

CHAPTER I



INTRODUCTION

1.1 Mixed Crystals

Molecular crystals¹ 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 the host component, while the minor component is designated as the guest. In the heavily doped mixed crystal, these designations become meaningless.

When the two components are molecules which contain different isotopes of the same element, the mixed crystal is called an isotopic mixed crystal. Since the isotopes of the element have the same atomic 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. The "guest" molecules can enter substitutionally into the "host" lattice without disturbing the crystal structure. 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 research is the naphthalene- h_8 and naphthalene- d_8 mixed crystal.² As is well known, naphthalene- h_8 is an aromatic compound which contains eight hydrogen atoms attached to the double benzene rings as shown in Fig. 1.1.1

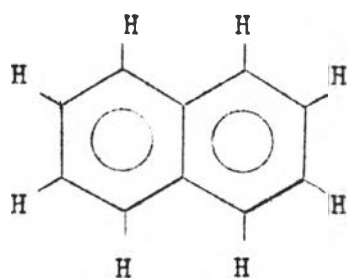


Fig.1.1.1 Naphthalene- h_8

Naphthalene- d_8 is obtained by replacing the eight hydrogen atoms by eight deuterium atoms to give the compound shown in Fig.1.1.2.

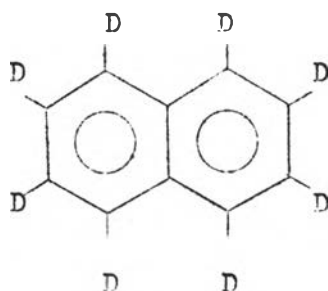


Fig.1.1.2 Naphthalene- d_8

Since the chemical bonds between the hydrogen atom and the carbon atom in naphthalene- h_8 are the same as the bonds between the carbon atom and the deuterium atom in naphthalene- d_8 , the change in the frequencies of the internal vibration (or excitations) in the naphthalene- h_8 and the naphthalene- d_8 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 difference in properties such as the diffusion coefficient of normal and fully deuterated hydrocarbons.

1.2 Symmetry Elements of Naphthalene Crystal³

The Site Group

Individual molecules in a molecular crystal retain their identity since the intermolecular forces are much weaker than the chemical forces within molecules. It is useful to investigate the connection between the symmetry of the free molecule and the symmetry retained by it in its crystal environment.

The symmetry of an individual molecule is described by a point group.⁴ For the case of naphthalene the point group is D_{2h} consisting of the following operations, referred to in Fig.1.2.1

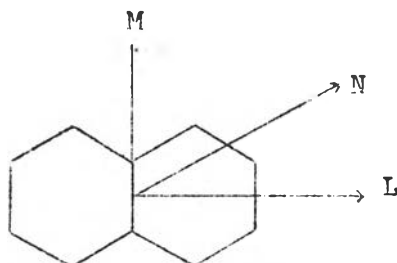


Fig.1.2.1 Axis convention in naphthalene crystal

1. Identity
2. 180° rotations about the axis L, M and N
3. Inversion in the origin
4. Reflection in the plane MN, NL and LM

In a crystal, a space group is identified by the symmetry of the array of molecules. In many systems, there are operations which are common to both the space group and the molecular point group. These are interpreted as operations that simultaneously leave one particular molecule and the whole crystal invariant. They form the site group, the elements of which must have the form $\{\alpha/o\}$.

In many organic molecules the site symmetry is much lower than the molecular symmetry. Thus for benzene, the molecular point group is D_{6h} , for naphthalene, D_{2h} and for anthracene, D_{2h} , but retaining only inversion symmetry, the site group is C_i for these molecular crystals. Naphthalene molecules form monoclinic unit cell, characterized by $a \neq b \neq c$; $\alpha = 90^\circ$, $\beta \neq 90^\circ$, $\gamma = 90^\circ$. The naphthalene crystal belongs to class C_{2h} and have cell dimensions $a = 8.24 \text{ \AA}$, $b = 6.00 \text{ \AA}$, $c = 8.62 \text{ \AA}$, $\beta = 122.9^\circ$.

The Schoenflies symbols C_{2h} , C_i , D_{2h} and D_{6h} are generally used in group theory.

In group theory⁴, C_{nh} is obtained from adjoining C_n to σ_h , where C_n denote the operation of rotation through an angle $2\pi/n$ (n integer) about a certain axis and σ_h denote reflection in a plane

perpendicular to this axis. Thus for C_{2h} , represent rotation $2\pi/n$ or π about a certain axis and reflection in a plane perpendicular to this axis. C_i is obtained from adjoining the inversion I to C_n . This group C_i has two elements E (identity) and I (inversion).

The group D_{nh} ($n = 2, 3, \dots$), symmetry elements are C_n and n two-fold axes, perpendicular to C_n , and a horizontal mirror plane σ_h , n vertical mirror planes $n \sigma_v$ (σ_v denote vertical plane, i.e., plane contains the principal axis C_n).

The naphthalene unit cell is shown in Fig.1.2.2.

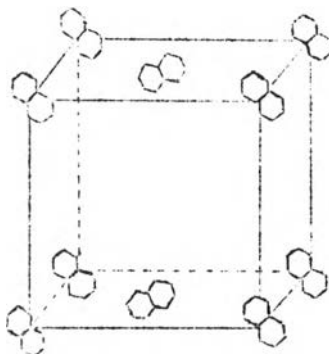


Fig.1.2.2 The naphthalene unit cell.

The nature of a lattice structure implies that, corresponding to any arbitrary molecule in an unit cell, there is a molecule in any other unit cell with exactly the same orientation and exactly the same relative position in the unit cell. The operations which take us from one molecule to an equivalent molecule in another unit cell forms a translationally equivalent set. This set is left invariant by lattice translation T and also by the operations at the site group. There are

two molecules per unit cell, the centers of which have coordinate 000 and $\frac{1}{2} \frac{1}{2} 0$. This arises because the eight molecules at the corners of cube are each shared by eight unit cells while the molecules in the $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 1)$ are each shared by two unit cells.

1.3 Excitons and Exciton bands

The excitation of an atom within the molecules can be passed from one molecule to another molecule. When this happens, the excitation is said to be travelling through the crystal and is then called an exciton⁵. 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 also known as excitons. They correspond to a bound electron-hole pair state. The energy of these excitons lies within the gap. The pair is the result of the attractive coulomb interaction between an electron which has been excited from the valence band into the conduction band and the hole left behind in the valence band. The properties of the exciton depend on its size and some properties of the excitations. The exciton can be classified as a Wannier (or Mott-Wannier) exciton or a Frenkel exciton.

1.3.1 Mott-Wannier Excitons

When the size of the excitation is such that the electron-hole pair or the excited atom type excitons, overlap neighboring atoms, the exciton must be treated as a Mott-Wannier excitons. The Mott-Wannier

excitons are often referred to as weakly bound excitons. A typical Wannier exciton is shown in Fig.1.3.1⁶

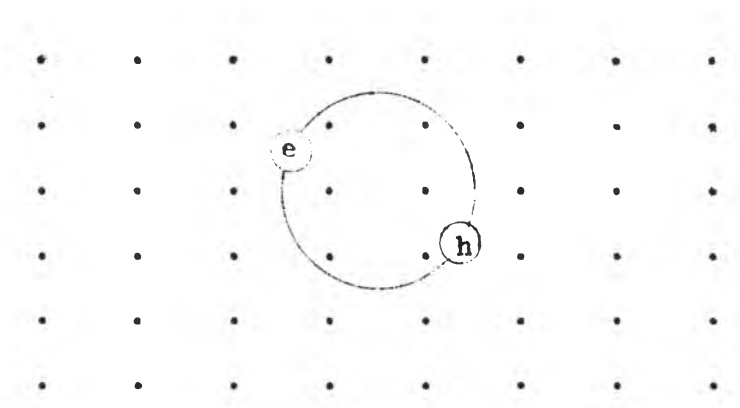


Fig.1.3.1 picture of a typical Wannier exciton

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

1.3.2 Frenkel Excitons

Frenkel excitons are the tight binding excitons. To be called Frenkel excitons, the excitation must be localized on or near a single atom or molecule. In the case of excited atoms for instance, the hole and excited electron are located on the same atom. The electron-hole pair (or excitation) can hop from one atom to another depending on the strength of the coupling between the neighbors. An example of an excited atom type exciton is seen in the alkali halide crystals. In these crystals (See Fig.1.3.2⁵) the excitons of lowest energies are localized on the negative halogen ions, since the excitation energy levels for negative ions are lower than the levels for positive ions.

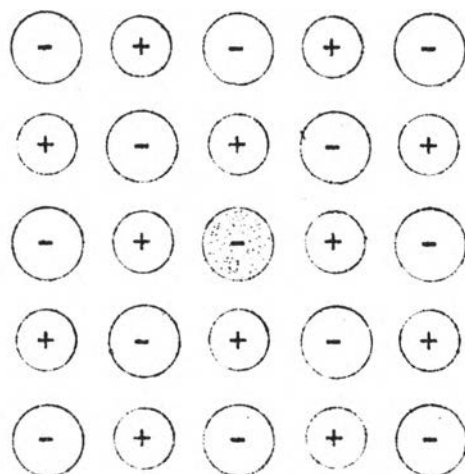


Fig.1.3.2 Schematic representation of a tightly bound or Frenkel exciton localized on one atom in the (100) plane of an alkali halide crystal. An ideal Frenkel exciton will travel as a wave throughout the crystal, but the electron is always close to the hole.

In many crystals including 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 ground state molecules. The excited molecules in this case can also be treated as Frenkel excitons.

1.3.3 Restricted Frenkel Excitons Limit.

In the restricted Frenkel exciton limit, 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 exciton 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.

1.3.4 Exciton Band ³

According to the theory of a two-molecule system, the nondegenerate excited state of the individual molecules would split into two excited states when they are incorporated into the two-molecule system. The amount of the splitting depends on the strength of the interactions between the molecules, the relative orientation of the molecules and on the properties of the one (or free) molecule state. Extending the theory to N-molecule system, one would expect the N single-molecule states (all having the same energy E) would combine together 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 band). The width of the excitation absorption band depends on the intermolecular coupling strength and can be related to the intensity through the transition dipole moments.

1.4 The Density of States

Of interest to solid state physicists is the density of states function. One way to calculate the density of states is simply by counting. If the system can be in an energy state E_1 , we count it

$$\rho(E) = N^{-1} \sum_1 \delta(E - E_1), \quad (1.4.1)$$

where E_1 are the allowed energy states. N is the total number of molecules or states. The same energy can have one or more time of the allowed energy states which correspond to Pauli exclusion principle.

In the ${}^1B_{2u}$ state of a $C_{10}H_8 - C_{10}D_8$ mixed crystal at low temperature, high-resolution resonance pair data were fitted by an iterative computer program, with the help of the well-known Davydov components. Hong and Kopelman⁸ pointed out that this leads to a restricted-Frenkel-model exciton dispersion relation in terms of six pairwise interaction parameters, pertaining to the sixteen nearest, next-nearest, etc., neighbors :

$$E(\vec{k}) = \sum_e M_e e^{i\vec{k} \cdot \vec{R}_e} + \sum_i M_i e^{i\vec{k} \cdot \vec{R}_i}, \quad (1.4.2)$$

where $e = a, b, c, (a + c)$; and $i = \frac{1}{2}(a + b), \frac{1}{2}(a + b) + c$. Here a, b and c are the primitive lattice vectors, \vec{k} is the reduced wave vector, \vec{R}_e is the pair vector for translationally equivalent molecules, and \vec{R}_i is that for interchange equivalent molecules. The \vec{k}^+ state designates the symmetric branch (interchange group C_2); The \vec{k}^- state, the antisymmetric branch. M_e and M_i are the parameters.

When intermolecular distances alone are considered, the leading interaction terms are those listed in Table 1.4.1. The corresponding exciton dispersion relation can be written as⁷

$$\begin{aligned}
 E(\vec{k}^{\pm}) &= 2M_a \cos(\vec{k} \cdot \vec{a}) + 2M_b \cos(\vec{k} \cdot \vec{b}) + 2M_c \cos(\vec{k} \cdot \vec{c}) \\
 &+ 2M_{a+c} \{ \cos(\vec{k} \cdot \vec{a}) \cos(\vec{k} \cdot \vec{c}) - \sin(\vec{k} \cdot \vec{a}) \sin(\vec{k} \cdot \vec{c}) \} \\
 &+ \left[4M_{12} \cos\left\{ \vec{k} \cdot \left(\frac{\vec{a}}{2} \right) \right\} \cos\left\{ \vec{k} \cdot \left(\frac{\vec{b}}{2} \right) \right\} + 4M_{12}' \right. \\
 &\times \left[\cos(\vec{k} \cdot \vec{c}) \cos\left\{ \vec{k} \cdot \left(\frac{\vec{a}}{2} \right) \right\} \cos\left\{ \vec{k} \cdot \left(\frac{\vec{b}}{2} \right) \right\} \right. \\
 &\left. \left. - \sin(\vec{k} \cdot \vec{c}) \sin\left\{ \vec{k} \cdot \left(\frac{\vec{a}}{2} \right) \right\} \cos\left\{ \vec{k} \cdot \left(\frac{\vec{b}}{2} \right) \right\} \right] \right] \quad (1.4.3)
 \end{aligned}$$

where M_{12} designates the pair interaction for $\vec{R} = \frac{1}{2}(\vec{a} + \vec{b})$, M_{12}' for $\vec{R} = \frac{1}{2}(\vec{a} + \vec{b}) + \vec{c}$, M_a for $\vec{R} = \vec{a}$, M_b for $\vec{R} = \vec{b}$, M_c for $\vec{R} = \vec{c}$ and M_{a+c} for $\vec{R} = \vec{a} + \vec{c}$

Table 1.4.1 Excitation exchange interaction parameters for the ${}^1B_{2u}$ state of naphthalene.⁹

M^b (cm^{-1})			
Position ^a	Set 1	Set 2	Set 3
$\frac{1}{2}(a + b)^c$	18.0	18.0	18.0
$\frac{1}{2}(a + b) + c^c$	2.0	1.0	1.0
a^d	-0.6	-4.3	-1.2
b^d	-3.9	1.9	1.6
c^d	6.1	-6.1	-8.9
$a + c^d$	-3.7	6.0	6.0

^a Position of the second molecule of the pair with respect to the first

^b Pairwise interaction, Hong and Kopelman⁷

^c Interchange equivalent pairs

^d Translationally equivalent pairs

1.5 Quantitative Tests of Mixed Molecular Crystal Theory

⁹
Ochs and Kopelman have attempted to relate quantitative experimental observations with the theories proposed by Hong and Kopelman. In their first paper, Ochs, Prasad and Kopelman¹⁰ believed that they were successful in relating quantitative experiments involving isolated

isotopic naphthalene guest molecules ("monomer") in a host lattice, with Hong and Kopelman's theory. They found excellent agreements between the observed quasiresonance shifts and the theoretical predictions, between the observed spectral polarization and the theoretical predictions, and between the degree of exciton localization at the monomer site and the theory. In a later paper⁹, they sought to retest the theory by looking at the dimer states. To be specific, they sought to relate the peaks in the optical absorption by mixed crystals of 1-D₁C₁₀H₇, 2-D₁C₁₀H₇ and 1,4-D₂C₁₀H₆ with C₁₀D₈ over a concentration range of 0.009 % to 5 % mole, at 2 K, with a resolution of 0.5 cm⁻¹. Their assignment of peaks to monomer quasiresonances or to dimer resonances was based entirely on whether the area underneath the peaks increased linearly or non-linearly as the concentration of the guest molecules was increased. The reason for this type of differentiation was that in Hong and Kopelman's theory, the spectral weight of the optical intensity at the monomer energy was proportional to c while the spectral weight at the dimer energy was proportional to c^2 .

With their assignment of peaks, they were successful in showing that the relevant formulae in Hong and Kopelman's theory would develop singularities at the observed absorption energies when three sets of previously determined parameters were used the formulae. However, several dimer resonance peaks predicted by the appearances of singularities in Hong and Kopelman dimer self energy expression were not observed. Ochs and Kopelman explained away most of the nonappearances as being due to the fact that the unobserved resonances were too close to monomer

quasiresonance peaks and could therefore not be resolved experimentally or that the unobserved resonances were very broad resonance which could not be identified as being a resonant peak.

The purpose of this research is to obtain the monomer self energy for mixed naphthalene crystal self consistently. Our treatment involves the calculation $P_n(c)$ using only monomer case. By expanding $P_n(c)$ in term of diagram, and count only monomer graphs, we get the monomer self energy. Our result is similar to that of Leath and Goodman's¹¹ work on the mass disorder problem which was symmetric in two constituents and depending on concentration of impurity.