Growth of fullerene thin films and oxygen diffusion in fullerites 
\((C_{60} \text{ and } C_{70})\)

Undergraduate project in solid state physics

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Objectives

The objectives of the project were:

1. to learn about the molecular structure of\(C_{60}\) and \(C_{70}\) and crystalline structure of \(C_{60}\) and \(C_{70}\) fullerites;

2. to learn literature data on oxygen diffusion in fullerites and in particular the relation between oxygen diffusion and EPR measurements;

3. to grow thin films of \(C_{60}\) and \(C_{70}\) by vacuum deposition method and prepare samples for EPR measurements in order to study the differences of oxygen diffusion in \(C_{60}\) and \(C_{70}\).

Fullerenes

Fullerenes \((C_{20}, C_{24}, \ldots C_{60}, C_{70}, \ldots)\) are closed-cage molecules of pure carbon. \(C_{60}\) and \(C_{70}\) are the most abundant and stable members of the fullerene family. Fullerenes can form molecular crystals -fullerites –that are recognized as a third stable crystalline form of carbon, after graphite and diamond [1]. Fullerenes existed in nature long before they were discovered by humans, in interstellar dust and geological formations on earth. In a joint experiment conducted by Kroto and Smalley [2], the laser beam ablation of graphite in helium gas was studied and it was discovered by mass spectroscopy that there is a single peak with the mass of 720 amu. That implied that a single molecule of 60 carbon atoms was formed. The research group proposed a shape of truncated icosahedron cage
for this molecule. The molecule was named Buckminster fullerene after the American architect Buckminster Fuller who designed the geodesic dome. Five years later, the proposed structure was proved to be correct. This could happen only after the discovery of a simple technique of producing $C_{60}$ by using electric arc discharge between two graphite electrodes in a helium atmosphere [3].

Soon after its discovery the $C_{60}$ and other fullerenes raised great interest among scientists because of several unique features of theoretical and practical value. Some of them are:

1. unique symmetry of the molecule (see below);
2. use of fullerene as a semiconductor, conductor and even superconductor;
3. use of fullerene as a lubricant;
4. use of the fullerene molecules as a holder for drugs (inside the hollow ball) that would be slowly released.

The methods of producing fullerene are being studied until these days. The main ways of production are:

1. arc discharge – fullerene is created by using arc discharge between two graphite electrodes to create fullerene soot. The soot contains different kinds of fullerenes and hydrocarbon species. The fullerenes are extracted from the soot by the use of different organic solvents. The fullerenes are then purified to their different masses by chromatographic separation.
2. laser ablation of graphite – carbon vapor is created by intense laser beam.
3. ablation of graphite by ultrahigh solar flux – this method uses concentrated sunlight to create carbon vapor. Fullerene molecules are formed in the vapor environment (in a partial vacuum).
Structural properties of fullerene molecules

$C_{60}$:
In the preparation of fullerenes by any of the conventional methods (carbon arc-discharge, laser pyrolysis or solar light concentration) the fullerene species of greatest abundance by far is the $C_{60}$, the most stable of the fullerenes, and the fullerene molecule with the greatest symmetry (Fig. 1). The 60 carbon atoms arrange a truncated icosahedron with in 12 pentagonal and 20 hexagonal faces, in a way that there are no adjacent pentagons. Every carbon site on the molecule is equivalent to every other site. However, the three C-C bonds emanating from each C atom are not equivalent. Each of the 5 atoms on the pentagon perimeter has two single bonds that are electron poor while the bond between two adjacent hexagons is an electron rich double C=C bond. At room temperature, $C_{60}$ molecular crystal has FCC structure (Fig. 2). The forces between the molecules are weak Van-der-Vaals interactions.

$C_{70}$:
In synthesis of fullerenes, larger molecular weight fullerenes are also formed, by far the most abundant being $C_{70}$.

$C_{70}$ has been found to exhibit a rugby-ball shape and its form can be envisioned either by adding a ring of ten carbon atoms or a belt of 5 hexagons around the equatorial plane of the $C_{60}$ molecule normal to one of the five-fold axes (figure 3). $C_{70}$ crystallizes mostly in a FCC or HCP structures.

Chart 1 summarizes some of the physical properties of $C_{60}$ and $C_{70}$.
Chart 1: Physical properties of C\textsubscript{60} and C\textsubscript{70}.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>C\textsubscript{60}</th>
<th>C\textsubscript{70}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>FCC</td>
<td>FCC</td>
</tr>
<tr>
<td>Average c-c distance</td>
<td>0.144 nm</td>
<td></td>
</tr>
<tr>
<td>c-c bond length on a pentagon</td>
<td>0.146 nm</td>
<td>0.146 nm (maximal)</td>
</tr>
<tr>
<td>c-c bond length on a hexagon</td>
<td>0.140 nm</td>
<td>0.140 nm (minimal)</td>
</tr>
<tr>
<td>Mean molecule diameter</td>
<td>0.710 nm</td>
<td>0.798 nm (long)</td>
</tr>
<tr>
<td>Number of distinct c sites</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Number of distinct c-c bonds</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>$2.65 \pm 0.05$ eV</td>
<td>$2.72 \pm 0.05$ eV</td>
</tr>
<tr>
<td>Lattice constants</td>
<td>Fcc: 1.417 nm</td>
<td>Fcc: 1.501 nm</td>
</tr>
<tr>
<td></td>
<td>Hcp: $a=1.090$ nm</td>
<td>$c=1.750$ nm</td>
</tr>
<tr>
<td>$C\textsubscript{60}$-$C\textsubscript{60}$ distance in crystal</td>
<td>1.002 nm</td>
<td></td>
</tr>
<tr>
<td>$C\textsubscript{60}$-$C\textsubscript{60}$ cohesive energy</td>
<td>1.6 eV</td>
<td></td>
</tr>
<tr>
<td>Mass density</td>
<td>$1.65 \frac{g}{cm^2}$</td>
<td>$1.7 \frac{g}{cm^2}$</td>
</tr>
<tr>
<td>Band gap</td>
<td>1.7 eV</td>
<td>1.45 eV</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>1477 K</td>
<td>937 K</td>
</tr>
<tr>
<td>Sublimation temperature</td>
<td>731 K</td>
<td>937 K</td>
</tr>
</tbody>
</table>

Oxygen diffusion in C\textsubscript{60} and C\textsubscript{70}

A variety of experiments [for review, see Ref. 4] has strongly suggested that oxygen affects electronic and optical properties of C\textsubscript{60} films. Among them some studies have revealed a drastic but reversible reduction of dark and photo-conductivity in C\textsubscript{60} films upon their exposure to air. The diffused oxygen quenches the conductivity but does not react chemically with the C\textsubscript{60} molecules. On the other hand, illumination of C\textsubscript{60} films in air causes larger and irreversible changes in conductivity. It has been suggested that air/light exposure promotes C-O binding that damages the C\textsubscript{60} molecules, producing dangling bonds or other defects with deep levels in the gap. Furthermore, a re-distribution between fast and slow components of photoconductivity under the air/light exposure of
C$_{60}$ films also points to a generation of recombination centers with deep levels. In a joint EPR/SPV experiment [5] it has been demonstrated that the air/light exposure of C$_{60}$ films leads to the generation of the C$_{60}^+$ paramagnetic centers and deep acceptor states at $E_v + 1.3 eV$. These acceptors act as recombination and/or scattering centers. The paramagnetic and recombination/scattering centers were suggested to have the same origin. Thus, it is believed that monitoring the evolution of the EPR signal may be a relevant probe for studying the interaction of C$_{60}$ films with oxygen and the corresponding effects on the material properties.

The EPR signal of C$_{60}$ samples exhibits two distinguished regions of fast ($0 < t < 24$ h) and slow ($t > 24$ h) growth. It was also studied experimentally that the improvement of the crystalline structure of C$_{60}$ films, and in particular the increase in the grain size, leads to a deceleration of the EPR signal growth in the “fast” period of the exposure and vice versa. Thus it has been suggested that oxygen diffuses in fullerene films in two distinct ways. In the first few minutes of exposure oxygen diffuses along the grain boundaries rapidly decreasing conductivity by an order of magnitude. Then, in a slow process that can run for days, oxygen diffuses into the grains, lowering conductivity by about two more orders of magnitude. Measurements of the EPR signal while lowering the air pressure to $10^{-2}$ torr show a decrease of the intensity. The intensity grows back when the pressure is back to normal. For samples with small grain sizes the effect of air pumping is stronger than for samples with large grain sizes.

**Vacuum deposition of C$_{60}$ and C$_{70}$**

Vacuum deposition is one of the most popular ways of creating thin films. The selected material is vaporized in a vacuum chamber and crystallizes on a chosen substrate. The temperature of the material and the temperature of the substrate can be varied according to the physical characteristics. The vacuum is necessary to prevent interaction of the deposited material with the air.
Experimental setup:

Vacuum was created using mechanical air pump and diffusion pump. The substrate we used was glass. Six glass plates of the dimensions 3x20x1 mm were in the holder. Powder C$_{60}$ or C$_{70}$ was heated to evaporate in the vacuum chamber. Both C$_{60}$ and C$_{70}$ were deposited on glass at room temperature until a thickness of 1000Å was achieved. The rate of deposition on the substrate was kept stable by controlling the source temperature during the deposition. Generally, the source temperature was near the sublimation temperature. For C$_{60}$ the deposition rate was between the values of 12 and 25 Å/s and the pressure was between $2.3 \times 10^{-6} - 2.8 \times 10^{-6}$ torr. For C$_{70}$ the deposition rate was between 7 and 14 Å/s and the pressure was between $2.4 \times 10^{-6} - 3.5 \times 10^{-6}$ torr. Fig. 4 describes the experimental setup.

![Figure 4: The experimental setup](image-url)
After deposition, the samples were moved to the glove box with a small exposure (approx. 30 seconds) to air in a very weak light. In the glove box the samples were sealed in a dark nitrogen environment. The samples were then sent to the Physics Dept. of Ben Gurion University for EPR measurements. The EPR measurements were conducted by Dr. Alex Shames (BGU Dept. of Physics) and Dr. Eugene Katz (Blaustein Institute for the Desert Research).

Results

In agreement with previous experiments [5], oxygen-free C$_{60}$ and C$_{70}$ thin films are practically EPR silent and only air/light exposure leads to the appearance of a sharp ($\Delta H_{pp} = 0.124 \pm 0.005$ mT) Lorentzian EPR signal with g-factor $g = 2.0026 \pm 0.0002$. Meanwhile no other EPR signals were observed. The signal was attributed to C$^+_{60}$ centers which are located in the bulk of the films and generated due to oxygen diffusion into the C$_{60}$ and C$_{70}$ films. The experimental data on the intensity of such EPR signal as a function of air exposure are shown in figures 5 and 6.

![Graph showing EPR signal intensity of C$_{60}$ and C$_{70}$ in the first hours of exposure to air/light.](image)

**Figure 5:** EPR signal intensity of C$_{60}$ and C$_{70}$ in the first hours of exposure to air/light.
Discussion

Our EPR data clearly demonstrate that the oxygen diffusion rate in the C\textsubscript{70} film is much slower than in the C\textsubscript{60} sample. I will bring here several speculation that might explain the phenomenon.

1. By the results of an X-ray diffraction of the samples (not shown) it is clear that the average grain size in the C\textsubscript{70} sample is much smaller than in the C\textsubscript{60} sample. Intuitively, this should suggest that at least in the first few hours the oxygen diffusion rate in C\textsubscript{70} should be greater than in C\textsubscript{60}, because it is believed that oxygen diffuses faster into the grain boundaries [6]. As we can see from figure 5, this is not what happened. The intensity of the EPR signal in C\textsubscript{60} is greater from the beginning to the end. Therefore I suspect there ought to be another mechanism that is more crucial to the diffusion of oxygen than the diffusion into grain boundaries.

2. One example of such mechanism can perhaps be found by looking at the symmetries of the two samples. The C\textsubscript{60} film has a higher symmetry than the C\textsubscript{70} one because the C\textsubscript{70} molecules rotate at room temperature in all directions. It is possible that oxygen atoms get "locked" in preferred points near the surface of the C\textsubscript{70} crystal because of the lack of symmetry and therefore preventing other oxygen atoms from diffusing deeper into the solid. In C\textsubscript{60}, where the symmetry is much
greater, there are no such preferred points for the oxygen atoms and they continue diffusing into the solid.

3. Another explanation for the slower diffusion into $C_{70}$ is related to the different paths that oxygen molecule has to pass in order to enter the crystal. Calculations show that in $C_{70}$ this distance is larger than in $C_{60}$, and that might be a reason for the slower diffusion rate.

References


