

## Thermal decomposition of a fullerene mix

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Experiments to characterize fullerene decomposition at temperatures above 973 K were conducted by spectroscopic analysis of samples heated *in vacuo*. The thermal decomposition can be described by first-order kinetics with an activation energy of  $266 \pm 9$  kJ/mol and a preexponential factor of  $1.24 \times 10^9$  s<sup>-1</sup>. Though scanning electron micrographs display structures with a distinctly faceted appearance, x-ray diffraction, Raman spectroscopy, and transmission-electron microscopy all show that the material is composed of amorphous carbon and graphite, indicating that pyrolysis of the fullerite occurs without destroying crystal facets.

### I. INTRODUCTION

Since fullerenes became available in macroscopic quantities in 1991,<sup>1</sup> there have been several experimental studies of the thermal stability of C<sub>60</sub>.<sup>2-4</sup> These investigations are important for practical applications such as effusive fullerene sources. In addition, decomposition kinetics can provide insights into the chemistry of fullerene formation, because ring-rearrangement steps are believed to be involved in both processes.<sup>5,6</sup>

Frum *et al.*<sup>7</sup> observed thermal degradation of C<sub>60</sub> heated to 1223 K while studying its infrared emission spectrum, while Sundar *et al.*<sup>4</sup> observed that solid C<sub>60</sub> decomposes into amorphous carbon upon heat treatment beyond 993 K for 24 h. However, neither of these studies attempted to quantify the decomposition kinetics.

Two studies have reported rate constants for thermal decomposition of gas-phase C<sub>60</sub> at higher temperatures.<sup>2,3</sup> Von Gersum, Kruse, and Roth<sup>2</sup> studied pyrolysis of shock-heated C<sub>60</sub> dispersed in argon over the temperature range from 2370 to 3500 K. They report an activation energy of 120 kJ/mol for the decay of broadband emission near 490 nm which they attribute to C<sub>60</sub>, and a value of 190 kJ/mol for the appearance of C<sub>2</sub> spectral emission features.

Kolodney, Tsipinyuk, and Budrevich<sup>3</sup> used a two-stage effusive source of C<sub>60</sub> to study thermal decomposition in the temperature range between 1720 and 1970 K. They report an Arrhenius activation energy of  $385 \pm 30$  kJ/mol for unimolecular decay.

At higher energies, there are numerous reports of electron-impact-induced<sup>8</sup> and laser-induced fragmentation<sup>9,10</sup> of C<sub>60</sub>. The primary decomposition channel at high excitation energy is believed to be



which is endothermic by 6–13 eV.<sup>8-11</sup>

Thermal decomposition has also been the subject of several theoretical studies.<sup>6,12-14</sup> Molecular-dynamics

simulations show that C<sub>60</sub> decomposes within a few hundred vibrational periods when heated to a temperature of 4900–5500 K.<sup>12-14</sup> In at least one study,<sup>6</sup> simulations show the C<sub>60</sub> decaying via reaction (1) without the cage opening.

In this work, we report measurements of the thermal decomposition of a solid fullerene mix over the temperature range from 973 to 1273 K. To our knowledge, this is the first report of solid-state fullerene decomposition kinetics.

### II. EXPERIMENTAL PROCEDURE

#### A. Sample preparation

We employed a method similar to that of Sundar *et al.*<sup>4</sup> to determine the thermal stability of fullerene mix. Quartz ampoules were each filled with approximately 10 mg of fullerene extract containing C<sub>60</sub> and C<sub>70</sub> in a ratio of approximately 85% to 15%. The fullerene mix was Soxhlet extracted with toluene from soot produced by Ulvick Industries. Pure C<sub>60</sub> from MER Corporation and pure C<sub>70</sub> from Term Ltd. were used as standards for compositional analysis.

The fullerene-containing ampoules were placed under dynamic vacuum in the mid-10<sup>-6</sup>-Torr range and heated to temperatures between 473 and 523 K to eliminate solvent and hydrocarbon impurities.<sup>15</sup> Partial pressures of monatomic and diatomic oxygen, CO and N<sub>2</sub>, CO<sub>2</sub>, OH, H<sub>2</sub>O, toluene, and benzene were monitored using a MKS model 600A PPT Residual Gas Analyser. The preheating of the samples lasted anywhere from 6 to 16 h, depending upon the concentration of solvent impurities in the powder. Upon initial heating, there was a rapid and significant increase in toluene partial pressure, with moderate increases in O<sub>2</sub> and H<sub>2</sub>O. Some of the observed oxygen may have come from C<sub>60</sub> epoxide.

The ampoules were then vacuum sealed and placed in a tube furnace for durations of 5 min to 6 h. We prepared sets of samples heated to 873, 973, 1073, 1098, 1123,

1148, 1173, and 1273 K. After removing the samples from the tube furnace, we noted that, in most cases, the fullerene powder had remained at one end of the ampoule with only a slight coating of soot on the walls. However, samples heated to 1273 K for a few minutes or to 1173 K for 1 h formed a thick black coating on the entire inner surface of the ampoules.

### B. UV-VIS absorption spectroscopy

The remaining fullerene content was determined by UV absorption spectroscopy using a Cary 5E UV-VIS-NIR spectrophotometer and a Hewlett-Packard model HPUV 8452A spectrometer. A 1.0-cm path length was used with blank solvent as the reference. The powder samples were placed in 200 ml of methylene chloride or toluene and sonicated. A further dilution of 1:10 was made for analysis. The concentrations of  $C_{60}$  and  $C_{70}$  were determined by monitoring the 336- and 384-nm ab-

sorption features, respectively. The 260-nm peak of  $C_{60}$  was also monitored in the methylene-chloride-dissolved samples, but was obscured by the strong absorption by toluene at this wavelength. Significant quantities of seemingly insoluble material were observed in the methylene chloride solutions after sonicating for several hours, even though the solubility of  $C_{60}$  in methylene chloride has been reported<sup>16</sup> as 0.26 mg/ml. We found that some of the residual solid was soluble in toluene. Subsequently, all remaining samples were analyzed in toluene.

Peak intensities were corrected for initial sample weight, then correlated to remaining fullerene material. Repeatability of dilution preparation and inhomogeneity of the fullerene mix were the main sources of error. As a result, the peak height of the 336-nm absorption feature exhibited sample-to-sample variations of  $\pm 3.7\%$ . The contribution to absorption at this wavelength by a 15%  $C_{70}$  content is approximately 12%. The amount of higher fullerenes ( $C_n$  for  $n > 70$ ) contained in the samples was not determined.

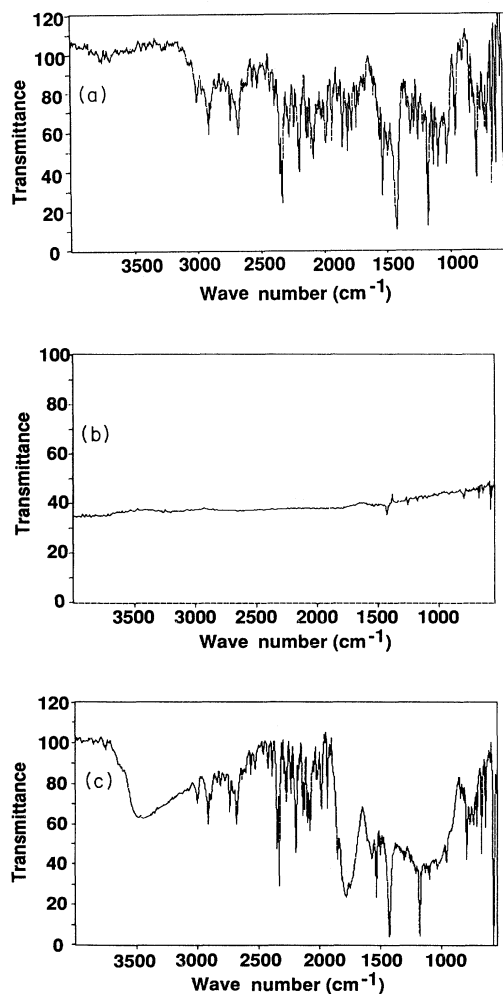


FIG. 1. Diffuse reflectance FTIR spectra of fullerene mix (a) heated to 523 K for 12 h under vacuum, (b) heated to 1073 K for 1 h under vacuum, and (c) heated for 18 h in nitrogen and air.

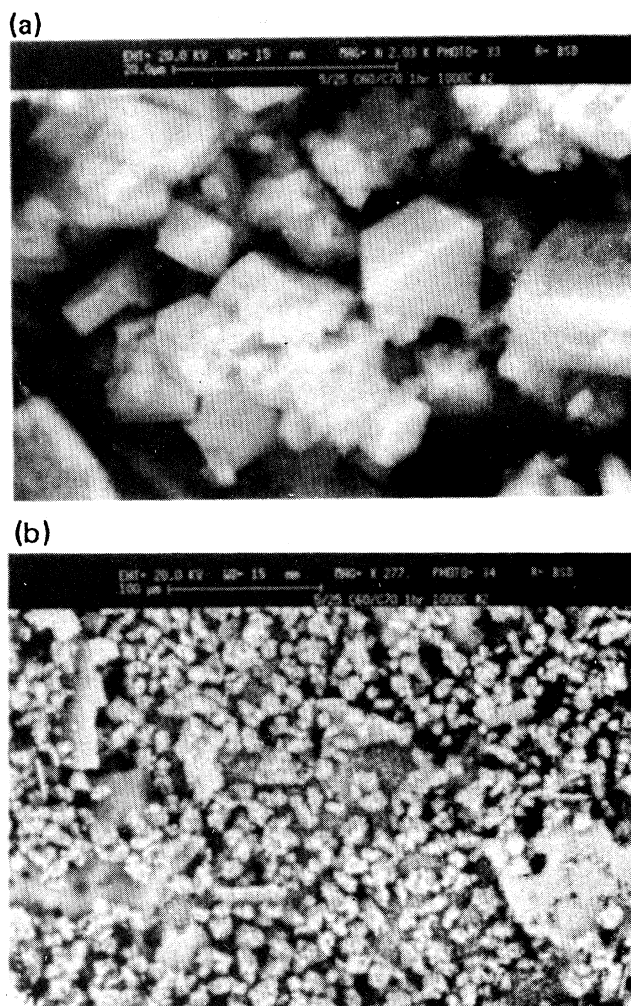


FIG. 2. SEM micrographs of carbon powder obtained from heating mixed fullerenes to 1273 K for 1 h (a) 2030  $\times$  magnification, (b) 277  $\times$  magnification.



FIG. 3. Diffraction pattern of decomposed fullerene material showing rings attributed to graphite polycrystals.

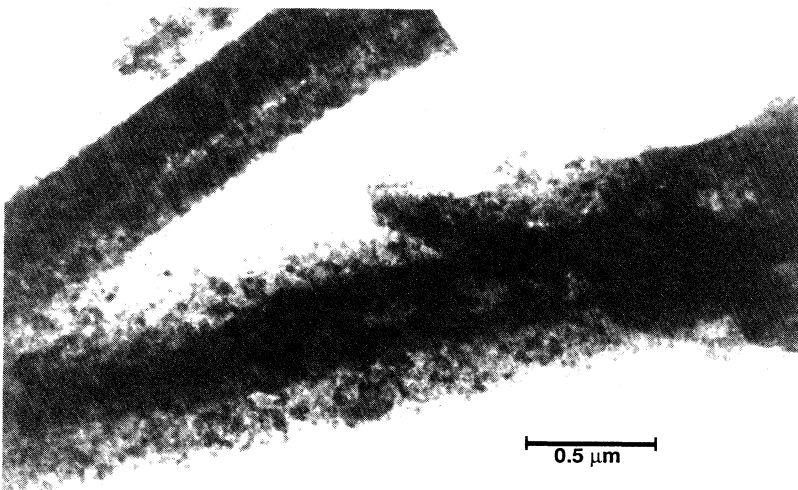


FIG. 4 Bright-field TEM micrograph of a decomposed fullerite structure.

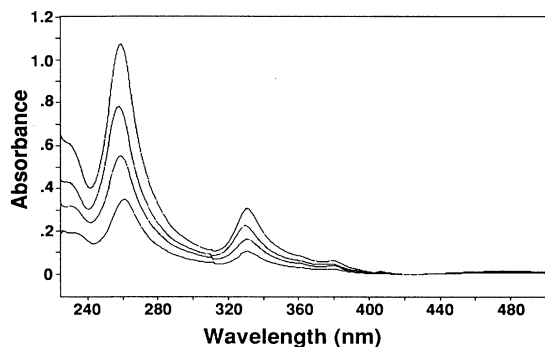


FIG. 5. UV-VIS absorption spectrum of mixed fullerene samples heated at 1073 K for 20, 60, 180, and 360 min. The solutions were prepared with methylene chloride.

### III. RESULTS AND DISCUSSION

#### A. Diffuse reflectance FTIR spectroscopy

To verify that decomposition was not a result of reaction or catalysis with impurities, diffuse reflectance Fourier transform infrared (FTIR) spectroscopy was used to analyze the decomposed material. Figures 1(a)–1(c) shows three spectra: (a) untreated fullerene mix, (b) a sample heated to 1073 K in vacuum for 1 h, and (c) a sample heated for 18 h at 523 K in nitrogen and air. Note the appearance of cyclic anhydride features in the 1800–1000-cm<sup>-1</sup> region of Fig. 1(c), similar to those reported elsewhere.<sup>17</sup> However, no oxidation products are evident in the 1073 K sample, although only 50% of the material remained as fullerene. The high concentration of carbon black in the sample heated to 1073 K resulted in the relatively low transmittance seen in Fig. 1(b). Small amounts of hydrocarbon impurities are evident in all of the samples. Also, there is a possibility that at these temperatures, any intermediate compounds will have decomposed, leaving only CO<sub>2</sub> and CO as reaction products and catalysts. We have not attempted to determine whether these gases are present in the sealed ampoules after heating.

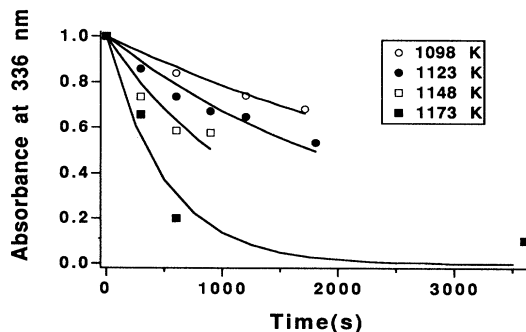


FIG. 6. Decomposition rate of the toluene-dissolved samples heated to 1098, 1123, 1148, and 1173 K. Data points are experimental, lines are exponential curve fits.

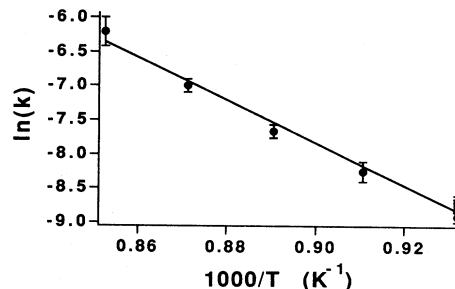


FIG. 7. Arrhenius plot of the thermal decay rate constant of a fullerene mix.

#### B. Microscopy

Samples that had been heated to temperatures greater than 1273 K were completely insoluble in toluene. This material was examined with an x-ray diffractometer, which showed no diffraction peaks. Raman spectroscopy also failed to show evidence of an ordered structure. Although all indications were that the fullerenes had decomposed into amorphous carbon, the material appeared distinctly faceted. Scanning-electron-microscope images of this material are shown in Figs. 2(a) and 2(b). A selected area diffraction pattern of one of the structures in a Phillips 301 transmission-electron microscope produced only rings (Fig. 3) from graphite polycrystals. Figure 4 is a bright-field image of the faceted structure. The fullerite appears to have pyrolyzed without destroying the crystal shape.

#### C. Decomposition kinetics

Figure 5 shows the UV absorption spectrum of mixed fullerene samples heated at 1073 K for 20, 60, 180, and 360 min. The solutions were prepared with methylene chloride. Figure 6 shows the decay of the 336-nm peak height of the toluene-dissolved samples heated to 1098, 1123, 1148, and 1173 K. We were not able to discern any significant changes in the ratio of C<sub>60</sub> to C<sub>70</sub>, and therefore conclude that the difference in their decay rates is within the uncertainty of this experiment.

By assuming the fullerene decay data shown in Fig. 6 may be described by unimolecular decomposition, we obtained decay constants  $k(T)$  such that the remaining ful-

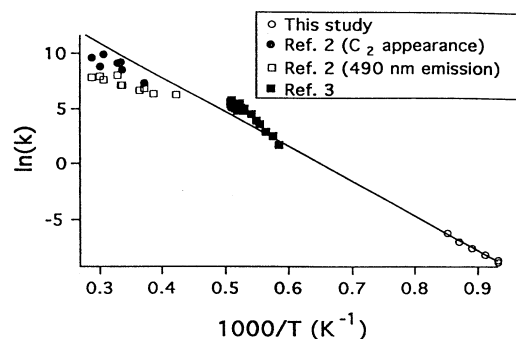


FIG. 8. Comparison of the decay rates of this study with data for gas phase decomposition (Refs. 2 and 3).

lerene concentration is proportional to  $\exp(-k(T)t)$ . The exponential curves which yield the best fit to the data are also shown in Fig. 6. An Arrhenius plot of the rate constants determined from the curve fits of Fig. 6 is shown in Fig. 7. The best-fit line gives a rate constant of

$$k(T) = 1.24 \times 10^9 \exp(E_a/RT) \text{ s}^{-1}, \quad (2)$$

where  $E_a = 266 \pm 9$  kJ/mol.

This activation energy is more than twice as high as the 120 kJ/mol, and approximately 30% smaller than the  $385 \pm 30$  kJ/mol previously reported for the thermal decomposition of pure  $C_{60}$  in the gas phase.<sup>2,3</sup> A comparison of our results with the previously published data is shown in Fig. 8. Remarkably, all three sets of data can be described by a single Arrhenius fit to within an order-of-magnitude uncertainty over eight orders-of-magnitude variation. A best-fit line to the combined data gives an activation energy of 228 kJ/mol.

All three sets of experimental data indicate thermal decomposition rates for  $C_{60}$  at low temperature which are much higher than one would predict for a single-step  $C_2$  ejection process. For example, if we assume this process has a rate of  $10^{11} \text{ s}^{-1}$  at 5000 K and an activation energy of 675 kJ/mol [consistent with the endothermicity of reaction (1)], then the rate at 1000 K would be  $6 \times 10^{-18} \text{ s}^{-1}$ —orders of magnitude below the experimental value of  $2 \times 10^{-5} \text{ s}^{-1}$ .

These results suggest that a second, low-barrier decay channel exists. This process may include one or more ring-rearrangement isomerization reactions prior to ejection of a  $C_2$ .<sup>3,6</sup> However, theoretical estimates of the barriers for ring-rearrangement steps suggest the lowest barrier is still 810 kJ/mol. Clearly, more theoretical work will be required to explain the low activation energy for thermal decomposition of  $C_{60}$ .

#### IV. CONCLUSIONS

We have found an activation energy of  $266 \pm 9$  kJ/mol for the solid-state thermal decomposition of a fullerene mix over a temperature range from 1073 to 1173 K. The

rate constant is consistent with the previously published experimental data for unimolecular decomposition of vapor phase  $C_{60}$ . Scanning electron microscope (SEM) images of the decomposed sample show a faceted structure, though x-ray diffraction, Raman spectroscopy, and transmission-electron microscopy (TEM) all show that the material is a combination of amorphous carbon and graphite. Diffuse reflectance FTIR spectroscopy does not detect the presence of intermediate compounds. The integrity of the fullerite crystal shape after decomposition makes it unlikely that the reaction mechanism is catalysis with impurities or quartz surfaces. Hence we attribute the degradation to solid-state unimolecular decay.

This result makes the existence of a liquid phase of  $C_{60}$  (Refs. 18–20) highly unlikely. It also places bounds on the range of operating temperatures of fullerene vapor sources and ionization techniques for producing fullerene plasmas.

Further work to extend the experimental data to temperatures higher than those explored in this study, yet lower than that of prior investigations<sup>2,3</sup> will require another technique. *In situ* monitoring of the Bragg peak intensity of heated fullerite samples<sup>20</sup> may be successful in yielding more insight into fullerene decomposition kinetics.

#### ACKNOWLEDGMENTS

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(a)



(b)

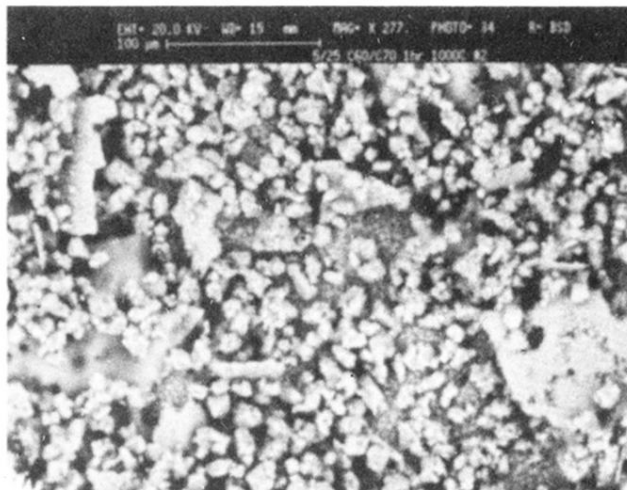


FIG. 2. SEM micrographs of carbon powder obtained from heating mixed fullerenes to 1273 K for 1 h (a) 2030  $\times$  magnification, (b) 277  $\times$  magnification.

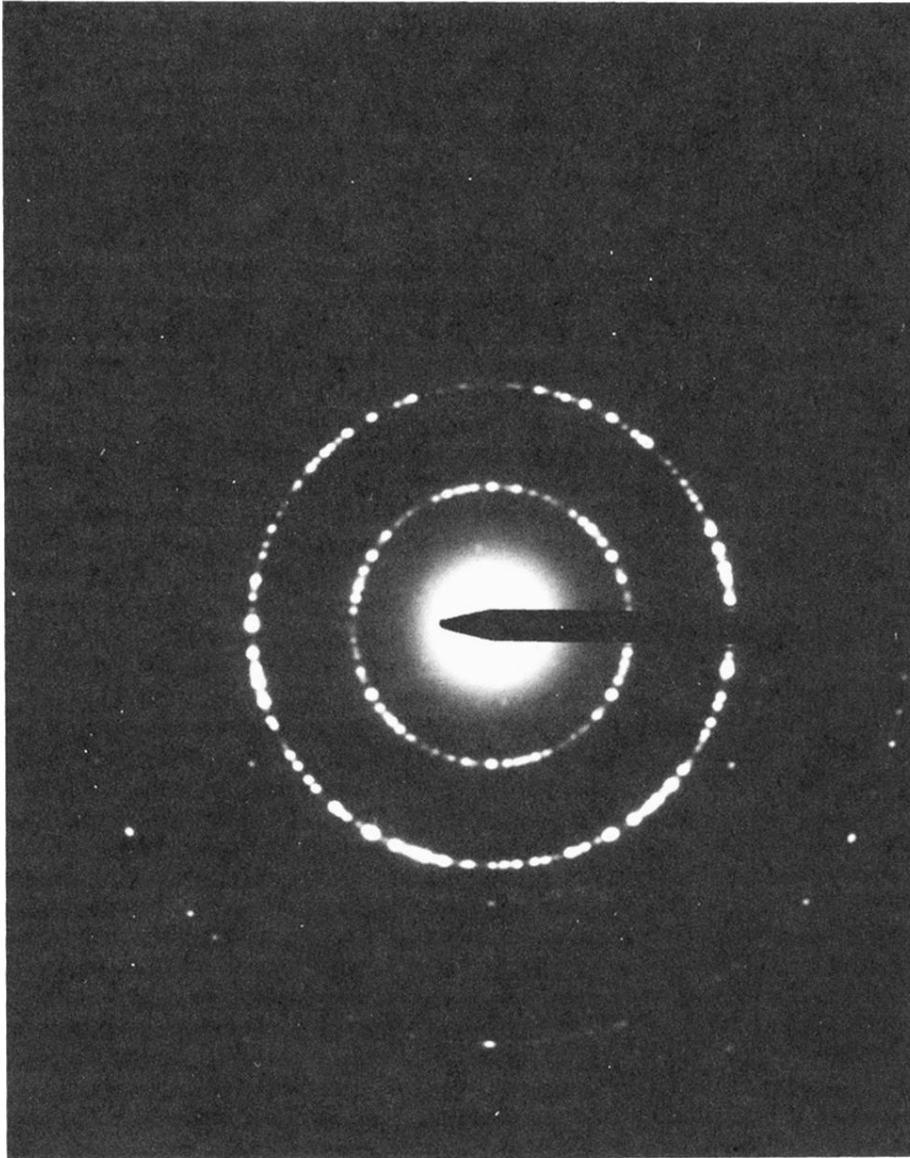


FIG. 3. Diffraction pattern of decomposed fullerene material showing rings attributed to graphite polycrystals.



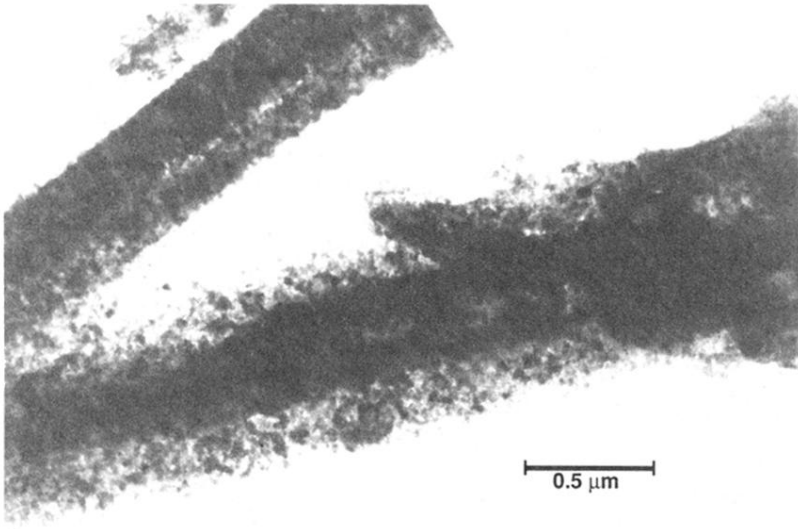


FIG. 4 Bright-field TEM micrograph of a decomposed fullerite structure.