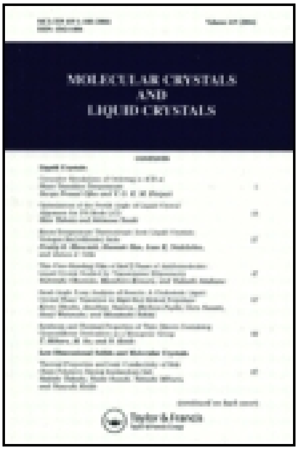

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Self Consistent Diagram Determination of the Monomer State in Isotopic Mixed Molecular Crystals

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The diagram approach is used to determine the locations of the singularities of the monomer self energy in isotopic mixed molecular crystals. The cumulant functions, which are the relative weights of the diagrams in the series, are evaluated in a self consistent manner. The resulting self energy expression is seen to contain singularities which are dependent on the concentration of guest molecules in the system. The formalism is used to obtain the locations of the singularities as a function of the reciprocal trap depth for different concentrations of naphthalene-h_8 in a host naphthalene-d_8 crystal.

I. INTRODUCTION

Hoshen and Jortner[1] have pointed out that the mixed molecular crystals such as naphthalene-h_8/naphthalene-d_8 crystals, benzene-h_6/benzene-d_6 crystals and durene-h_{14}/durene-d_{14} crystals should be ideal systems for testing the different methods introduced for studying disordered systems. Their idealness is due mainly to the fact that the two components differ to a good approximation only in their excitation energies. This means that the perturbation due to the disordering appears only in the diagonal elements of the Hamiltonian and not in the off diagonal elements. Another reason is that the entire range of mixing of the two components can be realized without having the underlying crystal structure altered. Furthermore, there exist experimental techniques[2,3] which can monitor the density of states of the lowest singlet exciton states of these crystals.

Hong and Robinson,[4] Hong and Kopelman,[5] and Hoshen and Jortner[6] have used the Onodera–Toyozawa approach[7] to study the effects of the disorder on the exciton band structures in these crystals. Hong and Kopelman[8] and Hoshen and Jortner[9] have also applied the coherent potential approximation (CPA) method to these crystals. The negative factor counting method,[10] and the cluster expansion method[11] are some of the other methods which have been used to study the disorder in these systems. More recently, Tokura, Koda and Nakada[12] used the dynamical CPA method of Sumi[13] to obtain the self energy of the exciton in isotopically mixed crystals of anthracene. The present paper is concerned with the Onodera–Toyozawa approach to the study of the exciton band structure in mixed molecular crystals of arbitrary concentrations.

The "exact" or closed form self energy expressions obtained by Hong and Kopelman[5] are valid only for the very dilute limit. While some of the approaches give reasonable results as the impurity concentration tends away from zero, the results obtained by Hong and Kopelman cannot be applied to mixed crystals of arbitrary concentrations since the basic assumption which allowed the self energy series to be summed is invalid as the concentration tends away from zero. Recently, Adjutamamus and Tang[14] were able to formally sum the monomer self energy series without having to use Hong and Kopelman's approximation that $P_n(c)$ (the cumulant function) was equal to c for all values of n. Their monomer self energy expression had a series of singular points which were not found in the self energy expression of Hong and Kopelman. Using the same Stirling number representation of the cumulant function used by Adjutamanus and Tang, Ratanapun and Tang[15] found that the dimer self energy expression also contained a series of singularities not present in Hong and Kopelman's results. Leath and Goodman[16] found that a similar set of additional poles appeared in the self energy expressions for the phonon band in mass disordered binary alloys when the Stirling number representation of the cumulant functions was used in their calculations. They argued, however, that the additional poles were unphysical and were due to an overcounting of diagrams implicit in the determination of the Stirling number representation of the cumulant function.

In this paper, we are interested in how the monomer self energy correction changes when different methods are used to calculate the cumulant functions. In Section II., the perturbative expansion of the exciton propagators in a mixed molecular crystal is briefly reviewed. The results of Hong and Kopelman[4] and of Adjutamanus and Tang[14] are rederived here. In Section III., an expression for the cumulant functions which does not contain the overcounting error mentioned by Leath and Goodman and which is obtained in a systematic way using the diagram reduction scheme proposed by Gaspard and Cryot-Lackmann[17] is used in the partial summation of the monomer self energy series. The positions of the singularities in the newly obtained monomer self energy expression as a function of the reciprocal trap depth are numerically evaluated for various concentrations of naphthalene-h_8 in a host naphthalene-d_8 crystals using the density of states of the plus branch of the excitons of the host crystal (the density of states of the excitons of the host crystal being calculated in Section II., using the dispersion relationship appropriate for the crystal structure of naphthalene).

II. MONOMER SELF ENERGY

In molecular crystals such as naphthalene, benzene and durene, the covalent bonding between the individual atoms within the molecules is much stronger than the Van der Waal binding between the molecules in the crystal. The excited atomic states tend, therefore, to be localized within the molecule and so the excitations can be treated as Frenkel excitons. Since the intermolecular interactions in these crystals are short ranged, the excitons in these crystals lie in the restricted Frenkel exciton limit.[5] In this limit, the molecules can be viewed as being geometric points occupying the lattice sites. This allows the orientational dependence of the pairwise interactions between the atoms within the molecule to be ignored. When this is done, the dispersion relation for crystals having the naphthalene structure takes on the simple form

$$\begin{aligned} E(k^{\pm}) = {} & 2M_a\cos(\vec{k}\cdot\vec{a})c + 2M_b\cos(\vec{k}\cdot\vec{b}) + 2M_c\cos(\vec{k}\cdot\vec{c}) \\ & +2M_{a+c}[\cos(\vec{k}\cdot\vec{a})\cos(\vec{k}\cdot\vec{c}) - \sin(\vec{k}\cdot\vec{a})\sin(\vec{k}\cdot c)] \\ & \pm\left\{4M_{12}\cos\left(\vec{k}\cdot\frac{\vec{a}}{2}\right)\cos\left(\vec{k}\cdot\frac{\vec{b}}{2}\right)\right. \\ & +4M'_{12}\left(\cos(\vec{k}\cdot\vec{c})\cos\left(\vec{k}\cdot\frac{\vec{a}}{2}\right)\right. \\ & \left.\left. -\sin(\vec{k}\cdot\vec{c})\sin\left(\vec{k}\cdot\frac{\vec{a}}{2}\right)\right)\cos\left(\vec{k}\cdot\frac{\vec{b}}{2}\right)\right\}^{1/2} \end{aligned} \tag{1}$$

where the M_i's are various interaction parameters. The density of states of the exciton band in naphthalene-d_8 can be obtained by substituting the following numerical values[18] -0.6, -3.9, $+6.1$, -3.7, $+18.0$ and $+2.0$ for the interactions M_a, M_b, M_c, M_{a+c}, M_{12} and M'_{12} appearing in Eq. (1) and then use the fact that the density of states is given by

$$p(E) = (1/N)\left\{\sum_{k^+}\delta(E - E(k^+)) + \sum_{k^-}\delta(E - E(k^-))\right\} \tag{2}$$

The density of states for naphthalene-d_8 shown in Figure 1 was obtained by evaluating $E(k^+)$ and $E(k^-)$ at 512,000 points in the Brillouin zone.

If H_0 is the Hamiltonian for the neat host molecular crystal, the isotopic substitution of some of the molecules in the crystal leads to the following Hamiltonian for the mixed molecular crystal

$$H = H_0 + \sum{}'\Delta_i \tag{3a}$$

where

$$\Delta_i = \epsilon_{\text{guest}} - \epsilon_{\text{host}} \tag{3b}$$

provided that the intermolecular interactions are invariant under the isotopic substitution. The summation in the above equation, Eq. (3a), is only over the sites on which the host molecules have been replaced by the guest molecules. To remove this restriction on the summation, we introduce the site occupancy operator c_i which is equal to one if the

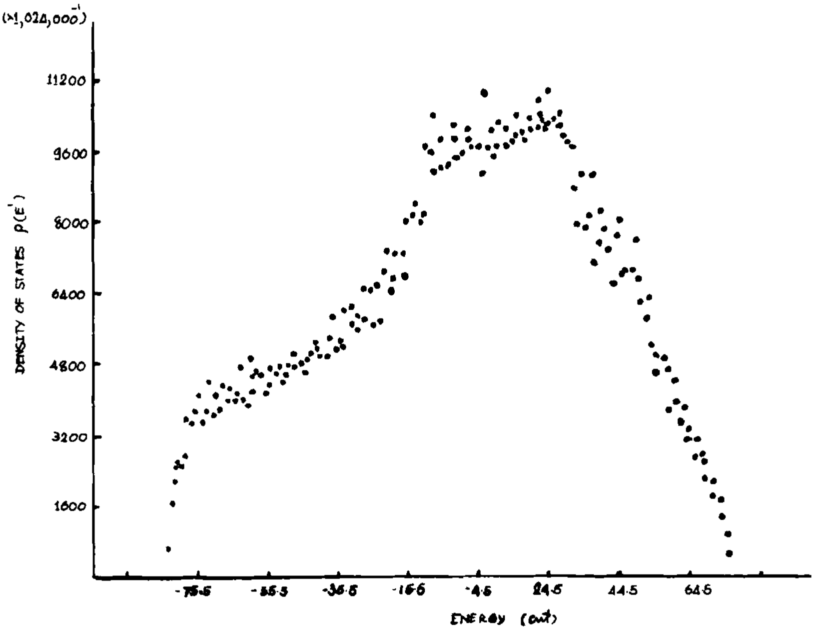

FIGURE 1 Density of states of the exciton band in naphthalene d_8. The density of states was obtained by evaluating the dispersion relations for $E(k^+)$ and $E(k^-)$, Eq. (1), at 512,000 points in the Brillouin zone using the numerical parameters listed as Set I. in ref. 18.

site i has a guest molecule on it or is equal to zero if the site still has a host molecule on it. A given crystal is, then, described by a set of c_i values giving the locations of all the guest molecules in the crystal. The Hamiltonian for a specific crystal can, therefore, be written as

$$H = H_0 + \sum \Delta_i c_i \tag{4}$$

where the summation now extends over every lattice site.

The exciton propagator for the mixed molecular crystal described by a set of c_i values is the diagonal matrix element of $1/(E - H)$ where H is given by Eq. (4). Since in an actual crystal, the guest molecules are randomly distributed and the detailed information about the locations of the guest molecules is not known, the diagonal matrix element must be averaged over all possible configurations of the impurity molecules, i.e., over all possible sets of c_i values. To accomplish this, $1/(E - H)$ must be expanded in powers of the perturbation $\Sigma_i \Delta_i c_i$. In averaging the perturbative expansion, config-

FIGURE 2 Monomer self energy series. The self energy corrections due to the isolated guest (monomer) level is the sum of one-vertex graphs, some of which are shown here.

uration averages of products of site occupancy operators will be encountered. The configuration averaging of these products then leads to the appearance of the cumulant functions. The self energy corrections are obtained by picking out those perturbative terms whose diagrammatic representations are irreducible graphs. Identifying the monomer self energy corrections as being the irreducible graphs which contain only a single interaction vertex, we obtain the monomer self energy series shown in Figure 2.

The analytical representation of each graph in the series is obtained by associating with each vertical line, the perturbation Δ (the trap depth); with each horizontal line, the host crystal propagator $G_0(k)$; with each interaction vertex of n perturbation lines, the cumulant function $P_n(c)$ and then summing over all the internal momentum $\vec{k}$. The analytical expression for the monomer self energy series is

$$\sum_{\text{monomer}} = P_1(c)\Delta + P_2(c)\Delta^2 G_0(E) + P_3(c)\Delta^3 G_0^2(E) + \cdots . \quad (5)$$

Hong and Kopelman were able to formally sum this series by making the approximation that $P_n(c) = c$ for all values of n. This approximation, however, is only valid for very dilute concentrations. Substituting $P_n(c) = c$ into Eq. (5), they obtained

$$\sum_{\text{monomer}} = \frac{c\Delta}{1 - \Delta G_0(E)} . \quad (6)$$

It can be easily shown that the singularities of the imaginary part of the Green's function (or propagator) for the mixed crystal lying outside the exciton band of the pure molecular crystal coincide with the singularities of the imaginary part of the self energy correction. Therefore, the singularities due to the monomer states are given by $G_0(E) = 1/\Delta$. The locations of the singularities as a function of the reciprocal trap depth for mixed naphthalene-d_8/naphthalene-h_8 crystal are shown in Figure 3. For a trap depth $\Delta = -115$ cm^{-1} (which is

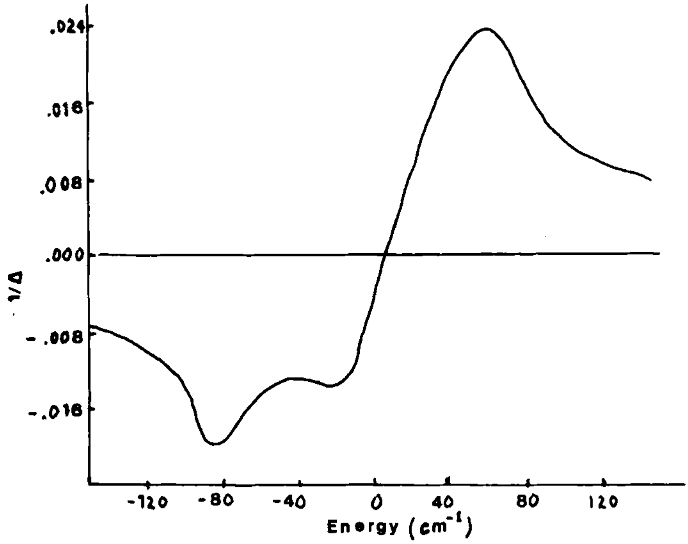

FIGURE 3 Locations of the singularities of Eq. (6) as a function of the reciprocal trap depth. The above curve was first obtained by Hong and Kopelman (ref. 5) and lead to the identification of the 31,540 cm^{-1} line as being due to the monomer states in the mixed naphthalene-h_8/naphthalene-d_8 crystals.

that for the mixed naphthalene-d_8/naphthalene-h_8 crystal), Hong and Kopelman's results predict an absorption peak at 31,541 cm^{-1} in the exciton band spectrum of this crystal. Such a peak was indeed seen by Sheka[19] and by Hanson.[20]

Since the approximation $P_n(c) = c$ is valid only for very low concentrations, Adjutamanus and Tang used a Stirling number representation of the cumulant function first proposed by Leath and Goodman,[16] to obtain a monomer self energy expression which would be valid for mixed molecular crystals of arbitrary concentrations. Using the connection between the cumulant functions and the Stirling numbers of the second kind first shown by Leath and Goodman

$$P_n(c) = \sum_{m=1}^{n} (-1)^{m-1}(m-1)!S(n,m)c^m \qquad (7)$$

where $S(n, m)$ is the Stirling number of the second kind, Adjutumanas and Tang were able to formally sum the monomer series by summing the terms which were proportional to c, than those proportional to c^2, to c^3 and so forth. Their expression for the monomer self energy is

$$\sum_{\text{monomer}}^{\text{AT}} = \sum_{n=1} (-1)^{n+1}\left\{\frac{c\Delta}{1 - n\Delta G_0(E)}\right\}\left\{\frac{(nc\Delta G_0(E))^{n-1}}{(1 - nc\Delta G_0(E))^{n}}\right\}. \quad (8)$$

As can be seen, the above expression contains two sets of singularities which are not present in the self energy expression obtained by Hong and Kopelman, Eq. (6). The above expression reduces to that of Hong and Kopelman in the limit $c \to 0$.

As was pointed out, Leath and Goodman[16] found similar sets of singularities in the phonon self energy corrections for mass disordered alloys. They argued that the additional poles were the result of overcounting errors in the determination of the cumulant functions, $P_n(c)$. Their arguments have been supported by some self consistent calculations of the self energy corrections for binary alloys by Elliott and Taylor[21] and by Aiyer, Elliott, Krumhansl and Leath.[22] To understand why there are overcounting errors, we refer to the systematic approach of Gaspard and Cryot–Lackmann[17] for calculating $P_n(c)$. Their approach involves the diagrammatic reduction of the individual graphs appearing in the monomer series. Starting with any graphs in the series, a single interaction line is cut in each level of reduction. Only the topologically distinct graphs are kept at each level. The full cumulant function is obtained by subtracting the weights of all the graphs appearing in the reduction scheme from the weight of the starting graph. The weights of the graphs in the reduction scheme are obtained in the same manner as that of the starting graph. As an example, the reduction of $P_4(c)$ leads to the set of diagrams shown in Figure 4. The evaluation of these diagrams yields

$$P_4(c) = c - 4P_1(c)P_3(c) - 3P_2^2(c) - 6P_1^2(c) - P_1^4(c). \quad (9)$$

The lower order cumulant functions, $P_1(c)$, $P_2(c)$ and $P_3(c)$, are themselves determined by a similar diagram reduction scheme. The result obtained by substituting the expressions for the other cumulant functions into Eq. (9) is

$$P_4(c) = c - 7c^2 + 12c^3 - 6c^4 \quad (10)$$

which is the same as that obtained by the use of Eq. (7). The overcounting error occurs when for instance $P_3(c) = c - 3c^2 + 2c^3$ is substituted into Eq. (9) since the reduction of $P_3(c)$ in terms of

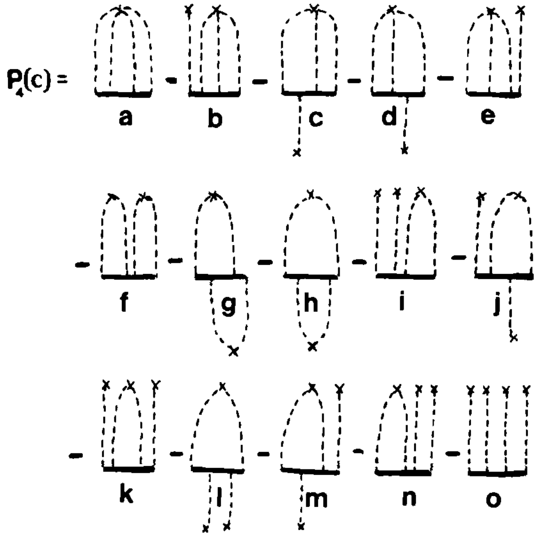

FIGURE 4 Diagrammatic reduction scheme for obtaining $P_4(c)$. In the reduction scheme, the contributions of the graphs resulting from the successive cutting of an interaction line are subtracted from the contribution due to the starting graph.

diagrams shows that diagrams like Figures 4i–4o are being recounted.

III. SELF CONSISTENT APPROACH

In addition to the appearance of the additional singularities, it has been pointed out[16,17,21,22] that inconsistency occurs when the full cumulant functions are used in the summation of the monomer self energy series given by Figure 2. Many diagrams in the expansion of the self energy correction are left out when the diagrams are collected into sets which are labelled as the monomer series, the dimer series, etc. since graphs such as the ones shown in Figure 5 are neglected. However, the reduction scheme of Gaspard and Cryot–Lackmann used to calculate the full cumulant functions clearly shows that the graphs which were neglected in the partial summations of the various series are kept in the determination of the cumulant function.

To overcome the inconsistency and prevent some of the overcounting from occurring, Gaspard and Cryot–Lackmann proposed that the cumulant functions to be used in the summation of the monomer series should be the functions which are obtained when only one-complex graphs (n-complex graphs are the irreducible graphs which contain n vertices) are considered in the reduction scheme. This leads to

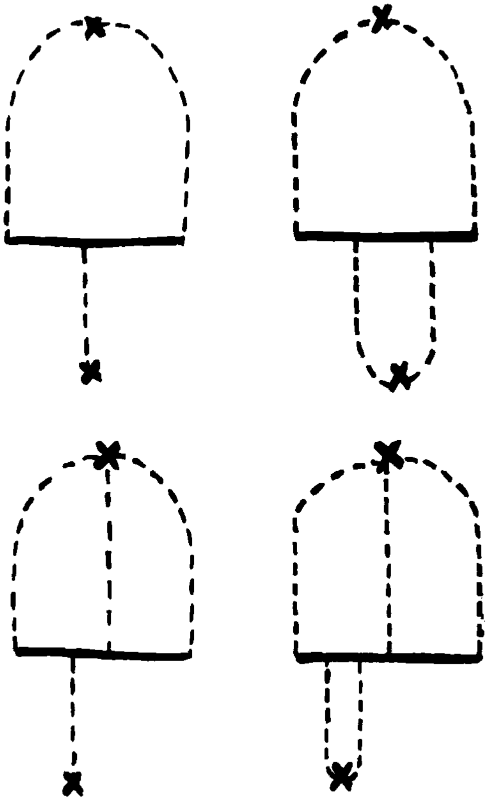

FIGURE 5 Some of the graphs which are left out in the partial summations of graphs leading to the self energy corrections due to the monomer states, dimer states, etc. but which are kept in the evaluation of the full cumulant functions.

the formation of new cumulant functions, $1 - P_n(c)$. Referring to the diagrams which yield $P_4(c)$, (See Figure 4) $1 - P_4(c)$ would be obtained if the 2-complex graphs (Figures 4c, 4d, 4g, 4h, 4l and 4m) are left out in the reductive scheme. A systematic derivation of the first few $1 - P_n(c)$ indicated that in general

$$1 - P_n(c) = c(1 - c)^{n-1}. \tag{11}$$

When the $1 - P_n(c)$ are used in the partial summation of the monomer series, we obtain

$$\sum_{\text{monomer}} = \frac{\Delta c}{1 - (1 - c)\Delta G_0(E)}. \tag{12}$$

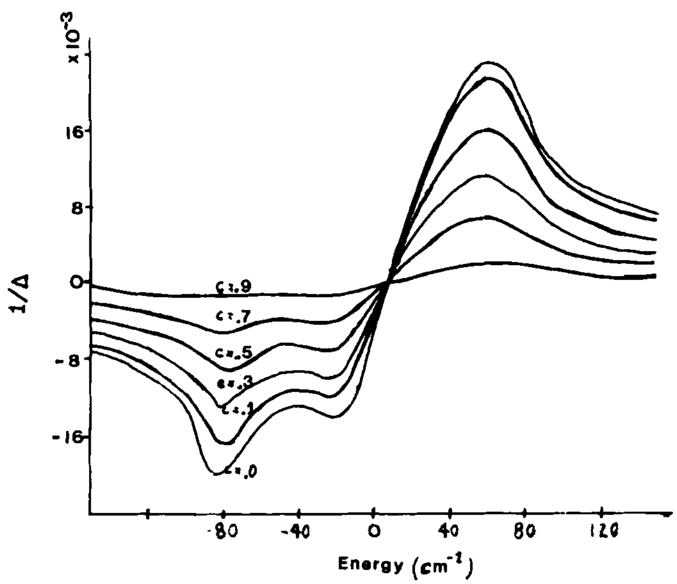

FIGURE 6 Locations of the singularities of Eq. (12) as a function of the reciprocal trap depth for different concentrations of naphthalene-h_8 in the host naphthalene-d_8 crystal. The fact that $1/\Delta$ line intercepts the different curves at different E values indicate that the maximum in the impurity band shifts as the concentration of the guest is increased.

The denominator of this expression indicated that the positions of the singularities are functions of the concentration of the guest molecules in the host crystal. This is clearly seen in Figure 6, where we have plotted the positions of the singularities as a function of the reciprocal trap depth for various concentrations of naphthalene-h_8 in the host naphthalene-d_8 crystal.

Since the excitation energies (taken to be the centers of the pure exciton bands) of the pure naphthalene-h_8 and -d_8 crystals are[19] 31556 cm^{-1} and 31671 cm^{-1}, respectively, the trap depth for these crystals would be -115 cm^{-1}. This would cause an isolated guest (monomer) level to appear at 31,541 cm^{-1}. Such a peak has been seen by Sheka,[19] by Hanson,[20] and by Hong and Robinson[23] in the spectra of various mixed naphthalene-h_8/naphthalene-d_8 crystals. Hanson finds that this line is present in the spectra of all the lightly doped crystals ($c \leq 0.05$) studied and that the intensity of this line increases linearly with c. In their studies of the heavily doped crystals, Sheka and Hong and Robinson found that the location of the maximum of the impurity band shifts from 31,541 cm^{-1} to 31,470 cm^{-1} as c increases from Q to 1. A similar shift of the maximum in the absorption spectra of isotropically mixed crystals of anthracene as the concentration of the guest molecules increased was recently reported by Tokura, Koda and Nakada.[12] An examination of the computer print outs of the zeros of the denominator of Eq. (12) for values of c less than 0.10 and of Figure 6 shows that the intersections of the zero curves with the $1/\Delta = -0.00869$ ($\Delta = -115$ cm^{-1}) line occur within a range of ± 1 cm^{-1} of the 31,541 cm^{-1} line for the lightly doped crystals and that they begin to shift towards more negative E values (corresponding to a shift towards the 31,470 cm^{-1} position) as the value of c increases. A similar discussion was used by Leath and Goodman[24] to account for the shift in the impurity peak in the frequency spectrum of mass disordered binary crystals.

The shift of the intersections (or positions of the impurity levels) predicted by the present study does not follow the strict linear dependence predicted by the virtual crystal model. The behavior is more like the predictions of the coherent potential approximation approach.[8,9] This is not surprising since the derivation of the modified cumulant functions $1 - P_n(c)$ is closely connected to the single site CPA.[17] In a later paper, we will give the results of a study in which another type of modified cumulant function, $2 - P_n(c)$, is used in the partial summation. Gaspard and Cryot-Lackmann[17] point out that the use of the $2 - P_n(c)$ cumulant functions, which are obtained if 2-complex graphs are also retained during the diagram reduction determination of the cumulant functions, would be equivalent to the two-site coherent potential approximation.[12,25]

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