

Cluster Expansion Method for the Density of Excited Electronic States of Substitutionally Disordered Crystals

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In this paper we introduce a cluster expansion method which is suitable for numerical calculations of the density of electronically excited states of substitutionally disordered molecular crystals. This method is based on an expansion of the density of states of the guest subband in terms of the localized densities corresponding to various clusters and is valid for a large scattering potential and for concentrations of guest molecules below the percolation concentration. The general features of the cluster expansion method are illustrated by calculations for a simple one-dimensional molecular crystal. These numerical calculations for the one-dimensional model are compared with the results obtained by the coherent potential approximation. The role of the localized states, which are not accounted for by the coherent potential method can be elucidated.

I. INTRODUCTION

The coherent potential approximation (CPA) has been recently utilized for the calculation of the densities of electron, phonon and exciton states in substitutionally disordered mixed crystals.¹⁻⁵ The CPA was introduced by Soven⁶ for the study of electronic states in substitutional alloys and by Taylor⁷ for the study of phonon states. An alternative systematic approach was developed by Yonezawa.⁸ The first order self-energy is identical to the one derived by the CPA.^{7,5} The same result was obtained by Onodera and Toyazawa⁹ for Frenkel exciton states and was utilized for the calculation of the density of excited electronic states and for the optical properties of isotopically substituted naphthalene crystals.^{4,5}

The attractive feature of the CPA is that only directly measurable physical quantities are required as input data for the calculations of the excited electronic states of isotopically mixed crystals. The pertinent parameters are the experimental density of states¹⁰ of the pure crystal and the difference of the single molecule excitation energies. The major shortcoming of the CPA involves an inadequate description of localized states. This theoretical scheme does not account for the fine structure of the density of states introduced by the clustering of the guest molecules. It has been shown by Taylor⁷ that the first order self-energy fails to explain the fine structure of the density of states in the "forbidden gap" below the percolation concentration of the mixed crystal.

The existence of the fine structure was demonstrated by machine calculations performed by Dean¹¹ and by Dean and Bacon¹² for one and for two dimensions, and by Payton and Visscher¹³ for one-, two-, and three-dimensional systems. Recently Bierman has presented a statistical theory of localized states for a one-dimensional crystal.¹⁴ The localized modes beyond the band edges which are not accounted for by the CPA are important for the understanding of the optical absorption spectra^{4,5,15} of mixed crystals. These optical prop-

erties are sensitive to the behavior of the band edges. Recent activity aimed towards the elucidation of the electronic and optical properties of amorphous semiconductors emphasized the crucial role of the density of states near the band edges.¹⁶⁻¹⁸

In this paper an attempt is made to estimate the effect of the localized modes on the densities of electronic excited states of a substitutionally disordered crystal. In Sec. II, we briefly survey the CPA¹⁻³ and its application^{4,5,9} to Frenkel exciton states. In Sec. III we introduce a new cluster expansion scheme for calculating the densities of the localized states. The method which is applicable for the strong scattering case below the percolation concentration. In Sec. IV the cluster expansion method is applied to a one-dimensional crystal. Numerical data obtained by the cluster expansion method and by the CPA are compared in Sec. V. The numerical data presented in this paper focus attention on a simple one-dimensional model. These results do not pertain only to model systems, but may be of considerable interest for the elucidation of the electronic states of polymers¹⁹ where a one-dimensional model is strictly applicable. It should be noticed also that in certain three-dimensional crystals the exciton band structure is determined by (short range) intermolecular interactions in one dimension. A good example was provided recently by Hochstrasser and Whiteman²⁰ who have demonstrated that triplet exciton states in 1,4-dibromonaphthalene correspond to a one-dimensional chain.

II. THE COHERENT POTENTIAL APPROXIMATION FOR EXCITED STATES OF MIXED MOLECULAR CRYSTALS

In this section we present some of the general results which were obtained by Soven⁶ and Velicky *et al.*,⁷ and which were applied later by us⁵ for the study of exciton states in isotopically mixed molecular crystals. We shall limit the discussion for a crystal containing one molecule per unit cell, although the method can be

readily generalized.⁵ In the CPA we are searching for an unknown effective Hamiltonian determined in a self-consistent manner. The procedure is based upon the restriction that a single molecule which scatters the electronic excitation should not produce on the average further scattering.⁵⁻⁷ The crystal Hamiltonian for a particular configuration is given in the form

$$H = H_0 + \Delta \sum_n \hat{\xi}_n, \quad (\text{II.1})$$

while the effective Hamiltonian for a configurationally averaged mixed crystal is

$$H_{\text{eff}}(z) = H_0 + \sum_n \hat{\Sigma}_n(z). \quad (\text{II.2})$$

$\hat{\Sigma}_n(z)$ represents the self-energy operator in the localized representation. The virtual crystal Hamiltonian H_0 is given by

$$H_0 = \sum_n |n\rangle \bar{\epsilon} \langle n| + J. \quad (\text{II.3})$$

$\bar{\epsilon}$ is the mean excitation energy

$$\bar{\epsilon} = C_A(\Delta\epsilon_A' + d') + C_B(\Delta\epsilon_B' + d'), \quad (\text{II.4})$$

where $\Delta\epsilon_A'$ and $\Delta\epsilon_B'$ correspond to the excitation energies of the isolated molecules A and B while C_A and C_B denote the concentrations of the two components. d' is the environmental shift (which is assumed to be independent of the nature of the particular component). J represents the excitation transfer operator while Δ is the difference in the excitation energies between the two components

$$\Delta = \Delta\epsilon_A' - \Delta\epsilon_B'. \quad (\text{II.5})$$

$\hat{\xi}_n$ is a random operator given by

$$\hat{\xi}_n = \xi_n |n\rangle \langle n|, \quad (\text{II.6})$$

where $\xi_n = -C_A$ when site n is occupied by a molecule of type B, and $\xi_n = C_B$ when the site is occupied by a molecule of type A.

We shall now define a general perturbation W representing the deviation of the crystal Hamiltonian from its configurationally averaged behavior

$$W = H - H_{\text{eff}} = \sum_n (\hat{\xi}_n \Delta - \hat{\Sigma}_n) \equiv \sum_n \omega_n. \quad (\text{II.7})$$

The excitation scattering can be described by total T matrix

$$T = W + W \langle G \rangle T, \quad (\text{II.8})$$

where $\langle G \rangle$ is the configurationally averaged Green's function defined by

$$\langle G(z) \rangle = \langle 1/(z-H) \rangle = 1/[z - H_{\text{eff}}(z)] \quad (\text{II.9})$$

$G(z)$ and its configurational average $\langle G(z) \rangle$ are related by

$$G(z) = \langle G(z) \rangle + \langle G(z) \rangle T \langle G(z) \rangle. \quad (\text{II.10})$$

When the configurationally averaged system is considered, the self-consistency condition⁵⁻⁷ implies that

the spatial average of the T matrix vanishes,⁵⁻⁶

$$\langle T(z) \rangle = 0. \quad (\text{II.11})$$

T can be expanded in the local scattering matrices, t_n , associated with each site,⁵⁻⁷

$$t_n = \omega_n + \omega_n \langle G \rangle t_n, \quad (\text{II.12})$$

so that T is given by the expansion

$$T = \sum_n t_n + \sum_n \sum_{m \neq n} t_n \langle G \rangle t_m + \dots \quad (\text{II.13})$$

Now it is assumed that higher order terms in Eq. (II.13), arising from multiple scattering effects are neglected, whereupon the exact equation (II.11) is replaced by the approximate relation

$$\langle t_n(z) \rangle = 0. \quad (\text{II.14})$$

The diagonal matrix elements of the configurationally averaged Green's function in the local misrepresentation are given in the form

$$\begin{aligned} \langle n | \langle G \rangle | n \rangle &= \int \{ \rho^0(E') / [z - \hat{\Sigma}(z) - \bar{\epsilon} - E'] \} dE' \\ &\equiv f^0 [z - \bar{\epsilon} - \hat{\Sigma}(z)], \end{aligned} \quad (\text{II.15})$$

where ρ^0 is the density of states of the pure crystal. Utilizing Eqs. (II.12) and (II.14) one obtains the final equation for the self energy^{5-7,15}

$$\begin{aligned} f^0 [z - \bar{\epsilon} - \hat{\Sigma}(z)] \\ = \Sigma(z) / \{ C_A C_B \Delta^2 - \hat{\Sigma}(z) \Delta (C_A - C_B) - [\hat{\Sigma}(z)]^2 \}. \end{aligned} \quad (\text{II.16})$$

The density of states ρ of the configurationally averaged crystal is

$$\rho(E) = (1/\pi N) \text{Im Tr} \langle G(E) \rangle, \quad (\text{II.17})$$

where N denotes the number of unit cells in the crystal. In the CPA one gets

$$\rho(E) = (1/\pi N) \text{Im} \langle 0 | 1/[z - H_0 - \hat{\Sigma}(z)] | 0 \rangle, \quad (\text{II.18})$$

where $\hat{\Sigma}(z)$ is obtained from Eq. (II.16).

III. A CLUSTER EXPANSION METHOD FOR THE DENSITY OF STATES

Consider an isotopically mixed crystal where the concentration of one of its components is below the percolation concentration. The two component molecules which differ just in their (free molecule) excitation energies will be referred to as the guest (minority component) and as the host (majority component). An expression for $\text{Tr} G(E)$, which determines the exciton density of states can be derived by the application of the identity²¹

$$G(E) = G^0(E) + G^0(E) V [1 - G^0(E) V]^{-1} G^0(E), \quad (\text{III.1})$$

where V is the perturbation matrix, which for an isotopically mixed crystal is given by

$$\langle n | V | n \rangle = \Delta \eta \delta_{nm}, \quad (\text{III.2})$$

where $\eta=1$ when the site n is occupied by a guest molecule, while $\eta=0$ when the site n is occupied by a host molecule. Δ [see Eq. (II.5)] is the difference between the excitation energy of a single guest molecule and a single host molecule. This definition implies that in the present case V is a diagonal matrix in the localized representation. The diagonal elements Δ and 0 are randomly distributed with probabilities C_A and $1-C_A$, respectively. The trace of $G(E)$ can now be represented in the form²¹

$$\text{Tr}G(E) = NG_0^0(E) + d \ln D(E) / dE, \quad (\text{III.3})$$

where $D(E)$ is the determinant

$$D(E) = |1 - \mathbf{G}^0(E)\mathbf{V}| \quad (\text{III.4})$$

and

$$G_0^0(E) = \langle n | G^0(E) | n \rangle \quad (\text{III.5})$$

is the diagonal matrix element of the unperturbed (pure crystal) Green's function $G^0(E)$. The density of states of the mixed crystal is given by²²

$$\begin{aligned} \rho(E) &= (1/\pi N) \text{Im Tr}G(E) \\ &= \rho^0(E) + (1/\pi N) \text{Im}[d \ln D(E) / dE]. \end{aligned} \quad (\text{III.6})$$

Provided that the matrices $G^0(E)$ and V are properly constructed, the factorization of $D(E)$ can be easily accomplished. The pure crystal Green's function in the localized representation can be partitioned into four submatrices

$$\mathbf{G}^0(E) = \begin{pmatrix} \mathbf{G}_{gg}^0(E) & \mathbf{G}_{gh}^0(E) \\ \mathbf{G}_{hg}^0(E) & \mathbf{G}_{hh}^0(E) \end{pmatrix}. \quad (\text{III.7})$$

The matrix $\mathbf{G}_{gg}^0(E)$ corresponds to sites occupied by guest molecules only, so that

$$[\mathbf{G}_{gg}^0(E)]_{nm} = \langle n | G^0(E) | m \rangle \quad (\text{III.8})$$

where sites n and m are occupied by guest molecules. In a similar manner the matrix $\mathbf{G}_{hh}^0(E)$ corresponds to sites occupied by host molecules, while \mathbf{G}_{hg}^0 and \mathbf{G}_{gh}^0 represent the guest-host matrix elements.

The matrix \mathbf{V} has the following form

$$\mathbf{V} = \begin{pmatrix} \mathbf{V}_g & \mathbf{O} \\ \mathbf{O} & \mathbf{O}_h \end{pmatrix}, \quad (\text{III.9})$$

where \mathbf{V}_g is a diagonal matrix of the same order of $\mathbf{G}_{gg}^0(E)$.

$$\mathbf{V}_g = \Delta \mathbf{1}_g, \quad (\text{III.10})$$

\mathbf{O}_h is a null matrix of the order of $\mathbf{G}_{hh}^0(E)$.

The matrix $[1 - \mathbf{G}^0(E)\mathbf{V}]$ can now be recast in the

form

$$1 - \mathbf{G}^0\mathbf{V} = \begin{pmatrix} \mathbf{1}_g - \Delta \mathbf{G}_{gg}^0(E) & \mathbf{O} \\ -\Delta \mathbf{G}_{hg}^0(E) & \mathbf{1}_h \end{pmatrix}. \quad (\text{III.11})$$

Employing Eq. (III.11), the determinant $D(E)$ is

$$D(E) = \det |\mathbf{1}_g - \Delta \mathbf{G}_{gg}^0(E)|. \quad (\text{III.12})$$

Equation (III.12) represents the Koster-Slater²³ result which implies that for a local perturbation the order of $D(E)$ is given by the number of guest molecules.

In order to facilitate a further reduction of $D(E)$, specific approximations have to be invoked. These approximations are closely related to the distribution of guest clusters in the crystal. It will be useful at this stage to survey briefly the notion of clusters.^{24,25} We shall examine an "island" of the guest molecules embedded in the crystal. Following the notations introduced by Rushbrook and Morgan²⁴ and by Elliot and Hemp,²⁵ a molecule A is considered to belong to a particular cluster if it is not separated from any other member of the cluster by more than a preassigned distance. In the present work, only the nearest neighbor clusters are considered. Let $N_{n\alpha}$ denote the number of clusters of size n and of shape α , and let $P_{n\alpha}$ be the probability of finding a cluster $n\alpha$. It was previously demonstrated that^{24,25}

$$P_{n\alpha} \equiv N_{n\alpha} / N = K C_A^n (1 - C_A)^m, \quad (\text{III.13})$$

where m is the number of peripheral host molecules isolating the cluster from the rest of the crystal. K is the number of geometrically equivalent clusters. For example, the probability of finding an isolated impurity is given by $P_1 = C_A(1 - C_A)^z$, where z is the coordination number of the lattice. Behringer²⁶ gives the probability for doublet and triplet clusters for a simple cubic face centered and for a body centered cubic lattice.

Expression (III.12) for the determinant $D(E)$ is not manageable for a finite impurity concentration. The determinant $D(E)$ is still of an infinite order and cannot be simplified without invoking some approximations concerning off-diagonal matrix elements of the Green's function. Our aim is to factorize $D(E)$ into partial determinants $D_{n\alpha}(E)$ of finite order, each corresponding to the appropriate cluster $n\alpha$. To achieve this goal we assume that:

(a) The perturbation strength Δ is large relative to the pure crystal exciton bandwidth, $2a$. We thus neglect the off-diagonal matrix elements of the Green's function linking sites which correspond to different clusters. Since we consider clusters consisting only of nearest neighbor guest molecules, the off-diagonal matrix elements of Green's function are taken to be zero except for the matrix element connecting nearest neighbors.

(b) The concentration of the guest molecules is assumed not to exceed the percolation concentration.

of $D_{na}(E)$ in the form

$$\mu_i^{(g)} = (1/C_A) \sum_{na} P_{na} \sum_m [E_m(n\alpha)]^i \quad (\text{III.25})$$

The major limitations of the cluster expansion method are:

(1) When the ratio $\Delta/2a$ is not sufficiently large some of the roots $D(E)$ are located near the edge of the host band. Under these circumstances one cannot neglect the off diagonal elements of the Green's function linking different sites which are separated by more than one lattice distance. For the same reason the method collapses for the energy region within the host band.

(2) In order to separate the contributions of different clusters, off diagonal matrix elements of the Green's function connecting different clusters were neglected invoking assumption (a). For the sake of self consistency one has also to neglect the off diagonal contributions within a single cluster (of order higher than two) connecting cluster members separated by more than nearest neighbor distance. As a consequence, the determinants $D_{na}(E)$ for large clusters may yield some unphysical roots outside the allowed energy region for the mixed crystal.

These two limitations of the method can be checked in the light of a theorem originally introduced by Lifshitz,²⁷ which postulates that the mixed crystal cannot have states in the energy region which is forbidden for the pure crystals of components A and B. In the present context the components A and B correspond to the guest and to the host molecules, respectively. This theorem was proved for the special case of one dimensional alloy by Luttinger.²⁸ Kirkpatrick *et al.*² have recently proved this theorem for a substitutionally disordered crystal without referring to any specific dimensionality of the crystal. Taking advantage of these general arguments we may assert that the roots of $D(E)$ outside the pure host band are confined to an energy region spanned by the pure guest band.

IV. A ONE-DIMENSIONAL MODEL

Two- and three-dimensional clusters are rather complex, as a cluster of size n can appear in several different geometrical configurations. In a one-dimensional crystal any cluster of order n is characterized by a single geometrical shape. The probability of finding such a cluster [Eq. (III.13)] is just

$$P_n = C_A^n (1 - C_A)^2 \quad (\text{IV.1})$$

The probability of finding a guest molecule belonging to a cluster of order n is $nP_n = nC_A^n (1 - C_A)^2$, while the total probability, P , of finding a guest molecule in any cluster is

$$P = \sum_n nP_n = C_A (1 - C_A)^2 (1 + 2C_A^2 + \dots + nC_A^{n-1}) = C_A \quad (\text{IV.2})$$

P represents the probability of the occupation of any crystal site by the guest molecules [see Eq. (III.24)].

The determinant $D_n(E)$ [see Eq. (III.16)] is now characterized by the two matrix elements

$$g_0 = \langle 0 | G^0(E) | 0 \rangle \quad \text{and} \quad g_1 = \langle 0 | G^0(E) | 1 \rangle,$$

being characterized by the simple form

$$D_n(E) = \begin{vmatrix} 1 - g_0\Delta & -g_1\Delta & 0 & \dots & 0 \\ -g_1\Delta & 1 - g_0\Delta & 0 & \dots & 0 \\ 0 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & & & & 1 - g_0\Delta \end{vmatrix} \quad (\text{IV.3})$$

This determinant can now be transformed into

$$D_n(E) = (-g_1\Delta)^n \begin{vmatrix} X & 1 & 0 & & \\ & 1 & X & 1 & 0 \\ 0 & 1 & X & & \\ & & 0 & \cdot & 1 \\ & & & \cdot & \\ & & & 1 & X \end{vmatrix}, \quad (\text{IV.4})$$

where X is given by

$$X = (1 - g_0\Delta) / (-g_1\Delta) \quad (\text{IV.5})$$

The zeros of the n th order determinant are simply

$$X_m^{(n)} = 2 \cos[n\pi / (n+1)], \quad (\text{IV.6})$$

where $m = 1, 2, \dots, n$. The energy dispersion relation for the pure one dimensional crystal is taken in the form

$$E(k) = a \cos k, \quad -\pi \leq k \leq \pi \quad (\text{IV.7})$$

so that the matrix elements of the Green's function in the localized representation are

$$g_0(E) = \pm 1 / (E^2 - a^2)^{1/2} \quad (\text{IV.8})$$

and

$$g_1(E) = \pm u^{(\mp)} / (E^2 - a^2)^{1/2}, \quad (\text{IV.9})$$

where

$$u^{(\mp)} = [-E \mp (E^2 - a^2)^{1/2}] / a. \quad (\text{IV.10})$$

Here $u^{(-)}$ corresponds to the energy range $E > a$ while $u^{(+)}$ is taken for the energy range for $E < a$.

The combination of Eqs. (IV.5), (IV.6), (IV.8), and (IV.9) yields a quadratic equation for the zeros of the determinant $D_n(E)$

$$E^2 [(\alpha + X_m^{(n)})^2 - (X_m^{(n)})^2] - 2\alpha X_m^{(n)} E - a^2 [(\alpha + X_m^{(n)})^2 + 1] = 0, \quad (\text{IV.11})$$

where $\alpha = a/\Delta$. Finally we should note that the physi-

cally significant roots of Eq. (IV.11) satisfy the inequality

$$a - \Delta < E < a + \Delta. \quad (\text{IV.12})$$

A comment should be made concerning the results previously reported by Bierman¹⁴ for a one dimensional model. In this work,¹⁴ two guest subbands appear below and above the subband. This result is incompatible with the general theorem introduced by Lifshitz,²⁷ as these two subbands cannot be simultaneously located within the energy region defined by Eq. (IV.12). Bierman has neglected off-diagonal matrix elements of the Green's function except for nearest neighbors, in a similar way as done by us. Unfortunately, the physical implications of these approximations were not realized in the previous work.

Focusing attention on the CPA, it is possible to derive analytical expression for the density of states of a one-dimensional lattice.⁷ Setting $\Delta\epsilon_B^f = 0$, $\Delta = \Delta\epsilon_A^f$ and utilizing Eq. (II.15) the following expression is obtained for the matrix element (II.15):

$$f^0[E - C_A\Delta - \Sigma(E)] = i / \{a^2 - [E - C_A\Delta - \Sigma(E)]^2\}^{1/2}. \quad (\text{IV.13})$$

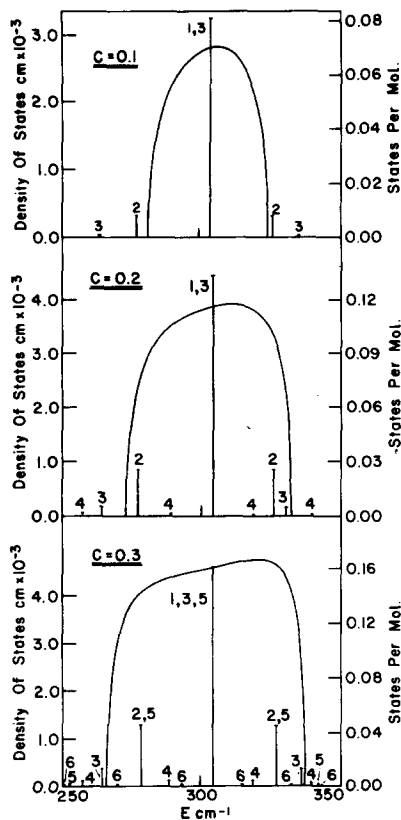


FIG. 1. Model calculations for the density of excited states in the guest band of a one dimensional isotopically substituted crystal. $a = 50 \text{ cm}^{-1}$ and $\Delta = 300 \text{ cm}^{-1}$. The solid curve is calculated by the CPA. The vertical segments represent the energy distribution of states per molecule calculated by the cluster expansion method, the numbers signifying the cluster size which contributes to the particular segment.

TABLE I. The zeroes of $D_n(E)$ for a one-dimensional crystal by the cluster expansion method.

Cluster size	Zeroes of $D_n(E)$ (cm^{-1})
A. $a = 50 \text{ cm}^{-1}$; $\Delta = 150 \text{ cm}^{-1}$	
1	158.11
2	178.57; 130.00
3	185.91; 150.11; 111.68
4	189.35; 171.29; 142.25; 95.57 ^a
B. $a = 50 \text{ cm}^{-1}$; $\Delta = 200 \text{ cm}^{-1}$	
1	206.15
2	227.77; 178.57
3	235.7; 206.15; 163.53
4	239.44; 219.99; 190.14; 154.50
5	241.48; 227.77; 206.15; 148.6 ^a
6	242.72; 232.56; 216.28; 194.91; 170.01; 144.6 ^a
7	243.53; 235.70; 223.05; 206.15; 185.87; 163.53; 141.78 ^a
C. $a = 50 \text{ cm}^{-1}$; $\Delta = 300 \text{ cm}^{-1}$	
1	304.13
2	326.9; 277.27
3	335.53; 304.13; 264.28
4	339.62; 318.58; 288.16; 257.28
5	341.87; 326.92; 304.13; 277.27; 253.10
6	343.24; 332.1; 314.67; 292.81; 269.69; 250.55
7	344.13; 335.53; 321.85; 304.13; 248.06; 269.27; 248.80 ^a

^a These roots represent nonphysical energy values whose appearance is due to neglecting high order off diagonal matrix elements of the Green's function.

Inserting the expression for f^0 in Eq. (II.16) results in a cubic equation for the self-energy⁷:

$$\Sigma^3(C_B\Delta - E) + \Sigma^2(E^2 - 2EC_A\Delta - C_B^2\Delta^2 + 4C_AC_B\Delta^2 - a^2) + 2\Sigma C_AC_B(C_A - C_B)\Delta^3 - C_A^2C_B^2\Delta^4 = 0. \quad (\text{IV.14})$$

Within the energy band of the mixed crystal the self energy has an imaginary component of finite magnitude. We therefore search for a solution of the cubic equation (IV.14) corresponding to E values for which two roots are complex conjugate. The density of states can be then easily obtained by substituting the value of Σ thus obtained in Eq. (II.16) and by making use of Eq. (II.18).

V. NUMERICAL CALCULATIONS

In this section we present some numerical results based on the cluster expansion method and on the CPA for a one-dimensional isotopically mixed crystal. Utilizing Eq. (IV.10) we have calculated the zeroes of the determinants $D_n(E)$ for various values of Δ (for $\Delta > 2a$). These results obtained by the cluster expansion method are presented in Table I. It is apparent that as the ratio

TABLE II. Moments of the density of states for a one-dimensional crystal [units (cm⁻¹)ⁱ]. $a = 50$ cm⁻¹; $\Delta = 300$ cm⁻¹.

Moments	Cluster method	CPA	Cluster method	CPA
	$C_A = 0.05$		$C_A = 0.1$	
1	303.9	303.9	303.7	303.7
2	62.23	60.56	124.8	121.5
3	-383.2	-16.66	-776.8	-65.73
4	4.402×10^4	7.253×10^3	9.971×10^4	2.886×10^4
5	-4.883×10^5	-4.945×10^3	-1.167×10^6	-3.878×10^4
6	3.542×10^7	1.081×10^6	9.111×10^7	8.505×10^6
7	-6.067×10^8	-1.23×10^6	-1.765×10^9	-1.912×10^7
	$C_A = 0.2$		$C_A = 0.3$	
1	303.3	303.3	302.9	302.9
2	251.2	244.6	378.3	368.6
3	-159.3	-235.9	-2436.4	-471.5
4	2.308×10^5	1.141×10^5	4.060×10^5	2.525×10^5
5	-3.084×10^6	-2.704×10^5	-5.685×10^6	-7.862×10^5
6	2.691×10^8	6.546×10^7	5.420×10^8	2.105×10^8
7	-5.892×10^9	-2.577×10^8	-1.253×10^{10}	-1.083×10^9

Δ/a increases, the number of "unphysical" energy levels (marked in Table I by crosses), which violate relation (IV.12), diminishes. The number of localized states per molecule derived by the cluster expansion method and which correspond to the guest subband are displayed in Fig. 1. These results are compared with the CPA density of states. The averaged CPA density of states cannot reflect the fine structure pattern exhibited by the results of the cluster expansion method, which may be revealed in the optical spectrum at relatively low ($C_A = 0.1-0.3$) concentration region of the isotopic impurity. In particular it should be noted that the CPA does not account for the "tails" of the density of states due to the contribution of large clusters which appear outside the energy region spanned by the averaged CPA density of states.

The moments of the density of states up to the seventh order computed by the cluster expansion method [employing Eq. (III.25)] and by the CPA [employing Eqs. (III.23) and (II.18)] are presented in Table II for $\Delta = 300$ cm⁻¹ and $a = 50$ cm⁻¹. Moments of higher order than one are given about the mean. The marked feature of the odd moments calculated by the CPA is that they are significantly smaller than those calculated by the cluster expansion method, indicating that the CPA density of states is more symmetrical. The negative values of the odd moments calculated by the cluster expansion method suggest that the number of "tail" states is greater in the gap between the host and the guest band than on the other side of the guest band.

The first moment of the density of states $\mu_1^0 \equiv E$ and the width of the guest band $\sigma = [\mu_2^0 - (\mu_1^0)^2]^{1/2} / \mu_0^0$ (the standard derivation of the distribution) are displayed in Fig. 2 for several values of Δ . The moments calculated

by the cluster expansion method and by the CPA, are compared with the results obtained by moment expansion^{1,5} method. The moment expansion method introduced by Velicky *et al.*¹ does not refer to any specific approximation and is valid for the separated band situation.^{1,5} These moments provide a good test for any approximate theory of substantial disorder. The first moment and the width of the distribution up to second order in $2a/\Delta$ are given by^{1,5}

$$\mu_0 = C_A,$$

$$\mu_1 = \Delta + (\mu_2^{(0)}/\Delta)(1 - C_A), \quad (\text{V.1})$$

$$\sigma = (C_A^2 \mu_2^{(0)})^{1/2}, \quad (\text{V.2})$$

where $\mu_2^{(0)} = a^2/2$ is the second moment of the pure crystal density of states.

There seems to be good agreement between the results for the first and for the second moment obtained by the three different methods. The slight deviations are easily understood on the basis of the approximations involved. The moment expansion method does not yield the exact zero concentration value because Eq. (V.1) depends on an expansion in Δ^{-1} up to second order. The smaller width of the guest band computed by the CPA is due to the "tail" states which are not properly accounted for by this method.

VI. DISCUSSION

It is useful to summarize the general features of the CPA and to compare them with the cluster expansion method. The inherent assumption involved in both schemes is that all statistical correlation between different crystal sites are neglected. In the CPA the physical characteristics of the mixed crystal are deter-

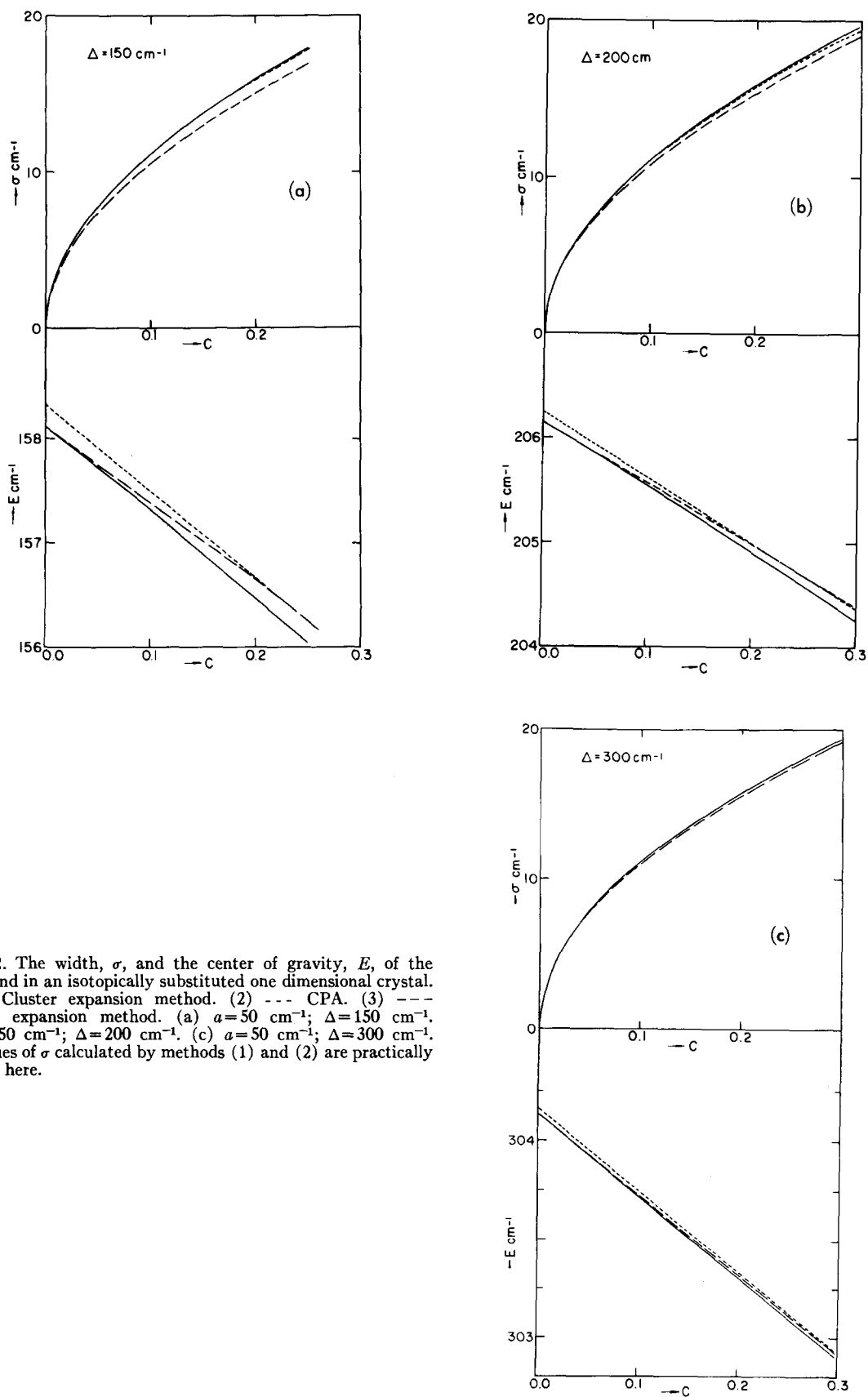


FIG. 2. The width, σ , and the center of gravity, E , of the guest band in an isotopically substituted one dimensional crystal. (1) — Cluster expansion method. (2) --- CPA. (3) --- Moment expansion method. (a) $a=50\text{ cm}^{-1}$; $\Delta=150\text{ cm}^{-1}$. (b) $a=50\text{ cm}^{-1}$; $\Delta=200\text{ cm}^{-1}$. (c) $a=50\text{ cm}^{-1}$; $\Delta=300\text{ cm}^{-1}$. The values of σ calculated by methods (1) and (2) are practically identical here.

mined by averaging over all possible configurations, while the cluster method assigns statistical weighting factors to any particular configuration of the binary crystal. In the limit of an infinite crystal the two methods correspond approximately to the same physical situation.

The major advantages of the CPA can be summarized as follows: (a) The scheme is symmetrical in the concentration (C_A and C_B). (b) This scheme faithfully reproduces the virtual crystal¹ and the atomic limit.⁵ (c) Finally, only directly measurable quantities, such as the density of states of the pure crystals are required as input data. Additional information concerning the exciton transfer integrals is not required. A major disadvantage of the CPA is that the effect of multiple scattering is neglected. In principle, this scheme can be systematically extended²⁹ by taking the higher terms in Eq. (II.13). Yonezawa⁸ has speculated that higher order terms in the self-energy, which represent the effect of clusters, are responsible for the fine structure in the density of states which was not exhibited by the results of the CPA. According to Yonezawa,⁸ the contribution of these higher order terms in Σ , should play an important role below the percolation concentration.

The cluster expansion method introduced herein is just applicable and useful in the (relatively low) concentration region where the CPA is unreliable. The major advantages of this scheme are: (a) The localized modes of the guest subband are explicitly represented below the percolation concentration. (b) It is useful for the strong scattering case. It seems that the multiple scattering effects which were ignored by the CPA are implicitly introduced by the cluster expansion method. The limitations of the cluster method are: (a) This method is suitable only for the concentration range below the percolation concentration. Above the critical concentration there is a major contribution from infinite clusters. In that case the cluster expansion diverges. Thus the cluster expansion method cannot yield an extended band structure. (b) Satisfactory results are obtained only for the strong scattering case when $\Delta/a \gg 1$. (c) The method is not applicable within the energy region of the host subband. (d) A detailed knowledge of the intermolecular exciton transfer integrals is required, at least for nearest neighbors.

It is possible to extend the cluster expansion method for a weaker scattering situation provided the cluster distance (as defined in Sec. II) is increased to include next nearest neighbors. This in turn will further complicate the cluster structure, and introduce additional off-diagonal Green's function matrix elements into the calculations. This method can be also applied to two and

three dimensional crystals, however, in these systems the number of geometrically equivalent clusters increases with the order of the clusters, thus making the calculations rather cumbersome.

The cluster expansion method should be regarded as complementary to the CPA, each of these schemes being useful in a different composition range of the mixed crystal. The most interesting conclusion emerging from the present model calculations, based on the cluster expansion method, is the appearance of a "tail" in the density of states, and that this "tail" extends in the gap between the host and the guest band. Although the present treatment is restricted to the problem of substitutional disorder, we should notice that these "tails" in the density of states play a central role in the Mott-Cohen-Fritzsche-Ovshinsky model^{16,17} for the electronic states of amorphous solids.

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