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Intercalation of AsF_5 in C_{60}

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The product of a solid solution reaction of C_{60} and AsF_5 in liquid SO_2 is reported. The change of weight of the C_{60} by the reaction indicates that there is $(AsF_5)_xC_{60}$ with $x=1.88\pm0.04$. Mass spectroscopy identifies the AsF_5 and C_{60}. The x-ray diffraction is distinctly different from that of C_{60} and can be indexed with a body-centered-tetragonal unit cell. The infrared spectrum has an absorption at 702 cm^{-1} which is not present in C_{60}.

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Many fullerene-based compounds have been prepared with interesting properties and potential applications. Some of these such, as the alkali-metal-doped C_{60} compounds, are intercalation compounds in which the introduced atoms occupy interstitial sites in the C_{60} lattice, and the fullerene host retains its molecular identity.[1] The AsF_5 molecule can be intercalated into graphite. In this Brief Report we show that the intercalation of AsF_5 with C_{60} is also possible.

Fluorinated and chlorinated fullerenes have been reported previously.[2-4] Reactions of C_{60} with Cl_2 produce species with 12–15 Cl's per C_{60}. Chlorine is extracted from these products by thermal, electrical, and electrochemical means. A product from the reaction of $SbCl_5$ and C_{60} has also been reported.[5] It was identified with x-ray, far-infrared and mass-spectromagnetic techniques.

A solid-solution method was adopted in order to prepare a homogeneous compound. A solution of AsF_5 dissolved in liquid SO_2 was reacted with C_{60} powder. The black C_{60} powder started to change to a suspension with a green color after 1 h. The complete reaction took place during three or four days at room temperature with continuous stirring. The final product had a uniformly dark green color. The excess SO_2 and AsF_5 were decanted, and the green compound was dried and removed from the reaction vessel for measurements.

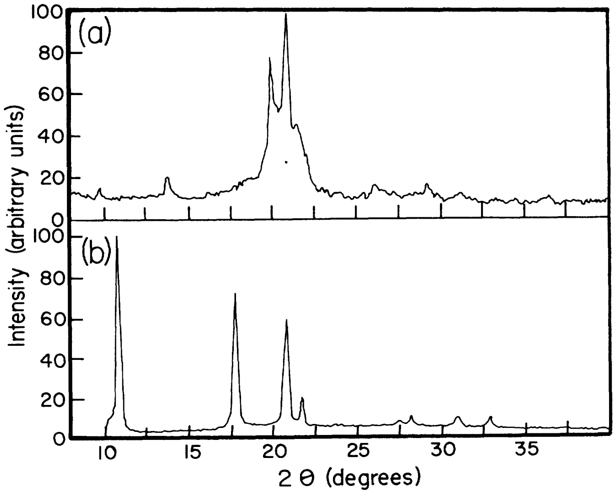

FIG. 1. X-ray diffraction with Cu K_α radiation of (a) $(AsF_5)_xC_{60}$, (b) C_{60}.

It was found that the compound changed to a brown color when it was exposed to room atmosphere. Thus the $(AsF_5)_xC_{60}$ was handled in a dry box and placed in sealed sample cells that were designed for each of the x-ray, mass spectrometric, and infrared measurements of its properties.

Several reactions were carried out to establish the stoichiometry of $(AsF_5)_xC_{60}$. A large amount of C_{60} was used so that the relative error of the weight analysis was small. All reactions with AsF_5 were done in a solution of SO_2 at room temperature for four or five days until a green solid was formed. The weights of the C_{60} before and after a reaction were used to determine the formula. It was found that with 550 mg of pure C_{60} as the starting material, x was 1.92. With 420 mg, x was 1.85. These two measurements indicate a formula $(AsF_5)_xC_{60}$ with $x=1.88\pm0.04$.

The Cu K_α X-ray powder patterns of the pure C_{60} and the $(AsF_5)_xC_{60}$ compound are shown in Fig. 1. The x-ray diffraction of the C_{60} in Fig. 1(b) is the same as that found previously with the fcc lattice parameter $a=14.172$ Å.[6] The pattern of the compound in Fig. 1(a) is distinctly different, indicating that it has a different lattice from that of C_{60}. Eight diffraction lines are discernable. They can be indexed with a body-centered-tetragonal (bct) unit cell with lattice parameters of $a=12.794$ Å and $c=12.426$ Å, as shown in Table I.

Mass analysis was made with a double-focusing mass

TABLE I. Observed and calculated x-ray diffraction with Cu K_α radiation of $(AsF_5)_xC_{60}$ for a tetragonal lattice with $a=12.794$ Å and $c=12.426$ Å.

h	k	l	$2\theta_{obs}$	$2\theta_{calc}$
1	1	0	9.783	9.769
2	0	0	13.769	13.832
2	0	2	19.933	19.906
2	2	1	20.851	20.883
0	0	3	21.466	21.436
3	2	1	26.122	26.095
2	2	3	29.178	29.212
4	2	0	31.240	31.144

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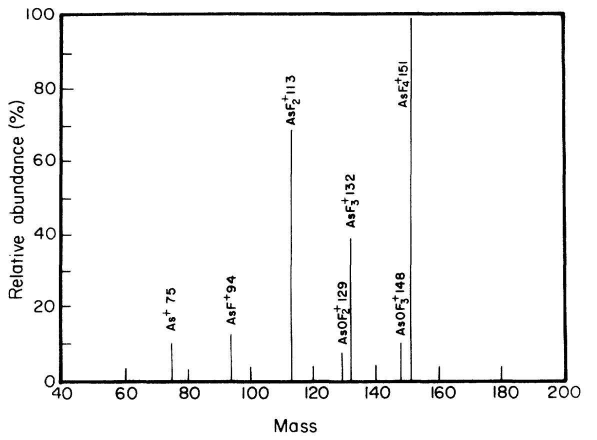

FIG. 2. Mass spectrum of $(AsF_5)_xC_{60}$.

spectrometer (ZAB-E) with the sample mounted in the source chamber of the spectrometer, and the vapor from a sample was bombarded by electrons with an energy of 70 eV. The mass spectrum of Fig. 2 has masses of AsF_x ($x=1$, 2, 3, and 4). The presence of these ions show that AsF_5 is in the sample because these ions are formed with the relative abundance of Fig. 2 from AsF_5 without the presence of AsF_5^+. The minor constituents of oxyfluorides were probably present in the commercial AsF_5. The spectrum of the sample in toluene gives the characteristic multiplit centered at 720 a.u. Thus the integrity of the C_{60} is maintained by the presence of the AsF_5. Mass spectra of polyfluorofullerenes were not observed, because they lose fluorine under ionization conditions of the electron bombardment.

The infrared spectra of C_{60} and $(AsF_5)_xC_{60}$ are shown in Fig. 3. The C_{60} spectrum has lines at 527, 575, 1182, and 1428 cm^{-1}, in agreement with previous reports for C_{60}.[7] The intensity of these lines is very small for $(AsF_5)_xC_{60}$. However, there is a strong absorption at 702 cm^{-1}. This absorption is characteristic of all samples with the peak in the range 702–709 cm^{-1}. The spectra of samples heated in vacuum to different temperatures for several hours were also recorded. The spectrum for heat treatment at 150 °C was similar to Fig. 3(a). However, treatments at 300 and 400 °C eliminated the absorption at 702 cm^{-1} and increased the intensity of the C_{60} lines, indicating that the sample was returned to the C_{60} state by the decalation of AsF_5.

TABLE II. Unit cells of bct C_{60} compounds and ionic radii r_0 of the intercalated species.

	a (Å)	c (Å)	c/a	$r/0$
K_4C_{60}	11.886	10.774	0.906	1.38
Rb_4C_{60}	11.962	11.022	0.921	1.47
Cs_4C_{60}	12.057	11.443	0.949	1.70
$(AsF_5)_xC_{60}$	12.794	12.426	0.971	1.577 axial 1.534 equatorial

The strongest lines of the infrared spectrum of gaseous AsF_5 at 798 and 819 cm^{-1} (Ref. 8) are not observed from $(AsF_5)_xC_{60}$, indicating that AsF_5 is not an isolated molecule in the material. Rather, there is the line at 702 cm^{-1}. This is not due to the C-F stretch mode which is expected in the range 1120–1350 cm^{-1} for CF_2 and CF_3.

Table II compares the cell parameters with those of A_4C_{60} (A =K,Rb,Cs) that forms a tetragonal lattice.[9] The lattice parameters and the c/a ratio increase as the size of the ion increases. The alkali ions occupy the four smaller lattice sites that are formed with $c<a$ from the six bcc tetrahedral sites. The two larger ones in the ab plane of the bct lattice are necessary for the AsF_5 ion. The AsF_5 molecule is a trigonal bipyramid and is similar to the PF_5 molecule with axial and equatorial distances of 1.577 and 1.534 Å, respectively.[8] This requires a larger site with some distortion. The weight of $(AsF_5)_xC_{60}$ with x close to 2 indicates that most of the larger sites are occupied.

Resistivity measurements indicate that the $(AsF_5)_xC_{60}$ is conducting at room temperature. The resistivity is of the order of 10^6 Ω cm, and increases as the temperature is

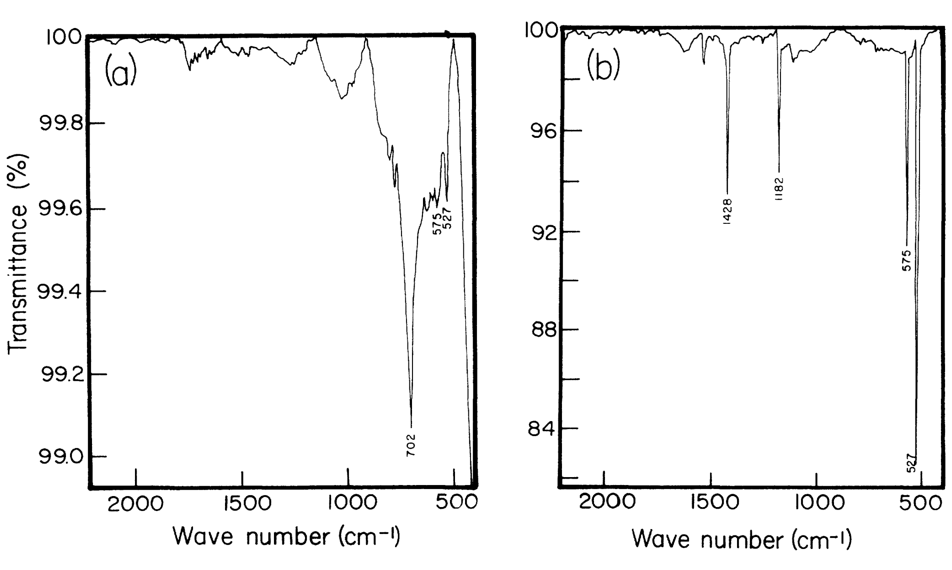

FIG. 3. Infrared spectra of (a) $(AsF_5)_xC_{60}$, (b) C_{60}.

lowered below room temperature. The resistivity is too large to be measured at temperatures below 170 K. Further tests at temperatures down to 4.2 K indicate that it remains insulating and does not become a superconductor. This was confirmed with susceptibility measurements taken with a superconducting quantum interference device (SQUID) magnetometer which showed no superconducting effects for temperatures down to 4.2 K.

In conclusion, $(AsF_5)_xC_{60}$ with $x = 1.88 \pm 0.04$ is formed by intercalation. It has a strong infrared absorption at 702 cm^{-1}. The x-ray diffraction indicates that there is a tetragonal lattice with $a = 12.794$ Å and $c = 12.426$ Å.

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