# II M.Sc., Physics

## Semester IV

## NANO PHYSICS - P16PYE5

**Unit II Carbon Nanostructures**

Carbon molecules and carbon bond -- $C_{60}$: Discovery and structure of $C_{60}$ and its Crystal -- Superconductivity in $C_{60}$ -- Carbon nanotubes: Fabrication – Structure – Electrical properties – Vibrational properties – Mechanical properties -- Applications (Fuel cells, chemical sensors, catalysts).

## 2.1. CARBON MOLECULES:

### 2.1.1 NATURE OF THE CARBON BOND:

In order to understand the nature of the carbon bond it is necessary it examine the electronic structure of the carbon atom. Carbon contains six electrons, which are distributed over the lowest energy levels of the carbon atom. The structure is designated as follows $(1s)^2$, (2s), $(2p_x)$, $(2p_y)$, $(2p_z)$ when bonded to atoms in molecules. The lowest energy level 1s with the quantum number N= 1 contains two electrons with oppositely paired electron spins. The electron charge distribution in an s state is spherically symmetric about the nucleus. These 1s electrons do not participate in the chemical bonding. The next four electrons are in the N=2 energy state, one is a spherically symmetric s orbit and three in $p_x$, $p_y$, and $p_z$ orbitals, which how the very direct charge distributions shown in *Fig. 2.1.*, oriented perpendicular to each other.

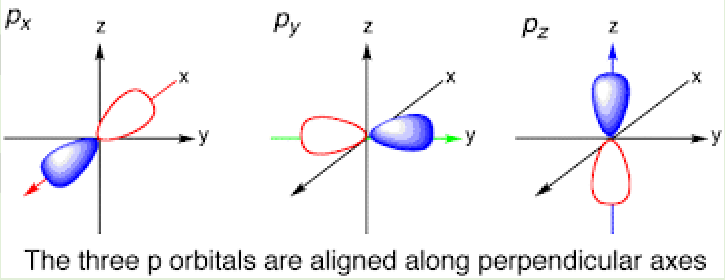

Fig. 2.1.,

The outer s orbital together with the p orbitals form the chemical bond of carbon with other atoms. The charge distribution associate with this orbitals mixes or overlaps with the charge distribution of each other atom being bonded as glue the holds the atoms together on the basis of the simple methane molecule, $CH_4$ might have the structural shown in *Fig 2.2.*

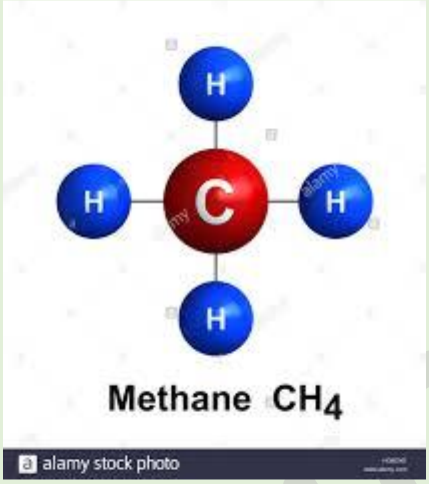

Fig 2.2.

Where the H-C bonds are at angle to each other. However, methane does not have this configuration; rather, it has the tetrahedral structure shown in *Fig. 2.3*, where the carbon bond make angel of 109°28' with each other.

Fig. 2.3

The explanation lies in the concept of hybridization. In the carbon atom energy separation between the 2s level and the 2p levels in the very small, and this allow an admixture of the 2s wavefunction with one or more of the $2p_i$ wavefunctions. The un-normalized wavefunction $\Psi$ in a valence state can be designated by the expression

$$\Psi = s + \lambda p \quad \text{-------------------} \quad (1)$$

Where p indicates an admixture of $p_i$ orbitals. With this hybridization the direction of the p lopes and the angles between them change. The angel will depend on the relative admixture λof the p states with the s states. Three kind hybridization are the band angle for various the possibilities, which are 180°,120°,and 109°28' for the linear compound acetylene , ($H-C{\equiv}C-H$), the planar compound ethylene ($H_2C = CH_2$) and tetrahedral methane ($CH_4$), respectively. In general most of the bond angle for carbon inorganic molecule have this values. For example, the carbon bond angle in diamond is 109°, and in graphite benzene it is 120°.

Solid carbon has two main structures called allotropic forms that are stable at room temperature: diamond and graphite. Diamond consists of carbon atoms that are tetrahedral bond to each other through sp3 hybrid bonds that form a three dimensional network. Each carbon atom as four nearest-neighbor carbons. Graphite has allayed structural with each layer called graphitic sheet, formed from hexagons of carbon atoms bond together by sp2 hybrid bonds that make 120°angels with each other. Each carbon atoms has three nearest-neighbor carbon in the planner layer.

### 2.1.2 New carbon structures

Until 1964 it was generally believed that no other carbon band angles were passible in hydrocarbons, that is, compounds only carbon and hydrogen atoms. In that year phil eaton of the university of chicago synthesized a square carbon molecules, $C_8H_8$ called *Cubane,* shown in *Fig. (2.4).*

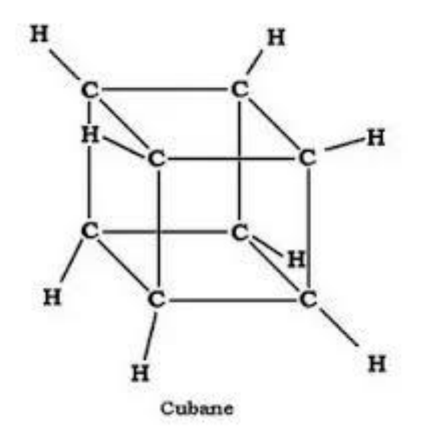

Fig. (2.4).

In 1983 L.paquettee of ohio states university synthesized a $C_{20}H_{20}$ molecule having a *dodecahedron* shape, shown in *Fig.(2.5)* formed by joining carbon pentagons, and having C-C band angles ranging from 108°.

Fig.(2.5)

### 2.1.3. Discovery of $C_{60}$

The discovery of the existence of a soccer ball-like molecule containing 60 carbon atoms was a somewhat fortuitous result of research on the natural of mater in out space involving studies of light transmission through interstellar dust, the small particle of matter that fill the regions of outer space between stars and galaxies. When light from a distant star passes through the cosmos and arrives on earth, the intensity of the light is reduced. This is referred to as optical extinction. It occurs because of the absorption and scattering of the light from the interstellar dust lying in the pathway of the light on its way to earth. Scientists study this extinction by measuring the intensity of light coming from the stars at different wavelengths, that is, with different colors. When these studies were made, it was noted that there was an increased extinction or absorption in the scattered from small particles of graphite that were believed to be present in the regions between the stars. Some researchers were not convinced of this explanation, their approach was to simulate the graphite dust in the dust in the laboratory and investigate light transmission through it. They made smoke like particles by striking an arc between two graphite electrodes in a helium gas environment, and then condensing the smoke on quartz glass plates. They did indeed obtain the spectral lines known to arise from graphite, but they also observed four additional IR absorption bands that did not originate from graphite and they found this very puzzling.

Although a soccer ball like molecules consisting of 60 carbon atoms with the chemical formula $C_{60}$ had been envisioned by theoretical chemists for an atom it becomes electrically conducting.

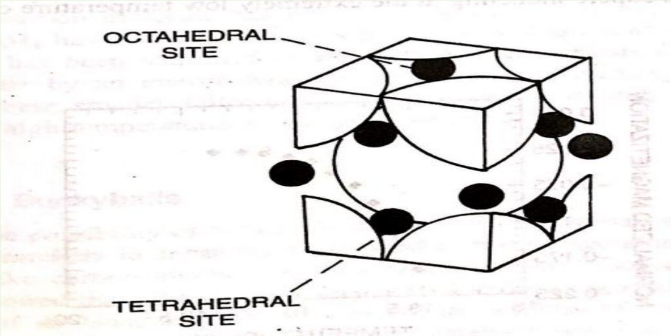

Fig (2.6)

*Fig (2.6)* shows the location of the alkali atoms in the lattice where they occupy the two vacant tetrahedral sites and a larger octahedral site per $C_{60}$ balls, and in the octahedral site there are six surrounding $C_{60}$ molecules .when $C_{60}$ is doped with potassium to from $K_3C_{60}$, the potassium atoms becomes ionized to from $K^+$ and their electrons becomes associated with the $C_{60}$. Which becomes a $C_{60}^{3-}$ triply negative ion. Thus each $C_{60}$ has three extra electrons that are loosely bonded to the $C_{60}$, and can move through the lattice making $C_{60}$ electrically conducting. In this case $C_{60}$ said to be electron doped.

### 2.1.4 Superconductivity in C60

Superconductivity is a state of matter in which the resistance of a sample becomes zero,and in which no magnetic field is allowed to penetrate the sample. The latter manifests itself as a reduction of the magnetic susceptibility $\chi$ of the sample to $\chi = -1$.in the year 1991,A.F. Hebard and co-workers at bell telephone laboratories doped C60 crystals with potassium by the methods described above and tested them for superconductivity, to the surprise of all, evidence was found for a superconducting transition at 18K

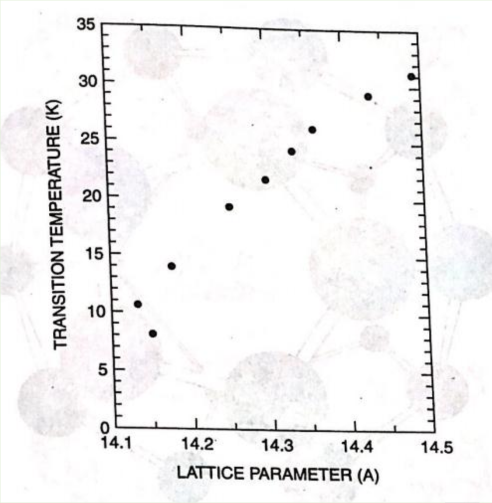

Fig (2.7)

*Fig.(2.7).* Shows the drop in the magnetization indicative of the presence of superconductivity. A new class superconducting materials had been found having a simple cubic structure and only two elements not long after the initial report it was found that many alkali atoms could be doped into the lattice, the transition temperature increased to as high as 33K in $Cs_2RbC_{60}$.as the radius of the dopant alkali atoms increased cubic $C_{60}$ lattice expands, and the superconducting transition temperature goes up. *Fig.(2.8).*is a plot of transition temperature versus the lattice parameter.

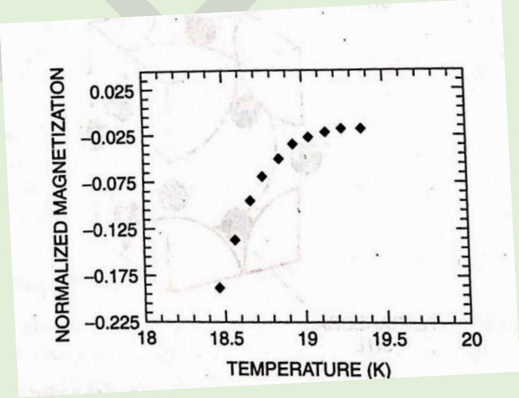

Fig (2.8)

It was mentioned above that graphite consist of parallel planer graphite sheets of carbon atom. It is possible to put other atom between the plans of this sheets, a procedure called *intercalation*. When intercalated with potassium atoms, crystalline graphite becomes superconducting at the extreme the low temperature of a few tenths of a Kelvin.

## 2.2. Carbon nanotubes

Carbon nanotube as a sheet of graphite rolled into a tube with bonds at the end of the sheet forming the bonds that close the tube. *Fig. (2.9).* Shows the structure of a tube formed by rolling the graphite sheet about an axis parallel to C-C bonds. A single walled nanotube can have a diameter of 2nm and a length of 100µm, making it effectively a one dimensional structure called a *nanowire.*

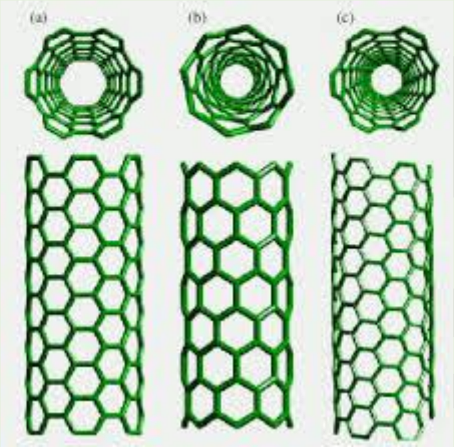

*Fig. (2.9).*

### 2.2.1. Fabrication

Carbon nanotube scan be made by laser evaporation, carbon arc methods, and chemical vapor deposition.

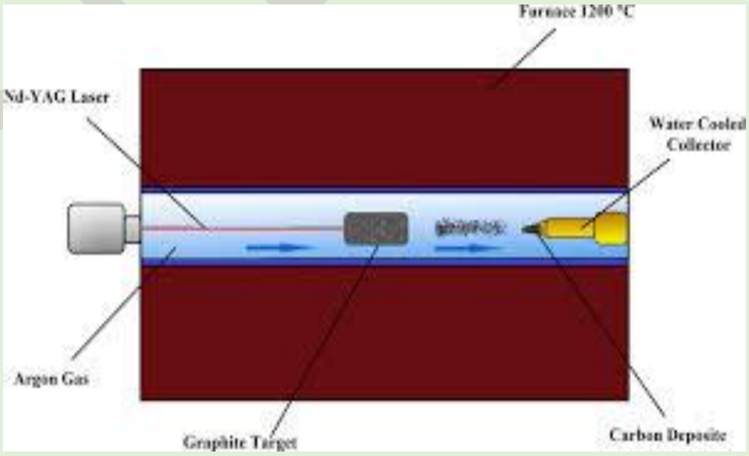

Fig. (2.10).

Fig. (2.10). illustrates the apparatus for making carbon nanotubes by laser evaporation. A quartz tube containing argon gas and a graphite target are heated to 1200°C. contained in the tube, but somewhat outside the furnace, is a water-cooled copper collector. The graphite target contains small amounts of cobalt and nickel that act as catalytic nucleation sites for the formation of the tubes. An intense pulsed laser beam is incident on the target, evaporating carbon from the graphite. The argon then sweeps the carbon atoms from the high temperature zone to the colder copper collector on which they condense into nanotubes. Tubes 10-20 nm in diameter and 100µm long can be made by this method.

Nanotubes can also be synthesized using a carbon arc. A potential of 20-2 V is applied across carbon electrode of 5-20µm diameter and separated by 1mm at 00 torr pressure of flowing helium. Carbon atoms are ejected from the positive electrode and from nanotubes on the negative electrode. As the tubes form, the length of the positive electrode decreases, and a carbon deposit forms on the negative electrode. To produce single walled nanotubes, a small amount of cobalt, nickel, or iron is incorporated as a catalyst in the central region of the positive electrode. If no catalysts are used, the tubes are nested or multi-walled types, which are nanotubes within nanotubes, as illustrated in *Fig.(2.11*). The carbon arc method can produce single-walled nanotubes of diameters 1-nm with a length of 1µm.

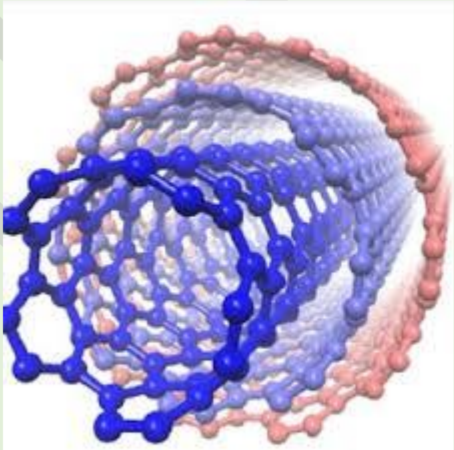

Fig. (2.11).

The chemical vapor deposition method involves decomposing a hydrocarbon gas such as methane ($CH_4$) at 1100°C. As the gas decomposes, carbon atoms are produced that then condense4 on a cooler substrate that may contain various catalysis such as iron. This method produced tubes with open ends, which does not occur when other methods are used.

This procedure allows continuous fabrication, and may be the most favorable method for scale up and production.

The mechanism of nanotubes growth is not understood. Since the metal catalyst is necessary for the growth of single wall nanotubes, the mechanism must involve the role of the Co or Ni atoms. One proposal referred to as scooter mechanism suggest that atoms of the metal catalyst attach to the dangling bonds at the open end of the tubes, and that these atoms scoot around the rim of the absorbing carbon atoms as they arrive.

A group at IBM has developed a method to separate the semiconducting from the metallic nanotubes. The separation was accomplished by depositing bundles of nanotubes, some of which are metallic and some semiconducting, on a silicon wafer. Metal electrodes were then deposited over the bundle. Using the silicon wafer as an electrode, a small bias voltage was applied that prevents the semiconducting tubes from conducting, effectively making those insulators. A high current through the metallic tubes to vaporize, leaving behind only the semiconducting tubes.

### 2.2.2 Structure

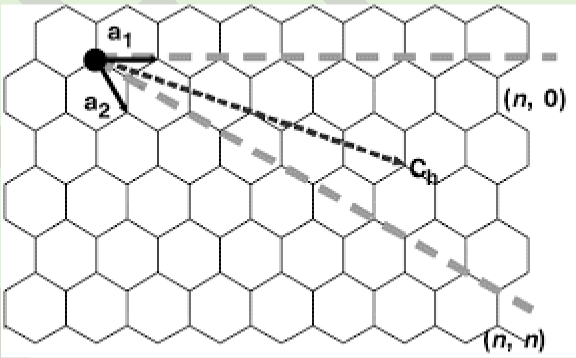

**Fig. (2.12).**

There are a variety of structure of carbon nanotubes, and these various structures have different properties. Although carbon nanotubes are not actually made by rolling graphite sheets, it is possible to explain the different structures by consideration of the way graphite sheet is rolled up about the axis T shown in Fig.(2.12). The $C_h$ vector is called the *circumferential vector*, and it is at right angles to T. Three examples of nanotubes structures constructed by rolling the graphite sheet about the T vector having different orientations in the graphite sheet are shown in Fig.(2.12) . When T is parallel to the C-C bonds of the carbon hexagons, the structure shown in Fig.(2.12) . Armchair, zigzag and chiral structures are formed by rolling about a T vector having different orientations in the graphite plane, but not parallel to C-C bonds. Looking down the tubes of the chiral structure, one would see a spiraling row of carbon atoms. Generally nanotubes are closed at both ends, which involves the introduction of a pentagonal topological arrangement on each to half of a large fullerene like structure.

### 2.2.3 Electrical properties

Carbon nanotubes have the most interesting property that they are metallic or semiconducting, depending on the diameter and chirality of the tube. Chirality refers to how the tubes are rolled with respect to the direction of the T vector in the graphite plane, as discussed above. Synthesis generally results in a mixture of tubes two –thirds of which are semiconducting and one-third metallic. The metallic nanotubes have the armchair structure shown in Fig.(2.13). Figure 2.13.is a plot of the energy gap of semiconducting chiral carbon nanotubes versus the reciprocal of the diameter, shown that as the tube increases, the band gap decreases.

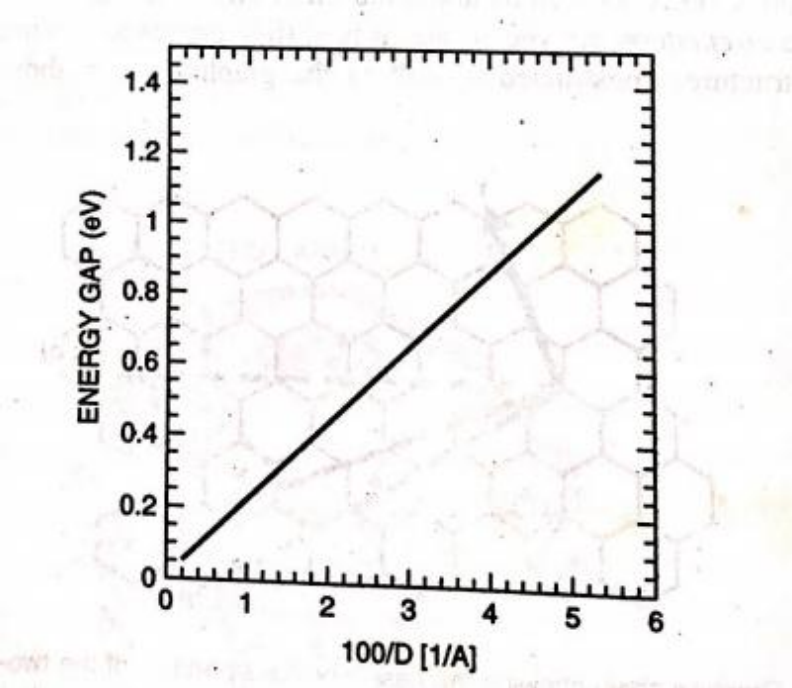

Fig. (2.13).

Scanning tunneling microscopy (STM) is used to investigate the electronic structure of carbon nanotubes.in this measurement the position of the STM tip is fixed above the nanotube,, and the voltage V between the tip and the sample is swept while the tunneling current I is monitored. The measured conductance G = I/V is a direct measure of the local electronic density of states. The density of states, is a measure of how close as the differential conductance, which is (dI/dV) (I/V), versus the applied voltage between the tip and carbon nanotube. The data show clearly the energy gap in materials at voltages where very little current is observed. The voltage width of this region measures the gap which for the semiconducting materials shown on the bottom of *Fig.(2.14).* is 0.7 eV.

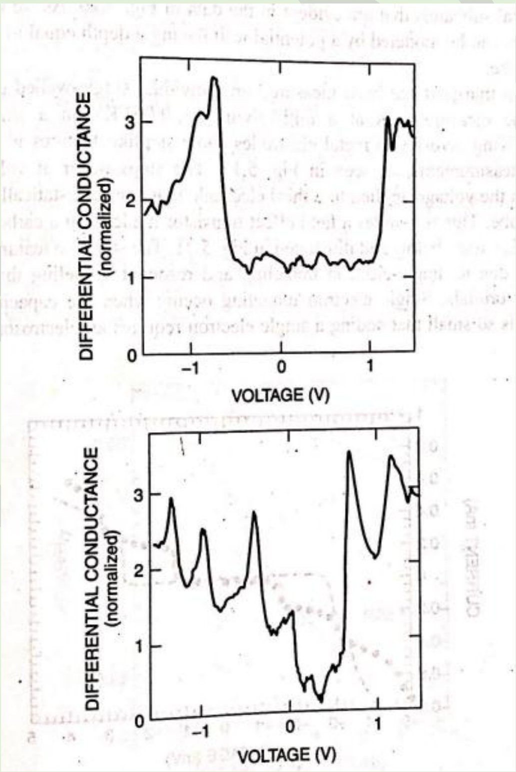

Fig. (2.14).

At higher energies sharp peaks are observed in the density of states, referred to as van hove singularities, and are characteristic of low dimensional conducting materials. The peaks occur at the bottom and top of a number of sub bands. As electrons in the quantum theory can be viewed as waves, If the electron wavelength is not a multiple of the circumference of the tube, it will destructively interfere with itself, and therefore only electron wavelengths that are integer multiples of the circumference of the tubes are allowed.

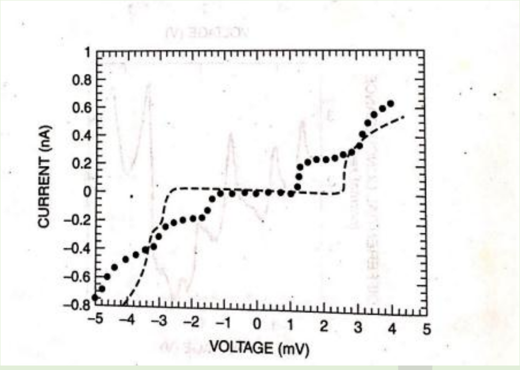

Fig. (2.15).

This severely limits the number of energy states available for conduction around the cylinder. The dominant remaining conduction path is along the axis of the tubes, making carbon nanotubes function as one –dimensional quantum wires. The electronic states of the tubes do not form a single wide electronic energy band, but instead split into one-dimensional sub bands at are evident in the data in *Fig.(2.15).*

Electron transport has been measured on individual single-walled carbon nanotubes. The measurements at a mill kelvin (T =0.001 K) on a single metallic nanotube lying across two metal electrodes show step like features in the current-voltage measurements, as seen in Fig.(2.15).

The step like features in the I-V curve are due to single-electron tunneling and resonate tunneling through single molecular orbits. Single electron tunneling occurs when the capacitance of the nanotube is so small that adding a single electron requires an electrostatic charging energy greater than the thermal energy $K_BT$. Electron transport is blocked at low voltages, which is called coulomb blockade.

In the metallic states the conductivity of the nanotubes is very high. It is estimated that they can carry a billion amperes per square centimeter. Copper wire fails at one million amperes per square centimeter because resistive heating melts the wire. The high conductivity of the carbon tubes is that they have very few defects to scatter electrons, and thus a very low resistance. Nanotubes also have a very high thermal conductivity, almost a factor of 2 more than that of diamond. This means that they are also very good conductors of heat.

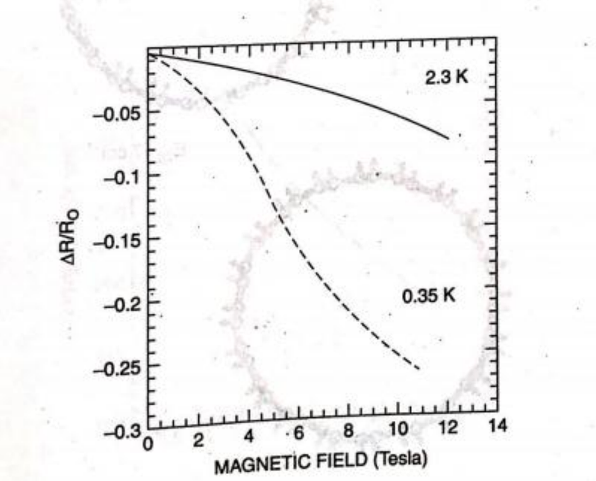

Fig. (2.16).

Magneto resistance is a phenomenon where by the resistance of a materials is changed by the application of a DC magnetic field. Carbon nanotubes display magneto resistive effects at low temperature. *Fig.(2.16).* Shows a plot of the magnetic field dependence of the change in resistance ΔR of nanotubes at 2.3 and 0.35 K compared to their resistance R in zero magnetic field. This is negative magneto resistance effect because the resistance decreases with increasing DC magnetic field, so its reciprocal, the conductance G = 1/R, increases. This occurs because when a Dc magnetic field is applied to the nanotubes, the conduction electrons acquires new energy levels associated with their spiraling motion about the field. It turns out that for nanotubes these levels, called Landau levels, lie very close to the topmost filled energy levels.

### 2.2.3 Vibrational properties

The atoms in a molecule or nanoparticle continually vibrate back and forth. Each molecule has a specific set of vibrational motions, called normal modes of vibration, which are determined by the symmetry of the molecule. For example carbon dioxide CO2, which has the structure O = C = O, is a bent molecule with three normal modes.One mode involves a bending of the molecule. QAnother, called the symmetric stretch, consists of an in-phase elongation of the two C = O bonds. The asymmetric stretch consists of out of phase stretches of the C = O bond length, where one bond length increase while the other decreases.

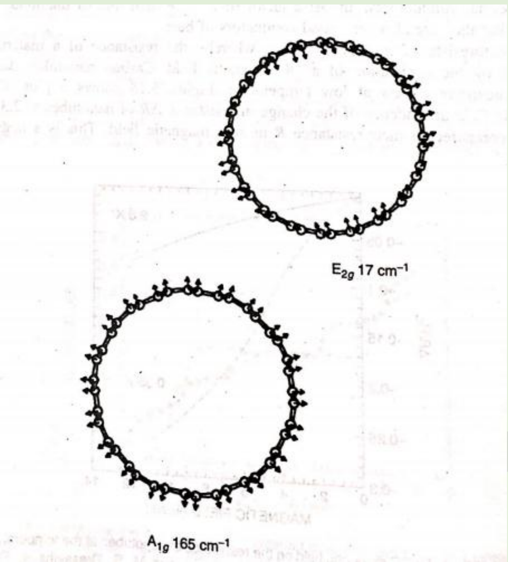

Fig. (2.17).

Similarly carbon nanotubes also have normal modes of vibration. *Fig.(2.17)* illustrates two of the normal modes of nanotubes.one mode, labeled $A_{1g}$, involves an ‘in and out’ oscillation of the diameter of the tube. Another mode, the $E_{2g}$ mode, involves a squashing of the tube where it squeezes down in one direction and expands in the perpendicular direction essentially oscillating between a sphere and an ellipse.

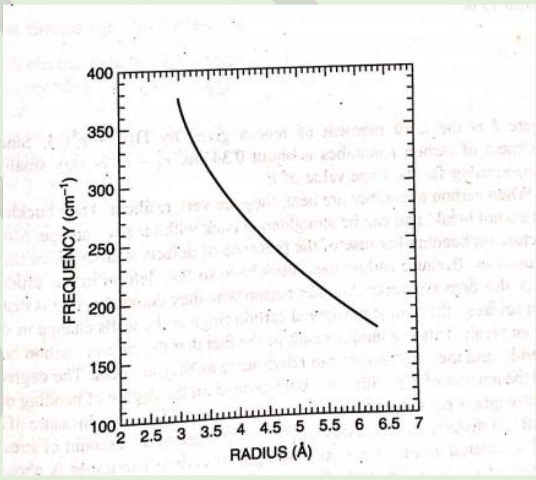

Fig. (2.18).

The frequencies of these two modes are Raman active and depend on the radius of the tube. *Fig.(2.18)* is a plot of the frequency of the A1g mode as a function of this radius. The dependence of this frequency on the radius is now routinely used to measure the radius of nanotubes.

### 2.2.4. Mechanical properties

Carbon nanotubes are very strong. If a weight W is attached to the end of a th n wire nailed to the root of the room, the wire will stretch. The stress S on the wire is defined as the load, or the weight per unit cross sectional area A of the wire,

$$S = W/A$$

The strain e is defined as the amount of stretch ΔL of the wire per unit length L,

$$e = \Delta L/L$$

Where L is the length of the wire before the weight is attached. Hooke's law says that the increase in the length of the wire is proportional to the weight at the end of the wire. More generally, we say stress S is proportional to strain e,

$$S = Ee$$

The proportionality constant E =LW / ΔL is young's modulus, and it is a property of a given material. It characterizes the elastic flexibility of a material. The larger the value of young's modules, the less flexible the material. Young's modulus of steel is about 30,000 times that of rubber. Carbon nanotubes have young's moduli ranging from 1.28 to 1.8 Terapascal. Which means that young's modulus of carbon tubes is almost 10 times that of steel.

## 2.3 Applications of carbon nanotubes

### 2.3.1 Fuel cells

Carbon nanotubes have applications in battery technology. Lithium, which is a charge carrier in some batteries, can be stored inside nanotubes, it is estimated that one lithium atom can be stored for every six carbons of the tube. Storing hydrogen in nanotubes is another possible application, one that is related to the development of fuel cells as sources of electrical energy for future automobiles. A fuel cell consists of two electrodes, to pass through it. Hydrogen is sent to the anode, where it is ionized. The freed electrons travel through an external circuit wire to the cathode. The hydrogen ions diffuse through the electrolyte to the cathode, where electrons, hydrogen, and oxygen combine to form water. The system needs a source of hydrogen. One possibility is to store the hydrogen inside carbon nanotubes. It is estimated that to be useful in this application, the tubes needs to hold 6.5% hydrogen by weight. At present only about 4% hydrogen by weight has been successfully put inside the tubes.

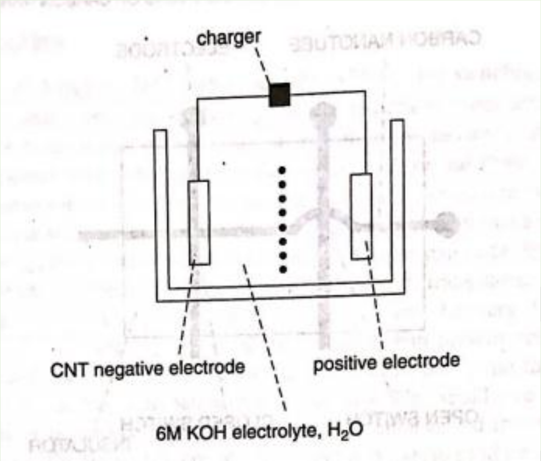

Fig. (2.19).

An elegant method to put hydrogen into carbon nanotubes employs the electro-chemical cell sketched *in Fig.(2.19).* Single –walled nanotubes in the form of paper are the negative electrode in a KOH electrolyte solution. A counter electrode consists of $Ni(OH)_2$. The water of the electrolyte is decomposed into positive hydrogen ions ($H^+$) that are attracted to the negative single wall nanotubes electrode. The presence of hydrogen bonded to the tubes is indicated by a decrease in the intensity of a Raman active vibration, as indicated in *Fig.(2.20)*,which shows the Raman spectrum before and after the material is subjected to the electrochemical process.

### 2.3.2 Chemical Sensors

A field effect transistor similar to the one shown in *Fig.(2.20)* made of the chiral semiconducting carbon nanotubes has been demonstrated to be a sensitive detector of various gases.

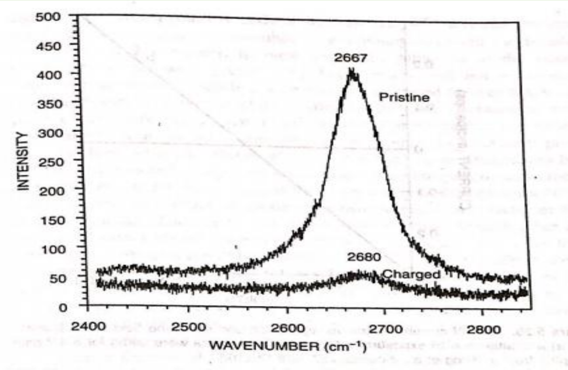

Fig. (2.20).

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The transistor was placed in a 00ml flask having electrical feed through and inlet and outlet valves to allow gases to flow over the carbon nanotubes of the FET. Two to 200 parts per million of NO2 flowing at a rate 700 ml /min for 10 min caused a threefold increase in the conductance of the carbon nanotubes. *Fig.(2.21)* shows the current – voltage relationship before and after exposure to NO2. These data were taken for a gate voltage of 4 V. The effect occurs because when NO2, increasing the hole concentration in the carbon nanotube and enhancing the conductance.

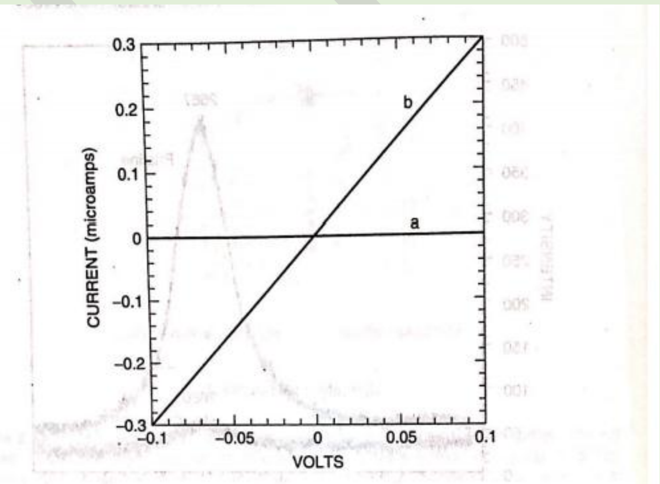

Fig.(2.21)

The frequency of one of the normal-mode vibrations of the nanotubes, which gives a very strong Raman line, is also very sensitive to the presence of other molecules on the surface of the tubes. The direction and the magnitude of the shift depends on the kind of molecule on the surface. This effect could also be the basis of a chemical gas sensor employing nanotubes.

### 2.3.3 Catalysis

A catalytic agent is a material, typically a metal or alloy that enhances the rate of a reaction between chemicals. Nanotubes serve as catalysts for some chemical reactions. For example, nested nanotubes with ruthenium metal bonded to the outside have been demonstrated to have a strong catalytic effect in the hydrogenation reaction of cinnamaldehyde ($C_6H_5CH = CHCHO$) in the liquid phase compared with the effect when the same metal Ru is attached to other carbon substrates. Chemical reactions have also been carried out inside nanotubes, such as the reduction of nickel oxide NiO to the base metal Ni, and the reduction $AlCl_3$ to its base metal Al. A stream of hydrogen gas $H_2$ at 475°C partially reduces $M0O_3$ to $MoO_2$, with the accompanying formation of stream $H_2O$, inside multi- walled nanotubes. Cadmium sulfide crystals have been formed inside nanotubes by reacting cadmium oxide crystal with hydrogen sulfide gas at 400°C.

### Reference:

**1. C.P. Poole and F.J. Owens, *Introduction to Nanotechnology* (Wiley, New Delhi, 2003).**