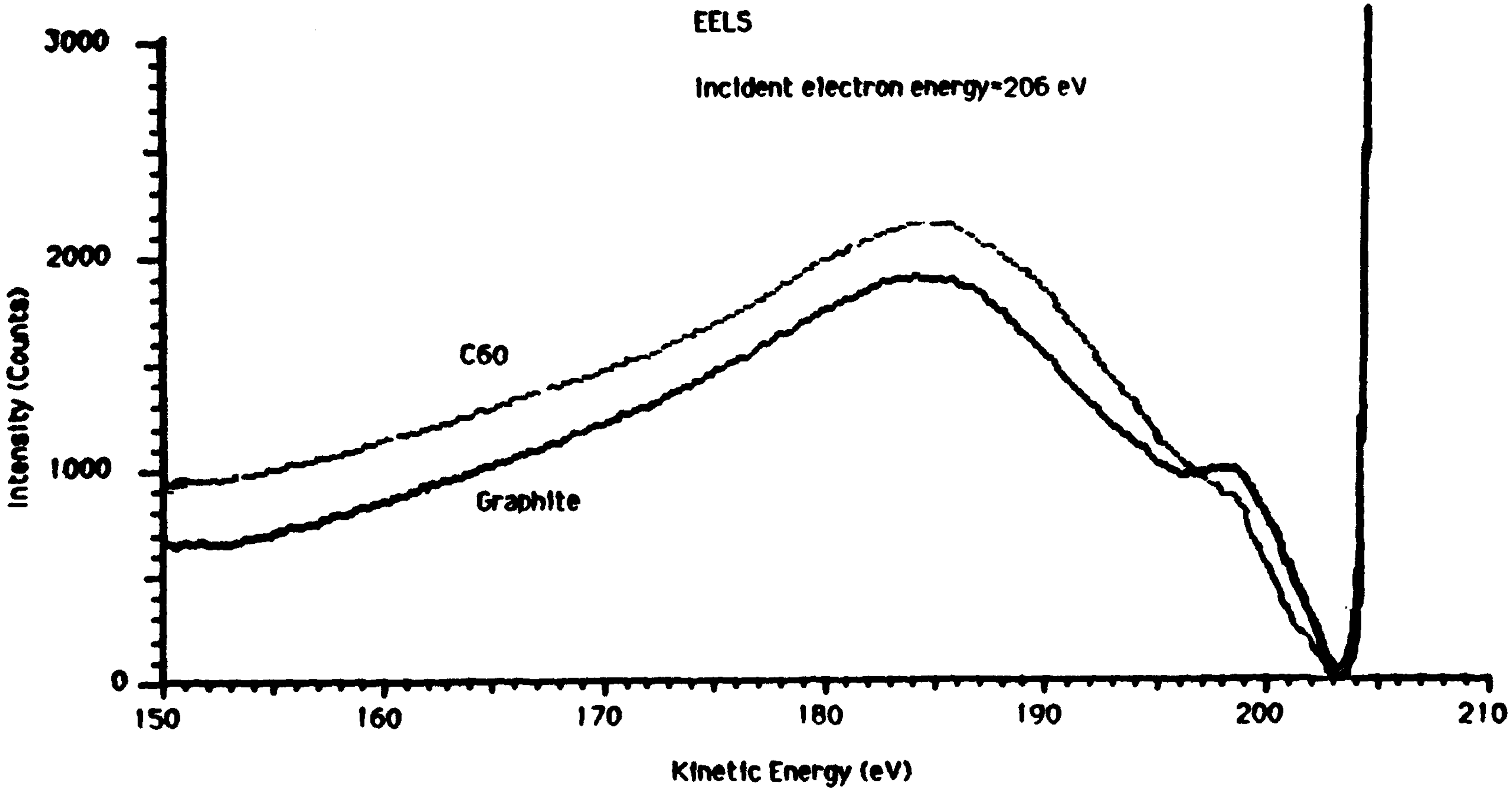
EELS
Incident electron energy=206 eV
C60
Graphite
Intensity (Counts)
3000
2000
1000
0
150
160
170
180
190
200
210
Kinetic Energy (eV)

Fig. 6