CHAPTER III

DIAGRAMMATIC INTERPRETATION OF MONOMER SERIES

3.1 Monomer Series Expansion.

From equation (I.28), Hong and Kopelman[18] and Chatuporn[19] and Tang[20] pull out the series of graphs which have one vertex. These series of graphs are labeled as the monomer series and which produced $\Sigma_{monomer}$, then

$$\Sigma_{monomer} \quad = \quad \text{}$$

III.1

Denoting $\Sigma_{monomer}$ by Σ_1, we find that the analytical form is

$$\Sigma_1 \quad = \quad (\Delta/N)NP_1(c) + (\Delta/N)^2 NP_2(c) \sum_{K'} G_0(K')$$

$$+ (\Delta/N)^3 NP_3(c) \sum_{K'K''} G_0(K')G_0(K'') + \ldots$$

III.2

Hong and Kopelman[18] used the approximation $P_n(c) = c$ which is valid for lightly doped crystals to get

$$\Sigma_1(K) \quad = \quad (\Delta/N)Nc \left[1 + \Delta G_0(E) + \Delta^2 G_0^2(E) + \ldots \right]$$

III.3

The resulting series is in the form $1 + x + x^2 + \ldots\ldots$ which is just the geometric power series expansion of $(1 - x)^{-1}$.

Thus equation (III.3) can be rewritten as

$$\Sigma_1(K) = \frac{c\Delta}{1 - G_0(K)\Delta} \qquad \text{III.4}$$

The Dyson's equation

$$<G(K)> = G_0(k) + G_0(K) \Sigma(K) <G(K)> \qquad \text{III.5}$$

can be rewritten as

$$<G(K)> = \left[G_0^{-1}(K) - \Sigma(K) \right]^{-1} \qquad \text{III.6}$$

or as

$$<G(K)> = \left[E - \epsilon(K) - \Sigma(K) \right]^{-1} \qquad \text{III.7}$$

where $\Sigma(K)$ is given by equation (III.3)

By taking the imaginary part of equation (III.7) we get

$$\text{Im} <G(K)> = \frac{\text{Im}\Sigma(K)}{\left[E - \epsilon(K) - \text{Re}\Sigma(K) \right]^2 + \left[\text{Im}\Sigma(K) \right]^2} \qquad \text{III.8}$$

Assuming that $\Sigma(k)$ is small (valid for very low concentrations of impurities), we find that

$$\text{Im} <G(K)> = \frac{\text{Im}\,\Sigma(K)}{\left[E - \epsilon(K) \right]^2} \qquad \text{III.9}$$

In other words, the singularities in the imaginary part of the configuration average Green's function for the mixed crystal outside the band are the same as the singularities of the imaginary part of the self energy and the residue of these two functions at their common poles are related by equation (III.9)

The optical spectrum can be obtained by the two relationships (these being the Krammer Kronig relationships)

$$I_b^O (E) \quad = \quad (1/\pi)\text{Im} < G(K^+ = 0) > \qquad \text{III.10}$$

$$I_{ac}^O (E) \quad = \quad (1/\pi)\text{Im} < G (K^- = 0) > \qquad \text{III.11}$$

where b and ac refer to the branches of the spectrums. The pole or singularity of equation (III.4) is given by

$$G_o(E(1)) \quad = \quad \frac{1}{\Delta} \quad = \quad \int \frac{\rho_o(E')}{E(1)-E'} \, dE' \qquad \text{III.12}$$

For convenience, Hong and Kopelman work with the total intensity attributable to the monomer impurity defined as

$$I_b (E(1)) \quad = \quad \int_{E(1)-\epsilon}^{E(1)+\epsilon} I_b^O (E) \, dE \qquad \text{III.13a}$$

$$I_{ac}(E(1)) \quad = \quad \int_{E(1)-\epsilon}^{E(1)+\epsilon} I_{ac}^O (E) \, dE \qquad \text{III.13b}$$

where E(1) is the monomer energy defined by equation (III.12). Because the Im <G(K)> is connected to Im Σ (K) by equation (III.10), we have

$$I_b(E(1)) \quad = \quad \text{Res} \frac{\Sigma(E = E(1) \,)}{(E(1) -\epsilon_b)^2} \qquad \text{III.14a}$$

$$I_{ac}(E(1)) \quad = \quad \text{Res} \frac{\Sigma(E = E(1) \,)}{(E(1) -\epsilon_{ac})^2} \qquad \text{III.14b}$$

Using equation (III.14a) and (III.14.b) and a similar set of equations

for the dimer contribution which also requires that $P_n(c) = c$ for

all value of n , Hong and Kopelman were then able to explain some of

the observed properties of mixed naphthalene crystal and to provide

some insights into the internal mechanism of resonance pairs.

Later Chatuporn[19] and Tang[20] extend the theory to crystals con-

taining higher concentrations of impurities. The modification consists

essentially of replacing the approximation $P_n(c) = c$ by a form for

$P_n(c)$ used by Leath and Goodman[21] for treating lattice vibration

in disordered binary system.

Leath and Goodman[21] pointed out that the function $P_n(c)$ can be

written as

$$P_n(c) = \sum_{m=1}^{n} (-1)^{m-1} (m-1)! \, c^m \, S(n,m) \qquad \text{III.15}$$

where S(n,m) is the number of ways of partitioning a set of order n

into m non-empty subsets and which is called " the stirling numbers

of the second kind " . The stirling numbers of the second kind can be

defined in terms of the binomial coefficient as

$$S_{(n,m)} = S_n^{(m)}$$

$$= \frac{1}{m!} \sum_{K=0}^{m} (-1)^{m-K} \binom{m}{K} K^n \qquad \text{III.16}$$

Substitution of equation (III.16) into equation (III.15) gives

$$P_n(c) = \sum_{m=1}^{n} (-1)^{m-1} (m-1)! \, c^m \, \frac{1}{m!} \sum_{k=0}^{m} (-1)^{m-k} \frac{m!}{(m-k)!K!} K^n \qquad III.17$$

The coefficients of the Nth power of c in the nth function $P_n(c)$ can be obtained by relationship

$$\text{Coefficient of } c^N \text{ in } P_n(c) = \frac{1}{N!} \frac{\partial^N}{\partial c^N} P_n(c)\Big|_{c=0} \qquad III.18$$

where $n > N$.

Substituting equation (III.17) into equation (III.18), we get coefficient of c^N in $P_n(c)$

$$= \frac{1}{N!} \sum_{m=N}^{n} (-1)^{m-1} (m-1)! \frac{m!}{(m-N)!} c^{m-N}\Big|_{c=0} \frac{1}{m!} \sum_{K=0}^{m} (-1)^{m-K} \frac{m!}{(m-K)!K!} K^n$$

$$= \frac{1}{N!} \sum_{m=N}^{n} (-1)^{m-1} (m-1)! \frac{m!}{(m-N)!} \delta_{mN} \frac{1}{m!} \sum_{K=0}^{m} (-1)^{m-K} \frac{m!}{(m-K)!K!} K^n$$

$$= \frac{1}{N!} (-1)^{N-1} (N-1)! N! \frac{1}{N!} \sum_{K=0}^{N} (-1)^{N-K} \frac{N!}{(N-K)!K!} K^n$$

$$= (N-1)! \sum_{K=0}^{N} (-1)^{K+1} \frac{1}{(N-K)!K!} K^n \qquad III.19$$

Again it should be emphazied that the n appearing in equation (III.19) is the subscript of the P(c) function while N is the

power of c in $P_n(c)$,

We are now in a position of being able to sum the self-energy arising from the monomer contribution. This monomer series is not the total self energy since diagrams such as

and

are not

included in the above series. These two terms are, of course, the simplest diagrams which appear in the dimer contribution to the self-energy. The summing of Σ_m is accomplished by summing those contribution from each diagram which proportional to c, then summing those proportional to c^3 and so forth. For example, the contribution to c^N is

$$(N-1)! \quad \Delta \sum_{K=0}^{N} (-1)^{K+1} \frac{K^L L^{L-1} G_o^{L-1}}{(N-K)!K!} \qquad \text{III,20}$$

Equation (III.20) is the product of eqn. (III.19) and the Green's function equivalent of L interactions connected to the impurities with the propagator $<G(E)>$ without the probability factor $P_n(c)$ present,

Putting everything together, we find that the self-energy written to all orders of c is

$$\Sigma_{monomer} \quad \text{or} \quad \Sigma_1 = c\Delta(1+\Delta G_o + \Delta^2 G_o^2 + \ldots \Delta^n G_o^n + \ldots) + \Sigma^{(2)} \qquad \text{III,21}$$

where

$$\Sigma^{(2)} = \Delta \sum_{N=2}^{\infty} c^N \sum_{n=N}^{N} (N-1)! \sum_{K=0} (-1)^{K+1} \frac{K^n \Delta^{n-1} G_o^{n-1}}{(N-K)!K!}$$

III.22

The first summation in $\Sigma^{(2)}$ represents summation over all the orders of c, the second summation represents the summing of all the contributions which are proportional to c^N, while the last summation arises from the definition of nth contribution. By rearranging the terms in the last two summations, we get

$$\Sigma^{(2)} = \Delta \sum_{N=2}^{\infty} \frac{c^N}{n} \sum_{n=N}^{\infty} \sum_{K=0}^{N} (-1)^{K+1} \binom{N}{K} K^n \Delta^{n-1} G_o^{n-1}$$

III.23

where $\binom{N}{K}$ is binomial coefficient. If we now adopt a convention that $\binom{N}{K} = 0$ for $k > n$, the summation over K can be extended to infinity. this allow us to interchange the two summation over n and K,

The summation over n can now be carried out as follows

$$\sum_{n=N}^{\infty} K^n \Delta^{n-1} G_o^{n-1} = \Delta^{-1} G_o^{-1} \sum_{n=N}^{\infty} K^n \Delta^n G_o^n$$

$$= \Delta^{-1} G_o^{-1} K^N \Delta^N G_o^N \sum_{n=0}^{\infty} K^n \Delta^n G_o^n$$

$$= \frac{K^N \Delta^{N-1} G_o^{N-1}}{1-K\Delta G_o}$$

III.24

where $K \Delta G_o < 1$

Thus the second part of the self-energy become

$$\Sigma^{(2)} = \Delta \sum_{N=2}^{\infty} \frac{c^N}{N} \sum_{K=o}^{\infty} (-1)^{K+1} \binom{N}{K} \frac{K^N \Delta^{N-1} G_o^{N-1}}{1-K\Delta G_o} \qquad \ldots \text{III.25a}$$

$$= G_o^{-1} \cdot \sum_{N=2}^{\infty} \frac{c^N \Delta^N G_o^N}{N} \sum_{K=o}^{\infty} (-1)^{K+1} \binom{N}{K} \frac{K^N}{1-K\Delta G_o} \qquad \text{III.25b}$$

$$= \Sigma_1^{(2)} + \Sigma_2^{(2)} + \Sigma_3^{(2)} + \Sigma_4^{(2)} + \ldots \qquad \text{III.26}$$

where

$$\Sigma_1^{(2)} = G_o^{-1} \sum_{N=2}^{\infty} \frac{1}{N} \binom{N}{1} \frac{c^N \Delta^N G_o^N}{1-\Delta G_o} \qquad \text{III.27a}$$

$$\Sigma_2^{(2)} = G_o^{-1} \sum_{N=2}^{\infty} \frac{1}{N} \binom{N}{2} \frac{(2c\Delta G_o)^N}{1-2\Delta G_o} \qquad \text{III.27b}$$

$$\Sigma_3^{(2)} = G_o^{-1} \sum_{N=3}^{\infty} \frac{1}{N} \binom{N}{3} \frac{(3c\Delta G_o)^N}{1-3\Delta G_o} \qquad \text{III.27c}$$

and where the general expression is

$$= G_o^{-1} \sum_{N=L}^{\infty} (-1)^{L+1} \frac{1}{N} \binom{N}{L} \cdot \frac{(Lc\Delta G_o)^N}{1-L\Delta G_o} \qquad \text{III.27d}$$

By writting out the binomial coefficient, equation (III.27a) to

(III.27d) become

$$\Sigma_1^{(2)} = \frac{c^2\Delta^2 G_o}{1- G_o} \quad \frac{1}{1-c\Delta G_o} \qquad \text{III.28a}$$

$$\Sigma_2^{(2)} = \frac{-c\Delta}{1-2\Delta G_o} \quad \sum_{n=o}^{\infty} n(2c\Delta C_o)^n \qquad \text{III.28b}$$

$$\Sigma_3^{(2)} = \frac{c\Delta}{1-3\Delta G_o} \quad \sum_{n=o}^{\infty} \frac{n(n-1)}{2}(3c\Delta G_o)^n \qquad \text{III.28c}$$

$$\text{and } \Sigma_L^{(2)} = (-1)^{L+1} \quad \frac{c\Delta}{1-L\Delta G_o} \quad \sum_{n=o}^{\infty} \frac{n(n-1)(n-2)\ldots(n-L+2)(Lc\Delta G_o)^n}{(L-1)!}$$

$$\text{III.28d}$$

The summation over n in equation (III.28b) to equation (III.28d) can be carried out by noting that[22]

$$\sum_{K=o}^{\infty} KX^K = \frac{X}{(1-X)^2} \qquad \text{III.29}$$

Dividing both sides of equation (III.29) by X, we get

$$\sum_{K=o}^{\infty} KX^{K-1} = \frac{1}{(1-X)^2} \qquad \text{III.30}$$

By differentiating equation (III.30), we get

$$\sum_{K=o}^{\infty} K(K-1)X^K = \frac{2X^2}{(1-X)^3} \qquad \text{III.31}$$

Dividing equation (III.31) by X^2 and differentiating with respect to X again gives

$$\sum_{K=0}^{\infty} K(K-1)(K-2)X^K = \frac{3!X^3}{(1-X)^4} \qquad \text{III.32}$$

Repeating this process N times, we get

$$\sum_{K=0}^{\infty} K(K-1)K-2)...(K-N+2)X^K = \frac{N!X^N}{(1-X)^{N+1}} \qquad \text{III.33}$$

Using the general result, equation (III.33), in equation (III.28d), we find that

$$\Sigma_2^{(2)} = (-1)^3 \frac{c\Delta}{1-2\Delta G_o} \frac{2c\Delta G_o}{(1-2c\Delta G_o)^2} \qquad \text{III.34a}$$

$$\Sigma_3^{(2)} = (-1)^4 \frac{c\Delta}{1-3\Delta G_o} \frac{(3c\Delta G_o)^2}{(1-3c\Delta G_o)^3} \qquad \text{III.34b}$$

and in general, we find

$$\Sigma_L^{(2)} = (-1)^{L+1} \frac{c\Delta}{1-L\Delta G_o} \frac{(Lc\Delta G_o)^{L-1}}{(1-L\Delta G_o)^L} \qquad \text{III.35}$$

Summing over all values of the variable L of equation (III.36) and replacing $1 + \Delta G_o + \Delta^2 G_o^2 + ..$ by its sum, we find that the self self-energy due to the monomer contribution is

$$\Sigma_{monomer} = \frac{c\Delta}{1-\Delta G_o} + \frac{c\Delta}{(1-\Delta G_o)}\frac{c\Delta G_o}{(1-c\Delta G_o)} +$$

$$\sum_{N=2}^{\infty} (-1)^{N+1} \frac{c\Delta}{1-N\Delta G_o} \frac{(Nc\Delta G_o)^{N-1}}{(1-Nc\Delta G_o)^N}$$

$$\text{or } \Sigma_1 = \frac{c\Delta}{1-\Delta G_o}\frac{1}{(1-c\Delta G_o)} +$$

$$\sum_{N=2}^{\infty} (-1)^{N+1} \frac{c\Delta}{1-N\Delta G_o} \frac{(Nc\Delta G_o)^{N-1}}{(1-Nc\Delta G_o)^N}$$

$$= c\Delta \sum_{N=1}^{\infty} (-1)^{N+1} \frac{(Nc\Delta G_o)^{N-1}}{(1-N\Delta G_o)(1-Nc\Delta G_o)^N} \qquad \text{III.36}$$

It should be noted that as $c \longrightarrow 0$, equation (III.36) reduces to the self-energy, equation (III.4), derived by Hong and Kopelman on the basis of the substitution $P_n(c) = c$ for all values of n.

3.2 Modified Monomer Series of Self Energy.

Tang [20] pull out a series of graphs to give a "modified monomer" series as in the figure (3.1)

Fig. 3.1 Modified monomer series

in place of monomer series obtained by Hong and Robinson.[23] The

additional diagram, which are shown in equation (III.1), are incorporated

into the series by replacing the internal bare propagators by the dressed

or true propagators.

When the monomer self energy series being replaced by the true

propagators $\langle G(E)\rangle = (G_o^{-1}(E) - \Sigma)^{-1}$ where Σ is the monomer

self energy series shown in figure 3.1, the partial series shown in

figure 3.1 can be summed to be the continued fraction

$$\Sigma = \cfrac{cV}{1 - \cfrac{V}{G_o^{-1} - \cfrac{cV}{1 - \cfrac{V}{G_o^{-1} - \cfrac{cV}{1 - V}}}}}$$

III.37

where V is the perturbation $\varepsilon_A - \varepsilon_B$; c is the concentration of the

impurities and $G_o(E)$ is the bare propagator of the system.

(18)

As was pointed out by Hong and Kopelman, the singularities lying outside the density of state band of the bare propagators are the zeros of the denominator of the self energy expression. By terminating the continued fraction at the first appearance of c in the denominator , at the second appearance, at the third and so on, we find that the singularities are the zeros of the following sequence of polynomials (which are the denominators of the first convergent, the second etc).

$$P_1(E) = 1 - VG_o(E)$$

$$P_2(E) = (1 - VG_o(E))P_1(E) - cVG_o(E)$$

$$P_3(E) = (1 - (1 + c)VG_o(E)) P_2(E) - cV^2G_o(E)P_1(E)$$

$$\vdots$$

$$P_n(E) = (1 - (1 + c)VG_o(E))P_{n-1}(E) - cV^2G_o(E)P_{n-2}(E)$$

III.38

The above sequence of polynomials is known as a Sturm sequence. Based on some theorems concerning the zeros of a Sturm sequence of polynomials, we find that the singularities of the propagators will lie on the real axis and will therefore be physically meaningful. The continued fraction can be terminated by writing the self energy as

$$\Sigma = \frac{cV}{1 - \dfrac{V}{G_o^{-1}(E) - \Sigma}} \qquad \text{III.39}$$

The solution of equation (III.39) is

$$\Sigma = \left[\frac{G_o V(c-1) + 1}{2G_o}\right]\left\{1 - \left[1 - \frac{4G_o cV}{(G_o V (c-1) + 1)^2}\right]^{1/2}\right\} \qquad \text{III.40}$$

The negative sign is taken in order to insure the proper behavior as E goes to infinity. As we see, the analytic expression for the self energy has a cut as a result of $\left[1 - \dfrac{4G_o cV}{(G_o V(c-1) + 1)^2}\right]^{1/2}$.

This cut will manifest itself as an impurity side band of width dependent on c in the dilute mixed molecular crystal.

From equation (III.40); the square root in the complex plane has a cut running from +1 to -1 . Which means that when the square root is zero, we have

$$\frac{4G_o cV}{(G_o V(c-1) + 1)^2} = 1 \qquad \text{III.41}$$

Inverting equation (III.41); we get two expressions for G_o

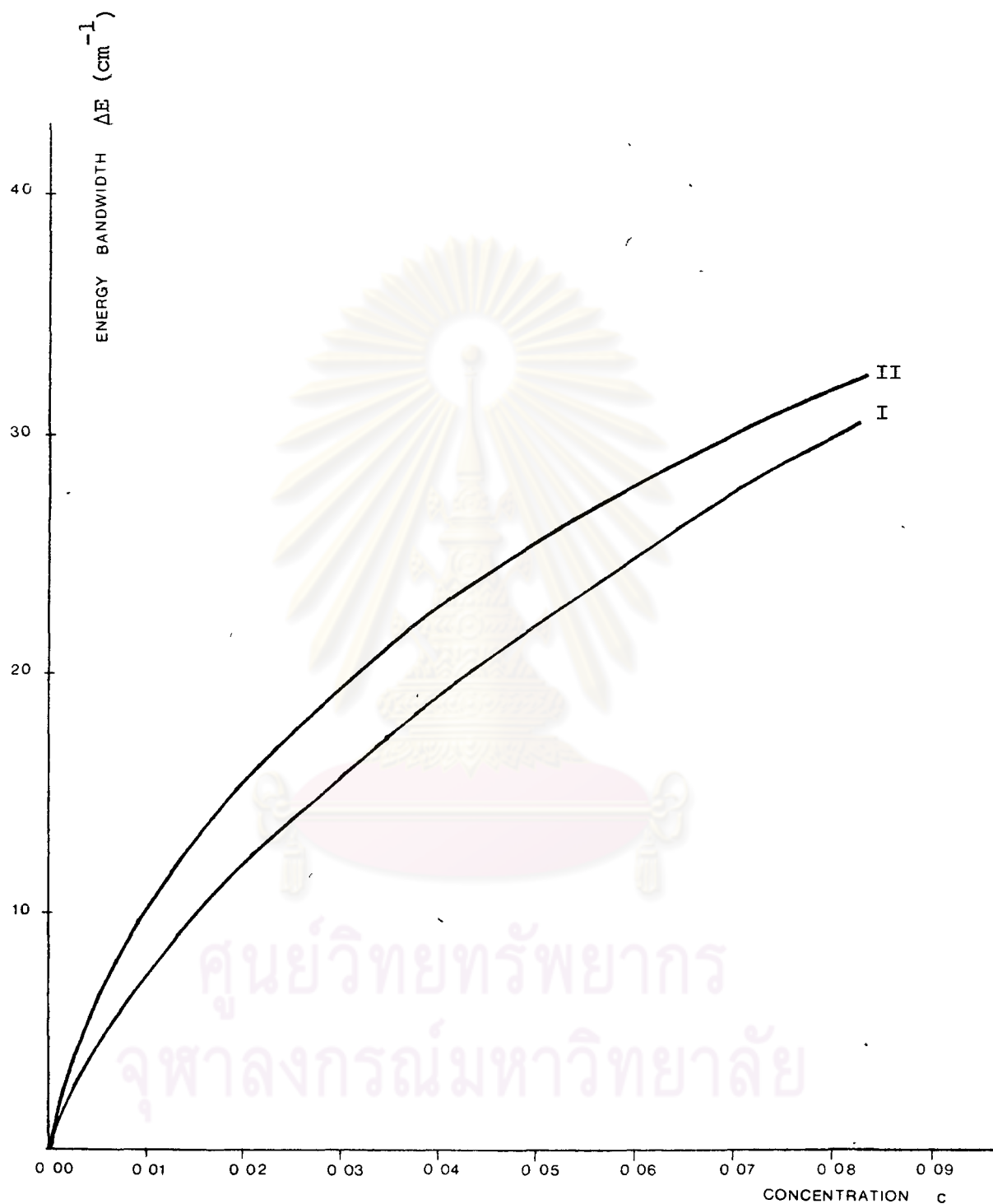$$G_o = \frac{(c+1) \pm 2\sqrt{c}}{V(c-1)^2} \qquad \text{III.42}$$

Fig. 3.2 Energy Bandwidths of Isotopic Mixed Molecular
Crystals in very low concentration

Each expression for G_o yields a value for E. We can see clearly that for every value of c we get two expressions of G_o and two values of E.

Using values of G_o obtained from Suporn[24], we find the values of G_o which satisfy equation (III.41). The difference in the E values is shown in fugure 3.2

Figure 3.2 showed two curves of impurity side band. Curve I corresponds to this result and Curve II corresponds to Hoshen and Jortner[25] who obtained their curve by solving the equation

$$\Delta E = \Delta \sqrt{c(1-c)} \qquad III.43$$

Numerical datas for these two curves will be in the chapter 4.