

## Force constant and mass disorder in vibrational systems in the coherent-potential approximation\*

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The coherent-potential approximation (CPA) for vibrational systems is extended to include force-constant changes as well as mass defects in alloys for which the force constants superimpose linearly. Such a model is correct at both the low- and high-concentration limits, and may be reasonable for broad concentration ranges in some real systems, for example, in diatomic alloys like mixed alkali halides. Results for one-dimensional systems with nearest-neighbor force constant and mass disorder have the same over-all agreement with exact results as was previously found for CPA calculations for mass defects only. Applications in three dimensions appear to be computationally feasible.

### I. INTRODUCTION

Considerable progress in understanding the properties of substitutional alloys has been made recently through the use of the coherent-potential approximation (CPA). As first described for phonons by Taylor<sup>1</sup> and electrons by Soven,<sup>2</sup> the CPA is a mean-field theory in which the random alloy is approximated by an effective medium. This medium is chosen self-consistently such that the average scattering from a single real atom in the otherwise perfect effective crystal vanishes. Within the confines of the single-site approximation, there have been numerous applications and refinements of the CPA for vibrational,<sup>3-7</sup> electronic,<sup>8-14</sup> and magnetic<sup>15</sup> systems.

For both theoretical and computational reasons, it has proven difficult to go beyond the single-site CPA to include either pair and higher cluster correlations or off-diagonal randomness, that is, randomness in phonon force constants or in electron-transfer integrals connecting different sites. A number of attempts<sup>16-21</sup> have been made to include correlations, which are known from exact machine calculations<sup>22,23</sup> to produce structure associated with identifiable pairs, triplets, and larger clusters. Butler<sup>21</sup> has recently succeeded in reproducing some of the detailed structure found in the density of states of one-dimensional alloys by embedding clusters self-consistently in a (super) periodic effective medium.

To a first approximation, the effects of off-diagonal randomness are to shift and distort features of the alloy spectrum, rather than to introduce a great deal of additional fine structure. For phonons, for example, force-constant changes may shift local or resonant modes away from the frequencies predicted by CPA mass-defect calculations; they may move a resonant mode out of the in-band region,<sup>7</sup> or a local mode back down into the continuum. Shiba<sup>24</sup> and Blackman *et al.*<sup>25</sup> have

proposed methods to include off-diagonal randomness for electrons which are much like standard CPA in using diagonal single-site averages, but there is some question as to whether their approaches are wholly consistent with known low-concentration-limit results.<sup>24,26</sup>

In this paper, we describe how the CPA may be extended to include both force constant and mass changes in vibrational systems for which a linear superposition of forces is a good approximation. In particular, the theory is applicable to diatomic crystals with nearest-neighbor force-constant changes. We make no effort to include clustering effects, preferring instead to focus on the incorporation of force-constant changes.

It is by now well known that local force-constant changes generally play an important role in determining the behavior of phonons around isolated defects. Diatomic alloys of the form  $A_{1-c}A'_cB$  are particularly well-suited for studies of the effects of force-constant disorder, since correlations between the alloyed constituents  $A, A'$  are to some extent buffered by the intervening stable constituent  $B$ . Furthermore, there are only two nearest-neighbor force constants ( $A-B, A'-B$ ) to deal with, rather than three as would be the case for a monatomic  $A-A'$  alloy. However, our approach is not limited to diatomic crystals, but also applies to other systems whose force constants superimpose linearly, for example, monatomic  $A-A'$  alloys in which the  $A-A'$  force constants are the average of the  $A-A$  and  $A'-A'$  force constants. While it is true that this is a special case, it should also be noted that real alloys do not have the simple Hamiltonians generally assumed, and that mappings of the real-alloy problem onto models are common practice.

We describe the theory in Sec. II. In Sec. III, we show that for one-dimensional alloys, our results for the CPA with force-constant changes have the same over-all agreement with exact calcula-

tions as those of Taylor<sup>1</sup> for mass defects. In Sec. IV, we indicate how practical extensions to three dimensions can be accomplished, and briefly summarize our conclusions.

## II. THEORY

To describe our approach, we will use notation similar to that of Taylor<sup>1</sup> and will parallel his development where possible. The time transform of the (retarded) phonon Green's function<sup>27</sup> is defined by

$$\begin{aligned} \underline{G}(lb, l'b'; \omega) = & \int d(t-t') e^{i\omega(t-t')} \\ & \times (i/\hbar) \Theta(t-t') \langle [\tilde{u}(l, b; t), \\ & \tilde{u}(l', b'; t')] \rangle, \end{aligned} \quad (1)$$

where  $\Theta(t-t')$  is the Heaviside step function, and  $\tilde{u}(l, b; t)$  is the displacement of the atom at the site  $b$  in the  $l$ th unit cell at time  $t$ . For conciseness, the frequency argument  $\omega$  will be suppressed in subsequent equations.

In the harmonic approximation, the perfect-crystal Green's function  $\underline{P}(lb, l'b')$  satisfies the equation

$$\begin{aligned} \underline{I}\delta(l, l')\delta(b, b') = & \sum_{l'', b''} \{M_b \omega^2 \underline{I}\delta(l, l'')\delta(b, b'') \\ & - \Phi^0(lb, l'b'')\} \cdot \underline{P}(l''b'', l'b'), \end{aligned} \quad (2)$$

where  $\underline{I}$  is the unit matrix,  $M_b$  is the atomic mass of  $b$ -type atoms, and  $\Phi^0(lb, l'b')$  is the force-constant matrix in the perfect crystal. When defects are present, the Green's function  $\underline{G}(lb, l'b')$  must be determined from

$$\begin{aligned} \underline{I}\delta(l, l')\delta(b, b') \\ = \sum_{l'', b''} \{ \underline{P}^{-1}(lb, l''b'') - [M_b - M(lb)] \omega^2 \underline{I}\delta(l, l'') \\ \times \delta(b, b'') - \Delta\Phi(lb, l''b'') \} \cdot \underline{G}(l''b'', l'b'), \end{aligned} \quad (3)$$

where  $M(lb)$  is the mass of the atom at the site  $lb$  in the imperfect crystal, and

$$\Delta\Phi(lb, l'b') = \Phi(lb, l'b') - \Phi^0(lb, l'b') \quad (4)$$

represents the changes in the force constants.

We treat the force-constant changes as a sum of individual defect matrices,

$$\Delta\Phi(lb, l'b') = \sum_{l_i b_i} \Delta\Phi^{\delta}(lb, l'b'; l_i b_i), \quad (5)$$

where  $\Delta\Phi^{\delta}(lb, l'b'; l_i b_i)$  is the change in force constants associated with the site  $l_i b_i$ ,  $\delta$  is the type of atom at  $l_i b_i$  [i. e.,  $\delta = \delta(l_i b_i)$ ], and the summation is over all sites in the crystal. If the atom at  $l_i b_i$  is a host atom,  $\delta = \text{host}$ , then the defect matrix for this site vanishes,  $\Delta\Phi^{\delta}(lb, l'b'; l_i b_i) = 0$ . Taylor<sup>1</sup> properly points out that Eq. (5) represents a restrictive assumption. However, it is valid for any system whose force constants superimpose linear-

ly, and it is also legitimate when the overlap of the individual defect perturbations can be neglected. It is therefore valid for either small or very large defect concentrations  $c$ , that is, for  $c$  or  $1-c$  small. We also expect Eq. (5) to be appropriate over more extended concentration ranges for short-range force-constant changes in polyatomic crystals like mixed alkali halides.

As an example of a system whose force constants superimpose linearly, consider a monatomic  $A-A'$  alloy whose force constants satisfy

$$\Phi_{AA'}(l, l') = \Phi_{A'A}(l, l') = \frac{1}{2} [\Phi_{AA}(l, l') + \Phi_{A'A'}(l, l')]. \quad (6)$$

Here  $\Phi_{AA'}(l, l')$  is the force constant between an  $A$  atom at the site  $l$  and an  $A'$  atom at the site  $l'$ . An equivalent model for the electronic alloy problem has been proposed by Schwartz *et al.*<sup>28</sup> If  $n_{A'}(l)$  has the value 1 when there is an  $A'$  atom at site  $l$  and 0 otherwise, then the force constants in the alloy differ from those of a pure  $A$  crystal by

$$\Delta\Phi(l, l') = \frac{1}{2} [\Phi_{A'A'}(l, l') - \Phi_{AA}(l, l')] [n_{A'}(l) + n_{A'}(l')]. \quad (7)$$

For this system, the individual defect matrices of Eq. (5) are

$$\Delta\Phi^{\delta}(l, l'; l_i) = \begin{cases} \frac{1}{2} [\Phi_{A'A'}(l, l') - \Phi_{AA}(l, l')] \\ \times [\delta(l, l_i) + \delta(l', l_i)], & \delta = A' \\ 0, & \delta = A \end{cases} \quad (8)$$

With the assumption of linear superposition for the force constants, Eq. (3) for the Green's function can be written in the form

$$\begin{aligned} \underline{G}(lb, l'b') \\ = \underline{P}(lb, l'b') + \sum_{l_1 b_1, l_2 b_2} \underline{P}(lb, l_1 b_1) \\ \cdot \sum_{l_i b_i} \underline{D}^{\delta}(l_1 b_1, l_2 b_2; l_i b_i) \cdot \underline{G}(l_2 b_2, l'b'), \end{aligned} \quad (9)$$

where the sum on  $l_i b_i$  is over all sites, and

$$\begin{aligned} \underline{D}^{\delta}(l_1 b_1, l_2 b_2; l_i b_i) = M_b \epsilon^{\delta}(l_i b_i) \omega^2 \underline{I}\delta(l, l')\delta(b, b')\delta(l, l_i) \\ \times \delta(b, b_i) + \Delta\Phi^{\delta}(lb, l'b'; l_i b_i), \end{aligned} \quad (10)$$

$$\epsilon^{\delta}(l_i b_i) = [M_b - M(l_i b_i)] / M_b. \quad (11)$$

The region in which the perturbation  $\underline{D}^{\delta}(lb, l'b'; l_i b_i)$  around the site  $l_i b_i$  may be nonzero will be called the defect space.

We now introduce the CPA Green's function  $\underline{G}^0(lb, l'b')$ ,

$$\begin{aligned} \underline{G}^0(lb, l'b') = \underline{P}(lb, l'b') \\ + \sum_{l_1 b_1, l_2 b_2} \underline{P}(lb, l_1 b_1) \cdot \underline{E}(l_1 b_1, l_2 b_2) \\ \cdot \underline{G}^0(l_2 b_2, l'b'), \end{aligned} \quad (12)$$

with the self-energy  $\underline{E}(lb, l'b')$  to be determined later by minimizing the difference between  $\underline{G}^0$  and

$\langle \underline{G} \rangle$  at some level of approximation. In terms of  $\underline{G}^0$  rather than  $\underline{P}$ , the equation for  $\underline{G}$  before averaging is

$$\begin{aligned} \underline{G}(lb, l'b') &= \underline{G}^0(lb, l'b') + \sum_{l_1 b_1, l_2 b_2} \underline{G}^0(lb, l_1 b_1) \\ &\cdot \left( \sum_{l_i b_i} \underline{D}^0(l_1 b_1, l_2 b_2; l_i b_i) - \underline{E}(l_1 b_1, l_2 b_2) \right) \\ &\cdot \underline{G}(l_2 b_2, l'b') \quad . \quad (13) \end{aligned}$$

We would like to recast this equation in a way that allows us to separate out the scattering from atoms in the defect space around any potential defect site and to set that scattering equal to zero on the average by proper choice of the self-energy.

To do this, we first express the crystal periodic self-energy function  $\underline{E}$  as a sum of local self-energy matrices  $\underline{K}$  associated with each site in the crystal. Adopting for the present a compressed notation in which  $L$  denotes both  $l$  and  $b$ , we can without loss of generality write

$$\underline{E}(L, L') = \sum_{L_i} \sum_{S, S'} \underline{K}(S, S'; L_i) \delta(L, S + L_i) \delta(L', S' + L_i), \quad (14)$$

where  $S, S'$  are site indices defined relative to  $L_i$ . Similarly, we rewrite the individual matrices defined in Eq. (10) in the same form,

$$\underline{D}^0(L, L'; L_i) = \sum_{S, S'} \underline{D}^0(S, S'; L_i) \delta(L, S + L_i) \delta(L', S' + L_i). \quad (15)$$

A scattering potential matrix around the site  $L_i$  can be defined by

$$\underline{V}^0(S, S'; L_i) = \underline{D}^0(S, S'; L_i) - \underline{K}(S, S'; L_i) \quad , \quad (16)$$

which depends on what type of atom  $\delta$  is at  $L_i$ . In terms of  $\underline{V}^0$ , equation (13) becomes

$$\begin{aligned} \underline{G}(L, L') &= \underline{G}^0(L, L') + \sum_{L_i} \sum_{S, S'} \underline{G}^0(L, S + L_i) \\ &\cdot \underline{V}^0(S, S'; L_i) \cdot \underline{G}(S' + L_i, L') \quad . \quad (17) \end{aligned}$$

The  $t$  matrix for the scattering from the potential  $\underline{V}^0$  is

$$\underline{T}^0(S, S'; L_i) = \sum_{S_1} \underline{V}^0(S, S_1; L_i) \cdot \underline{X}^0(S_1, S'; L_i)^{-1} \quad , \quad (18)$$

where

$$\underline{X}^0(S, S'; L_i) = \underline{I} \delta(S, S') - \sum_{S_1} \underline{G}^0(S, S_1) \cdot \underline{V}^0(S_1, S'; L_i) \quad . \quad (19)$$

We can now follow in the steps of Taylor's derivation for mass defects. From equations (17)–(19), a Green's function associated with the site  $L_i$  is defined by

$$\begin{aligned} \underline{G}^0(S + L_i, L'; L_i) &= \sum_{S_1} \underline{X}^0(S, S_1; L_i) \cdot \underline{G}(S_1 + L_i, L') \\ &= \underline{G}^0(S + L_i, L') + \sum_{L_j \neq L_i} \sum_{S_1 S_2} \underline{G}^0(S + L_i, S_1 + L_j) \end{aligned}$$

$$\cdot \underline{V}^0(S_1, S_2; L_j) \cdot \underline{G}(S_2 + L_j, L') \quad . \quad (20)$$

The average Green's function for the alloy can then be determined by solving the equations

$$\begin{aligned} \langle \underline{G}(L, L') \rangle &= \underline{G}^0(L, L') + \sum_{\delta, L_i} \sum_{S, S'} \underline{G}^0(L, S + L_i) \\ &\cdot c^\delta(L_i) \underline{T}^\delta(S, S'; L_i) \\ &\cdot \langle \underline{G}^\delta(S' + L_i, L'; L_i) \rangle_{\delta(L_i)} \quad , \quad (21) \end{aligned}$$

$$\begin{aligned} \langle \underline{G}^\delta(S + L_i, L'; L_i) \rangle_{\delta(L_i)} &= \underline{G}^0(S + L_i, L') \\ &+ \sum_{\gamma, L_j \neq L_i} \sum_{S_1 S_2} \underline{G}^0(S + L_i, S_1 + L_j) \\ &\cdot c^\gamma(L_j) \underline{T}^\gamma(S_1, S_2; L_j) \\ &\cdot \langle \underline{G}^\gamma(S_2 + L_j, L'; L_j) \rangle_{\delta(L_i), \gamma(L_j)} \quad . \quad (22) \end{aligned}$$

Here  $c^\delta(L_i)$  is the probability that there is an atom of type  $\delta$  at  $L_i$ , and  $\langle \underline{G}(L, L') \rangle$  is the configurational average of the Green's function.  $\langle \rangle_{\delta(L_i)}$  is the conditional average when there is an atom of type  $\delta$  at  $L_i$ , and  $\langle \rangle_{\delta(L_i), \gamma(L_j)}$  is the conditional average for atoms of types  $\delta$  and  $\gamma$  at the sites  $L_i$  and  $L_j$ , respectively.

An approximation is now made which omits pair and higher cluster correlations, and which leads to a local self-energy  $\underline{K}$  confined to the defect space around  $L_i$ . This approximation is to replace the two-site conditional average in Eq. (22) by a single-site average,

$$\langle \underline{G}^\gamma(S + L_j, L'; L_j) \rangle_{\delta(L_i), \gamma(L_j)} = \langle \underline{G}^\gamma(S + L_j, L'; L_j) \rangle_{\gamma(L_j)} \quad (23)$$

for  $L_j \neq L_i$ . With this approximation, Eqs. (21) and (22) form a closed system which can be solved to give

$$\begin{aligned} \langle \underline{G}(L, L') \rangle &= \underline{G}^0(L, L') + \sum_{L_i} \sum_{S_1, S_2, S_3} \underline{G}^0(L, S_1 + L_i) \\ &\cdot \underline{T}(S_1, S_2; L_i) \cdot \underline{Y}^{-1}(S_2, S_3; L_i) \\ &\cdot \langle \underline{G}(S_3 + L_i, L') \rangle \quad , \quad (24) \end{aligned}$$

where  $\underline{T}(S, S'; L_i)$  is the average  $t$  matrix in the defect space around  $L_i$ ,

$$\underline{T}(S, S'; L_i) = \sum_{\delta} c^\delta(L_i) \underline{T}^\delta(S, S'; L_i) \quad , \quad (25)$$

and  $\underline{Y}(S, S'; L_i)$  is defined in terms of  $\underline{G}^0$  and  $\underline{T}$  by

$$\underline{Y}(S, S'; L_i) = \underline{I} \delta(S, S') + \sum_{S_1} \underline{G}^0(S, S_1) \cdot \underline{T}(S_1, S'; L_i) \quad . \quad (26)$$

We now set the average  $t$  matrix equal to zero for each  $L_i$ ,

$$0 = \sum_{\delta} c^\delta(L_i) \underline{T}^\delta(S, S'; L_i) \quad , \quad (27)$$

so that  $\langle \underline{G}(L, L') \rangle$ , the average Green's function for the alloy, is equal to the CPA Green's function  $\underline{G}^0(L, L')$ . Since  $\underline{T}(S_1, S_2; L_i)$  is an averaged quantity, it has the symmetry of the perfect lattice and (27) therefore results in only one independent matrix equation for each site in the unit cell. The local self-energy matrix  $\underline{K}(S, S'; L_i)$  found by solving

Eq. (27) is nonzero only if  $L_i$  is a possible defect site. Furthermore,  $\underline{K}(S, S'; L_i) = 0$  if  $S$  or  $S'$  lies outside the defect space around  $L_i$ , where the defect space comprises the set of sites defined by the condition  $\underline{D}^{\delta} \neq 0$ . As is shown more explicitly in the illustrative calculations of Sec. III, however, nonzero values for  $\underline{K}(S, S'; L_i)$  may be obtained for combinations of  $S$  and  $S'$  within the defect space for which the defect perturbation matrix  $\underline{D}^{\delta}(S, S'; L_i)$  itself vanishes.

For the case where defects of only one type may be present at only one site in the unit cell, the equation for the local self-energy matrix is derived schematically as follows. From Eqs. (16), (18), (19) and (27), the condition to be satisfied for a concentration  $c$  of defects is

$$0 = -c(\underline{K} - \underline{D})[\underline{I} + \underline{G}^0(\underline{K} - \underline{D})]^{-1} - (1-c)\underline{K}(\underline{I} + \underline{G}^0\underline{K})^{-1}. \quad (28)$$

Here all quantities are matrices in the defect space, and  $\underline{D}$  now denotes the perturbation matrix for a defect,  $\underline{D} = \underline{D}^{\delta=d}$ . Using the identity

$$\underline{W}(\underline{I} + \underline{G}^0\underline{W})^{-1} = (\underline{I} + \underline{W}\underline{G}^0)^{-1}\underline{W}, \quad (29)$$

and performing some elementary algebra, we obtain from Eq. (28)

$$0 = \underline{K} - c\underline{D} + \underline{K}\underline{G}^0(\underline{K} - \underline{D}) = \underline{K} - c\underline{D} + (\underline{K} - \underline{D})\underline{G}^0\underline{K}, \quad (30)$$

which is of the same form as that found by Taylor for mass defects.

We now restore our full notation for the case of defects of one type at the site  $\beta$  in the unit cell. Then if  $s$  denotes unit cells in the space of a defect at  $0\beta$ , Eq. (30) for the local self-energy is

$$0 = \underline{K}(sb, s'b'; \omega) - c\underline{D}(sb, s'b'; \omega) + \sum_{s_1 b_1, s_2 b_2} \underline{K}(sb, s_1 b_1; \omega) \cdot \underline{G}^0(s_1 b_1, s_2 b_2; \omega) \cdot [\underline{K}(s_2 b_2, s'b'; \omega) - \underline{D}(s_2 b_2, s'b'; \omega)], \quad (31)$$

where  $\underline{K}(sb, s'b'; \omega) = \underline{K}(sb, s'b'; 0\beta)$  and  $\underline{D}(sb, s'b'; \omega) = \underline{D}^{\delta=d}(sb, s'b'; 0\beta)$ .

The crystal periodic self-energy  $\underline{E}(lb, l'b'; \omega)$  which determines the CPA Green's function in Eq. (12) is found from Eq. (14) as a sum of local self-energy matrices,

$$\underline{E}(lb, l'b'; \omega) = \sum_{s, s'} \underline{K}(sb, s'b'; \omega) \delta(l - l', s - s'). \quad (32)$$

Equations (12), (31), and (32) must be solved self-consistently to obtain the CPA self-energy and Green's function.

It is easy to show that these equations reduce to those of Taylor for the case of mass defects. The defect space then reduces to the defect site itself ( $s = 0, b = \beta$ ), and Eq. (32) simplifies to

$$\underline{E}(\omega) = \underline{E}(l\beta, l\beta; \omega) = \underline{K}(0\beta, 0\beta; \omega). \quad (33)$$

From Eqs. (10) and (32), the self-energy  $\underline{E}(\omega)$

must satisfy

$$0 = \underline{E}(\omega) - cM\epsilon\omega^2\underline{I} + \underline{E}(\omega) \cdot \underline{G}^0(l, l; \omega) \cdot [\underline{E}(\omega) - M\epsilon\omega^2\underline{I}], \quad (34)$$

which is Taylor's equation (3.9).

In order to meet the requirements of translational invariance, the force-constant changes in Eq. (10) must be such that

$$\underline{D}(sb, sb; \omega = 0) = - \sum_{s', b' \neq sb} \underline{D}(sb, s'b'; \omega = 0). \quad (35)$$

Every atom in the defect space of the impurity at  $0\beta$  therefore has a nonzero diagonal force constant change. Furthermore,

$$\underline{D}(sb, sb; \omega) = \underline{D}(sb, sb; \omega = 0) + M\beta\epsilon\omega^2\delta(s, 0)\delta(b, \beta)\underline{I} \quad (36)$$

is not independent of  $s$ , so that  $\underline{D}(sb, s'b'; \omega) \neq \underline{D}(s - s', bb'; \omega)$  is not translationally invariant, and from Eq. (31), neither is the local self-energy  $\underline{K}(sb, s'b'; \omega)$ . Since the full self-energy is determined as a sum of local contributions in Eq. (32),  $\underline{E}(lb, l'b'; \omega) = \underline{E}(l - l', bb'; \omega)$  does have the correct behavior.

### III. RESULTS IN ONE DIMENSION

In this section we present some illustrative results for one-dimensional alloys with nearest-neighbor force constants. For both a monatomic and a diatomic system, the separate and combined effects of light-mass defects and increased force constants are calculated in the CPA at several concentrations and compared with exact results obtained by Monte Carlo calculations.<sup>22</sup>

For substitutional impurities which introduce nearest-neighbor force-constant changes in either a diatomic or monatomic linear chain, the local equations (those confined to the space of the defect) of Sec. II can be written as  $3 \times 3$  matrix equations in which rows and columns are ordered by position relative to the central site as  $-1, 0, 1$ . With this convention, the defect perturbation in Eq. (31) is

$$\underline{D} = \begin{bmatrix} \Delta & -\Delta & 0 \\ -\Delta & M\epsilon\omega^2 + 2\Delta & -\Delta \\ 0 & -\Delta & \Delta \end{bmatrix}, \quad (37)$$

where  $\Delta$  is the force-constant change;  $\Delta > 0$  corresponds to an increase in the force constant. From general symmetry arguments, the local self-energy matrix  $\underline{K}$  is similar in form to  $\underline{D}$ ,

$$\underline{K} = \begin{bmatrix} K(1, 1) & K(0, 1) & K(1, -1) \\ K(0, 1) & K(0, 0) & K(0, 1) \\ K(1, -1) & K(0, 1) & K(1, 1) \end{bmatrix}, \quad (38)$$

but  $K(0, 1) \neq K(1, 1)$ , in general, and the  $1, -1$  element may have a nonzero value, corresponding

to an effective next-nearest-neighbor coupling between the atoms adjacent to the central site.

The Green's function  $\underline{G}^0$  and the crystal self-energy  $\underline{E}$  have somewhat different matrix representations in the defect space for diatomic alloys than they do for monatomic systems. For the diatomic case,  $\underline{G}^0$  and  $\underline{E}$  have the same form as  $\underline{K}$  in Eq. (38), and from Eq. (32), the elements of  $\underline{E}$  are equal to those of  $\underline{K}$  with the exception that  $E(1, 1) = 2K(1, 1)$ . For monatomic alloys, the diagonal elements of  $\underline{G}^0$  and  $\underline{E}$  are equal; that is  $G^0(1, 1) = G^0(0, 0)$  and  $E(1, 1) = E(0, 0)$ , and the elements of  $\underline{E}$  are related to those of the local self-energy  $\underline{K}$  by  $E(0, 0) = K(0, 0) + 2K(1, 1)$ ,  $E(0, 1) = 2K(0, 1)$ , and  $E(1, -1) = K(1, -1)$ .

Since  $\underline{K}$  has four distinct elements, the  $3 \times 3$  equation for the local self-energy [cf. Eq. (31)],

$$0 = \underline{K} - c\underline{D} + \underline{K} \cdot \underline{G}^0 \cdot (\underline{K} - \underline{D}) \quad , \quad (39)$$

provides a set of four complex nonlinear equations which must be solved self-consistently to determine  $\underline{E}$  from Eq. (32) and  $\underline{G}^0$  from Eq. (12). The variable metric method of Powell<sup>28</sup> was used to do the calculations, and although it was more difficult to find the roots of Eq. (39) for some frequencies and concentrations than for others, no pathologies were encountered in the solutions.

Figures 1-6 compare approximate CPA phonon densities of states for model one-dimensional alloys with essentially exact results obtained by using the techniques of Dean.<sup>22</sup> The phonon density of states for an alloy can be defined by

$$\nu(\omega^2) = -\frac{1}{3\pi sN} \text{Im} \sum_{lb} \text{Tr} \langle \underline{M}(lb) \underline{G}(lb, lb; \omega) \rangle \quad , \quad (40)$$

where  $s$  is the number of atoms in the unit cell and  $N$  is the number of unit cells in the crystal. When

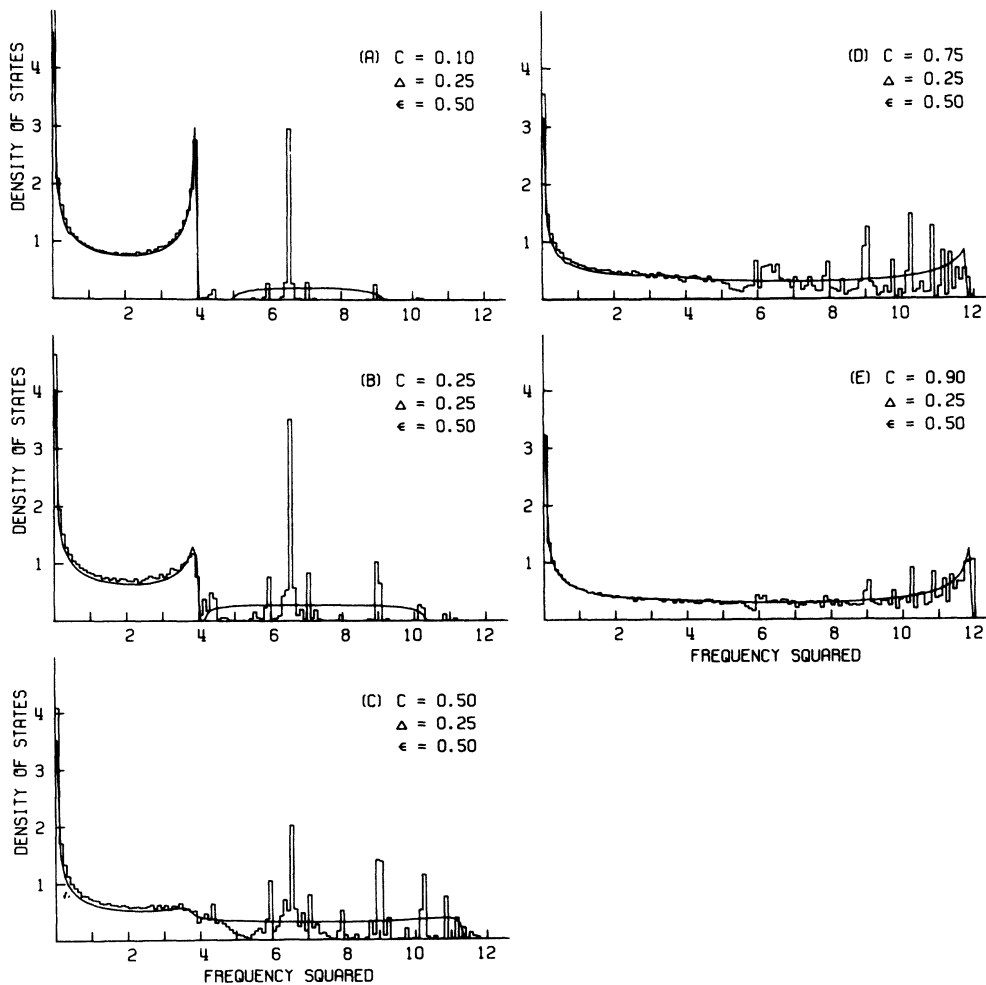


FIG. 1. CPA (smooth curve) and exact results (histogram) for the phonon density of states of a monatomic alloy  $A_{1-c}A'_c$  with nearest-neighbor force-constant changes and mass differences. For the exact calculations,  $M_A = 1.0$ ,  $M_{A'} = 0.5$ ,  $\Phi_{AA} = 1.0$ ,  $\Phi_{AA'} = 1.5$ . For the CPA calculations,  $\Phi = 1.0$ ,  $\Delta = 0.25$ , and  $\epsilon = 0.5$ .

defects of one type only are present at one site  $\beta$  in the unit cell, the configurational average in Eq. (40) at that site can, in principle, be evaluated exactly as

$$\langle \underline{M}(lb)\underline{G}(lb, lb; \omega) \rangle = M^d(\beta) \langle \underline{G}^{dd}(l\beta, l\beta; \omega) \rangle + M^h(\beta) \langle \underline{G}^{hh}(l\beta, l\beta; \omega) \rangle, \quad (41)$$

where  $d$  and  $h$  denote defect and host atoms, respectively. For the case of mass defects, the site diagonal defect and host Green's functions,  $\langle \underline{G}^{dd} \rangle$  and  $\langle \underline{G}^{hh} \rangle$ , in Eq. (41) can be related to the full CPA Green's function in a straightforward fashion, as discussed in Refs. (1) and (29). When off-diagonal disorder is present, however, the relationship between  $\langle \underline{G}^{dd} \rangle$ ,  $\langle \underline{G}^{hh} \rangle$ , and  $\underline{G}^0$  becomes less straightforward. For our purposes, we have found it sufficient to approximate the average,  $\langle \underline{M}\underline{G} \rangle$ , in Eq. (40) by the product of the averages,  $\langle \underline{M} \rangle \langle \underline{G} \rangle$ . The approximate CPA densities of states plotted in Figures 1-6 are therefore obtained from

$$\nu(\omega^2) = -\frac{1}{3\pi s} \text{Im} \sum_b \text{Tr} \langle M(b) \rangle \underline{G}^0(0b, 0b; \omega). \quad (42)$$

Figure 1 shows the approximate CPA phonon density of states determined from Eq. (42) for a monatomic alloy,  $A_{1-c}A'_c$ , with both mass difference and force-constant changes. The smooth curves are the CPA results, while the histograms are the exact results obtained by using the techniques of Dean<sup>22</sup> for chains of 10 000 atoms. The masses of the two constituents are  $M_A = 1.0$  and  $M_{A'} = 0.5$ , and the nearest-neighbor force constants for the exact calculation are  $\Phi_{AA} = 1.0$ ,  $\Phi_{AA'} = 1.25$ , and  $\Phi_{A'A'} = 1.5$ . Here and subsequently, the values given for the force constants are the spring constants for nearest-neighbor pairs of atoms; for example,  $\Phi_{AA} = -\Phi_{AA}(0, 1)$  for a pair of  $A$ - $A$  neighbors. Notice that we have chosen force constants which superimpose linearly,  $\Phi_{AA'} = (\Phi_{AA} + \Phi_{A'A'})/2$ . The maximum frequencies in the pure  $A$  and  $A'$  crystals are  $\sqrt{4}$  and  $\sqrt{12}$ , respectively. For the CPA calculations, the  $A$  crystal was used as the host mate-

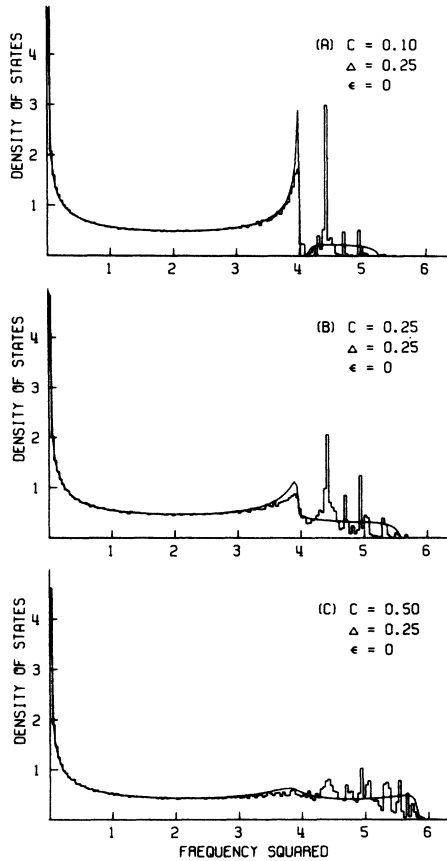


FIG. 2. CPA and exact densities of states for a monatomic alloy with force-constant changes only:  $M_A = M_{A'} = 1.0$ ,  $\Phi_{AA} = 1.0$ ,  $\Phi_{AA'} = 1.25$ ,  $\Phi_{A'A'} = 1.5$  (exact);  $\Phi = 1.0$ ,  $\Delta = 0.25$ ,  $\epsilon = 0$  (CPA).

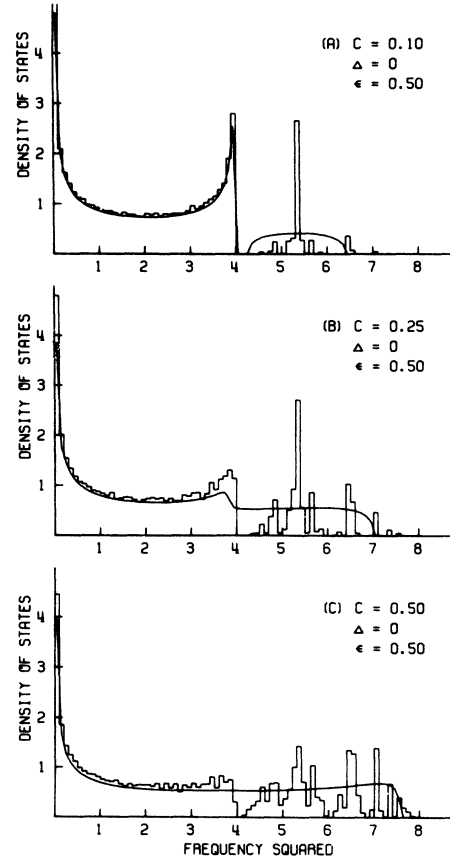


FIG. 3. CPA and exact densities of states for a monatomic alloy with mass changes only:  $M_A = 1.0$ ,  $M_{A'} = 0.5$ ,  $\Phi_{AA'} = \Phi_{A'A'} = 1.0$  (exact);  $\Phi = 1.0$ ,  $\Delta = 0$ ,  $\epsilon = 0.5$  (CPA).

rial so the mass defect is  $\epsilon = 0.5$  and the force-constant change is  $\Delta = 0.25$ .

For dilute concentrations  $c$  of  $A'$  atoms, the mass defect and the force-constant changes are such that a local-mode band is produced. As the concentration of  $A'$  atoms increases, this band increases in width and merges with the in-band modes around  $c = 0.25$ . As the concentration increases still further, the higher-frequency portion of the spectrum is filled in, and the agreement between the CPA and the exact results improves as the structure in the exact results diminishes in magnitude. The agreement between the CPA and the exact calculations is quite good over the frequency range  $0 < \omega^2 < 4$  of the pure  $A$  crystal for all concentrations. While the CPA of course fails to reproduce the fine structure at higher frequencies, it does give a good average description of the spectrum, and counts the number of modes in each region correctly.

Figure 2 shows the density of states for an alloy with the same force constants, but with no mass difference,  $M_A = M_{A'} = 1.0$ . For this case, the maximum frequency of the pure  $A'$  crystal is  $\sqrt{6}$ . Although a local-mode band still splits off at the lowest concentration shown, it is much closer to the band edge, and it merges with the in-band

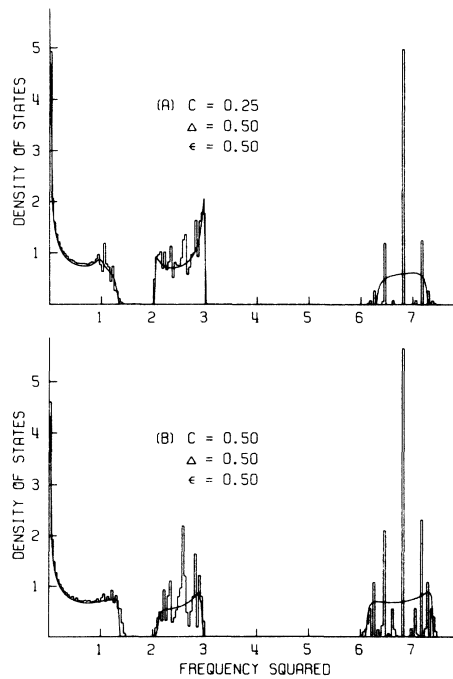


FIG. 4. CPA and exact results for the phonon density of states of a diatomic alloy  $A_{1-c}A'_cB$  with nearest-neighbor force-constant changes and mass differences. For the exact calculations,  $M_A = 1.0$ ,  $M_{A'} = 0.5$ ,  $M_B = 2.0$ ,  $\Phi_{AB} = 1.0$ ,  $\Phi_{A'B} = 1.5$ . For the CPA calculations,  $\Phi = 1.0$ ,  $\Delta = 0.5$ , and  $\epsilon = 0.5$ .

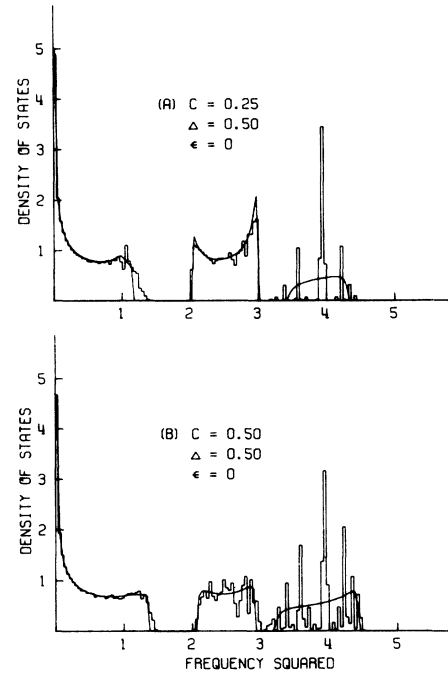


FIG. 5. CPA and exact densities of states for a diatomic alloy with force constant changes only:  $M_A = M_{A'} = 1.0$ ,  $M_B = 2.0$ ,  $\Phi_{AB} = 1.0$ ,  $\Phi_{A'B} = 1.5$  (exact);  $\Phi = 1.0$ ,  $\Delta = 0.5$ ,  $\epsilon = 0$  (CPA).

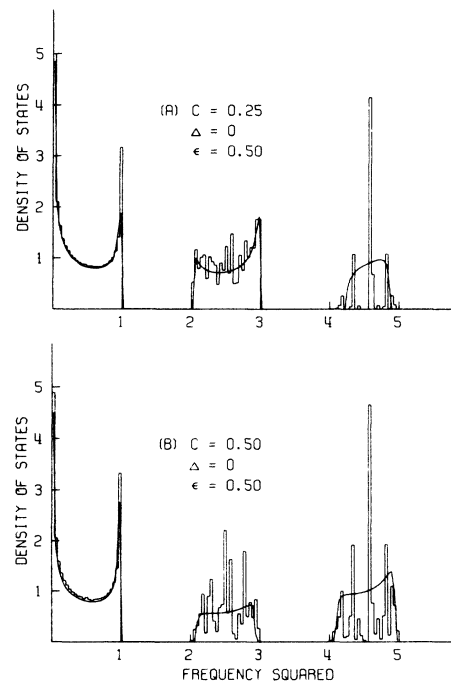


FIG. 6. CPA and exact densities of states for a diatomic alloy with mass changes only:  $M_A = 1.0$ ,  $M_{A'} = 1.5$ ,  $M_B = 2.0$ ,  $\Phi_{AB} = \Phi_{A'B} = 1.0$  (exact);  $\Phi = 1.0$ ,  $\Delta = 0$ ,  $\epsilon = 0.5$  (CPA).

modes more quickly. The structure in the exact results is also somewhat smaller in magnitude, and the agreement between the CPA and the exact calculations is generally better than for the more extreme case of Fig. 1.

Figure 3 compares the CPA and exact densities of states when there are no force-constant changes, but only mass differences:  $M_A = 1.0$ ,  $M_{A'} = 0.5$ ,  $\Phi_{AA} = \Phi_{AA'} = \Phi_{A'A'} = 1.0$ . Here the maximum pure  $A'$  frequency is  $\sqrt{8}$ . Qualitatively, much the same behavior is observed as in the preceding example, although the structure in the exact results diminishes less rapidly as the  $A'$  concentration increases. Figures 1–3 show that the in-band phonon spectrum is relatively insensitive to force-constant changes at modest concentrations of light mass defects, while the local modes depend much more strongly on the force-constant changes. Furthermore, the combined effects of lighter masses and stiffer springs may be to split off a local-mode band which neither change can produce separately,<sup>7</sup> as is illustrated by the results for  $c = 0.25$  in Figs. 1–3.

Figures 4–6 compare the approximate CPA density of states determined from Eq. (42) with exact results for a diatomic alloy,  $A_{1-c}A'_cB$ , with force-constant changes and mass differences together and separately. Chains of 20 000 atoms were used for the exact calculations. The masses of the constituents are  $M_B = 2.0$ ,  $M_A = 1.0$ , and  $M_{A'} = 0.5$  except for Fig. 5, where  $M_A = M_{A'} = 1.0$ . For Figs. 4 and 5, the force constants for the exact calculations are  $\Phi_{AB} = 1.0$  and  $\Phi_{A'B} = 1.5$ , and since the  $AB$  crystal was used as the host, the force-constant change for the CPA calculations is  $\Delta = 0.5$ . Figure 6 is for mass differences only, so there  $\Phi_{AB} = \Phi_{A'B} = 1.0$  and  $\Delta = 0$ .

With the values chosen for the masses and force constants, there is a gap in the spectrum of the pure  $AB$  crystal, and a local-mode band splits off above the  $AB$  optic-mode band as  $A'$  atoms are added in. The increase in force constant and the light mass defect cause this to happen separately, so again their combined effect is more pronounced. The CPA again is in good average agreement with the exact calculations, and counts the modes in the three bands seen at these concentrations correctly.

#### IV. DISCUSSION

For one-dimensional alloys with nearest-neighbor force-constant differences as well as mass disorder, the local self-energy matrix  $\underline{K}$  can be found by solving a difficult but tractable set of four com-

plex nonlinear equations which follow quite directly from Eq. (28). For three-dimensional systems, slightly more effort is required to obtain a manageable set of equations. Written as a single matrix spanning the central site and its nearest neighbors,  $\underline{K}$  has dimensions  $21 \times 21$ ,  $39 \times 39$ , and  $27 \times 27$  for NaCl, fcc, and bcc crystals, respectively, in contrast to the  $3 \times 3$  found for the one-dimensional case. However, these large matrices can be reduced in dimension by projection onto the irreducible representation of the  $(O_h)$  point group.<sup>30</sup>

The  $3 \times 3$  matrix equation encountered for one-dimensional alloys can itself be further simplified by a coordinate transformation, with results that are instructive for cubic materials. If  $u_0$  and  $u_{\pm 1}$  denote unit displacements along the chain for the three atoms in the defect space, then the symmetrized coordinates for the system are  $u_0$  and  $(u_{+1} + u_{-1})/\sqrt{2}$ , and the even mode  $(u_{+1} - u_{-1})/\sqrt{2}$ . Transformation to these coordinates reduces the  $3 \times 3$  equation (39) to a  $2 \times 2$  and a  $1 \times 1$  equation.

For many alloys, a simple but reasonable first approximation to include force-constant changes would be to allow changes only in the nearest-neighbor force constants along the nearest-neighbor directions. For this case in cubic crystals, Eq. (31) can be reduced to a  $T_{1u}(\Gamma_{15})$   $2 \times 2$  and two, four, or three  $1 \times 1$  equations for the NaCl, fcc, and bcc lattices, respectively.<sup>31</sup> The number of equations to be solved (5, 7, or 6) is not very much larger than for the one-dimensional alloys. A more serious computational problem is that of evaluating the real-space CPA Green's function  $\underline{G}^0(s, b, s', b'; \omega)$  in three dimensions rather than one. Work is now in progress toward including force-constant changes in cubic crystals in this approximation.

From the comparison between the extended CPA and exact results for one-dimensional alloys presented in Sec. III, we can hope to obtain good over-all agreement between theory and experiment for the effects of force-constant changes in real alloys, particularly for diatomic systems where the underlying assumption of linear superposition of the defect perturbations is most acceptable.

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<sup>1</sup>D. W. Taylor, Phys. Rev. **156**, 1017 (1967).

<sup>2</sup>P. Soven, Phys. Rev. **156**, 809 (1967).

<sup>3</sup>W. A. Kamitakahara and B. N. Brockhouse, in *Neutron Inelastic Scattering*, 1972 (IAEA, Vienna, 1972),



- Vol. I, p. 73.
- <sup>4</sup>D. W. Taylor, *Solid State Commun.* **13**, 117 (1973).
- <sup>5</sup>W. A. Kamitakahara and D. W. Taylor (unpublished).
- <sup>6</sup>N. Wakabayashi, *Phys. Rev. B* **8**, 6015 (1973).
- <sup>7</sup>T. Kaplan and M. Mostoller, *Phys. Rev. B* **9**, 353 (1974).
- <sup>8</sup>B. Velický, S. Kirkpatrick, and H. Ehrenreich, *Phys. Rev.* **175**, 747 (1968).
- <sup>9</sup>S. Kirkpatrick, B. Velický, and H. Ehrenreich, *Phys. Rev. B* **1**, 3251 (1970).
- <sup>10</sup>P. Soven, *Phys. Rev.* **178**, 1136 (1969).
- <sup>11</sup>G. M. Stocks, R. W. Williams, and J. S. Faulkner, *Phys. Rev. B* **4**, 4390 (1971).
- <sup>12</sup>D. Stroud and H. Ehrenreich, *Phys. Rev. B* **2**, 3197 (1970).
- <sup>13</sup>B. Velický and K. Levin, *Phys. Rev. B* **2**, 938 (1970).
- <sup>14</sup>J. S. Faulkner, *Phys. Rev. B* **1**, 934 (1970).
- <sup>15</sup>W. J. L. Buyers, D. E. Pepper, and R. J. Elliot, *J. Phys. C* **5**, 2611 (1972).
- <sup>16</sup>W. H. Butler, *Phys. Lett. A* **39**, 203 (1972).
- <sup>17</sup>B. G. Nickel and J. A. Krumhansl, *Phys. Rev. B* **4**, 4354 (1971).
- <sup>18</sup>B. G. Nickel and W. H. Butler, *Phys. Rev. Lett.* **30**, 373 (1973).
- <sup>19</sup>F. Cyrot-Lackmann and F. Ducastelle, *Phys. Rev. Lett.* **27**, 287 (1971).
- <sup>20</sup>E-Ni Foo, Shyamalendu M. Bose, and M. Ausloos, *Phys. Rev. B* **7**, 3454 (1973).
- <sup>21</sup>W. H. Butler, *Bull. Am. Phys. Soc.* **18**, 415 (1973); *Phys. Rev. B* **8**, 4499 (1973).
- <sup>22</sup>P. Dean, *Proc. R. Soc. Lond. A* **260**, 263 (1961); *Rev. Mod. Phys.* **44**, 127 (1972).
- <sup>23</sup>D. N. Payton and W. M. Visscher, *Phys. Rev.* **154**, 802 (1967).
- <sup>24</sup>Hiroyuki Shiba, *Prog. Theor. Phys.* **46**, 77 (1971).
- <sup>25</sup>J. A. Blackman, D. M. Esterling, and N. F. Berk, *Phys. Rev. B* **4**, 2412 (1971).
- <sup>26</sup>L. Schwartz, H. Krakauer, H. Fukuyama, *Phys. Rev. Lett.* **30**, 746 (1973).
- <sup>27</sup>D. N. Zubarev, *Usp. Fiz. Nauk.* **71**, 71 (1960) [*Sov. Phys.-Usp.* **3**, 320 (1960)].
- <sup>28</sup>J. M. Ortega and W. C. Rheinhold, *Iterative Solution of Non-Linear Equations in Several Variables* (Academic, New York, 1970).
- <sup>29</sup>R. J. Elliot and D. W. Taylor, *Proc. R. Soc. Lond. A* **296**, 161 (1967).
- <sup>30</sup>Katja Lakatos and J. A. Krumhansl, *Phys. Rev.* **175**, 841 (1968).
- <sup>31</sup>For force constant changes only, the  $T_{1u}$   $2 \times 2$  equations can be further reduced to  $1 \times 1$  equations by unitary transformations.