

Theory of the Excitation Spectrum of Nondiagonal Disordered Systems

A. I. ONIPKO

Academy of Sciences of the Ukrainian S.S.R., Institute for Theoretical Physics, Kiev, U.S.S.R.

Abstract

The spectrum of a two-component solid solution with a nondiagonal disorder is studied in the framework of the average T matrix method. For a one-dimensional system in the nearest-neighbor approximation the criteria for the system parameters are given such that at an in-band resonance, one or two "impurity bands" may be realized, and the corresponding model calculation is performed. In the single-site approximation an expression of the self-energy part of a nondiagonal disordered system Green's function is found taking into account multiple occupancy corrections. The possibility of using it to describe a disordered system excitation spectrum and the calculation of state density moments are discussed.

0. Introduction

Two-component solid solutions consisting of two subsystems* randomly distributed in the points of a regular spatial structure belong to systems of great physical interest and have been the subject of much theoretical and experimental investigation.

The application of approximations, based on a partial summation of a series of the Green's function, to the above systems proved to be very useful in describing the phonon [1-3] and electron [4, 5] spectra of binary alloys, the exciton spectra of mixed ionic [6] and molecular [7-9] crystals in studying structural transitions in the quasi-one-dimensional systems [10], and other related problems. We also note a certain correspondence of the model under consideration to some macromolecules, for example, nucleonic acids [11] whose physical properties are essentially defined by a random sequence of Watson-Crick pairs of bases: $\cdots ABBABBBBAAAB \cdots$ (A, B are the different pairs of bases).

The theory of disordered systems is developed in detail for the case of diagonal disorder, i.e., when the component molecules differ in their individual properties (mass or excitation energy) and the integrals of intermolecular interactions are supposed to be independent of the type of molecules (see reviews, Refs. 12 and 13). The study of a nondiagonal disorder is a more complex mathematical problem, and the methods developed here are actually valid only under restrictions on a nondiagonal perturbation which allow one to reduce a formal solution of the problem to the case of diagonal disorder [14-16].

The present paper deals with the model of a disordered system taking into account the dependence of the excitation energy as well as the integrals of

* In what follows we shall call the subsystem a molecule, implying that it may be an atom as well as a certain group of atoms or molecules.

excitation resonance transfer between molecules on the type of the component molecules (nondiagonal disorder).

An expression for the self-energy operator in the average T matrix approximation is found using the diagrammatic technique (Sec. 2)

$$\langle \mathbf{G} \rangle = \mathbf{G}^0 + \mathbf{G}^0 \mathbf{T} \mathbf{G}^0 + \mathbf{G}^0 \mathbf{T} \mathbf{G}^0 \mathbf{T} \mathbf{G}^0 + \dots \quad (1)$$

where $\langle \mathbf{G} \rangle$ is the averaged Green's function of a disordered system, \mathbf{G}^0 is its zero approximation, characterized by translational invariance, \mathbf{T} is an average T matrix of a single defect.

This approximation is then used to analyze and calculate the excitonic state density of a one-dimensional chain with nondiagonal disorder (Sec. 3).

A more correct approximation of the Green's function may be obtained by taking into account multiple occupancy corrections in the expansion yielding Eq. (1) [13]. Different methods of calculating these corrections have been developed for diagonal disordered systems (see, for example, Refs. 17 and 18). Their inclusion results in an interpolation formula for $\langle \mathbf{G} \rangle$, which satisfactorily describes the one-particle excitation spectrum at arbitrary concentrations of the components [3].

The possibility of the approach mentioned above is investigated in connection with nondiagonal disordered systems (Sec. 4). The expression for the Green's function self-energy part is derived taking into account multiple occupancy corrections. The expression obtained takes the known form if the nondiagonal perturbation is put equal to zero. But an analysis of the interpolation formula leads us to the conclusion that the single-site approximation cannot give an appropriate interpolation of the Green's function of a nondiagonal disordered system. Moreover, for some values of the system parameters this approximation leads to meaningless physical results (like spurious spikes in the state density and so on) even if the concentration of one of the components is small. In this connection an attempt to improve the approximation based on Eq. (1) by including some cluster effect corrections is made and the calculation of the state density and spectral density moments of a nondiagonal disordered system is discussed (Sec. 5).

1. Hamiltonian Operator and Green's Function of the System

Assuming that the Gautler-London approximation is valid the Hamiltonian operator of one-particle excitations in the occupation number representation has the following form

$$H = \sum_{\mathbf{R}, \mathbf{R}'} [\varepsilon_{\mathbf{R}} \delta_{\mathbf{R}\mathbf{R}'} + M_{\mathbf{R}\mathbf{R}'} (1 - \delta_{\mathbf{R}\mathbf{R}'})] B_{\mathbf{R}}^+ B_{\mathbf{R}'} \quad (2)$$

where $B_{\mathbf{R}}^+$, $B_{\mathbf{R}}$ are the creation and annihilation operators of the excitation on the \mathbf{R} th site, $\varepsilon_{\mathbf{R}}$ is the molecule excitation energy in the site with coordinate \mathbf{R} , $M_{\mathbf{R}\mathbf{R}'}$ are the matrix elements of the resonance energy transfer of the excitation from the molecule \mathbf{R} to \mathbf{R}' .

The results obtained below do not depend on the commutation properties of the operators $B_{\mathbf{R}}^+$, $B_{\mathbf{R}}$ and therefore refer equally (except the model calculation) to the phonon, electron, and exciton branches of excitations.

For the two-component system under consideration we have $\epsilon_{\mathbf{R}} = \epsilon^A$ or $\epsilon_{\mathbf{R}} = \epsilon^B$ depending on whether the R th site is occupied by a molecule of type A or B . The energy of the excitation resonance transfer between A type molecules is equal to $M_{\mathbf{R}\mathbf{R}}^A$, between B type molecules it is equal to $M_{\mathbf{R}\mathbf{R}}^B$, and between molecules of different components it is equal to $M_{\mathbf{R}\mathbf{R}}^{AB}$.

The distribution of molecules A and B on the sites of a regular lattice is assumed to be random, therefore the operator (2) has no translational invariance. Using the numbers $\nu_{\mathbf{R}}$ equal to 1 if the site with \mathbf{R} coordinates is occupied by molecule B , or 0 if this site is occupied by A molecule, we represent (2) in the form

$$H = H^A + W \tag{3}$$

where the translationally invariant part of the Hamiltonian H^A coincides with the energy operator of a system constructed of A molecules and the perturbation operator is equal to

$$W = \sum_{\mathbf{R}, \mathbf{R}'} W_{\mathbf{R}\mathbf{R}'} B_{\mathbf{R}}^+ B_{\mathbf{R}'} \tag{4}$$

where

$$W_{\mathbf{R}\mathbf{R}'} = V_{\mathbf{R}\mathbf{R}'} (\nu_{\mathbf{R}} + \nu_{\mathbf{R}'}) + v_{\mathbf{R}\mathbf{R}'} \nu_{\mathbf{R}} \nu_{\mathbf{R}'} \tag{5}$$

$$V_{\mathbf{R}\mathbf{R}'} = \frac{1}{2} \Delta \delta_{\mathbf{R}\mathbf{R}'} + (M_{\mathbf{R}\mathbf{R}'}^{AB} - M_{\mathbf{R}\mathbf{R}'}^A) (1 - \delta_{\mathbf{R}\mathbf{R}'}), \quad \Delta = \epsilon^B - \epsilon^A \tag{6}$$

$$v_{\mathbf{R}\mathbf{R}'} = (M_{\mathbf{R}\mathbf{R}'}^A + M_{\mathbf{R}\mathbf{R}'}^B - 2M_{\mathbf{R}\mathbf{R}'}^{AB}) (1 - \delta_{\mathbf{R}\mathbf{R}'}) \tag{7}$$

The properties of a binary disordered system connected with one-particle excitations are defined by the configurationally averaged Green's function

$$\langle \mathbf{G} \rangle = \mathbf{G}^A + \mathbf{G}^A \langle \mathbf{W} \mathbf{G} \rangle \tag{8}$$

where

$$\mathbf{G}^A = [(E + i0)\mathbf{I} - \mathbf{H}^A]^{-1} \tag{9}$$

E is the energy of the system under consideration, \mathbf{I} is the unit operator, the angular brackets denote the configurational averaging. Since the distribution of molecules A and B in the lattice sites is assumed to be random each configuration is taken with equal weight

$$\langle \nu_{\mathbf{R}} \rangle = c_B, \quad 1 - c_B = c_A \tag{10}$$

where c_B is the relative concentration of B molecules in the binary mixture.

The relation (8) may be represented in an equivalent form

$$\langle \mathbf{G} \rangle = [\mathbf{E}\mathbf{I} - \mathbf{H}_{\text{eff}}(E)]^{-1}, \quad \mathbf{H}_{\text{eff}}(E) = \mathbf{H}^A + \underline{\Sigma}(E) \tag{11}$$

after the self-energy operator

$$\Sigma = \mathbf{G}^A{}^{-1} - \langle \mathbf{G} \rangle^{-1} \tag{12}$$

is defined.

2. Diagram Technique: One-Vertex Approximation

The problem of defining the self-energy of elementary excitations of the system with the effective Hamiltonian (11) is connected with the summation over the series

$$\langle \mathbf{G} \rangle = \mathbf{G}^A + \mathbf{G}^A \langle \mathbf{W} \rangle \mathbf{G}^A + \mathbf{G}^A \langle \mathbf{W} \mathbf{G}^A \mathbf{W} \rangle \mathbf{G}^A + \dots \tag{13}$$

The matrix elements of the Green's function represented by Eq. (13) may be expressed diagrammatically (Fig. 1) denoting $\langle \mathbf{G}_{RR'} \rangle$ and $\langle \mathbf{G}_{RR'}^A \rangle$ by solid thick and

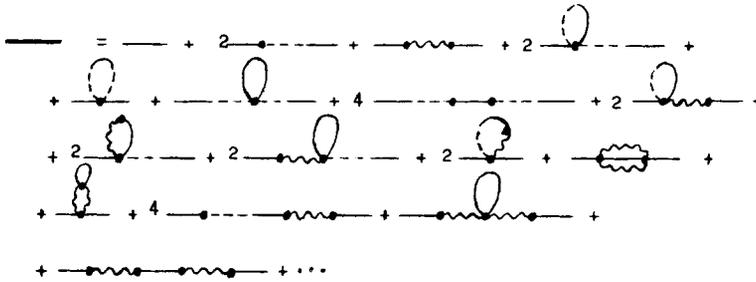


Figure 1. Diagram representation of an exact expansion of matrix elements of the Green's function.

solid thin lines, the matrix elements $V_{RR'}$, $v_{RR'}$ by dotted and wavy lines, respectively, and assuming the summation over the points of the convergence lines.

In Figure 1 the series is written in such a way that the terms containing multipliers ν_R with coinciding indices (loop diagrams) are explicitly taken into account. Therefore under summation in terms of the series with two and more vertices (thick points) the terms in which any indices of vertices coincide should be omitted. Each vertex corresponds to the multiplier $\langle \nu_R^n \rangle = c_B$ where n is equal to the number of the interaction lines convergent in this vertex. Thus, the diagram order with respect to concentration is equal to the number of vertices.

Let us calculate the contribution to the Green's function from one-vertex diagrams. In this approximation the expansion of the Green's function after its terms are regrouped in a certain way may be represented in the form given in Figure 2.

The first term in Figure 2(a) describes the propagation of an undisturbed excitation wave of the system with the Hamiltonian H^A . The corrections to the undisturbed Green's function, unlike an exact expansion, are taken into account

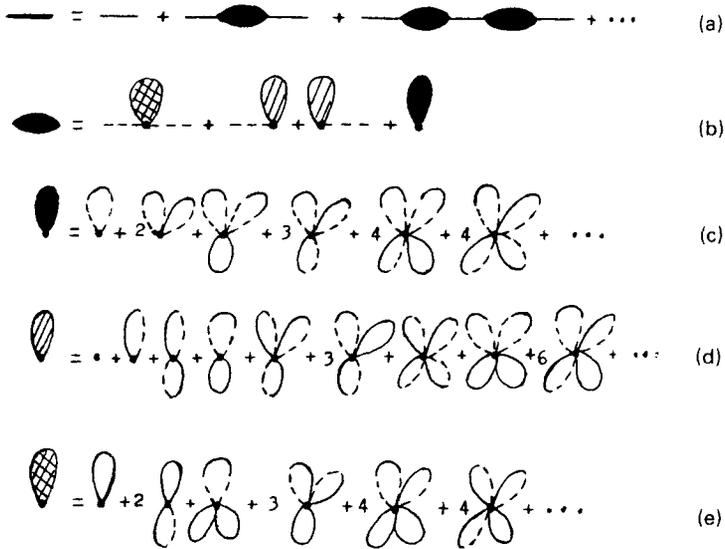


Figure 2. Series of the Green's function taking into account the total contribution of diagrams containing only one-vertex irreducible parts.

only relative to consecutive scatterings by single centers of B molecules. In this case the role of perturbation is played by a configurationally averaged T matrix of the single scattering center. Indeed, the analytical expression of the diagram [Fig. 2(b)] defining this matrix has the form

$$\begin{aligned}
 T_{\mathbf{R}\mathbf{R}'} = & c_B \delta_{\mathbf{R}\mathbf{R}'} Y_0 \sum_{i,j=0}^{\infty} X_0^i (Y_0 G_0^A)^j \left[\binom{2j+i}{i} + X_0 \binom{2j+i+1}{i} \right] \\
 & + 2c_B V_{\mathbf{R}\mathbf{R}'} \left\{ 1 + \sum_{i,j=0}^{\infty} X_0^i (Y_0 G_0^A)^j \left[X_0 \binom{2j+i}{i} + Y_0 G_0^A \binom{2j+i+1}{i} \right] \right\} \\
 & + c_B \sum_{\mathbf{R}''} V_{\mathbf{R}\mathbf{R}''} V_{\mathbf{R}''\mathbf{R}'} \sum_{i,j=0}^{\infty} X_0^i (Y_0 G_0^A)^j \left[\binom{2j+i}{i} + X_0 \binom{2j+i+1}{i} \right] \quad (14)
 \end{aligned}$$

$$\begin{aligned}
 X_{\mathbf{R}\mathbf{R}'} & \equiv \sum_{\mathbf{R}''} G_{\mathbf{R}\mathbf{R}''}^A V_{\mathbf{R}''\mathbf{R}'}, & Y_{\mathbf{R}\mathbf{R}'} & \equiv \sum_{\mathbf{R}'',\mathbf{R}'''} V_{\mathbf{R}\mathbf{R}''} G_{\mathbf{R}''\mathbf{R}'''}^A V_{\mathbf{R}'''\mathbf{R}'}, \\
 A_{\mathbf{R}\mathbf{R}} & \equiv A_0 & (\mathbf{A} = \mathbf{G}^A, \mathbf{X}, \mathbf{Y}) & \quad (15)
 \end{aligned}$$

where the coefficients of $\delta_{\mathbf{R}\mathbf{R}'}$, $2V_{\mathbf{R}\mathbf{R}'}$, $\sum_{\mathbf{R}''} V_{\mathbf{R}\mathbf{R}''} V_{\mathbf{R}''\mathbf{R}'}$ correspond to the diagrams (Figs. 2(c)–(e)). Reducing the obtained series by means of the generating function

$$(1-q)^{-i} = \sum_{j=0}^{\infty} \frac{(i+j-1)!}{j!(i-1)!} q^j, \quad \left. \frac{d^i(1-q)^{-i}}{dq^i} \right|_{q=0} = j! \binom{i+j-1}{j} \quad (16)$$

we find

$$T_{\mathbf{R}\mathbf{R}'} = c_B \frac{Y_0 \delta_{\mathbf{R}\mathbf{R}'} + 2(1-X_0)V_{\mathbf{R}\mathbf{R}'} + G_0^A \sum_{\mathbf{R}''} V_{\mathbf{R}\mathbf{R}''} V_{\mathbf{R}''\mathbf{R}'}}{(1-X_0)^2 - Y_0 G_0^A} \quad (17)$$

which coincides with the average T matrix of a single scattering center [19].

We now turn to the summation of the series [Fig. 2(a)]. In the simplest approximation the noncoincidence of the vertex indices need not be considered. Then the Green's function expression reduces to (1) ($\mathbf{G}^0 \equiv \mathbf{G}^A$) and

$$\underline{\Sigma} = \underline{\mathbf{T}} \quad (18)$$

The above approximation is equivalent to neglecting the correlation between the excitation wave scattering at different centers, which is justified in the limit of small concentrations of B molecules.

In the nearest-neighbor approximation, which will be used in what follows, the self-energy operator matrix elements in the momentum representation are equal to

$$\Sigma_{\mathbf{k}\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'} \frac{c_B}{G_0^A} \left\{ \frac{[\alpha + (1-\alpha)(E - \varepsilon^A - M_{\mathbf{k}}^A)G_0^A]^2}{\alpha^2 + [(E - \varepsilon^A)(1 - \alpha^2) - \Delta]G_0^A} - 1 \right\} \quad (19)$$

where

$$M_{\mathbf{k}}^A = \sum_{\mathbf{R}'} M_{\mathbf{R}\mathbf{R}'}^A \exp [i\mathbf{k}(\mathbf{R} - \mathbf{R}')], \quad \alpha = M^{AB}/M^A$$

\mathbf{k} is the wave vector.

Note certain general consequences of the obtained relation. In the region of the continuous spectrum of eigenvalues of the operator H^A , the value $\Sigma_{\mathbf{k}}$ is complex and defines the shift and the broadening of the levels of elementary excitations caused by the scattering by B molecules. At the values $\alpha \geq 1$ the correction to $\varepsilon^A + M_{\mathbf{k}}^A$ is small, since $c_B \ll 1$. But at small α the $\Sigma_{\mathbf{k}}$ dependence on energy acquired a resonance character and near the resonance ($E \approx \varepsilon^B$) the spectrum of the disordered system greatly differs from the eigenvalues of H^A even at small concentrations of B molecules. In the region of energies close to resonance the self-energy operator and the Green's function are approximately equal to

$$\begin{aligned} \Sigma_{\mathbf{k}\mathbf{k}'} &\approx \delta_{\mathbf{k}\mathbf{k}'} \gamma (E - \varepsilon^A - M_{\mathbf{k}}^A)^2 \\ \langle \mathbf{G} \rangle &\approx \mathbf{G}^A(E) - \mathbf{G}^A(E - \gamma^{-1}) \\ \gamma &= c_B [\alpha^2 G_0^{A-1} - \Delta + (E - \varepsilon^A)(1 - \alpha^2)]^{-1} \end{aligned} \quad (20)$$

In the limit $c_B \rightarrow 0$ we have

$$\langle \mathbf{G} \rangle = \mathbf{G}^A + \gamma \mathbf{I} \quad (21)$$

Hence it is seen that in the state density

$$\rho(E) = -\pi^{-1} \text{Im} \langle G_0 \rangle \quad (22)$$

at $E \approx \varepsilon^B$ and small α a spike with a half-width equal to $2\pi\alpha^2\rho^A(\varepsilon^B)|G_0^A(\varepsilon^B)|^{-2}$ and a maximum proportional to the concentration of B molecules will be

observed. A spike in the state density corresponds to a quasi-stationary level which appears if the excitation energy of *B* molecules is within the *A* band.

We now turn to the case when the levels isolated from the *A* band appear in the spectrum of the system after the molecule *A* is singly substituted by *B*. Then in the region of eigenvalues of H^A the state density of the disordered system is close to $\rho^A(E)$ [particular points of $\rho^A(E)$ may be an exception]. Outside this region $\rho^A(E) = 0$ but $\rho(E)$ will be different from zero near the energy values which determine the position of isolated levels. Thus, in a mixed system spectrum in the energy region, where $\Sigma_k(E)$ has poles an "impurity band" may appear.

3. State Density of a Two-Component Disordered Chain in the Average *T* Matrix Approximation

We use the expression for the self-energy operator (18) to calculate the state density of the exciton branch of excitations of a molecular chain. The diagonal matrix element of the Green's function in the nearest-neighbor approximation has the form

$$\langle G_0 \rangle = \frac{1}{2|M^A|(b^2 + 4ag)^{1/2}} \left[\frac{\text{sgn Im } x_1}{(x_1^2 - 1)^{1/2}} - \frac{\text{sgn Im } x_2}{(x_2^2 - 1)^{1/2}} \right] \tag{23}$$

at the complex values of x_1, x_2 and

$$\langle G_0 \rangle = \frac{1}{2|M^A|(b^2 + 4ag)^{1/2}} \left[\frac{\Theta(y_1) \text{sgn } x_1 - i\Theta(-y_1)}{|x_1^2 - 1|^{1/2}} - \frac{\Theta(y_2) \text{sgn } x_2 + i\Theta(-y_2)}{|x_2^2 - 1|^{1/2}} \right] \tag{24}$$

where

$$y_{1,2} = |x_{1,2}| - 1, \quad \Theta(y) = \begin{cases} 1, & y \geq 0 \\ 0, & y < 0 \end{cases}$$

at real values of x_1, x_2 . In Eqs. (23) and (24) the following notations are used:

$$\begin{aligned} x_{1(2)} &= \frac{\pm(b^2 + 4ag)^{1/2} - b}{2a} \\ a &= c_B(1 - \alpha)^2 \bar{G}_0^A d^{-1} \\ b &= 1 - 2c_B(1 - \alpha)[\alpha + (1 - \alpha)\bar{E}\bar{G}_0^A] d^{-1} \\ g &= \bar{E} + \frac{c_B}{\bar{G}_0^A} \{1 - [\alpha + (1 - \alpha)\bar{E}\bar{G}_0^A]^2 d^{-1}\} \\ d &= \alpha^2 + [\bar{E}(1 - \alpha^2) - \bar{\Delta}]\bar{G}_0^A \\ \bar{G}_0^A &= (2\pi)^{-1} \int_{-\pi}^{\pi} \frac{dx}{\bar{E} - \cos x + i0} \\ \bar{E} &= (E - \varepsilon^A)/2|M^A| \\ \bar{\Delta} &= \Delta/2|M^A| \end{aligned} \tag{25}$$

The behavior of the state density depending on energy is defined by the relations (23), (24) and specific values of the system parameters. For some of them Figure 3 represents the calculated results.

The curves in Figure 3(a) ($\alpha = 0.2, \bar{\Delta} = -0.5, 0$) correspond to the situation when in the region of excitations of A molecules there is a quasistationary level

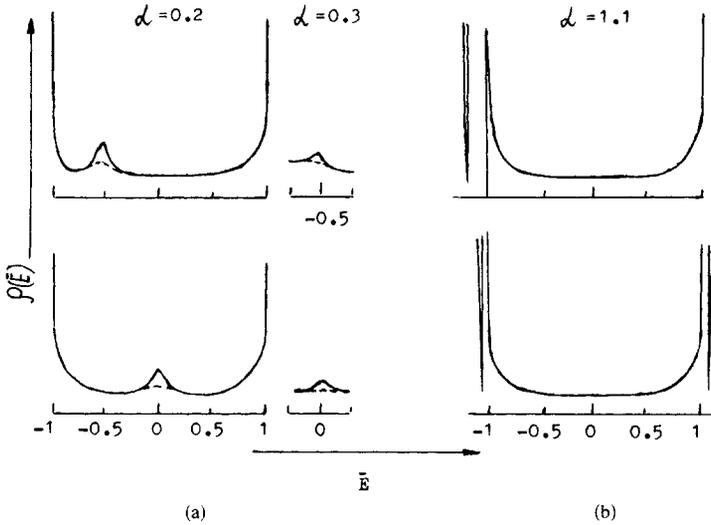


Figure 3. State density of the binary chain of A and B molecules with nondiagonal disorder in the average T matrix approximation ($c_B = 0.05$): (a) Case of the in-band resonance ($\alpha = 0.2, 0.3$). (b) Case of isolated excitation bands ($\alpha = 1.1$). Curves of the upper half of the figure correspond to the value $\bar{\Delta} = -0.5$ and those of the lower one to $\bar{\Delta} = 0$. Trend of the state density at $c_B = 0.01$ is shown by a dotted line.

caused by the presence of B molecules and expressed by the spike in the state density. The dependencies at $\alpha = 0.3$ and the same values of $\bar{\Delta}$ show that when $|\alpha|$ increases a shift occurs and the resonance spike "spreads." The dotted line illustrates a proportional decrease of the spike of the state density when the concentration of B molecules decreases.

From the analysis of the equation $d = 0$ (its graphical solution is shown in Fig. 4), which defines the poles of the self-energy part of the Green's function, it follows that at $\alpha^2 < 1$, as distinct from the case of the diagonal perturbation ($\alpha = 1$) when at any infinitely small perturbation the self-energy part has poles outside the A band, there is a limit value of $\bar{\Delta}$ for systems with nondiagonal disorder defined by the inequality

$$1 - \alpha^2 < |\bar{\Delta}| \quad (26)$$

when this inequality is satisfied d may become zero with excitation energies outside the A band region. Since the inequality (26) for the parameters given in

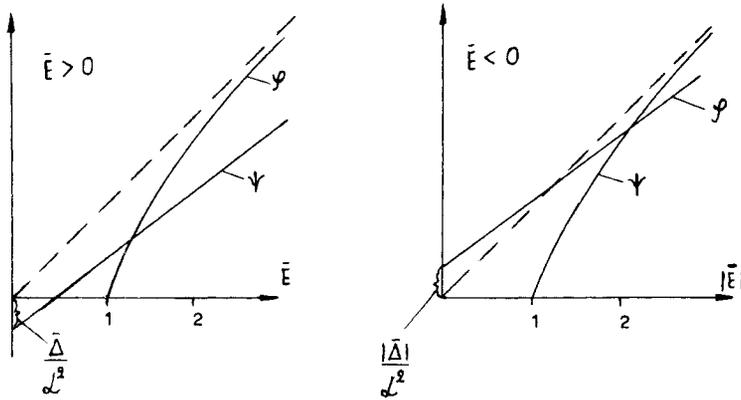


Figure 4. Graphic solution of the equation defining the poles of the self-energy part (19): $(\bar{E}^2 - 1)^{1/2} = (\bar{\Delta}\bar{E}^{-1}\alpha^{-2} - \alpha^{-2} + 1)|\bar{E}|$. Left-hand and the right-hand sides of the equation are denoted by φ and ψ . Plots correspond to the case when the system parameters satisfy the following relations: $\bar{\Delta} < 0, \alpha^2 - 1 > |\bar{\Delta}|$.

Figure 3(a) is not satisfied, the state density of a mixed system outside the *A* band is equal to zero in the average *T* matrix approximation.

At $\alpha^2 > 1$ the equation $d = 0$ always has a solution outside the *A* band, which lies above it if $\bar{\Delta}$ is positive and below it if $\bar{\Delta}$ has an opposite sign. However, in a one-dimensional system the self-energy part may also have two poles situated on both sides of the *A* band if the relation

$$\alpha^2 - 1 > |\bar{\Delta}| \tag{27}$$

is satisfied.

Accordingly, in the spectrum of a mixed system, in addition to the band caused by the excitation of *A* molecules, one or two isolated bands associated with the excitation of *B* molecules may exist, which is illustrated graphically in Figure 3(b).

At $\alpha = 1.1, \bar{\Delta} = -0.5$ one impurity band [inequality (27) is not satisfied] exists, and the singularity of the state density near the lower edge of the excitation band of host molecules becomes smooth. At $\alpha = 1.1, \bar{\Delta} = 0$ there exist two impurity bands arranged symmetrically with respect to the *A* band. The impurity band splitting is due to a strong resonance interaction of *A* and *B* molecules.

4. Modified Averaged *T* Matrix Approximation

Multiple occupancy corrections were not included in the discussion of previous sections, and the self-energy operator turned out to be equal to the averaged *T* matrix of a single defect. To improve the approximation one must keep in mind that the terms containing two and more vertices in Fig. 2(a) with coinciding indices should be omitted.

We shall take into account the excluded terms, known as multiple occupancy corrections, in which only adjacent vertex indices do not coincide. Such an

approximation was used in the theory of diagonal disordered systems in Refs. 2 and 3, for example. For this purpose let us introduce the matrices

$$\begin{aligned} G'_{RR'} &= G_{RR'}^A - \delta_{RR'} G_0^A \\ X'_{RR'} &= X_{RR'} - \delta_{RR'} X_0 \\ Y'_{RR'} &= Y_{RR'} - \delta_{RR'} Y_0 \end{aligned} \tag{28}$$

with the help of which the operator $\langle G \rangle$ may be transformed into

$$\begin{aligned} \langle G \rangle &= G^A \{ \mathbf{I} + (\mathcal{A}\mathbf{I} + \mathcal{B}\mathbf{V}) [G^A + \mathbf{K}G^A + \mathbf{L}X + (\mathbf{K}^2 + \mathbf{L}\mathbf{M})G^A + (\mathbf{K}\mathbf{L} + \mathbf{L}\mathbf{N})X + \dots] \\ &+ (\mathcal{B}\mathbf{I} + \mathcal{C}\mathbf{V}) [X + \mathbf{N}X + \mathbf{M}G^A + (\mathbf{N}^2 + \mathbf{M}\mathbf{L})X + (\mathbf{N}\mathbf{M} + \mathbf{M}\mathbf{K})G^A + \dots] \} \end{aligned} \tag{29}$$

where

$$\begin{aligned} \mathbf{K} &\equiv \mathcal{A}G' + \mathcal{B}X', & \mathbf{M} &\equiv \mathcal{A}X' + \mathcal{B}Y' \\ \mathbf{L} &\equiv \mathcal{B}G' + \mathcal{C}X', & \mathbf{N} &\equiv \mathcal{B}X' + \mathcal{C}Y' \\ \mathcal{A} &\equiv c_B Y_0 / d, & \mathcal{B} &\equiv c_B (1 - X_0) / d, & \mathcal{C} &\equiv c_B G_0^A / d \\ d &\equiv (1 - X_0)^2 - Y_0 G_0^A \end{aligned} \tag{30}$$

Using the rule

$$G^A \begin{matrix} \nearrow \mathbf{K}G^A \\ \searrow \mathbf{L}X \end{matrix}, \quad X \begin{matrix} \nearrow \mathbf{N}X \\ \searrow \mathbf{M}G^A \end{matrix} \tag{31}$$

one can get each successive term of Eq. (29). Therefore, we can write

$$\langle G \rangle = G^A + G^A \bar{\mathbf{T}} G^A \tag{32}$$

where

$$\bar{\mathbf{T}} = (\mathcal{A}\mathbf{I} + \mathcal{B}\mathbf{V})(\mathbf{q}_1 + \mathbf{q}_2\mathbf{V}) + (\mathcal{B}\mathbf{I} + \mathcal{C}\mathbf{V})(\lambda_1\mathbf{V} + \lambda_2) \tag{33}$$

and \mathbf{q}_i, λ_i ($i = 1, 2$) are expressed in terms of the expansion in powers of K, L, M, N operators.

Taking into account (31) we find

$$\mathbf{q}_1 = (\mathbf{I} - \mathbf{K})^{-1} + \sum_{i=1}^{\infty} (\mathbf{L}\mathbf{M})^i \sum_{j=0}^{\infty} \binom{i+j-1}{j} \mathbf{N}^j \sum_{l=0}^{\infty} \binom{i+l}{l} \mathbf{K}^l \tag{34}$$

$$\mathbf{q}_2 = \mathbf{L}(\mathbf{I} - \mathbf{K})^{-1}(\mathbf{I} - \mathbf{N})^{-1} \sum_{i=0}^{\infty} (\mathbf{L}\mathbf{M})^i \sum_{j=0}^{\infty} \binom{i+j-1}{j} \mathbf{N}^j \sum_{l=0}^{\infty} \binom{i+l-1}{l} \mathbf{K}^l \tag{35}$$

Then, having performed the summation of expansions (34), (35) and noted that after permutation of operators \mathbf{K} and \mathbf{N} , \mathbf{L} and \mathbf{M} , $\mathbf{q}_1, \mathbf{q}_2$ turn into λ_1, λ_2 correspondingly, we get

$$\bar{\mathbf{T}} = \frac{(\mathcal{A}\mathbf{I} + \mathcal{B}\mathbf{V})(\mathbf{I} - \mathbf{N} + \mathbf{L}\mathbf{V}) + (\mathcal{B}\mathbf{I} + \mathcal{C}\mathbf{V})(\mathbf{V} - \mathbf{K}\mathbf{V} + \mathbf{M})}{(\mathbf{I} - \mathbf{K})(\mathbf{I} - \mathbf{N}) - \mathbf{L}\mathbf{M}} \tag{36}$$

Taking into account the definitions (15), (28), (30) we can write the final expression for the needed operator $\bar{\mathbf{T}}$:

$$\begin{aligned} \bar{\mathbf{T}} = & c_B [2\mathbf{V} + c_A(Y_0\mathbf{I} - 2X_0\mathbf{V} + G_0^A\mathbf{V}^2)] \\ & \times \{[(1 - X_0)^2 - Y_0G_0^A]\mathbf{I} - c_B[Y_0\mathbf{G}' + 2(1 - X_0)\mathbf{X}' + G_0^A\mathbf{Y}'] \\ & - c_B^2(\mathbf{G}'\mathbf{Y}' - \mathbf{X}'^2)\}^{-1} \end{aligned} \quad (37)$$

Now one can derive an equation for the self-energy operator by substituting (37) into the known relation

$$\bar{\Sigma} = \frac{\bar{\mathbf{T}}}{\mathbf{I} + \mathbf{G}^A\bar{\mathbf{T}}} \quad (38)$$

Thus we have for matrix elements of $\bar{\Sigma}$

$$\bar{\Sigma}_{\mathbf{RR}'} = \frac{c_A c_B [Y_0 \delta_{\mathbf{RR}'} + 2(c_A^{-1} - X_0)V_{\mathbf{RR}'} + G_0^A(\mathbf{V}^2)_{\mathbf{RR}'}]}{(1 - c_A X_0)^2 - c_A^2 Y_0 G_0^A} \quad (39)$$

The expression derived above leads to an averaged T matrix approximation without multiple occupancy corrections (18) if c_A is taken equal to unity. As compared to the latter, Eq. (39) increases the number of exact terms included in the self-energy part from the Green's function expansion. These corrections are caused by the fact that any given site in the "average" system may be occupied either by A or by B molecules. Formally it is expressed in a c_A -fold decrease of the amplitude of every virtual consecutive scattering of an excitation wave of A molecules by B centers.

In the case of the diagonal perturbation, $V_{\mathbf{RR}'} = \frac{1}{2}\delta_{\mathbf{RR}'}\Delta$, Eq. (39) reduces to the known relation [2]

$$\bar{\Sigma}_{\mathbf{RR}'}^{\text{diag}} = \delta_{\mathbf{RR}'} c_B \frac{\Delta}{1 - \Delta G_0^A c_A} \quad (40)$$

and, therefore, provides the correct atomic limit ($\Delta \rightarrow \infty$) of the $\bar{\Sigma}$ operator.

Note, that Eq. (39) does not satisfy requirements for $A \rightleftharpoons B$ permutation symmetry, which naturally arises for the Green's function of binary system with random distribution of the components.

Following Secs. 2 and 4 but substituting zero approximation \mathbf{G}^A by \mathbf{G}^{vc} , which is the "virtual" crystal Green's function, we obtain instead of (39)

$$\begin{aligned} \bar{\Sigma}_{\mathbf{RR}'} = & c_A c_B \{ \delta_{\mathbf{RR}'} \tilde{Y}_0 + 2\tilde{V}_{\mathbf{RR}'} [\tilde{X}_0 - (c_A - c_B)\tilde{X}_0^2 + (c_A - c_B)\tilde{Y}_0 G_0^{\text{vc}}] + G_0^{\text{vc}}(\tilde{\mathbf{V}}^2)_{\mathbf{RR}'} \} \\ & \times \{ [1 - (c_A - c_B)\tilde{X}_0]^2 - (c_A - c_B)^2 G_0^{\text{vc}} \tilde{Y}_0 \}^{-1} \end{aligned} \quad (41)$$

where $\tilde{\mathbf{Y}}$, which also appears in the definitions of $\tilde{\mathbf{X}}$ and $\tilde{\mathbf{V}}$ similarly to (15), is defined as

$$\tilde{V}_{\mathbf{RR}'} = \frac{1}{2}\Delta\delta_{\mathbf{RR}'} + [c_B(M_{\mathbf{RR}'}^B - M_{\mathbf{RR}'}^{AB}) - c_A(M_{\mathbf{RR}'}^A - M_{\mathbf{RR}'}^{AB})](1 - \delta_{\mathbf{RR}'})) \quad (42)$$

and

$$G_{\mathbf{R}\mathbf{R}'}^{\text{vc}} = N^{-1} \sum_{\mathbf{k}} \frac{\exp [i\mathbf{k}(\mathbf{R} - \mathbf{R}')] }{E - \varepsilon - M_{\mathbf{k}}^{\text{av}} + i0}, \quad \varepsilon = c_A \varepsilon^A + c_B \varepsilon^B$$

$$M_{\mathbf{k}}^{\text{av}} = \sum_{\mathbf{R}'} M_{\mathbf{R}\mathbf{R}'}^{\text{av}} \exp [i\mathbf{k}(\mathbf{R} - \mathbf{R}')] \quad (43)$$

$$M_{\mathbf{R}\mathbf{R}'}^{\text{av}} = c_A^2 M_{\mathbf{R}\mathbf{R}'}^A + c_B^2 M_{\mathbf{R}\mathbf{R}'}^B + 2c_A c_B M_{\mathbf{R}\mathbf{R}'}^{AB}$$

where N is a full number of molecules.

One can see that now the definition (41) of the self-energy has the necessary property of $A \rightleftharpoons B$ permutation symmetry. In addition, in the limiting case of the diagonal perturbation it reduces to

$$\tilde{\Sigma}_{\mathbf{R}\mathbf{R}'}^{\text{diag}} = \delta_{\mathbf{R}\mathbf{R}'} c_A c_B \frac{\Delta^2 G_0^{\text{vc}}}{1 - (c_A - c_B) \Delta G_0^{\text{vc}}} \quad (44)$$

which was used in Ref. 3 for the calculation of the binary chain phonon state density in the arbitrary range of component concentrations.

The limiting expressions for the self-energy operator have been written to compare the possibilities of describing systems with the diagonal and nondiagonal randomness in the framework of a single-site approximation. For the first of them Eq. (40) and (44) give the Green's function expansion correct up to the second and the third term in perturbation inclusively, and it is correct up to the first term only if multiple occupancy corrections are not included, i.e., when $c_A = 1$ in (40). As to the nondiagonal randomness a quite different situation is realized. Multiple occupancy corrections included in the framework of the single-site approximation do not increase the occurrence of listed approaches and all of them are strictly correct only in zero approximation. The reason for such a discrepancy lies in the fact that the truncation procedure used above is not equivalent for the systems with diagonal and nondiagonal disorder, because in the latter two-vertex irreducible diagrams are already contained in the first-order perturbation theory, but they are ignored in single-site approximations. Thus, it is natural to expect that any approximation, based on the summation of diagrams involving one-vertex irreducible parts only (including self-consistent approaches like the coherent potential approximation), do not provide proper interpolation for Σ even for small but finite concentrations.

Especially for (39) and (41) it can be easily shown that for the very small resonant interaction between molecules of different components and for the Δ less than the bandwidth the binary linear chain state density has spurious spikes in the single-site approximations used above. In the other case of a big Δ the equation defining the Green's function poles with the self-energy part (41) in the linear approximation in concentration c_B and resonant interaction leads to the following result:

$$E^A = \varepsilon^A + c_A M_{\mathbf{k}}^A \quad (45)$$

$$E^B = \varepsilon^B + c_B (2\alpha - 1) M_{\mathbf{k}}^A \quad (46)$$

which defines the two excitation branches of a binary disordered system in the nearest-neighbor approximation.

As one can see the B molecule excitation bandwidth dependence on parameters of intermolecular interaction resulting from (46) is physically meaningless.

To avoid these difficulties it is necessary to include (even for small concentrations) the corrections which arise from diagrams with two vertices. We restrict ourselves to a sampling summation of two-vertex diagrams which give a correction to (39) of the following type:

$$c_B^2 \frac{v_{\mathbf{R}\mathbf{R}'}(1 - \delta_{\mathbf{R}\mathbf{R}'})}{[(1 - X_0)^2 - Y_0 G_0^A]^2} \quad (47)$$

Taking it into account we get instead of (46)

$$E^B = \varepsilon^B + c_B M_{\mathbf{k}}^B \quad (48)$$

The latter together with Eq. (45) corresponds to the Broude–Rashba approach [20] in the theory of disordered systems.

Thus, even two-vertex diagram corrections roughly included into consideration lead to the reasonable Green's function interpolation formula. A more realistic approach requires the summation of more diagrams. But even the full summation of two-vertex diagrams (and what is more, of three and more vertices) is a very difficult problem in the case of nondiagonal disordered systems. Therefore, it is instrumental to find some other parameters of the excitation spectrum, to enable one to make an exact calculation.

5. Moments of the State Density and Spectral Density

Such parameters of the excitation spectrum shape of a disordered system which may be defined exactly in the arbitrary range of concentrations are state density moments

$$\mu_p = \int_{-\infty}^{\infty} E^p \rho(E) dE \quad (49)$$

and spectral density moments

$$\begin{aligned} M_p(\mathbf{k}) &= \int_{-\infty}^{\infty} E^p S(\mathbf{k}, E) dE \\ S(\mathbf{k}, E) &= -\pi^{-1} \text{Im} \langle \mathbf{k} | \langle G \rangle | \mathbf{k} \rangle \\ |\mathbf{k}\rangle &= N^{-1/2} \sum_{\mathbf{R}} \exp(i\mathbf{k}\mathbf{R}) B_{\mathbf{R}}^+ |0\rangle \end{aligned} \quad (50)$$

where $|0\rangle$ is the vacuum wave function.

From definitions (49), (50), and Green's function dispersion relations [21] it follows [5]

$$\mu_p = N^{-1} Sp \langle H^p \rangle \quad (51)$$

$$M_p(\mathbf{k}) = \langle \mathbf{k} | \langle H^p \rangle | \mathbf{k} \rangle \quad (52)$$

To calculate these quantities it is convenient to present the disordered system Hamiltonian in the form

$$H = \langle H \rangle + \tilde{W} \quad (53)$$

$$\langle H \rangle = \sum_{\mathbf{R}, \mathbf{R}'} [\varepsilon \delta_{\mathbf{R}\mathbf{R}'} + M_{\mathbf{R}\mathbf{R}'}^{\text{av}} (1 - \delta_{\mathbf{R}\mathbf{R}'})] B_{\mathbf{R}}^+ B_{\mathbf{R}'} \quad (54)$$

$$\tilde{W} = \sum_{\mathbf{R}, \mathbf{R}'} [\tilde{V}_{\mathbf{R}\mathbf{R}'} (\xi_{\mathbf{R}} + \xi_{\mathbf{R}'}) + v_{\mathbf{R}\mathbf{R}'} \xi_{\mathbf{R}} \xi_{\mathbf{R}'}] B_{\mathbf{R}}^+ B_{\mathbf{R}'}, \quad \xi_{\mathbf{R}} = \nu_{\mathbf{R}} - c_B \quad (55)$$

where $\langle H \rangle$ corresponds to the virtual crystal approximation, and configurational averages $\langle \xi_{\mathbf{R}}^n \rangle$ are calculated as

$$\langle \xi_{\mathbf{R}}^n \rangle = c_A c_B [c_A^{n-1} + (-1)^n c_B^{n-1}] \quad (56)$$

Using the Hamiltonian in the form (53) simplifies the moment calculation. From its definition it follows that $\langle \tilde{W} \rangle = 0$ and a few first moments are easily found

$$\mu_0 = 1, \quad \mu_1 = \varepsilon, \quad (57)$$

$$\mu_2 = c_A \varepsilon^A + c_B \varepsilon^B + \sum_{\mathbf{R}'} (c_A^2 M_{\mathbf{R}\mathbf{R}'}^{A^2} + c_B^2 M_{\mathbf{R}\mathbf{R}'}^{B^2} + 2c_A c_B M_{\mathbf{R}\mathbf{R}'}^{AB^2})$$

$$M_0(\mathbf{k}) = 1, \quad M_1(\mathbf{k}) = \varepsilon + M_{\mathbf{k}}^{\text{av}},$$

$$M_2(\mathbf{k}) = c_A (\varepsilon^A + c_A M_{\mathbf{k}}^A + c_B M_{\mathbf{k}}^{AB})^2 + c_B (\varepsilon^B + c_B M_{\mathbf{k}}^B + c_A M_{\mathbf{k}}^{AB})^2 + c_A c_B \sum_{\mathbf{R}'} [c_A (M_{\mathbf{R}\mathbf{R}'}^A - M_{\mathbf{R}\mathbf{R}'}^{AB})^2 + c_B (M_{\mathbf{R}\mathbf{R}'}^B - M_{\mathbf{R}\mathbf{R}'}^{AB})^2] \quad (58)$$

The expressions for the third and other moments are too cumbersome and, therefore, are not given.

The quantities (57) and (58) are measured experimentally and define certain characteristics of the excitation spectrum [22]. Besides, in various papers (for example, Refs. 5, 9, 23) it is shown that the moment method is a very useful tool for investigating the disordered system's basic properties. Specifically, spectral density moments define the effective Hamiltonian's asymptotic behavior for large E :

$$H_{\text{eff}} = \langle H \rangle + \sum_{l=1}^{\infty} \frac{\Pi_l}{E^l} \quad (59)$$

where

$$\begin{aligned} \Pi_1 &= \langle H^2 \rangle - \langle H \rangle^2 = \langle \tilde{W}^2 \rangle \\ \Pi_2 &= \langle H^3 \rangle - \langle H \rangle \langle H^2 \rangle - \langle H^2 \rangle \langle H \rangle + \langle H \rangle^3 \\ &= \langle \tilde{W} \langle H \rangle \tilde{W} \rangle + \langle \tilde{W}^3 \rangle \end{aligned} \quad (60)$$

from which it follows that the asymptotic form of $\tilde{\Sigma}$ is an operator diagonal in \mathbf{k} -representation ($\tilde{\Sigma} = H_{\text{eff}} - \langle H \rangle$)

$$\tilde{\Sigma}_{\mathbf{k}} = \frac{M_2(\mathbf{k}) - M_1^2(\mathbf{k})}{E} + O\left(\frac{1}{E^2}\right) \quad (61)$$

Note, for comparison, that in the case of diagonal disordered systems the self-energy operator is presented by a number series up to E^{-5} [5]. In addition all moments of the systems mentioned above are expressed in terms of moments of the components and that is impossible to be done in the case of nondiagonal disorder.

The asymptotic properties of the self-energy are to be taken into account when an interpolation Green's function formula is required. And the moment calculation serves as a very useful method to check the chosen approximation.

Bibliography

- [1] D. W. Taylor, Phys. Rev. **156**, 1017 (1966).
- [2] R. J. Elliott and D. W. Taylor, Proc. Roy. Soc. Lond. A **296**, 161 (1967).
- [3] P. L. Leath and B. Goodman, Phys. Rev. **181**, 1062 (1969).
- [4] P. Soven, Phys. Rev. **156**, 809 (1967); **178**, 1136 (1969).
- [5] B. Velicky, S. Kirkpatrick and H. Ehrenreich, Phys. Rev. **175**, 747 (1968); B **1**, 3250 (1970).
- [6] Y. Onodera and Y. Toyozawa, J. Phys. Soc. Jpn. **24**, 341 (1968).
- [7] V. I. Sugakov, Fiz. Tverd. Tela **10**, 2995 (1968).
- [8] O. A. Dubovskij and Yu. V. Konobeev, Fiz. Tverd. Tela **12**, 405 (1970).
- [9] J. Hoshen and J. Jortner, J. Chem. Phys. **56**, 933 (1972); **56**, 4138 (1972).
- [10] L. N. Bulaevskij, Usp. Fiz. Nauk. **115**, 263 (1975).
- [11] J. Ladik and M. Seel, Phys. Rev. B **13**, 5338 (1976).
- [12] I. M. Lifshitz, Usp. Fiz. Nauk. **83**, 617 (1964).
- [13] R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. **46**, 465 (1974).
- [14] S. Takeno, Prog. Theor. Phys. **40**, 942 (1968).
- [15] H. Shiba, Prog. Theor. Phys. **46**, 77 (1971).
- [16] L. Schwartz, H. Krakauer, and H. Fukuyama, Phys. Rev. Lett. **30**, 746 (1973).
- [17] F. Yonezawa, Prog. Theor. Phys. **40**, 734 (1968).
- [18] R. N. Aiyer, R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Phys. Rev. **181**, 1006 (1969).
- [19] R. Bass and P. L. Leath, Phys. Rev. B **9**, 2769 (1974).
- [20] V. L. Broude, E. I. Rashba, Fiz. Tverd. Tela **3**, 1941 (1961).
- [21] D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Nauka, Moscow, 1971).
- [22] A. S. Davydov, *Solid State Theory* (Nauka, Moscow, 1976).
- [23] H.-K. Hong and R. Kopelman, J. Chem. Phys. **55**, 3490 (1971).

Received October 23, 1978

Accepted for publication January 18, 1979