THE JOURNAL OF CHEMICAL PHYSICS VOLUME 56, NUMBER 2 15 JANUARY 1972

On the Electronic States of Substitutionally Disordered Molecular Crystals

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(Received 5 August 1970)

In this paper we consider the optical properties of heavily doped molecular crystals where the constituents differ by isotopic substitution. Four different situations were considered determined by the perturbation strength relative to the second moment and to the width of the density of states in the pure crystal: (a) separated bands; (b) persistence case; (c) incipient band gap; (d) amalgamation limit. The properties of the effective Hamiltonian for a configurationally averaged mixed molecular crystal containing an arbitrary number of molecules per unit cell were explored. Information on the intensity distribution in optical absorption by a binary crystal can be obtained from the moments of the spatially averaged mixed crystal Hamiltonian. In the amalgamation limit the crystal exhibits the gross features of a virtual crystal and the number of the polarized intensity distributions is equal to that of the pure crystal, while in the separated band case and in the persistence case the number of polarized intensity distributions is double that in the pure crystal. The coherent potential approximation based on a local approximation for the self-energy and on neglecting multiple scattering effects was extended to handle the general case of a multiply branched exciton band. Concerning the general question of the persistence of the Davydov splitting in a mixed crystal, general arguments are provided that symmetry restrictions can be relaxed and that the Davydov splitting is exhibited by a substitutionally disordered system described by a Hamiltonian which is characterized by a random diagonal part and by a translationally invariant off-diagonal part. The number of these Davydov components is determined by the perturbation strength.

I. INTRODUCTION

In recent studies of Frenkel–Davydov exciton states[1–3] in pure molecular crystals it has become fashionable to search for some general unified experimental and theoretical information concerning the entire exciton band structure. A major breakthrough in this direction was provided by the theoretical work of Rashba[4] and of Colson *et al.*[5] and by the experimental work of Shpak and Sheka[6] and of Colson, Hanson, Kopelman, and Robinson[7] who have applied the technique of hot band spectroscopy to monitor the density of states of the lowest singlet exciton states of crystalline benzene and naphthalene. Complementary information on the density of states function can be obtained from the study of low-concentration isolated impurity states in molecular crystals.[8–13] Extensive use was made of the Koster–Slater Green's function method[14] with a recent emphasis on the connection between the one-particle Green's function and the density of states function for the pure crystal.[12,13]

The most challenging problem in the theoretical study of mixed molecular crystals involves the understanding of the band structure and the optical properties of heavily doped molecular crystals. This problem is of considerable general interest in relation to the vigorous current activity aimed towards the elucidation of the electronic structure of disordered systems.[15–17] Combined experimental and theoretical studies of isotopically mixed substitutionally disordered molecular crystals can be extremely useful in this context because of the following reasons:

(a) In isotopically mixed crystals of organic molecules the two components differ to a good approximation in the molecular excitation energies. Thus the theoretical model of a binary crystal, where the two components just differ in the diagonal matrix elements of the Hamiltonian while the off-diagonal matrix elements (in the localized excitation representation) are invariant,[11,12] can be applied to a real physical system.

(b) The study of the optical properties of isotopically mixed molecular crystals will provide a powerful tool to explore the "one-particle" properties of the elementary excitations. This type of a direct information cannot be easily obtained for one-particle (equilibrium) properties of other elementary excitations such as electrons or phonons in binary alloys.

The excited electronic states of a rigid, perfect, pure crystal reveal some universal features which result from perfect translational symmetry of the system:

(a) The crystal quasimomentum $\mathbf{k}$ is a good quantum number so that the crystal wavefunction possesses perfect phase coherence and all states are extended in the ideal crystal.

(b) The dispersion relation $\epsilon_j^f(\mathbf{k})$ describes the energy for the jth branch of the f exciton band, which is a continuous analytic function of $\mathbf{k}$ within each branch except at certain points.

(c) Well-defined band edges which correspond to extremum points of $\epsilon_j^f(\mathbf{k})$ occur for each exciton band.

(d) The density of state reveals Van Hove singularities at extremum and saddle points of the energy dispersion relation.

(e) The optical absorption bands correspond to delta functions located at $\mathbf{k}=0$ of each exciton branch.

Now all these features break down when a (substitutionally) disordered system is considered, and the following questions are then pertinent:

(a) *The localization problem*: The "breakdown" of **k** as a good quantum number provides just a necessary but by no means a sufficient condition for energy localization, as it is well known from the theory of isolated impurity states[11–14,17,18] that virtual scattering (delocalized) states can be induced by a moderately weak local perturbation. Current theories[16,17] of amorphous semiconductors assume the existence of regions of exclusively localized states separated by "critical energies" from regions of exclusively extended state. A similar classification of electronic excitation in a mixed crystal will be of interest.

(b) *Energy of excited states of the disordered system*: In this context it is interesting to inquire under what circumstances the pseudoparticle concept is still valid. Extended excited states in a substitutionally disordered system may be then characterized to a good approximation by a complex energy where the imaginary part describes the strength of the scattering.[19] If the impurity scattering effects are strong localization might be encountered. Such a general approach will be pertinent for the understanding of energy transfer phenomena in disordered systems.

(c) *Density of states in disordered systems*: A proper theoretical description of the density of exciton states in a substitutionally disordered crystal may lead to "forbidden zones" (density of states zero), "allowed zones" (density of states finite), and "almost forbidden" energy regions (where the density of states is nonzero but small). In this context interesting questions arise whether one can define an effective band edge (which provides a boundary between the "allowed" and the "almost forbidden" zones).[20]

(d) *Erosion of Van Hove singularities*: Obviously, topological concepts are no longer applicable and critical points do not exist in the density of states of disordered systems. However, it is interesting to inquire how fast are these singularities erased, as this problem may be pertinent for the understanding of the optical properties of some disordered systems, in particular polymers[21] where a one-dimensional model is applicable.

(e) *Optical properties*: In view of disorder scattering in a disordered system the absorption bands are expected to be broadened. (This effect is similar to the consequences of exciton–phonon coupling in a vibrating crystal.) The most interesting question arising in this context is concerned with the number of the (broadened) absorption bands in the disordered crystal, and whether the Davydov splitting of the crystal energy levels arises primarily from symmetry relations or can orginate from resonance coupling between randomly distributed molecules on the lattice sites.[3,12,22,23]

Experimental work on heavily mixed isotopically substituted benzene and naphthalene crystals was reported by Broude and Oprienko,[24] Broude and Rashba,[25] Sheka,[26,27] and recently by Hong and Robinson.[28] The major conclusions follow.

(a) *Persistence of the Davydov splitting in some binary mixed crystals*: In isotopically mixed crystals of naphthalene and deuterated naphthalene, where the difference in the electronic excitation energies exceeds the half-bandwidth of the exciton band, three polarized Davydov components were experimentally observed. The energies of these components exhibit a monotonic (roughly linear) concentration dependence.[26,27]

(b) *Line broadening*: Considerable line broadening of the Davydov components is encountered in the mixed crystal.[24–27] The experimental failure[27] to detect the second ac polarized component in naphthalene–deuteronaphthalene mixtures (which is very weak in the pure crystal) may be attributed to these line broadening effects.

Early theoretical studies[25] of the electronic states of heavily doped mixed molecular crystals were based on physical intuition. Broude and Rashba[25] have proposed a simple scheme designed to yield the center of gravity of the absorption bands in a mixed crystal invoking the hypothesis of "exciton democracy," that is, the amplitudes of the local excitations are determined only by the site occupation and by the molecular orientation in the unit cell. Phillpott and Craig[11] have bypassed the problem of the random distribution of impurities and have performed numerical calculations of the electronic states of a superlattice compatible with the guest concentration. An interesting machine calculation of the electronic states of a substitutionally disordered polymer was reported by Herzenberg and Miomides.[21] An important development in this field was provided by the exhaustive studies of Yonezawa and Matsubara who were concerned with the problem of the electronic structure of binary alloys.[29] In a series of formal papers it was demonstrated how to sum a selected class of terms in a perturbation series for a random alloy Green's function. This general scheme[29] was further extended by Onodera and Toyozawa[30] who have derived a manageable approximate interpolation formula for the self-energy of Frenkel excitons and electron states, which is valid for various limiting situations (i.e., zero bandwidth, zero concentration limit). An important application first considered by Onodera and Toyozawa involved the optical properties of mixed crystals. Recently Hong and Robinson[22] and somewhat later the present authors[23] utilized the Onodera–Toyozawa approach[30] for the study of isotopically mixed molecular crystals. On the basis of numerical calculations[22,23] several important conclusions were obtained concerning the persistence of the Davydov splitting for an isotopically mixed crystal when a band gap appears in the density of states function.

The purpose of the present paper is to discuss the electronically excited states of isotopically mixed crystals, with an emphasis on general relations and correlations rather than on numerical calculation based on approximate theoretical schemes. We shall proceed in two stages: first we shall consider the general properties of the excited electronic states of a random, isotopically substituted, heavily doped crystal without referring to any specific approximation.[31] Second, we shall adopt the coherent potential approximation (CPA) recently developed by Taylor for phonon states[32] and by Soven[33,34] Valicky, Kirkpatrick, and Ehrenreich[31] for electron states of binary alloys to the study of exciton states in isotopically mixed crystals.

The most general approach to the problem of the electronic states of an isotopically mixed crystal can be based on a single assumption invoking the hypothesis of complete random distribution of molecules on the lattice sites. An effective Hamiltonian determined only by the concentration and by the strength of the random perturbation can be defined[31] for the spatially averaged mixed crystal. The physical situation is somewhat more complex than previously considered[31] since for a crystal containing several molecules per unit cell the effective Hamiltonian is nondiagonal in the exciton representation. The moments of the density of states and of the spectral absorption bands of the mixed crystal can be expressed in terms of the density of states and the positions of the Davydov components in the pure crystal. General properties of the (complex) self-energy can be established which determine the conditions for the appearance of a band gap[31] and determine the number of the Davydov components in the mixed crystal. The general properties of the self-energy provide a basis for the introduction of the CP approximation.

The CP approximation[31–34] is extended to handle the case of multiple-branched exciton bands. This approximation, which invokes the hypothesis that multiple scattering effects are negligible, turns out[31] to be equivalent to the Onedora–Toyozawa expression.[30] The CP approximation is generalized for a crystal containing an arbitary number of molecules per unit cell and for any general form of the pure crystal exciton band. This approach will be useful to determine the range of validity of the CP approximation and to provide practical recipes for the systematic evaluation of correction terms and for extensions of this scheme. It will be shown how the optical properties derived by the CP approximation are obtained in various limiting cases such as the low concentration case, the virtual crystal, and the atomic limit. In this context the nature of the Broude–Rashba approximation[25] can be clarified.

We hope that the results of the present study will lead to a better understanding of the numerical calculations performed by Hong and Robinson[22] and by us,[23] and will provide impetus for further experimental work on the optical properties of heavily doped crystals which will contribute to a better understanding of the general phenomena arising from substitutional disorder.

II. THE EFFECTIVE HAMILTONIAN

Consider an isotopically mixed molecular crystal consisting of two types of molecules characterized by the concentrations (i.e., molar factions) C_A of component A and $C_B = 1 - C_A$ of component B. Furthermore, we shall make the following assumptions:

Assumption (A) The two components substitute the sites of the perfect empty lattice without any change in molecular orientation.

Assumption (B) The tight binding Heitler–London scheme is applicable for the description of the excited states.

Assumption (C) The excited state of a pure crystal of either one of the two components can be described in terms of a single configuration (multiply branched) exciton band, so that crystal field mixing effects between different electronic states are negligible.

Assumption (D) The environmental shift terms[1] D^f for the two components are equal and concentration independent.

Assumption (E) The intermolecular transfer integrals[1] are invariant under isotopic substitution.

Assumption (F) The two components are characterized by the same electronic wavefunctions and differ only in the molecular (gas phase) excitation energies $\Delta\epsilon_A^f$ and $\Delta\epsilon_B^f$. This difference results, of course, from the isotope effect on the zero point vibrations. As previously demonstrated, changes in nuclear kinetic energy due to isotopic substitution can be regarded as a local perturbation.[11,12]

As in the theory of dilute impurity states[10–12] two different zero-order basis sets can be used for the expansion of the crystal states. The localized excitation representation

$$|n\alpha\rangle \equiv a_{n\alpha}^f = \mathcal{A}\varphi_{n\alpha}^f \prod_{n\alpha\neq m\beta} \varphi_{m\beta}^0 \qquad \text{(II.1)}$$

is given in terms of an antisymmetrized product of the free molecule wavefunctions $\varphi_{n\alpha}$ (the indices 0 and f referring to the grand and excited state, respectively, while the double index $n\alpha$ labels the number of the unit cell $n = 1\cdots N$ and the molecule in the unit cell $\alpha = 1\cdots\sigma_D$). The exciton delocalized representation is given in the form

$$|\mathbf{k}j\rangle \equiv \psi_j^f(\mathbf{k}) = N^{-1/2} \sum_n \sum_\alpha B_{\alpha j}(\mathbf{k}) \exp(i\mathbf{k}\cdot\mathbf{R}_n)\, a_{n\alpha}^f. \qquad \text{(II.2)}$$

The coefficients $B_{\alpha j}(\mathbf{k})$ represent the elements of the unitary transformation matrix from one site exciton states to the pure crystal states. $j = 1\cdots\sigma_D$ corresponds to the σ_D branches of the exciton band.

The isotopically mixed crystal Hamiltonian can be now displayed in the form

$$H = \sum_n \sum_\alpha |n\alpha\rangle \epsilon_{n\alpha} \langle n\alpha| + J - E_0, \qquad \text{(II.3)}$$

where E_0 is the ground state energy, J is the excitation transfer operator

$$J = \sum\sum_{n\alpha<m\beta} |n\alpha\rangle J_{n\alpha m\beta} \langle m\beta|, \qquad \text{(II.3')}$$

and $J_{n\alpha m\beta}$ are the excitation transfer matrix elements which constitute of Coulomb $C_{n\alpha m\beta}$ and exchange $K_{n\alpha m\beta}$ contributions. As we are interested in the weak (electronic–vibrational) coupling limit[2,3] we set $J_{n\alpha m\beta}=(C_{n\alpha m\beta}+K_{n\alpha m\beta})S_v$, where S_v is the vibrational overlap Franck–Condon factor. $\epsilon_{n\alpha}$ is a random variable so that $\epsilon_{n\alpha}=\Delta\epsilon_A{}^f+D^f\equiv\epsilon_A$ when the site $n\alpha$ is occupied by a molecule A and $\epsilon_{n\alpha}=\Delta\epsilon_B{}^f+D^f\equiv\epsilon_B$ when this site is occupied by a molecule of type B.

This simple Hamiltonian is characterized in the localized representation by translationally invariant off-diagonal part and by random diagonal matrix elements. It will be convenient now to separate the translationally invariant part H_0 and the random contributions H_1:

$$H=H_0+H_1, \qquad \text{(II.4)}$$

where

$$H_0=\sum_n\sum_\alpha |n\alpha\rangle\bar{\epsilon}\langle n\alpha| +J-E_0, \qquad \text{(II.4a)}$$

$\bar{\epsilon}$ corresponds to the mean excitation energy

$$\begin{aligned}\bar{\epsilon}&=C_A(\Delta\epsilon_A{}^f+D^f)+C_B(\Delta\epsilon_B{}^f+D^f)\\ &\equiv C_A\epsilon_A+C_B\epsilon_B, \qquad \text{(II.5)}\end{aligned}$$

while

$$H_1=\Delta\sum_n\sum_\alpha \hat{\xi}_{n\alpha}, \qquad \text{(II.4b)}$$

where

$$\hat{\xi}_{n\alpha}=|n\alpha\rangle\xi_{n\alpha}\langle n\alpha|. \qquad \text{(II.4c)}$$

$\xi_{n\alpha}$ is a random variable which takes the values $\xi_{n\alpha}=-C_A$ when the site $n\alpha$ is occupied by B, $\xi_{n\alpha}=C_B$ when the site is occupied by A;

$$\Delta=\Delta\epsilon_A{}^f-\Delta\epsilon_B{}^f\equiv\epsilon_A-\epsilon_B \qquad \text{(II.6)}$$

is the difference in the single molecule excitation energies. Finally it will be convenient to choose the zero energy so that

$$\Delta\epsilon_A{}^f+D^f=\Delta/2 \qquad \text{(II.7a)}$$

and

$$\Delta\epsilon_B{}^f+D^f=-\Delta/2 \qquad \text{(II.7b)}$$

so that on this energy scale

$$\bar{\epsilon}=\tfrac{1}{2}\Delta(C_A-C_B). \qquad \text{(II.5')}$$

The virtual crystal Hamiltonian H_0 is translationally invariant and diagonal in the $|\mathbf{k}j\rangle$ representation, so that

$$\langle\mathbf{k}j|H_0|\mathbf{k}'j'\rangle=\delta_{\mathbf{k}\mathbf{k}'}\delta_{jj'}[\bar{\epsilon}+e_j(\mathbf{k})], \qquad \text{(II.8)}$$

where the exciton dispersion relation $e_j(\mathbf{k})$ is

$$e_j(\mathbf{k})=\sum_\alpha\sum_\beta B_{\alpha j}(\mathbf{k})B_{\beta j}(\mathbf{k})L_{\alpha\beta}(\mathbf{k}) \qquad \text{(II.9)}$$

with the energy matrix $\mathbf{L}$ determined by the exciton transfer integrals

$$L_{\alpha\beta}(\mathbf{k})=\sum_m J_{n\alpha m\beta}\exp[i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_m)]. \qquad \text{(II.10)}$$

All the pertinent physical information is contained in the Green's function

$$G(z)=1/(z-H). \qquad \text{(II.11)}$$

The "honest" way to proceed is to solve the problem for a fixed configuration and then average over all possible distribution of molecules on the lattice site. However, for a given crystal configuration the solution of the problem is unmanageable. We shall therefore employ a "dishonest" procedure invoking the assumption.

Assumption (G) Molecule–molecule spatial correlations are neglected. The properties of the configurationally averaged system will be thus considered. The configurationally averaged Green's function is

$$\langle G(z)\rangle=\langle 1/(z-H)\rangle, \qquad \text{(II.12)}$$

where $\langle\ \rangle$ corresponds to an ensemble average over all distribution of the two components.

An effect Hamiltonian H_{eff} which describes the averaged crystal is defined by the relations

$$\langle G(z)\rangle=1/[z-H_{\text{eff}}(z)]=1/[z-H_0-\hat{\Sigma}(z)] \qquad \text{(II.13)}$$

$$H_{\text{eff}}(z)=H_0+\hat{\Sigma}(z), \qquad \text{(II.14)}$$

where $\hat{\Sigma}(z)$ is the self-energy operator of the mixed crystal with respect to the virtual crystal, which describes the shift and the broadening of the states of the virtual crystal. This operator can be formally represented as a sum of site operators $\hat{\Sigma}_{n\alpha}$ (of unknown form):

$$\hat{\Sigma}(z)=\sum_{n\alpha}\hat{\Sigma}_{n\alpha}(z). \qquad \text{(II.14')}$$

Unlike in conventional generalized perturbation schemes, one should not attempt to break down the effective Hamiltonian into unperturbed and perturbed parts. Rather, the effective Hamiltonian is considered as an unknown of the problem.[31]

In view of the configurational averaging procedure employed, the effective Hamiltonian has the following general properties[31]:

(a) It possesses the full crystal symmetry.

(b) The effective Hamiltonian is energy dependent, determined by the (complex) energy z.

(c) The effective Hamiltonian is non-Hermitian.

(d) The effective Hamiltonian is analytic in both complex half-planes for all z not on the branch cut.

(e) The poles of $(z-H_{\text{eff}})^{-1}$ determine the positions and the widths of the states of the configurationally averaged crystals.

Since H_{eff} has full crystal symmetry and so has H_0 we expect that $\Sigma(z)$ is invariant under all the crystal space group operations. This conclusion implies that $\hat{\Sigma}(z)$ is diagonal in $\mathbf{k}$; however, it is nondiagonal in the excitation branch index j (i.e., the pure crystal exciton branch). The situation is reminiscent of the treatment of exciton states in a pure crystal containing several molecules per unit cell, but further complications are introduced as the complex energy plane is considered. Without any loss in generality we can display the level shift operator in the localized representation

$$\hat{\Sigma}(z)=\sum_n\sum_m\sum_\alpha\sum_\beta |\,n\alpha\rangle\sigma_{n\alpha m\beta}(z)\langle m\beta\,|, \quad \text{(II.15)}$$

where

$$\sigma_{n\alpha m\beta}(z)=\langle n\alpha\,|\,\hat{\Sigma}(z)\,|\,m\beta\rangle. \quad \text{(II.16)}$$

Turning our attention to the $|\,\mathbf{k}j\rangle$ representation we can write the general matrix elements

$$\langle\mathbf{k}j\,|\,\hat{\Sigma}(z)\,|\,\mathbf{k}'j'\rangle=N^{-1}\sum_n\sum_m\sum_\alpha\sum_\beta B_{\alpha j}{}^*(\mathbf{k})B_{\beta j'}(\mathbf{k}')$$
$$\times\exp[i(\mathbf{k}'\cdot\mathbf{R}_n-\mathbf{k}\cdot\mathbf{R}_m)]\sigma_{n\alpha m\beta}(z) \quad \text{(II.17)}$$

which can be easily reduced to the form

$$\langle\mathbf{k}j\,|\,\hat{\Sigma}(z)\,|\,\mathbf{k}'j'\rangle=\delta_{\mathbf{kk}'}\sum_\alpha\sum_\beta B_{\alpha j}{}^*(\mathbf{k})B_{\beta j'}(\mathbf{k})l_{\alpha\beta}(z,\,\mathbf{k}), \quad \text{(II.18)}$$

where

$$l_{\alpha\beta}(z,\,\mathbf{k})=\sum_n\exp(i\mathbf{k}\cdot\mathbf{R}_n)\sigma_{0\alpha n\beta}(z). \quad \text{(II.19)}$$

The following conclusions are immediately apparent:

(a) For a crystal characterized by a center of symmetry we can write

$$l_{\alpha\beta}(z,\,\mathbf{k})=2\sum_n\cos(\mathbf{k}\cdot\mathbf{R}_n)\sigma_{0\alpha m\beta}(z) \quad \text{(II.19}')$$

and choose the expansion coefficients $B_{\alpha j}(\mathbf{k})$ to be real. However, (II.18) is still, of course, complex.

(b) The diagonal matrix elements $l_{\alpha\alpha}(z,\,\mathbf{k})$ are in general equal for all values of α only for special directions of the $\mathbf{k}$ vector (i.e., perpendicular to or lying in a symmetry plane of the pure crystal).

(c) When the exciton dispersion relation in the pure crystal is dominated by short-range intermolecular interactions the $B_{\alpha j}(\mathbf{k})$ coefficients are independent of k and are determined by the factor group operations.[1,5] In this case we expect that

$$\langle\mathbf{k}j\,|\,\hat{\Sigma}(z)\,|\,\mathbf{k}'j'\rangle=\delta_{\mathbf{kk}'}\sum_\alpha\sum_\beta B_{\alpha j}(0)B_{\beta ji}(0)l_{\alpha\beta}(z,\,\mathbf{k})$$

and that the diagonal term $l_{\alpha\alpha}(z,\,\mathbf{k})$ is independent of α.

(d) The restriction of short-range interactions is not sufficiently discussed in (c) to lead to the vanishing of the off-diagonal matrix elements $\langle\mathbf{k}j\,|\,\Sigma\,|\,\mathbf{k}j'\rangle$. It should be borne in mind that $H_{\text{eff}}(z)$ and $\Sigma(z)$ are non-Hermitian and satisfy the relations[31]

$$H_{\text{eff}}{}^\dagger(z)=H_{\text{eff}}(z^*)$$
$$\hat{\Sigma}^\dagger(z)=\hat{\Sigma}(z^*), \quad \text{(II.20)}$$

whereupon even in a crystal characterized by a center of symmetry where the coefficients $B_{\alpha j}(0)$ can be chosen to be real we still have

$$[l_{\alpha\beta}(z)]^*=l_{\beta\alpha}(z^*) \quad \text{(II.21)}$$

and the off-diagonal matrix element of $\hat{\Sigma}(z)$ in the $|\,\mathbf{k}j\rangle$ representation does not vanish.

To summarize this discussion the effective Hamiltonian can be displayed in the form

$$\langle\mathbf{k}j\,|\,H_{\text{eff}}\,|\,\mathbf{k}'j'\rangle=\delta_{\mathbf{kk}'}\{\delta_{jj'}[\tilde{\epsilon}+e_j(\mathbf{k})]$$
$$+\langle\mathbf{k}j\,|\,\Sigma(z)\,|\,\mathbf{k}j'\rangle\}. \quad \text{(II.22)}$$

The mixed crystal energy levels can be determined (in principle!) by solving the secular equation $\det|\,z-H_{\text{eff}}\,|=0$, the (complex) solutions leading to the energies and the widths of the states.

In view of these complications we have to proceed with some caution. Let us define the matrix elements of the averaged Green's function in the $|\,\mathbf{k}j\rangle$ representation

$$\langle\mathbf{k}j\,|\langle G(z)\rangle|\,\mathbf{k}j'\rangle\equiv g(\mathbf{k}j,\,\mathbf{k}j',\,z);\qquad j\neq j'$$
$$\equiv g(\mathbf{k},j,\,z);\qquad j=j'. \quad \text{(II.23)}$$

We should note in passing that the Dyson equation which relates $\langle G(z)\rangle$ to the Green's function $G^0(z)=(z-H_0)^{-1}$ of the virtual crystal

$$\langle G(z)\rangle=G^0(z)+G^0(z)\hat{\Sigma}(z)\langle G(z)\rangle \quad \text{(II.24)}$$

leads to the relations

$$g(\mathbf{k}j,\,\mathbf{k}j',\,z)=g^0(\mathbf{k},j,\,z)\sum_{j''}\langle\mathbf{k}j\,|\,\hat{\Sigma}\,|\,\mathbf{k}j''\rangle$$
$$\times g(\mathbf{k}j'',\,\mathbf{k}j',\,z), \quad \text{(II.25a)}$$

$$g(\mathbf{k},j,\,z)=g^0(\mathbf{k},j,\,z)+g^0(\mathbf{k},j,\,z)$$
$$\times\sum_{j''}\langle\mathbf{k}j\,|\,\Sigma\,|\,\mathbf{k}j''\rangle g(\mathbf{k}j'',\,\mathbf{k}j,\,z), \quad \text{(II.25b)}$$

where

$$g^0(\mathbf{k},j,\,z)=\langle\mathbf{k}j\,|\,G^0(z)\,|\,\mathbf{k}j\rangle=1/[z-\tilde{\epsilon}-e_j(\mathbf{k})] \quad \text{(II.26)}$$

corresponds to the elements of the diagonal matrix of $G^0(z)$ in the $|\,\mathbf{k}j\rangle$ representation. Equation (25) reflects again the fact that in general H_{eff} is nondiagonal in j.

It will be useful at this stage to define the spectral density matrix S which is intimately connected to the optical properties of the mixed crystal. The matrix elements $S(\mathbf{k}j,\,\mathbf{k}j',\,E)$ are defined in terms of an integral representation

$$g(\mathbf{k}j,\,\mathbf{k}j',\,z)=\int_{-\infty}^{\infty}\frac{S(\mathbf{k}j,\,\mathbf{k}j',\,E')dE'}{z-E'}, \quad \text{(II.27)}$$

whereupon when z approaches the real axes

$$S(\mathbf{k}j,\,\mathbf{k}j',\,E)=\pi^{-1}\,\mathrm{Im}g(\mathbf{k}j,\,\mathbf{k}j',\,E-i0^+). \quad \text{(II.28)}$$

In particular we shall be interested in the diagonal matrix elements which we shall refer to as the spectral density functions

$$S(\mathbf{k},j,\,E)\equiv S(\mathbf{k}j,\,\mathbf{k}j',\,E)=\pi^{-1}\,\mathrm{Im}g(\mathbf{k},j,\,E-i0^+). \quad \text{(II.29)}$$

This formal definition leads to a convenient representation of the density of states and of the optical properties. The density of excited states (per molecule) in the averaged crystal is

$$\rho(E)=(1/\pi N\sigma_D)\ \mathrm{Im}\ \mathrm{Tr}\langle G(E-i0^+)\rangle \qquad (\mathrm{II}.30)$$

which can be expressed in view of (II.28) and (II.29) by the spectral density functions

$$\rho(E)=(1/N\sigma_D)\sum_{\mathbf{k}}\sum_{j}S(\mathbf{k},j,E). \qquad (\mathrm{II}.31)$$

Alternatively, the density of states can be expressed in terms of the localized representation

$$\rho(E)=(1/\pi N\sigma_D)\ \mathrm{Im}\sum_{n}\sum_{\alpha}\langle n\alpha\,|\langle G(E-i0^+)\rangle|\,n\alpha\rangle$$
$$=(1/\pi\sigma_D)\ \mathrm{Im}\sum_{\alpha}\langle n\alpha\,|\langle G(E-i0^+)\rangle\,|\,n\alpha\rangle. \qquad (\mathrm{II}.32)$$

If the molecules in the unit cell are crystallographically equivalent this expression can be further simplified by noting that $\langle G(z)\rangle$ possesses full crystal symmetry, whereupon

$$\rho(E)=\pi^{-1}\,\mathrm{Im}\langle n\alpha\,|\langle G(E-i0^+)\rangle|\,n\alpha\rangle. \qquad (\mathrm{II}.32')$$

Finally, in a manner formally equivalent to the Koster–Slater scheme, one can define a generalized dispersion relation for the complex function[30,31]

$$f(z)=(1/N\sigma_D)\ \mathrm{Tr}\langle G(z)\rangle \qquad (\mathrm{II}.33)$$

which in view of (II.32)

$$\rho(E)=\pi^{-1}\,\mathrm{Im}f(E-i0^+) \qquad (\mathrm{II}.34)$$

so that

$$f(z)=\int_{-\infty}^{\infty}\frac{dE'}{z-E'}\,\rho(E'). \qquad (\mathrm{II}.33')$$

The optical properties of the system can be expressed in terms of the susceptibility term induced by the electromagnetic field.[35,36] The dipole strength per unit energy, $I(E)$, is

$$I(E)=\pi^{-1}\,\mathrm{Im}\langle 0\,|(\boldsymbol{\mu}\cdot\mathbf{e})\langle G(E-i0^+)\rangle(\boldsymbol{\mu}\cdot\mathbf{e})|\,0\rangle, \qquad (\mathrm{II}.35)$$

where $|\,0\rangle$ is the ground state wavefunction, $\boldsymbol{\mu}$ the electric dipole operator, and $\mathbf{e}$ the polarization vector of the exciting light.

Making use again of the $|\,\mathbf{k}j\rangle$ representation and of Eqs. (II.23), (II.28), and (II.29), and bearing in mind the $\mathbf{k}=0$ selection rule for excitation of the pure crystal, the following result is obtained:

$$I(E)=\sum_{j}\sum_{j'}\langle 0\,|\,\boldsymbol{\mu}\cdot\mathbf{e}\,|\,\mathbf{0}j\rangle S(\mathbf{0}j,\mathbf{0}j',E)$$
$$\times\langle \mathbf{0}j'\,|\,\boldsymbol{\mu}\cdot\mathbf{e}\,|\,0\rangle. \qquad (\mathrm{II}.36)$$

The matrix elements of the dipole operator which appear in Eq. (II.36) are nothing but the transition moments for the pure (or virtual) crystal exciton branches

$$\mathbf{m}(j)=\langle 0\,|\,\boldsymbol{\mu}\,|\,\mathbf{0}j\rangle=\sum_{\alpha}\langle 0\,|\,\boldsymbol{\mu}\,|\,n\alpha\rangle B_{\alpha j}(\mathbf{0}), \qquad (\mathrm{II}.37)$$

where $\langle 0\,|\,\boldsymbol{\mu}\,|\,n\alpha\rangle$ is the transition dipole element of a single molecule. In special directions of the polarization vector say $\mathbf{e}=\mathbf{e}_j'$, we get for crystals of interest $\mathbf{m}(j)\cdot\mathbf{e}_{j'}=\mathbf{m}(j)\cdot\mathbf{e}_j\delta_{jj'}\equiv m(j)\delta_{jj'}$ so that only one Davydov component is excited by the linearily polarized light.[1,2] (Thus, for example, in a monoclinic crystal containing two molecules in unit cell these special directions are $\mathbf{e}_{j'}\parallel\mathbf{b}$ and $\mathbf{e}_{j'}\perp\mathbf{b}$, where $\mathbf{b}$ is the monoclinic axes.) Under these circumstances only one of the diagonal matrix elements of the spectral density is retained in Eq. (II.36). We can then define the dipole strength for polarized absorption to the jth excitation branch in the form

$$I_j(E)=|\,m(j)|^2S(0,j,E). \qquad (\mathrm{II}.38)$$

Hence the pertinent information on the optical properties can be extracted solely from the diagonal matrix elements of the spectral density.

To conclude the exposition of notation and definitions, it will be useful to list the Greenions and the corresponding physical properties of the virtual crystal

$$g^0(\mathbf{k},j,z)=1/[z-\tilde{\epsilon}-e_j(\mathbf{k})], \qquad (\mathrm{II}.39)$$
$$f^0(z)\equiv f^0(z-\tilde{\epsilon})=(1/N\sigma_D)\sum_{\mathbf{k}}\sum_{j}[z-\tilde{\epsilon}-e_j(\mathbf{k})]^{-1},$$
$$S^0(\mathbf{k},j,E)=\delta[E-\tilde{\epsilon}-e_j(\mathbf{k})],$$
$$\rho^0(E)=(1/N\sigma_D)\sum_{\mathbf{k}}\sum_{j}\delta[E-\tilde{\epsilon}-e_j(\mathbf{k})],$$
$$I_j^0(E)=|\,m(j)|^2\delta[E-\tilde{\epsilon}-e_j(\mathbf{k})].$$

III. MOMENTS OF THE DENSITY OF STATES AND OF THE SPECTRAL DENSITY

Without referring to any specific approximations, it will be useful to consider the asymptotic behavior of the configurationally averaged Green's function for large z. Such expansion will lead to useful information concerning the moments of the density of states and of the diagonal elements of the spectral density, and how these quantities are related to the moments of the density of states and to the energy levels of the virtual crystal, or rather to those of a pure crystal of one of the constituents.[37] In this section we shall follow closely the work of Velicky *et al.*[31] on the electronic states of binary alloys. This treatment is of interest to us as it will lead to some general results for the optical properties.

Considering the asymptotic behavior of $\langle G(z)\rangle$ for z we can write for energies far removed from the allowed band (or bands) of the mixed crystal:

$$\langle G(z)\rangle=\langle z-H\rangle^{-1}=\sum_{p=0}^{\infty}\frac{\langle H^p\rangle}{z^{p+1}}. \qquad (\mathrm{III}.1)$$

It will be useful now to introduce the basic definitions of the moments of the density of states

$$\mu_p = \int_{-\infty}^{\infty} dE \rho(E) E^p \tag{III.2}$$

and of the spectral density function

$$M_p(\mathbf{k}, j) = \int_{-\infty}^{\infty} dE S(\mathbf{k}, j, E) E^p \tag{III.3}$$

which in view of Eq. (II.32) are related by

$$\mu_p = \sum_{\mathbf{k}} \sum_{j} M_p(\mathbf{k}, j). \tag{III.4}$$

These definitions can be used to expand the following quantities, making use of Eqs. (II.12), (II.23), (II.27), (II.29), (II.33), and (III.1):

$$\begin{aligned} g(\mathbf{k}, j, z) &= \int_{-\infty}^{\infty} \frac{dE'}{z-E'} S(\mathbf{k}, j, E') = \sum_{p=0}^{\infty} \frac{M_p(\mathbf{k}, j)}{z^{p+1}} \\ &= \langle \mathbf{k}j \,|\langle G(z)\rangle|\, \mathbf{k}j \rangle \\ &= \sum_{p=0}^{\infty} \frac{\langle \mathbf{k}j \,|\langle H^p\rangle|\, \mathbf{k}j \rangle}{z^{p+1}}, \end{aligned} \tag{III.5}$$

$$\begin{aligned} f(z) &= \int_{-\infty}^{\infty} \frac{\rho(E') dE'}{z-E'} \\ &= \sum_{p=0}^{\infty} \frac{\mu_p}{z^{p+1}} \\ &= (N\sigma_D)^{-1} \operatorname{Tr}\langle G(z) \rangle \\ &= (N\sigma_D)^{-1} \sum_{p=0}^{\infty} \frac{\operatorname{Tr}\langle H^p \rangle}{z^{p+1}}. \end{aligned} \tag{III.6}$$

One immediately obtains the following relations:

$$\mu_p = (N\sigma_D)^{-1} \operatorname{Tr}\langle H^p \rangle \tag{III.7}$$

and

$$M_p(\mathbf{k}, j) = \langle \mathbf{k}j \,|\langle H^p\rangle|\, \mathbf{k}j \rangle. \tag{III.8}$$

The moments of the virtual crystal Hamiltonian are obviously

$$\langle H_0^p \rangle = H_0^p = (\tilde{\epsilon}+J)^p \tag{III.9}$$

so that the moments of the density of states of the virtual crystal $[\![\mu_p^0]\!]$ are just

$$[\![\mu_p^0]\!] = (1/N\sigma_D) \operatorname{Tr} H_0^p = (1/N\sigma_D) \sum_{\mathbf{k}} \sum_{j} [\tilde{\epsilon}+e_j(\mathbf{k})]^p. \tag{III.10}$$

It will be convenient to choose the moments μ_p^0 of the virtual (or pure) crystal so that $\mu_1^{(0)} = 0$ whereupon

$$\mu_p^0 = (1/N\sigma_D) \operatorname{Tr} J^p = (1/N\sigma_D) \sum_{\mathbf{k}} \sum_{j} (e_j(\mathbf{k}))^p. \tag{III.11}$$

The moments of the spectral density of the virtual crystal are obviously[12]

$$M_p^0(\mathbf{k}, j) = [\tilde{\epsilon}+e_j(\mathbf{k})]^p \tag{III.12}$$

and the moments of the optical spectrum are given by $M_p^0(\mathbf{0}j)$.

The averaged moments of the mixed crystal Hamiltonian (II.4) can be readily obtained from the expansion[31]

$$\langle H^p \rangle = \langle H_0^p \rangle + \cdots \langle H_1^p \rangle \tag{III.13}$$

and by making use of the relation $\tilde{\epsilon}^2 + \Delta^2 C_A C_B = \Delta^2/4$. In this way one obtains[31]

$$\begin{aligned} \langle H^0 \rangle &= 1, \\ \langle H' \rangle &= \langle H_0^1 \rangle = \tilde{\epsilon}+J, \\ \langle H^2 \rangle &= \langle H_0^2 \rangle + \Delta^2 C_A C_B = \tfrac{1}{4}\Delta^2 + 2\tilde{\epsilon}J + J^2, \\ \langle H^3 \rangle &= \tfrac{1}{4}\tilde{\epsilon}\Delta^2 + (\tfrac{1}{2}\Delta^2 + \tilde{\epsilon}^2)J + 2\tilde{\epsilon}J^2 + J^3. \end{aligned} \tag{III.14}$$

The lower moments of the density of states of the mixed crystal are

$$\begin{aligned} \mu_0 &= 1, \\ \mu_1 &= [\![\mu_1^0]\!] = \tilde{\epsilon}, \\ \mu_2 &= \mu_2^0 + \tfrac{1}{4}\Delta^2. \end{aligned} \tag{III.15}$$

Finally the lower moments of the spectral density are

$$\begin{aligned} M_0(\mathbf{k}, j) &= M_0^0(\mathbf{k}, j) = 1, \\ M_1(\mathbf{k}, j) &= M_1^0(\mathbf{k}, j) = \tilde{\epsilon} + e_j(\mathbf{k}), \\ M_2(\mathbf{k}, j) &= M_2^0(\mathbf{k}, j) + \Delta^2 C_A C_B. \end{aligned} \tag{III.16}$$

As pointed out by Velicky *et al.*[31] these results make it possible to derive the asymptotic behavior of the effective Hamiltonian. This result will provide us with some insight concerning the asymptotic form of the self-energy and its matrix elements in the $|\,\mathbf{k}j\rangle$ representation.

From Eqs. (II.12) and (III.1) one can write

$$\begin{aligned} H_{\text{eff}} &= z - \langle G \rangle^{-1} = z - \left(z^{-1} + \sum_{p=1}^{\infty} \frac{\langle H^p \rangle}{z^{p+1}} \right)^{-1} \\ &= \tilde{\epsilon} + J + \sum_{p=1}^{\infty} \frac{\hat{\Lambda}_p}{z^p} \end{aligned} \tag{III.17}$$

and the self-energy operator can be expanded in the asymptotic form[31]

$$\hat{\Sigma}(z) = \sum_{p=1}^{\infty} \frac{\hat{\Lambda}_p}{z^p}, \tag{III.18}$$

where the operators $\hat{\Lambda}_p$ can be determined by using (III.14). The lowest terms are[31]

$$\begin{aligned} \hat{\Lambda}_1 &= C_A C_B \Delta^2, \\ \hat{\Lambda}_2 &= -C_A C_B (C_A - C_B) \Delta^2, \\ \hat{\Lambda}_3 &= C_A C_B \Delta^2 (\tilde{\epsilon}^2 + \mu_2^0), \\ \hat{\Lambda}_4 &= -C_A C_B \Delta^2 (\tilde{\epsilon}^3 - \mu_3^0 + \tilde{\epsilon}\mu_2^0). \end{aligned} \tag{III.18$'$}$$

The following interesting feature of this result should be noticed:

(a) The asymptotic form of the self-energy operator is determined by a numerical power series up to the fifth order.

(b) The matrix elements of the self-energy operator in the $|\mathbf{k}j\rangle$ representation for asymptotic values of z are independent of $\mathbf{k}$.

(c) These asymptotic matrix elements are diagonal in the exciton branch j and the diagonal terms are equal for all j.

These conclusions are of importance for choosing an approximate form for the self-energy operator.

In order to utilize the results obtained herein for the moments of the density of states and of the optical spectrum (i.e., the moments of the spectral density at $\mathbf{k}=0$), some further information is required regarding the problem whether the density of states does or does not reveal an energy gap. This problem plays a central role in the theory of disordered systems and was considered for a binary alloy[38] by Luttinger,[39] Soven,[36] Toyozawa and Oneduna,[30] and by Velicky *et al.*[31]

In a binary mixed crystal under consideration the following physical situations can be encountered[40]:

(a) *Separated bands*: The mixed crystal cannot have states in the energy region which is simultaneously forbidden for the pure crystal of both A and B. Therefore, if the energy difference Δ exceeds the total bandwidth W of (either) pure crystal, i.e.,

$$\Delta > W \qquad (\Delta > 0), \tag{III.19}$$

two separate bands result. Condition (III.19) provides a condition for a band gap in the disordered system, specifying the existence of forbidden regions (between the two bands and outside the bands) where the density of states is strictly zero. One should note in passing that the "atomic limit" when $W\rightarrow 0$ (or $J\rightarrow 0$) will always correspond to separated bands.

(b) *The persistence case:* As previously pointed out by Soven[33] and by Onodera and Toyozawa[30] there are "nearly forbidden" energy regions, inside the range spanned by the two bands of the pure components where the density of states is extremely small. Therefore, Condition (III.15) is too strong for obtaining a bandgap between allowed energy regions. For a binary substitutionally disordered system it was demonstrated by Velicky *et al.*[31] that for reasonably large Δ values, the Green's function $g(\mathbf{k},j,z)$ can be expanded in the moments of the subbands, around $z=-(\tilde{\epsilon})$. The following behavior is then exhibited around this point[31]

$$g(\mathbf{k},j,z) = -[C_AC_B\Delta^2-\mu_2^0](z+\tilde{\epsilon})+O[(W/\Delta)^3]. \tag{III.20}$$

Therefore, to a good approximation one expects $g(\mathbf{k},j,z)$ to vanish for all values of $\mathbf{k}$ and j whereupon $\rho(-\tilde{\epsilon})\approx 0$. These conclusions are valid only provided that the density of states is a nonnegative quantity, whereupon one obtains the following necessary condition for the vanishing of the density of states (at one point $E=-\tilde{\epsilon}$) between the bands:

$$C_AC_B\Delta^2 \geq \mu_2^0. \tag{III.21}$$

Thus when (III.21) is fulfilled we expect that the bands will be split at least at one point, and we can further speculate that a band gap of "nearly forbidden" levels is formed between the bands. It should be noted, however, that these arguments do not hold for $C_A\rightarrow 0$. We shall thus define the persistence limit by the following relation:

$$W^2 \geq C_AC_B\Delta^2 \geq \mu_2^0. \tag{III.21$'$}$$

(c) *Incipient bandgap*: When

$$C_AC_B\Delta^2 \lesssim \mu_2^0, \tag{III.22}$$

an intermediate situation between the persistence [case (b)] and the amalgamation [case (d)] limits is encountered. One may expect that there will be a minimum in the density of states around $-\tilde{\epsilon}$. Such a conclusion cannot be proved from general considerations; however, it is made plausible on the basis of approximate models.[31,22,23]

(d) *The amalgamation limit*: Finally, when

$$\Delta^2 \ll \mu_2^0 < W^2, \tag{III.23}$$

one band exists in the density of states function. The electronic properties of the crystal can be then reasonably well described by using the virtual crystal Hamiltonian, whereupon just the center of gravity of the band is shifted relative to the pure crystal.

For general orientation purposes we have displayed in Fig. 1 a schematic representation of the pertinent energy regions for the excited states of a binary crystal. We have chosen a model band of the pure substance characterized by $W=1$ and $\mu_2^0=0.125$. All the electronic states are restricted to the strips parallel to ϵ_A and to ϵ_B, when $|\Delta|$ is varied. For $\Delta>1$ the subbands must be separated. The zero of $g(\mathbf{k},j,z)$ (or rather vanishing of the density of states at that point) is presented by heavy lines which were drawn for the two concentrations $C_A=0.1$ and $C_A=0.5$. This feature appears first at $\Delta=0.83$ and at $\Delta=0.5$ for $C_A=0.1$ and for $C_A=0.5$, respectively, thus separating the two subbands and providing a reasonable condition for persistence of a bandgap.

To apply these general considerations to a real life problem we have summarized in Table I the lowest singlet exciton bandwidths and the second moment of the exciton band for pure crystalline naphthalene and benzene as obtained from hot band spectroscopy[7,12,13] as well as the corresponding data for the lowest triplet band in naphthalene[12] obtained from theoretical calculation of the electron exchange terms, which concur with the experimental spectroscopic data.[41] The differences in the molecular excitation energies for the different isotopically substituted molecules are well known.[12,13] We can now state for which isotopically mixed crystals

TABLE I. Empirical data on the nature of some of the lowest excited electronic states of binary isotopically mixed crystal (data refer to the lowest vibronic component of the given electronic state).

Components	Molecular excited state	Pure crystal exciton states	W [a] (cm^{-1})	$\mu_2{}^0$ (cm^{-2})	$\lvert\Delta\rvert$ [b] (cm^{-1})	Physical situation in mixed crystal
C_6H_6/C_6D_6	$^1B_{2u}$	^1A_u, $^1B_{1u}$, $^1B_{2u}$, $^1B_{3u}$	60	110	200	Separated bands
C_6DH_5/C_6H_6	$^1B_{2u}$	^1A_u, $^1B_{1u}$, $^1B_{2u}$, $^1B_{3u}$	60	110	35	Persistence
$C_{10}H_8/C_{10}D_8$	$^1B_{3u}$	^1A_u, ^1B_u	160	1410	115	Persistence
$C_{10}H_8/\beta$-$C_{10}D_4H_4$	$^1B_{3u}$	^1A_u, ^1B_u	160	1410	78(74)	Incipient bandgap
$C_{10}H_8/\alpha$-$C_{10}D_4H_4$	$^1B_{3u}$	^1A_u, ^1B_u	160	1410	55(51)	Amalgamation
$C_{10}H_8/\alpha$-$C_{10}H_7D$	$^1B_{3u}$	^1A_u, ^1B_u	160	1410	21	Amalgamation
$C_{10}H_8/\alpha$-$C_{10}H_7D$	$^3B_{2u}$	^3A_u, ^3B_u	11.2	9	21	Separated bands

[a] Pure crystal exciton bandwidth and second moment for singlet states from hot band spectroscopy (Ref. 7) and for triplet naphthalene from theoretical calculation (Ref. 12).

[b] Perturbation strength from Refs. 11–13.

a band gap is expected to appear in the density of states. These conclusions concur with the results of the approximate calculations reported by Hong and Robinson[22] and by us.[23]

In the case of separated bands or in the persistence case one expects a splitting of the density of excited states. Let us then consider the two subbands—which will be labeled by α and β. Some useful information can be then obtained concerning the moments and spectral density in each subband.

The total density of states can be now decomposed into two separate contributions

$$\rho(E)=\rho_\alpha(E)+\rho_\beta(E) \tag{III.24}$$

and it will be useful to define the moments of the subbands relative to the centers of gravity of the exciton bands of the pure components ϵ_A and ϵ_B:

$$\mu_p{}^\alpha=\int_{-\infty}^{\infty} dE(E-\epsilon_A)^p\rho_\alpha(E),$$

$$\mu_p{}^\beta=\int_{-\infty}^{\infty} dE(E-\epsilon_B)^p\rho_\beta(E). \tag{III.24$'$}$$

The moments of the total density of states can be then expanded in terms of the moments of the subbands

$$\begin{aligned}\mu_p&=\int_{-\infty}^{\infty} dEE^p[\rho_\alpha(E)+\rho_\beta(E)]\\&=\int_{-\infty}^{\infty} dE(E-\epsilon_A+\epsilon_A)^p\rho_\alpha(E)\\&\qquad+\int_{-\infty}^{\infty} dE(E-\epsilon_B+\epsilon_B)^p\rho_\beta(E)\\&=\sum_{l=0}^{p}\binom{p}{l}[(\epsilon_A)^l\mu_{p-l}{}^\alpha+(\epsilon_B)^l\mu_{p-l}{}^\beta].\end{aligned} \tag{III.25}$$

The resulting equations involve in principle an infinite set which for reasonably large Δ values (i.e., $\mu_2{}^0/\Delta^2<1$) can be solved by truncation. This restriction is reminiscent of the intermediate and deep trap limit for a single impurity state. The solution of Eq. (III.24) including terms up to second order in Δ leads to the following results for the lower moments of the density of states in the subbands:

$$\begin{aligned}&\mu_0{}^\alpha=C_A; &&\mu_0{}^\beta=C_B,\\&\mu_1{}^\alpha=C_AC_B\mu_2{}^0/\Delta; &&\mu_1{}^\beta=-C_AC_B\mu_2{}^0/\Delta,\\&\mu_2{}^\alpha=C_A{}^2\mu_2{}^{(0)}; &&\mu_2{}^\beta=C_B{}^2\mu_2{}^0.\end{aligned} \tag{III.26}$$

From these results we conclude that:

(a) There are C_A states in one subband and C_B in the other subband. The sum rule $\mu_0{}^\alpha+\mu_0{}^\beta=1$ is obeyed.

(b) The centers of gravity $E_b{}^{\alpha,\beta}$ of the two subbands are located at

$$\begin{aligned}E_b{}^\alpha&=\Delta\epsilon_A{}^f+D^f+(C_B\mu_2{}^0/\Delta),\\E_b{}^\beta&=\Delta\epsilon_B{}^f+D^f-(C_A\mu_2{}^0/\Delta).\end{aligned} \tag{III.27}$$

(c) In the limit of zero concentration of one of the components (say $C_B\rightarrow0$)

$$\begin{aligned}E_b{}^\alpha&=\Delta\epsilon_A{}^f+D^f,\\E_b{}^\beta&=\Delta\epsilon_B{}^f+D^f-(\mu_2{}^0/\Delta)\end{aligned} \tag{III.27$'$}$$

which reduces to the situation in the single impurity deep trap limit where the host band is unshifted and the guest impurity level outside the band is determined by second-order perturbation theory.

(d) The "widths" $\tilde{Y}_\alpha$ and $\tilde{Y}_\beta$ of the two subbands are given by

$$\tilde{Y}_{\alpha,\beta}{}^2=(\mu_2{}^{\alpha,\beta}/\mu_0{}^{\alpha,\beta})-(\mu_1{}^{\alpha,\beta}/\mu_0{}^{\alpha,\beta})^2 \tag{III.28}$$

which to second order in Δ^{-1} take the form

$$\begin{aligned}\tilde{Y}_\alpha&=(C_A\mu_2{}^0)^{1/2},\\\tilde{Y}_\beta&=(C_B\mu_2{}^0)^{1/2}.\end{aligned} \tag{III.28$'$}$$

Thus the widths of the two distributions are given by

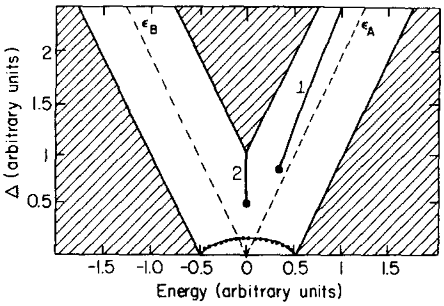

FIG. 1. A schematic representation of the different energy regions for the excited electronic states of an isotopically mixed crystal. •••, exciton density of states in pure crystal. Hatched area, absolutely forbidden energy regions. Unhatched area, allowed and nearly allowed energy regions. – (1), vanishing of density of states for $C_A=0.1$. – (2), vanishing of density of states for $C_A=0.5$. Heavy dots represent the lower limit of Δ required for the vanishing of the density of states at one point at the given concentration.

the square of the second moment of the pure crystal density of states scaled by the squares of the concentration.

These general model-independent conclusions are useful to test the results of numerical calculations based on approximate schemes. Of greater interest are the moments of the spectral density in the two subbands. Obviously in the forbidden and almost forbidden energy regions $S(\mathbf{k},j,E)=0$ or is vanishingly small (except for delta function singularities in the almost forbidden regions). The spectral density can be then decomposed into separate contributions from the two subbands (for each $\mathbf{k}$ and j):

$$S(\mathbf{k},j,E)=S_\alpha(\mathbf{k},j,E)+S_\beta(\mathbf{k},j,E). \qquad \text{(III.29)}$$

The moments of the spectral density in the regions of the two subbands can be defined as follows:

$$M_p^\alpha(\mathbf{k},j)=\int_{-\infty}^{\infty} dE(E-\epsilon_A)^p S_\alpha(\mathbf{k},j,E),$$

$$M_p^\beta(\mathbf{k},j)=\int_{-\infty}^{\infty} dE(E-\epsilon_B)^p S_\beta(\mathbf{k},j,E). \qquad \text{(III.30)}$$

The total moments of the spectral density for each branch j can be expressed in a manner analogous to that of (III.25)

$$\begin{aligned}M_p(\mathbf{k},j)=&\int_{-\infty}^{\infty} dE(E-\epsilon_A+\epsilon_A)^p S_\alpha(\mathbf{k},j,\epsilon)\\&+\int_{-\infty}^{\infty} dE(E-\epsilon_B+\epsilon_B)^p S_\beta(\mathbf{k},j,E)\\&=\sum_{l=0}^{p}\binom{p}{l}[M_{p-l}^\alpha(\epsilon_A)^l+M_{p-l}^\beta(\epsilon_B)^l].\end{aligned} \qquad \text{(III.31)}$$

The lowest moments of the spectral density can be now expressed in the form[31]

$$\begin{aligned}M_0^\alpha(\mathbf{k},j)&=C_A+2C_AC_Be_j(\mathbf{k})\Delta^{-1}\\&\quad-3C_AC_B(C_A-C_B)b_j(\mathbf{k})\Delta^{-2}+O(\Delta^{-3}),\\M_0^\beta(\mathbf{k},j)&=C_B-2C_AC_Be_j(\mathbf{k})\Delta^{-1}\\&\quad+3C_AC_B(C_A-C_B)b_j(\mathbf{k})\Delta^{-2}+O(\Delta^{-3}),\\M_1^\alpha(\mathbf{k},j)&=C_A^2e_j(\mathbf{k})\\&\quad+C_AC_B[3C_Ab_j(\mathbf{k})+\mu_2^0]\Delta^{-1}+O(\Delta^{-2}),\\M^\beta(\mathbf{k},j)&=C_B^2e_j(\mathbf{k})\\&\quad-C_AC_B[3C_Bb_j(\mathbf{k})+\mu_2^0]\Delta^{-1}+O(\Delta^{-2}),\\M_2^\alpha(\mathbf{k},j)&=C_A^2C_B\mu_2^0+C_A^3[e_j(\mathbf{k})]^2+O(\Delta^{-1}),\\M_2^\beta(\mathbf{k},j)&=C_AC_B^2\mu_2^0+C_B^3[e_j(\mathbf{k})]^2+O(\Delta^{-1}),\\b_j(\mathbf{k})&=[e_j(\mathbf{k})]^2-\mu_2^0.\end{aligned} \qquad \text{(III.32)}$$

From these results we conclude that:

(a) For a given excitation branch j the sum rule $M_0^\alpha(\mathbf{k},j)+M_0^\beta(\mathbf{k},j)=1$ is obeyed for all $\mathbf{k}$.

(b) When

$$e_j(\mathbf{k})/\Delta\ll 1, \qquad \text{(III.33)}$$

the zero moments or areas of the spectral density scale linearily with the respective concentrations, i.e.,

$$M_0^\alpha(\mathbf{k},j)\rightarrow C_A; \qquad M_0^\beta(\mathbf{k},j)\rightarrow C_B. \qquad \text{(III.34)}$$

When Condition (III.33) is not obeyed deviations determined by the Δ^{-1} term will be appreciable.

(c) When (III.33) is obeyed, the centers of gravity of the two generalized spectral distributions behave like

$$\begin{aligned}E_s^\alpha(\mathbf{k},j)&=\Delta\epsilon_A^f+D^f+C_Ae_j(\mathbf{k}),\\E_s^\beta(\mathbf{k},j)&=\Delta\epsilon_B^f+D^f+C_Be_j(\mathbf{k}).\end{aligned} \qquad \text{(III.35)}$$

Again correction terms to this linear behavior are expected to be important in the persistence case.

(d) The "widths" Y_α and Y_β of the distributions will take the limiting form for sufficiently large Δ

$$Y_\alpha(\mathbf{k},j)=Y_\beta(\mathbf{k},j)=(C_AC_B\mu_2^0)^{1/2} \qquad \text{(III.36)}$$

being then independent of $\mathbf{k}$ and j in this limit.

From these results we are able to extract some features of the intensity distribution in optical absorption. Obviously, the general treatment as presented up to this point does not provide us with direct information concerning the shape of the (polarized) absorption bands; however, useful information concerning these distributions can be obtained from the moments of the spectral density function. The moments $N_p(j)$ of the polarized absorption bands are obtained from Eqs.

(II.38) and (III.3):

$$N_p(j)=\int_{-\infty}^{\infty} I_j(E)E^p dE$$
$$=|m(j)|^2 M_p(0,j). \qquad \text{(III.37)}$$

Let us now consider two different physical situations:

(a) When a gap exists in the density of states function (separated bands and persistence cases), we can consider $2\sigma_D$ different intensity distributions in the binary crystal. In the region of each subband, σ_D intensity distributions, each characterized by a different polarization, are encountered. We can then assign moments $N_p^{\alpha}(j)$ and $N_p^{\beta}(j)$ to the optical lines in the two different subbands.

(b) In the amalgamation case σ_D different intensity distributions, each characterized by a different polarization, will appear.

The only information required to express the moments of the optical absorption bands in the mixed crystal involves the positions of the Davydov components (relative to the center of gravity) in the pure crystal $t_j \equiv e_j(\mathbf{0})$ and the moments of the density of states in the pure crystal (see Table I). In the case of split bands we have the following physical parameters for the $2\sigma_D$ spectral intensity distributions:

(a1) The relative integrated intensities of the absorption bands $A^{\alpha}(j)$ and $A^{\beta}(j)$, up to second order in Δ^{-2}, are

$$A^{\alpha}(j)=N_0^{\alpha}(j)/|m(j)|^2$$
$$=C_{\mathrm{A}}+2C_{\mathrm{A}}C_{\mathrm{B}}t_j\Delta^{-1}-3C_{\mathrm{B}}(C_{\mathrm{A}}-C_{\mathrm{B}})b_j\Delta^{-2},$$
$$A^{\beta}(j)=N_0^{\beta}/|m(j)|^2$$
$$=C_{\mathrm{B}}-2C_{\mathrm{A}}C_{\mathrm{B}}t_j\Delta^{-1}+3C_{\mathrm{A}}(C_{\mathrm{A}}-C_{\mathrm{B}})b_j\Delta^{-2}, \qquad \text{(III.38)}$$

where $b_j \equiv b_j(\mathbf{0})$ [see Eq. (III.32)].

(a2) The centers of gravity $E_c^{\alpha}(j)$ and $E_c^{\beta}(j)$ of the optical absorption bands are given up to first order in Δ^{-1} in the form

$$E_c^{\alpha}(j)=\Delta\epsilon_{\mathrm{A}}^{f}+D^{f}$$
$$+(C_{\mathrm{A}}t_j+3C_{\mathrm{A}}C_{\mathrm{B}}b_j\Delta^{-1}+C_{\mathrm{B}}\mu_2^0\Delta^{-1})/(1+2C_{\mathrm{B}}t_j\Delta^{-1}),$$
$$E_c^{\beta}(j)=\Delta\epsilon_{\mathrm{B}}^{f}+D^{f}$$
$$+(C_{\mathrm{B}}t_j-3C_{\mathrm{A}}C_{\mathrm{B}}b_j\Delta^{-1}-C_{\mathrm{A}}\mu_2^0\Delta^{-1})/(1-2C_{\mathrm{A}}t_j\Delta^{-1}). \qquad \text{(III.39)}$$

Strictly speaking, these results are valid for the deep trap limit. However, if $2C_{\mathrm{A}}t_j\Delta^{-1}\sim 2C_{\mathrm{B}}t_j\Delta^{-1}<0.5$ the terms of the order of Δ^{-2} will be relatively small. Furthermore, in this case Eq. (III.39) can be recast in the form

$$E_c^{\alpha}(j)=\Delta\epsilon_{\mathrm{A}}^{f}+D^{f}+C_{\mathrm{A}}t_j+C_{\mathrm{A}}C_{\mathrm{B}}t_j^2\Delta^{-1}$$
$$-3C_{\mathrm{A}}C_{\mathrm{B}}\mu_2^0\Delta^{-1}+C_{\mathrm{B}}\mu_2^0\Delta^{-1},$$
$$E_c^{\beta}(j)=\Delta\epsilon_{\mathrm{B}}^{f}+D^{f}+C_{\mathrm{B}}t_j-C_{\mathrm{A}}C_{\mathrm{B}}t_j^2\Delta^{-1}$$
$$+3C_{\mathrm{A}}C_{\mathrm{B}}\mu_2^0\Delta^{-1}-C_{\mathrm{A}}\mu_2^0\Delta^{-1}. \qquad \text{(III.39')}$$

The resulting energies behave properly in the zero concentration limit (for $C_{\mathrm{A}}\rightarrow 0$ or $C_{\mathrm{B}}\rightarrow 0$) leading to the "deep trap" values $E_c^{\alpha}(j)=\Delta\epsilon_{\mathrm{A}}^{f}+D^{f}+\mu_2^0\Delta^{-1}$ and $E_c^{\beta}(j)=\Delta\epsilon_{\mathrm{B}}^{f}+D^{f}-\mu_2^0\Delta^{-1}$. As demonstrated in the study of single impurity states,[12,13] these "zero concentration" energy levels provide a good approximation for both the deep and the intermediate impurity case. Thus Eq. (39a) will be considered as a useful interpolation formula, which is strictly applicable for the case of separated bands but will be also used for the persistence case.

(a3) The standard deviations (i.e., widths) $Y^{\alpha}(j)$ and $Y^{\beta}(j)$ of the distribution of intensities are given (to the lowest approximation) by

$$Y^{\alpha}(j)=[(C_{\mathrm{A}}C_{\mathrm{B}}\mu_2^0+C_{\mathrm{A}}^2t_j^2)-(C_{\mathrm{A}}t_j)^2]^{1/2}=(C_{\mathrm{A}}C_{\mathrm{B}}\mu_2^0)^{1/2},$$
$$Y^{\beta}(j)=[(C_{\mathrm{A}}C_{\mathrm{B}}\mu_2^0+C_{\mathrm{B}}^2t_j^2)-(C_{\mathrm{B}}t_j)^2]^{1/2}=(C_{\mathrm{A}}C_{\mathrm{B}}\mu_2^0)^{1/2}. \qquad \text{(III.40)}$$

We should note that for the separated bands and for the persistence case the optical properties are derived in terms of a power series in Δ^{-1}. These results [Eqs. (III.38)–(III.40)] can be safely applied for the case of separated bands. On the other hand, in the persistence case these results are of somewhat limited applicability. The intensity ratios (III.38) are expected to be reasonably good, while Eq. (III.40′) for the energy levels can be considered only as an interpolation formula.

In the amalgamation limit exact results can be easily obtained for the lower moments of the spectral density. The characteristics of the σ_D intensity distributions are readily obtained from Eq. (III.16) and reveal the following simple features:

(b1) The areas of each "absorption band" (for a given j value) are equal to the integrated intensities of the corresponding Davydov component in the pure crystal

$$A(j)=N_0(j)/|m(j)|^2=1. \qquad \text{(III.41)}$$

(b2) The center of gravity of each intensity distribution corresponds to the position of the Davydov component in the virtual crystal, being thus linear in concentration:

$$E_c(j)=C_{\mathrm{A}}(\Delta\epsilon_{\mathrm{A}}^{f}+D^{f})+C_{\mathrm{B}}(\Delta\epsilon_{\mathrm{B}}^{f}+D^{f})+t_j. \qquad \text{(III.42)}$$

(b3) The "width" of each intensity distribution is independent of the excitation branch and is determined by the perturbation strength Δ:

$$Y(j)=|\Delta|(C_{\mathrm{A}}C_{\mathrm{B}})^{1/2}. \qquad \text{(III.43)}$$

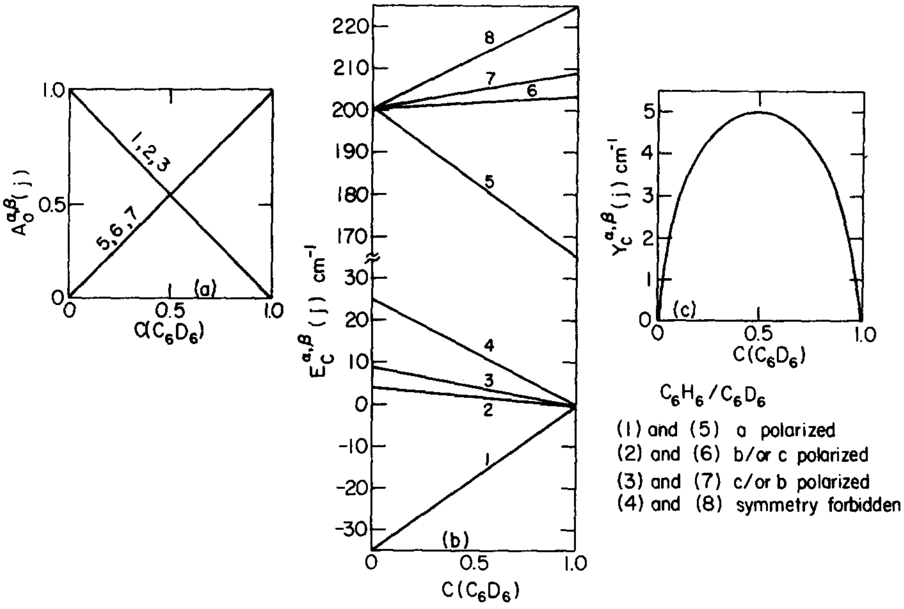

FIG. 2. Relative intensities (a), centers of gravity of the Davydov components (b), and line broadening (c) in C_6H_6/C_6D_6 mixed crystals. This situation corresponds to the separated bands case.

To demonstrate the usefulness of these results we have performed simple calculations for the intensity distribution in the lowest singlet state of isotopically mixed crystals of naphthalene and of benzene. We have considered the following representative cases:

(1) C_6H_6/C_6D_6, which corresponds to the separated band limit. For this system[7,12,42] $|\Delta| = 200$ cm^{-1} and $\mu_2^0 = 110$ cm^{-2}. The positions of the three allowed Davydov components are according to Colson[42]: $t_1 = -35$ cm^{-1}; $t_2 = +4$ cm^{-1}; $t_3 = +9$ cm^{-1} while the forbidden component is located at $t_4 = +25$ cm^{-1}. The physical situation can be faithfully accounted for by Eqs. (III.38)–(III.40). Eight intensity distributions are obtained, while six of these transitions are allowed. The results presented in Fig. 2 demonstrate the behavior of the system in the separated bands case limit when $\Delta \gg \mu_2^0$. In this limit the deviations of the relative intensities of the absorption bands from unity is small, the centers of gravity exhibit a linear concentration dependence, while the bandwidths just depend on $(C_AC_B)^{1/2}$. This situation corresponds to a good approximation to two independent subbands where molecules of one type contribute to each subband. It should be noted, however, that even in this case the effects of "impurity scattering" on the broadening of the optical absorption lines is appreciable. As is evident from Fig. 2, the *b* and *c* polarized components in the mixed crystal will not be resolved.

(2) $C_{10}H_8/C_{10}D_8$, which corresponds to the persistence case. The pertinent data are[7,12,13]

$$|\Delta| = 115 \text{ cm}^{-1}; \qquad \mu_2^0 = 1410 \text{ cm}^{-1}$$

and the positions of the two Davydov components[1,2,11] are:

$$t_1 = -78 \text{ cm}^{-1}; \qquad t_2 = +78 \text{ cm}^{-1}.$$

The results for this system are displayed in Fig. 3. The integrated relative intensities reproduce faithfully the results of the approximate intensity calculations reported by us.[23] The intensity of the higher-energy ac component diminishes with increasing concentration and this may be the reason that this weak transition was not detected. The deviation of the relative intensities from unity demonstrates the fact that in the persistence case each of the subbands cannot be associated just with molecules of one type.

A rough idea concerning the location of the four Davydov components is the mixed crystal we have made use of, Eq. (III.39′), which is only approximate for this case.

The centers of gravity of the intensity distributions are in qualitative agreement with the experimental results of Sheka[27] [reproduced in Fig. 3(b)] for the maxima of the polarized absorption maxima in this system. A quantitative comparison with these photographic data cannot be made as the concentration of Sheka's mixed crystals was not determined but rather inferred on the basis of the Broude–Rashba[25] approximate scheme. Furthermore, the general theory just yields an approximate value for the center of gravity and not the maximum of the absorption band.

Finally the widths of the form absorption components reveal a typical $(C_AC_B)^{1/2}$ behavior as demonstrated in Fig. 3. This broadening of the bands with increasing concentration reflects again some quantitative consequences of impurity scattering and its effects on the optical linewidths.

(3) $C_{10}H_8/C_{10}H_7D$ corresponds to the amalgamation limit. For this system

$$|\Delta| = 21 \text{ cm}^{-1}; \qquad \mu_2^0 = 1410 \text{ cm}^{-1};$$

$$t_1 = -78 \text{ cm}^{-1}; \qquad t_2 = +78 \text{ cm}^{-1}.$$

The features of the two polarized intensity distributions are summarized in Fig. 4.

The results obtained herein are gratifying but incomplete because of the following reasons: (a) exact results cannot be obtained for the persistence case; (b) these data do not provide any information concerning the actual shape of the absorption bands which may "come in such a questionable shape."[43] For this purpose we have to start introducing some approximations.

IV. LOCAL APPROXIMATION FOR THE SELF-ENERGY

A feasible approximation based on physical intuition involves the ansatz.

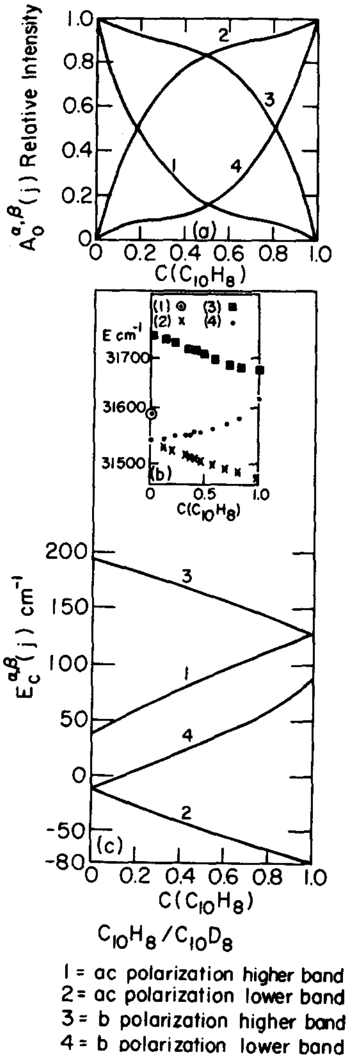

FIG. 3. Relative intensities (a), experimental data[27] for the location of the Davydov components (b), and theoretical data for the centers of gravity of the Davydov components (c), for $C_{10}H_8/C_{10}D_8$ mixed crystals. The curves in (3c) were calculated by the interpolation formula (III.39′).

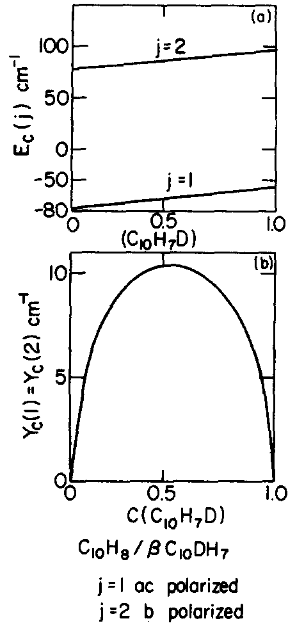

FIG. 4. Center of gravity of the two Davydov components (a) and line broadening (b) in $C_{10}H_8/\alpha$-$C_{10}DH_7$ mixed crystals which correspond to the amalgamation limit.

Assumption (H) The self-energy operator in Eq. (II.14) is assumed to be local in the localized excitation representation.[31,33]

Equation (II.16) will be now replaced by

$$\sigma_{n\alpha m\beta}(z)\equiv\langle n\alpha\,|\,\hat{\Sigma}(z)\,|\,n\alpha\rangle\delta_{nm}\delta_{\alpha\beta}\equiv\sigma_{n\alpha}(z)\delta_{nm}\delta_{\alpha\beta} \qquad \text{(IV.1)}$$

or, alternatively, using the superposition (II.14′) we set

$$\hat{\Sigma}_{n\alpha}=|\,n\alpha\rangle\sigma_{n\alpha}(z)\langle n\alpha\,|. \qquad \text{(IV.1′)}$$

Since $\hat{\Sigma}$ is invariant under crystal space group operations, we can set $\sigma_{n\alpha}(z)\equiv\sigma_\alpha(z)$ for all n. Equation (II.19) is greatly simplified, being just

$$l_{\alpha\beta}(z,\,\mathbf{k})=\sigma_\alpha(z)\delta_{\alpha\beta}, \qquad \text{(IV.2)}$$

and the matrix element of $\hat{\Sigma}$ in the $|\,\mathbf{k}j\rangle$ representation [Eq. (II.18)] is reduced to the form

$$\langle\mathbf{k}j\,|\,\hat{\Sigma}(z)\,|\,\mathbf{k}'j'\rangle=\delta_{\mathbf{k}\mathbf{k}'}\sum_{\alpha}B_{\alpha j}^{*}(\mathbf{k})B_{\alpha j'}(\mathbf{k})\sigma_\alpha(z). \qquad \text{(IV.3)}$$

If the molecules in the unit cell are crystallographically equivalent and can be mapped one to another by the factor group operations, the matrix elements $\sigma_\alpha(z)\equiv\sigma(z)$ are independent of the site index α. From now on we shall limit ourselves to this situation. The orthogonality of the $|\,\mathbf{k}j\rangle$ basis set now implies

$$\langle\mathbf{k}j\,|\,\hat{\Sigma}(z)\,|\,\mathbf{k}'j'\rangle=\delta_{\mathbf{k}\mathbf{k}'}\delta_{jj'}\sigma(z). \qquad \text{(IV.4)}$$

Thus the local approximation to the self-energy combined with a mild symmetry restriction leads to a self-energy operator which is diagonal in the $|\,\mathbf{k}j\rangle$ representation. The general treatment of Sec. II can be now greatly simplified. The effective Hamiltonian is now

$$\langle\mathbf{k}j\,|\,H_{\text{eff}}\,|\,\mathbf{k}'j'\rangle=\delta_{\mathbf{k}\mathbf{k}'}\delta_{jj'}[\bar{\epsilon}+e_j(\mathbf{k})+\sigma(z)]. \qquad \text{(IV.5)}$$

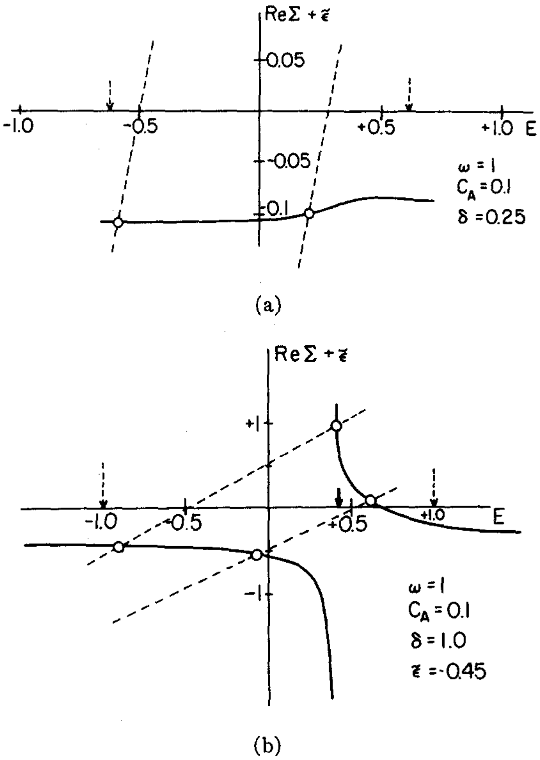

FIG. 5. A schematic representation of the location of the maxima of the Davydov components in a binary isotopically mixed crystal containing two molecules per unit cell. This figure displays the features of a graphical solution of Eq. (IV.10). The dashed arrows represent the limit of the allowed and almost allowed excited states. (a) corresponds to the amalgamation limit while (b) represents the persistence or separated bands cases. The heavy arrow in (b) represents the position of the pole of the self-energy. The intersections of the two straight lines with the curve $\mathrm{Re}\hat{\Sigma}+\bar{\epsilon}$ yield the location of the Davydov components in the mixed crystal.

The diagonal representation of the averaged Green's function takes the simple form (for the diagonal elements)

$$g(\mathbf{k},j,z)=1/[z-\bar{\epsilon}-e_j(\mathbf{k})-\sigma(z)], \qquad \text{(IV.6)}$$

while the off-diagonal elements (II.23) vanish. $g(\mathbf{k},j,z)$ is related to $g^0(\mathbf{k},j,z)$ by the Dyson equation

$$g(\mathbf{k},j,z)=g^0(\mathbf{k},j,z)+g^0(\mathbf{k},j,z)\sigma(z)g(\mathbf{k},j,z). \qquad \text{(IV.7)}$$

Finally the spectral density matrix (II.28) is diagonal, and its diagonal elements (i.e., the spectral density functions) can be conveniently displayed in terms of the "pseudo-Lorentzian" shape

$$S(\mathbf{k},j,E)=(\pi^{-1}) \times \frac{\mathrm{Im}\sigma(E-i0^+)}{[E-\bar{\epsilon}-e_j(\mathbf{k})-\mathrm{Re}\sigma(E-i0^+)]^2+[\mathrm{Im}\sigma(E-i0^+)]^2} \qquad \text{(IV.8)}$$

where we have separated the (complex) function $\sigma(E-i0^+)=\mathrm{Re}\sigma(E-i0^+)+i\,\mathrm{Im}\sigma(E-i0^+)$. The shape of the optical absorption bands is obtained in the form

$$I_j(E)=\left(\frac{|m(j)|^2}{\pi}\right) \times \frac{\mathrm{Im}\sigma(E-i0^+)}{[E-\bar{\epsilon}-t_j-\mathrm{Re}\sigma(E-i0^+)]^2+[\mathrm{Im}\sigma(E-i0^+)]^2}. \qquad \text{(IV.9)}$$

The broadening is determined by Imσ while the term Reσ can be considered as a level shift. This result provides us with further insight concerning the intensity distribution in absorption. Provided that $\mathrm{Im}\sigma(E-i0^+)$ is a relatively slowly varying function of E over the band region in the amalgamation case and over the region of each of the two subbands in the separated band and persistence cases, we can then assert that the peak of the distribution of intensity in the absorption bands will occur at the energies which satisfy the relation

$$E-\bar{\epsilon}-t_j-\mathrm{Re}\sigma(E-i0^+)=0; \qquad j=1\cdots\sigma_D. \qquad \text{(IV.10)}$$

This result is of interest as the behavior of Reσ determines the number and location of the absorption maxima. Using the moment expansion method it was demonstrated by Velicky *et al.*[31] that $g(\mathbf{k},j,z)$ is expected to vanish at $z=-\bar{\epsilon}$ for all $\mathbf{k}$ and j [see Eq. (III.20)], whereupon the self-energy in the local approximation takes the form [see (IV. 6)], in the vicinity of this point,

$$\begin{aligned}\sigma(z)&\approx z-\bar{\epsilon}-e_j(\mathbf{k})-[g(k,j,z)]^{-1}\\&=z-\bar{\epsilon}+e_j(\mathbf{k})+(C_AC_B\Delta^2-\mu_2^0)/(z+\bar{\epsilon})\end{aligned}$$

which has a pole at $z=-\bar{\epsilon}$. In the vicinity of $E=-\bar{\epsilon}$

$$\mathrm{Re}\sigma(E-i0^+)=[C_AC_B\Delta^2-\mu_2^0](E+\bar{\epsilon})^{-1}$$

so that the level shift diverges and changes sign at this point. Furthermore, when $E\rightarrow\infty$ we expect, of course, that $\mathrm{Re}\sigma\rightarrow E^{-1}$. On the other hand, in the amalgamation limit we expect that Reσ will be a slowly varying function of the energy throughout the whole band region decaying at large distances as E^{-1}. From these general considerations we can assert that:

(a) In the amalgamation limit Eq. (IV.10) is expected to exhibit σ_D solutions which correspond to the maxima of the σ_D differently polarized Davydov components in the mixed crystal. Thus in the amalgamation limit the number of the Davydov components in the mixed and in the pure crystal is equal. This result is not surprising as the amalgamation limit corresponds closely to the virtual crystal.

(b) In the separated bands and in the persistence case Eq. (IV.10) is expected to exhibit $2\sigma_D$ solution (σ_D within the region of each subband). Thus the number of Davydov components in the mixed crystal will be doubled relative to that of the pure crystal. The spectral distribution of intensity in these Davydov components was discussed in Sec. III.

In Fig. 5 we present the general features of the real part of the self-energy in the two cases discussed above with an application to a crystal characterized by two molecules per unit cell where the Davydov components in the pure crystal are located at the two band edges.

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

Following the work of Soven[33] and of Velicky *et al.*,[31] we shall now proceed to present the general expression for the self-energy based on a self-consistent approximation, which rests on multiple scattering theory. The effective Hamiltonian is considered as an unknown of the problem and one is seeking a self-consistent approximation based on the restriction that a single molecule (of type A or B) which scatters the electronic excitation should not produce on the average further scattering. Let us rewrite the crystal Hamiltonian

$$H=H_0+\Delta\sum_{n\alpha}\xi_{n\alpha} \tag{V.1}$$

and the (exact) effect Hamiltonian

$$H_{\mathrm{eff}}=H_0+\sum_{n\alpha}\hat{\Sigma}_{n\alpha}. \tag{V.2}$$

The generalized perturbation resulting from the deviations of the crystal from its average behavior is

$$V=H-H_{\mathrm{eff}}=\sum_{n\alpha}(\Delta\hat{\xi}_{n\alpha}-\hat{\Sigma}_{n\alpha})\equiv\sum_{n\alpha}v_{n\alpha}. \tag{V.3}$$

Excitation scattering due to the deviation of the mixed crystal configuration from its averaged behavior can be described by the total T matrix

$$T=V+V\langle G\rangle T. \tag{V.4}$$

The relation between $G(z)$ [Eq. (II.11)] and $\langle G(z)\rangle$ [Eq. (II.12)] is just given by the following version of the Dyson equation:

$$G(z)=\langle G(z)\rangle+\langle G(z)\rangle T\langle G(z)\rangle \tag{V.5}$$

which leads to the exact condition for neglecting molecule–molecule spatial correlations [Assumption (G), Sec. II]. This self-consistency condition implies that the spatial average of T vanishes, i.e.,

$$\langle T(z)\rangle=0, \tag{V.6}$$

whereupon Eq. (V.6) can be considered as an exact definition of $\langle G(z)\rangle$. Now the T matrix can be expanded in terms of "molecular" $t_{n\alpha}$ matrixes associated with each site[44,45]

$$t_{n\alpha}=v_{n\alpha}+v_{n\alpha}\langle G\rangle t_{n\alpha} \tag{V.7}$$

so that

$$T=\sum_{n\alpha}t_{n\alpha}+\sum_{n\alpha}t_{n\alpha}\langle G\rangle\sum_{m\beta\neq n\alpha}t_{m\beta}+\cdots. \tag{V.8}$$

The second- and higher-order terms in Eq. (V.8) represent multiple scattering effects. The CPA rests on the following assumption.[31,33]

Assumption (I) Multiple scattering contributions to the self-consistency condition (V.6) are negligible.

Thus Eq. (V.6) is replaced by the approximate relation

$$\langle t_{n\alpha}(z)\rangle=0 \qquad \text{for all } n\alpha. \tag{V.9}$$

Making use of Eqs. (V.3) and (V.7) we can write the operators

$$t_{n\alpha}(z)=[1-v_{n\alpha}(z)\langle G(z)\rangle]^{-1}v_{n\alpha}(z), \tag{V.10}$$

$$v_{n\alpha}(z)=\Delta\xi_{n\alpha}\mid n\alpha\rangle\langle n\alpha\mid-\hat{\Sigma}_{n\alpha}(z). \tag{V.11}$$

The spatially averaged $\langle t_{n\alpha}\rangle$ is

$$\langle t_{n\alpha}\rangle=C_{\mathrm{A}}t_{\mathrm{A}}+C_{\mathrm{B}}t_{\mathrm{B}}, \tag{V.12}$$

where t_{A} and t_{B} correspond to the t matrices for an impurity of type A and B, respectively, located on the lattice site $n\alpha$. Making use of the definition of $\xi_{n\alpha}$ [see Eq. (II.4b)] we immediately have

$$\begin{aligned}t_{\mathrm{A}}&=(1-v_{\mathrm{A}}\langle G\rangle)^{-1}v_{\mathrm{A}},\\ t_{\mathrm{B}}&=(1-v_{\mathrm{B}}\langle G\rangle)^{-1}v_{\mathrm{B}},\end{aligned} \tag{V.13}$$

where

$$\begin{aligned}v_{\mathrm{A}}&=\Delta C_{\mathrm{B}}\mid n\alpha\rangle\langle n\alpha\mid-\hat{\Sigma}_{n\alpha},\\ v_{\mathrm{B}}&=-\Delta C_{\mathrm{A}}\mid n\alpha\rangle\langle n\alpha\mid-\hat{\Sigma}_{n\alpha}.\end{aligned} \tag{V.14}$$

Equations (V.9) and (V.12) now imply

$$C_{\mathrm{A}}(1-v_{\mathrm{A}}\langle G\rangle)^{-1}v_{\mathrm{A}}+C_{\mathrm{B}}(1-v_{\mathrm{B}}\langle G\rangle)^{-1}v_{\mathrm{B}}=0 \tag{V.15}$$

which leads to the Soven equation[33]

$$C_{\mathrm{A}}v_{\mathrm{A}}+C_{\mathrm{B}}v_{\mathrm{B}}=v_{\mathrm{A}}\langle G\rangle v_{\mathrm{B}}, \tag{V.16}$$

or alternatively one can write the operator equation:

$$\hat{\Sigma}_{n\alpha}=(\Delta C_{\mathrm{B}}\mid n\alpha\rangle\langle n\alpha\mid-\hat{\Sigma}_{n\alpha})\langle G(z)\rangle\times(\Delta C_{\mathrm{A}}\mid n\alpha\rangle\langle n\alpha\mid+\hat{\Sigma}_{n\alpha}). \tag{V.17}$$

This result is somewhat more general than that obtained previously by Velicky *et al.*[31] However, in order to obtain a manageable expression we have to invoke again the local approximation for the self-energy (see Sec. IV) so that

$$\hat{\Sigma}_{n\alpha}=\sigma_\alpha(z)\mid n\alpha\rangle\langle n\alpha\mid, \tag{V.18}$$

whereupon

$$\sigma_\alpha(z)=[\Delta C_{\mathrm{B}}-\sigma_\alpha(z)]\langle n\alpha\mid\langle G(z)\rangle\mid n\alpha\rangle[\Delta C_{\mathrm{A}}+\sigma_\alpha(z)]. \tag{V.19}$$

For a crystal characterized by crystallographically equivalent molecules in the unit cell the matrix element of $\langle G\rangle$ in the localized approximation can be displayed in the form

$$\begin{aligned}\langle n\alpha|\langle G\rangle|n\alpha\rangle &= (1/N\sigma_D)\sum_{\mathbf{k}}\sum_{j}\{|B_{\alpha j}(\mathbf{k})|^2/[z-\tilde{\epsilon}-e_j(\mathbf{k})-\sigma(z)]\}\\ &= (1/N\sigma_D)\sum_{\mathbf{k}}\sum_{j}[z-\tilde{\epsilon}-e_j(\mathbf{k})-\sigma(z)]^{-1}\\ &= \int\{\rho^0(E')dE'/[z-\sigma(z)-E']\}=f^0[z-\tilde{\epsilon}-0(z)].\end{aligned} \tag{V.20}$$

Furthermore, in this case $\sigma_\alpha(z)=\sigma(z)$. This leads to the equation of Velicky *et al.*[31]

$$\sigma(z)=[\Delta C_{\mathrm{B}}-\sigma(z)]f^0[z-\tilde{\epsilon}-\sigma(z)][\Delta C_{\mathrm{A}}+\sigma(z)]. \tag{V.21}$$

This last result can be recasted in the form

$$\begin{aligned}&f^0[z-\tilde{\epsilon}-\sigma(z)]\\ &=\sigma(z)/\{C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2-\sigma(z)\Delta(C_{\mathrm{A}}-C_{\mathrm{B}})-[\sigma(z)]^2\}\end{aligned} \tag{V.21$'$}$$

which is equivalent[31] to the Toyozawa–Onodera result[30] previously applied by Hong and Robinson[22] and by us[23] for excited states of isotopically mixed organic solids. In this approximation all the physical information can be derived from the density of states function of the pure crystal, without invoking any approximations for the nature (short or long range) of the intermolecular interactions.

It seems to us that it was useful to derive the CPA results for a multiply branched exciton band and to discuss carefully the approximations involved in this somewhat extended treatment. We shall now consider some limiting cases within the framework of the CPA approximation with emphasis on the optical properties:

(a) *Low concentration of one component*: As it is well known,[30,33,22,23] the CPA reduces to the Koster Slater[14] single impurity equation. It will be, however, useful to consider in this context the intensity ratios in somewhat greater detail than done before. In the low-concentration limit $C_{\mathrm{A}}\rightarrow 0$, $C_{\mathrm{B}}\rightarrow 1$, and $\sigma(z)\rightarrow 0$. Retaining terms up to the order C_{A} in Eq. (V.21) leads to the equation first derived by Edwards.[44]

$$\sigma(z)=C_{\mathrm{A}}\Delta^2f^0(z-\tilde{\epsilon})/[1-\Delta f^0(z-\tilde{\epsilon})]. \tag{V.22}$$

The transition dipole strength takes the form given by (IV.9). If f^0 is real (corresponding to a state outside the band), then $\mathrm{Im}\sigma=0$ and we get

$$I_j(E)=|m(j)|^2\delta\{E-\tilde{\epsilon}-d_j-[C_{\mathrm{A}}\Delta^2f^0/(1-\Delta f^0)]\}. \tag{V.23}$$

The position of the (narrow) line is obtained from the Koster Slater relation $1-\Delta f^0(E_r)=0$, while the intensity is given by the Rasba equation[8,9]

$$I_j(E_r)=|m(j)|^2C_{\mathrm{A}}/(E_r-\tilde{\epsilon}-d_j)^2. \tag{V.24}$$

(b) *The virtual crystal*: When $\Delta\rightarrow 0$ $\sigma(z)\rightarrow 0$; first-order correction terms to the self-energy take the form of the weak coupling equation[44,45]

$$\sigma(z)=C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2f^0(z-\tilde{\epsilon}). \tag{V.25}$$

This result is useful in the amalgamation limit. A reasonable approximation for the line shapes of the σ_D Davydov components are obtained from Eq. (IV.9). Let us split σ into its real and imaginary parts:

$$\begin{aligned}\mathrm{Re}\sigma(E-i0^+)&=C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2\,\mathrm{Re}f^0(E-\tilde{\epsilon}),\\ \mathrm{Im}\sigma(E-i0^+)&=C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2\pi\rho^0(E-\tilde{\epsilon}),\end{aligned} \tag{V.26}$$

where ρ^0 is the density of states of the pure crystal while $\mathrm{Re}f^0$ corresponds to the level shift in the single impurity Koster Slater scheme.[14] We thus obtain from (IV.9)

$$I_j(E)=|m(j)|^2\{\rho^0(E-\tilde{\epsilon})C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2/[E-\tilde{\epsilon}-t_j-C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2\,\mathrm{Re}f^0(E-\tilde{\epsilon})]^2+[\pi\rho^0(E-\tilde{\epsilon})C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2]^2\}. \tag{V.27}$$

The dependence of the linewidth on the product $C_{\mathrm{A}}C_{\mathrm{B}}$ is identical with the functional form of the second moment in the amalgamation case (see Sec. III).

(c) *The atomic limit*: When $\mu_2{}^0\rightarrow 0$ we expect that $f^0[z-\tilde{\epsilon}-\sigma(z)]\rightarrow 1/[z-\tilde{\epsilon}-\sigma(z)]$ and Eq. (V.20) to first order in $\sigma(z)$ reduces to the form

$$\sigma(z)=C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2/[z-\tilde{\epsilon}+\Delta(C_{\mathrm{A}}-C_{\mathrm{B}})]. \tag{V.28}$$

This limiting equation was derived previously by Hubbard,[46] Edwards,[44] and by Velicky *et al.*[31] It should be noted that $\mathrm{Im}\sigma(E-i0^+)=0$ in this limit, which is reasonable as the unperturbed band corresponds to a delta function. The real part of the self-energy is

$$\mathrm{Re}\sigma(E)=C_{\mathrm{A}}C_{\mathrm{B}}\Delta^2/[E-\tilde{\epsilon}+\Delta(C_{\mathrm{A}}-C_{\mathrm{B}})], \tag{V.28$'$}$$

while the optical properties are now obtained from Eq. (IV.9)

$$I_j(E)=|m(j)|^2\delta[E-\tilde{\epsilon}-t_j-\mathrm{Re}\sigma(E)]. \tag{V.29}$$

Let us define an auxiliary function

$$R(E)=E-\tilde{\epsilon}-\mathrm{Re}\sigma(E), \tag{V.30a}$$

whereupon

$$[R(E)]^{-1}=[C_{\mathrm{A}}/(E-\epsilon_{\mathrm{A}})]+[C_{\mathrm{B}}/(E-\epsilon_{\mathrm{B}})]. \tag{V.30b}$$

We develop the delta function in (V.29) in the conventional manner which results in

$$I_j(E)=|m(j)|^2\sum_{l}\frac{1}{|\partial R(E)/\partial E|_{E=E_l}}\delta(E-\epsilon_l), \tag{V.31}$$

where the roots E_l are determined from the equation

$$R(E_l)=t_j \tag{V.32}$$

or

$$[R(E_l)]^{-1}=C_A/(E-\epsilon_A)+C_B/(E-\epsilon_B)=t_j^{-1}. \quad (V.33)$$

Equation (V.33) is expected to yield two solutions for each j branch as the atomic limit corresponds obviously to the case of completely separated bands.

The intensities of the transitions are given by

$$I_j(E_l)=|m(j)|^2\left[\left(\sum_{i=A,B}\frac{C_i}{E\rho-\epsilon_i}\right)^2\bigg/\sum_{i=A,B}\frac{C_i}{(E\rho-\epsilon_i)^2}\right]. \quad (V.34)$$

The results just derived for the atomic limit are identical with the equations obtained by Broude and Rashba[25] on the basis of the "excitation democracy" hypothesis. Thus the Broude–Rashba scheme corresponds to the extreme case when the perturbation strength Δ greatly exceeds the pure crystal exciton bandwidth. Thus for most cases of physical interest this scheme is not applicable.

VI. DISCUSSION

In this paper an attempt was made to present a systematic study of the excited electronic states of isotopically mixed crystals with an emphasis on the optical properties. The mathematical techniques based on the time-independent Green's function method are completely general and very physical in nature, providing a powerful tool for the study of the variety of problems related to the electronic states of disordered systems. As approximate schemes using the Green's function methods have to be handled rather carefully, we hope that the present treatment minimizes the number of uncontrolled approximations and defines clearly the range of validity of the approxischemes. When these methods were applied to the excited electronic states of a simple mixed crystal the following information was obtained:

(a) The properties of an effective Hamiltonian for excited states of a mixed crystal characterized by a multiply branched exciton band were considered.

(b) Information on intensity distribution in optical absorption can be obtained from the moments of the spectral density function for a randomly substituted heavily doped crystal. The moments of the absorption bands can be expressed in terms of the positions of the Davydov components and the moments of the density of states in the pure crystal.

(c) In the amalgamation limit the configurationally averaged isotopically mixed binary crystal is characterized by σ_D (polarized) intensity distributions while in the persistence and separated band cases $2\sigma_D$ different (polarized) intensity distributions are observed.

(d) Invoking the local approximation for the self-energy operator it can be demonstrated that for any general form of the pure crystal exciton band the self-energy can be specified by σ_D complex functions. For a crystal characterized by a unit cell containing crystallographically equivalent molecules a single complex function can be used to describe the self-energy in the local approximation.

(e) General expressions for the line shapes and for the Davydov components can be obtained in the local approximation.

(f) The CPA approximation was extended for a multiply branched exciton band.

(g) The Soven–Velicky–Kirkpatrick–Ehrenreich–Onodera–Toyozawa equation for the self-energy in the local approximation is applicable for a multiply branched excited state in a crystal where the molecules in the unit cell are crystallographically equivalent.

(h) The optical properties of the virtual crystal can be applied to obtain the line shapes of the σ_D Davydov components in the amalgamation limit.

(i) The atomic limit, which exhibits the extreme case of separated bands, reduces to the Rashba Broude formula.

(j) Davydov splitting and the appearance of polarized absorption bands will be exhibited by a substitutionally disordered molecular crystal described by a Hamiltonian which is characterized by a random diagonal part and translationally invariant off-diagonal part. The number of the Davydov components is determined by the perturbation strength.

The coherent potential approximation is very satisfactory in view of the following features[30–34,22,23] (a) symmetry in the concentrations C_A and C_B of the two components; (b) faithful reproduction of various limiting cases such as the low concentration, the virtual crystal, and the atomic limits; (c) the asymptotic expansion of H_{eff} in powers of z^{-1} up to z^{-5} is identical with the exact result; (d) the CPA self-energy for $C_AC_B\Delta^2>\mu_2^0$ reveals a pole at $z=-\bar{\epsilon}$, whereupon in the persistence and split band limits $2\sigma_D$ Davydov components will result as in the exact treatment.

The major disadvantages of the scheme used in this work are:

(a) The "coarse graining" procedure which focuses attention on the configurationally averaged crystal neglects important clustering effects. "Fluctuations" of the Hamiltonian are averaged out. Such fluctuation may lead to localization near the band edges and to formation of localized states in the band gap.[16,17]

(b) The effects of multiple scattering effects were neglected. These may be considered[34] by taking the higher terms in Eq. (V.8).

We have performed[47] detailed numerical calculations based on the CPA for a number of model systems. These calculations demonstrate the general features of the density of states in substitutionally disordered organic crystals, the erosion of Van Hove singularities, and the intensity distribution in optical absorption. The general study was also extended to handle tertiary mixed crystals which are of some experimental interest.[27] The most interesting problems which deserve further theoretical study are the following:

(a) The localization problem with an attempt to provide criteria for excitation localization.

(b) The "spreading" of the bands near and within the gap in the persistence and the separated band cases. This effect may contribute to the experimental failure[27] to observe the fourth Davydov component in the $C_{10}H_8/C_{10}D_8$ system.

(c) Energy transfer phenomena and the role of impurity scattering on excitation transfer in heavily doped crystals.

ACKNOWLEDGMENTS

Partial support of this research was provided by the U.S. Air Force Office of Scientific Research and by the Advanced Research Projects Agency at the University of Chicago.

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