



## CHAPTER II

### ISOTOPIC MIXED CRYSTALS

#### 2.1 Elementary Excitations in Molecular Crystals .

In dielectric crystals, the first electronic excitation states do not give rise to electrical conductivity in a constant electric field. Such ' currentless ' excited states in dielectric crystals may be divided into three types.<sup>(10)</sup>

2.1.1 Phonon excitations. Which are elementary collective excitations that correspond to lattice vibrations, i.e., to vibrations about the equilibrium positions of ions in ionic lattices or to vibrations and rotational oscillations about the equilibrium positions of molecules in molecular crystals. These excitations are associated with comparatively low frequencies: from zero to a few hundreds of inverse centimeters,

2.1.2 Excitons. Which are currentless collective excitations that correspond to a change in the state of motion of loosely bound electrons in ions and molecules of crystals. These excitations are associated with frequencies on the order of tens of thousands of inverse centimeters. Excitations in molecular crystals that correspond to intramolecular vibrations with frequencies exceeding  $100 \text{ cm}^{-1}$  are often classified as excitons,

2.1.3 High-frequency excitons. Which are associated with a change in the state of motion of ' internal ' , tightly bound electrons in atoms or ions and with frequencies of the order of hundreds of thousands of inverse centimeters.

In this thesis we shall investigate the elementary excited states of crystals that correspond to excitons only.

## 2.2 Excitons.

As a consequence of electron-electron interaction in insulator and in certain semiconductors, there may exist well-defined elementary excitations within the energy gap which separates the valence-electron band from the conduction-electron band. These excitations are the formation of bounded electron-hole pairs which are called excitons. Because electrons and holes are oppositely charged, they attract each other, producing bound state levels similar to those of the hydrogen atom. Since the bound states have energies less than that of the separated (i.e., ionized) electron-hole pair, the exciton energy levels lie in the forbidden band gap below the fundamental absorption limit by an amount approximately equal to the hydrogenlike bound-state levels in the dielectric continuum. When the electron and hole are bounded to one another, the pair is a neutral entity and does not contribute to electrical conductivity.

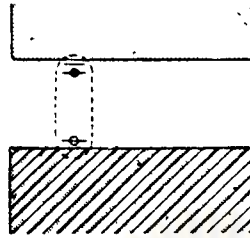
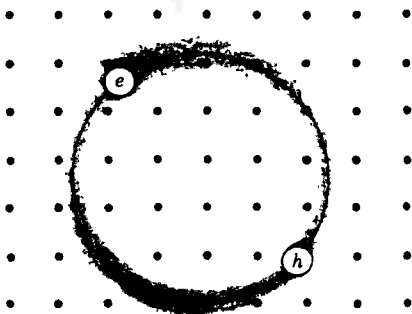


Fig. 2.1 Exciton States

In a semiconductor, with light carriers and a high dielectric constant, the expanded hydrogenic orbits of the Wannier exciton are the better approximation; while in a molecular crystal, such as solid argon, or anthracene, it is more accurate approximate them as a Frenkel exciton, whose wave-function lie mostly within a single unit cell.

2.2.1 Wannier Excitons. Wannier excitons are usually used to describe the collective electronic excited states of semiconductors and dielectrics with a high dielectric constant. In these cases the excitations will overlap neighboring atoms, so Mott-Wannier excitons are often refer to as weakly bound excitons. A typical Wannier exciton is shown in Figure 2.2


 (11)  
 Fig. 2.2 Mott-Wannier Excitons

Since the excitons which we are studying are not these type of excitons, we shall not go into any of the theories for the Mott-Wannier excitons.

### 2.2.2 Frenkel Excitons.

Frenkel excitons are used to describe the elementary collective electronic excitations of molecular crystals that consist of weakly interacting molecules. That is the excitation must be localized on or near a single atom or molecule. Thus we called Frenkel excitons to be the tight binding excitons or excitons of " Small radius " , as shown in Figure 2.3 . The excitation can hop from one atom to another depending on the strength of the coupling between the neighbors as shown in figure 2.4 . In crystal such as naphthalene crystal, the individual atoms within the molecules may become excited. Because the covalent binding between the atoms within the molecules are stronger than the Van der Waals binding between the molecules, the electrons tend to be localized within the molecule when the latter is in its ground state. The electron in the low lying molecule excited states of the molecule also tend to be localized in the sense that they do not overlap strongly with the neighboring bound state molecules. The excited molecules in this case can also be treated as Frenkel excitons.

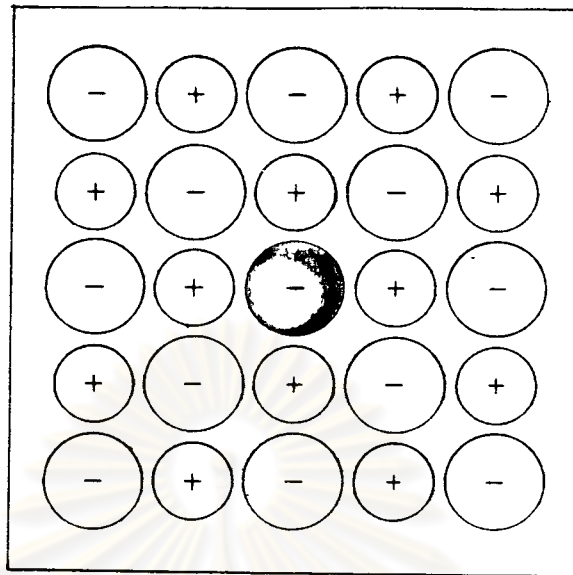


Fig. 2.3 Schematic representation of a tightly bound or Frenkel exciton

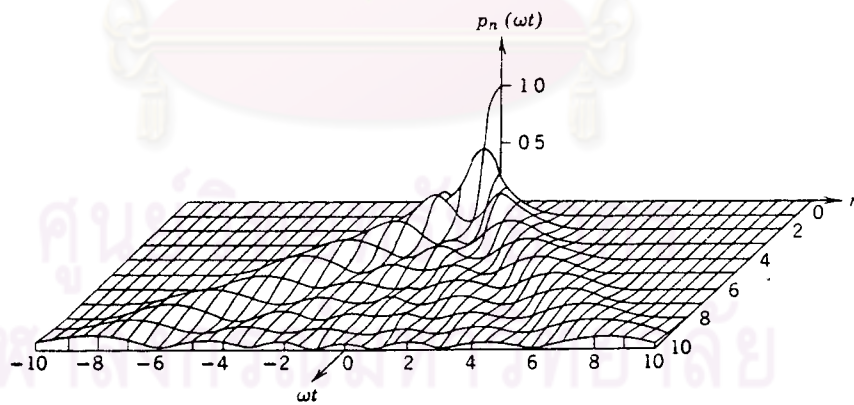


Fig. 2.4 Propagation of an exciton in a one-dimensional infinite crystal (12)

### 2.2.3 Restricted Frenkel Excitons Limit.

In the restricted Frenkel Exciton limit, (1) the intermolecular interaction is taken to be short range. This allows one to ignore some of the orientation dependence of the pairwise interaction. One can then treat the molecules as being geometric points occupying the lattice sites. Also in the short range interaction limit, the selection rules become very simple and the density of states of the excitation band, the total bandwidth and other quantities which depend on the intermolecular interaction can be easily calculated. The short range limit is applicable to the low lying excited states of benzene and naphthalene crystals.

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### 2.2.4 Exciton Band.

According to the theory of a two-molecule system, the degenerate excited state of the individual molecule would split into two excited states which are the strength of the interactions between the molecules, relative orientation of the molecules and on the properties of the one ( or free ) molecule state are taken into consideration . Extending the theory to N-molecule system, one would expect the N single-molecule states ( all having the same energy E ) would split into N energy states within a manifold or band. The spacing between the energy levels would depend on the same factors as the splitting in the two-molecule system. If the collection ( or aggregates ) of the N molecules is unorganized or they are in a random array, the individual energy levels will not be sharp but would be

spread out. The manifold of energy levels would therefore appear as a continuous band. Excitations of the molecules would then show up in the manifold or energy spectrum as an excitation of the whole band ( i.e. a broad absorption ). The width of the excitation absorption band depends on the intermolecular coupling strength and can be related to the internity through the transition dipole moments.

The relative orientation of the molecules in the N molecules can also give rise to some interesting features in the energy spectrum. These features are called Davydov components and splitting. (14) Their presences can be understood by considering first the two extreme orientations of the molecular planes of two adjacent molecules being parallel to each other ( and with their planes perpendicular to the lines joining the molecular centres ) and of the two molecular plane of the molecule, the transition moments line in the plane of the molecule, the transition moments of the adjacent molecules are parallel in the former orientation, while the transition moments lie along the same intermolecular axis in the latter orientation.

For both molecular orientation the two molecule system has two stationary states with energies varying with the inverse cube of the seperation. Of the two states, one has a higher energy than the free molecular case, while the other has lower. Thus transition moments which are not parallel is allowed while the other is not. If, however, the molecules are orientated so that their transition moments are not

parallel, the two stationary states are such that transition into both are allowed and so only one absorption line is seen. If the molecules are arranged to have the orientation in which one of the transition is not allowed, two absorption lines appear. The splitting is called the Davydov splitting and the absorption lines are called the Davydov components.

### 2.3 Molecular Crystals. (15)

For a theoretical description of the physical properties of a solid body, it is convenient to classify crystalline substances according to the magnitude of the ratio of the forces of interaction between the particles ( atoms or molecules ) which forms crystal to the forces of interaction between the component parts ( electrons and atoms, respectively ) of these particles. If the interaction between the component parts of one particle is larger than the interaction between the crystal forming parts, then individual parts preserve crystal. We define such bodies as molecular crystals. Usually molecular crystals are built with molecules which interact via the van der Waals forces. If the energy of inter-molecular interaction is close to magnitude of chemical energies ( the bond energies of atoms in a molecule or of electrons in an atom ) , then the molecules lose their individuality , and the crystals can now be identified as of the valence, metallic, or ionic type.

Molecular crystals, are formed from atoms of inert gases ( Ne, Ar, Kr, and others ) and from molecules with saturated



bonds (  $H_2$  ,  $CH_4$  , and others ). Molecular crystals have an especially wide occurrence among organic substances.

Molecular crystals are characterized by low melting and boiling points. Evaporation takes place by whole molecules. The heat of sublimation of typical molecular crystals amounts to several kcal/mole, i.e., is 10 to 20 times smaller than the dissociation energy of an isolated molecules or is much smaller than the dissociation energy of an ionic crystal lattice.

Molecular crystals are electrical nonconductors as shown in figure 2.5 . Almost all molecular crystals are diamagnetic . (except, for example, crystals of  $O_2$  and  $NO$  ), inasmuch as they consist of closed-shell molecules having no resultant spin.

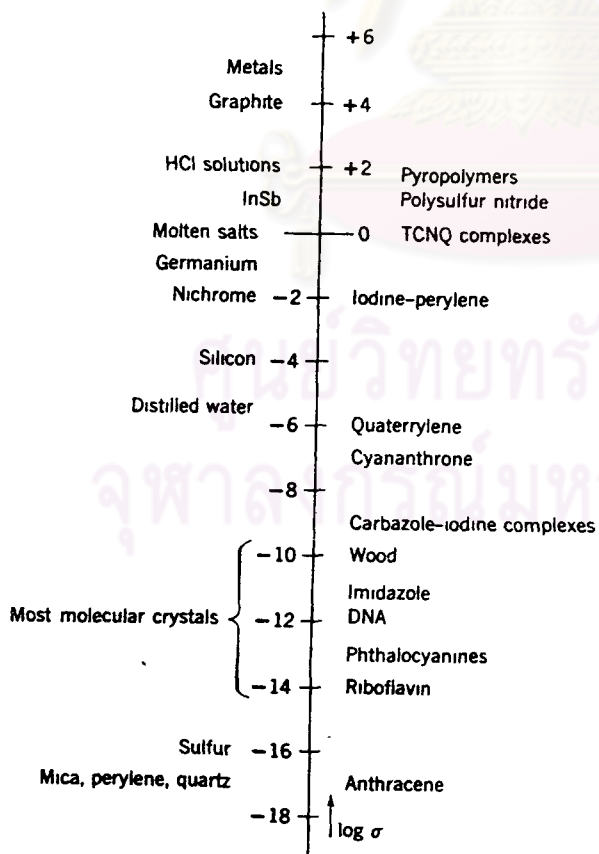


Fig. 2,5 Scale of approximate conductivities. ( on a logarithmic scale )

## 2.4 Naphthalene.

As is well known, Naphthalene- $\text{h}_8$  is an aromatic compound which contains eight hydrogen atoms attached to the double benzene rings. Naphthalene is a colorless crystalline hydrocarbon with melting point  $80^\circ\text{C}$  and boiling point  $218^\circ\text{C}$ . It sublimes readily and is isolated in quantity from coal tar. Naphthalene is the parent hydrocarbon of the series of fused benzene polycyclic structures given in figure 2.6a and 2.6b.

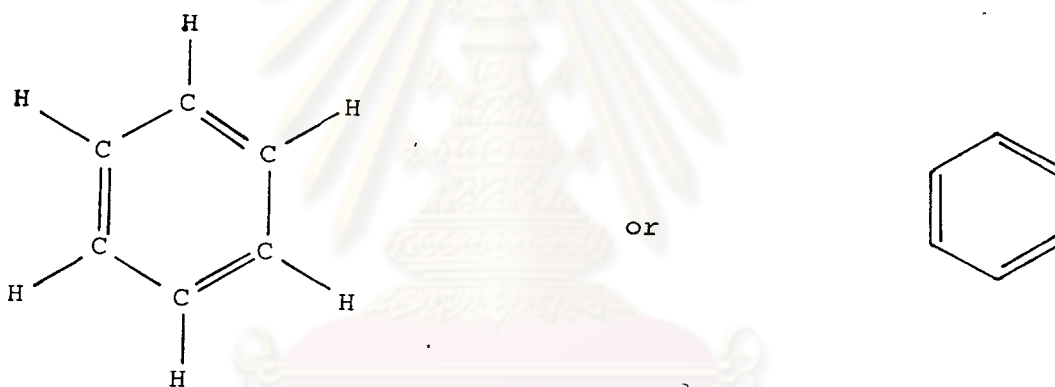


Fig. 2.6a Benzene

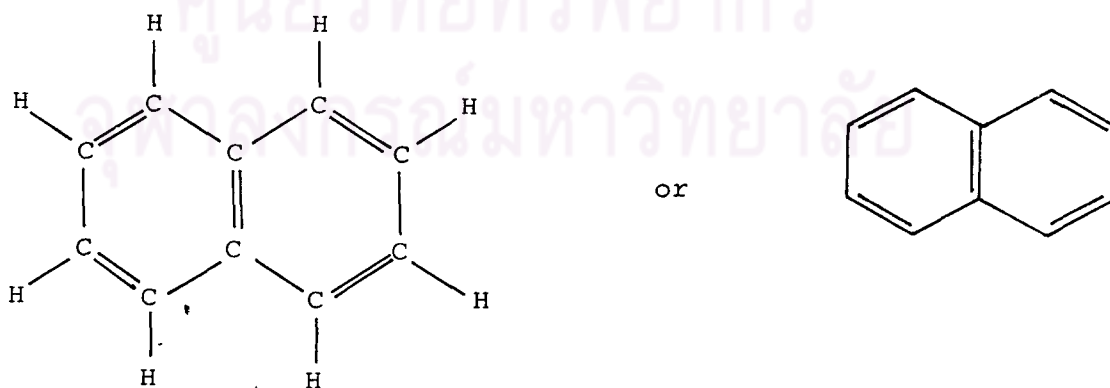
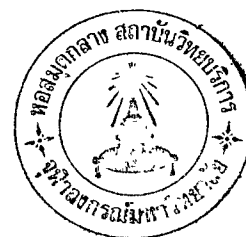
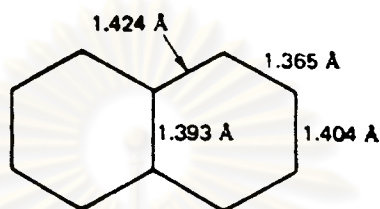


Fig. 2.6b Naphthalene

And X-ray analysis shows it to have the structure shown in figure. 2.7



(16)

Fig. 2.7 Structure of Naphthalene

As we see the bonds are not all of the same length, and naphthalene can be considered to be resonance hybrid of three structures.

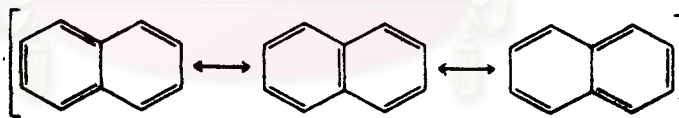
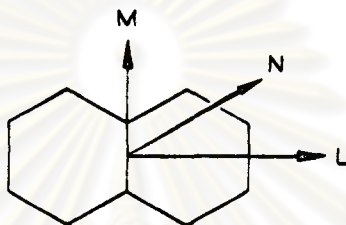


Fig. 2.8 Hybrid of three structures of Naphthalene.

and so the symmetry of an individual molecule is described by a point group. In the typical case of naphthalene the point group is  $D_{2h}$ , consisting of the following operations, referred to

1. Identity
2.  $180^\circ$  rotations about the axes L , M , and N
3. Inversion in the origin
4. Reflection in Planes MN , NL , LM

as shown in figure 2.9



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Fig. 2.9 Axis convection in naphthalene crystal

These molecules form into monoclinic unit cell , characterized by  
by

$$a \neq b \neq c$$

$$\alpha = 90^\circ \quad \beta \neq 90^\circ \quad \gamma = 90^\circ$$

where a , b , c are dimension of three noncoplanar vectors joining the lattice point at the origin to its near neighbors and angles  $\alpha$  ,  $\beta$  ,  $\gamma$  correspond to each pairs of vectors as shown in the figure 2.10

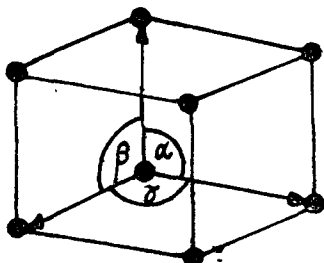


Fig. 2.10 Monoclinic unit cell

## 2.5 Mixed Crystals.

Molecular crystals which contain two or more types of molecules having different excitation energies are called mixed crystals. In the two component mixed crystals, the major component is usually designated as being the host component, while the minor component is designated as being the guest. In the heavily doped mixed crystals, these designation become meaningless.

When the two components are molecules which contain different isotopes of the same element, the mixed crystal is called an isotopes of the element have the same Z number the chemical properties of the different isotopes are almost the same. This means that the intermolecular interaction can be assumed to be invariant upon an isotopic substitution, that the "guest" molecules can enter substitutionally into the "host" lattice without disturbing the crystal structure, that the entire concentration range ( 0-100%) of impurities can be obtained and that the shift in the relative guest-host excitation energy differences can be changed by making different isotopic substitution. An example of isotopic substitution is the replacement of the hydrogen atoms in the naphthalene molecules by deuterium atoms.

The system to be studied in this thesis is the Naphthalene- $h_8$  and Naphthalene- $d_8$  mixed crystal. <sup>(12)</sup>

Naphthalene- $d_8$  is obtained by replacing the eight hydrogen atoms by eight deuterium atoms to give the compound shown in figure 2.11

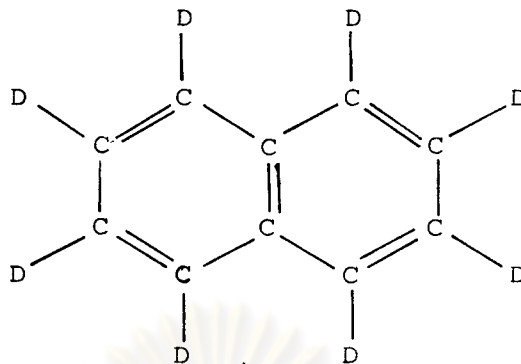


Fig. 2.11 Naphthalene-d<sub>8</sub>

Since the chemical bonds between the hydrogen atom and the carbon atom in Naphthalene-h<sub>8</sub> are the same as the bonds between the carbon atom and the deuterium atom in Naphthalene-d<sub>8</sub>, the change in the frequencies of the internal vibrations ( or excitations ) in the Naphthalene-h<sub>8</sub> and the Naphthalene-d<sub>8</sub> molecules would be due to the differences in the masses of the hydrogen and deuterium atom. The change in the frequencies resulting from the deuteration of the benzene ring in the naphthalene molecules is quite large. Similar changes can be seen in the deuteration of other aromatic hydrocarbons, e.g. , anthracene. These changes in the excitation energies can be seen in observed differences in properties such as the diffusion coefficients of normal and fully deuterated hydrocarbons.