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Phonons in mixed crystals

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Abstract. The simple example of phonons in a linear chain of atoms with substitutional disorder is reconsidered in order to determine the rearrangements of acoustic and localized mode branches with increasing concentration of light impurities. The coherent-potential approximation cannot be applied successfully to this problem. A new expression for the self-energy of phonons is derived, which is exact in the limits of $c \to 0$ and $c \to 1$, c being the impurity concentration, and which gives reliable results for intermediate c.

1. Introduction

Since the famous work of Velický *et al* [1] it is well known that the coherent-potential approximation (CPA) [2] does not correctly describe the spectral densities of elementary excitations, e.g. of phonons localized at impurities. Instead of Lorentzian shapes the CPA yields half-egg-like shapes for low impurity concentrations. Band tails are missing entirely, the peak positions are not well defined and the half-widths are too large. The δ-like shape of the spectral density in the limit of vanishing impurity concentration is not reproduced. Densities of states show, in general, the same shortcomings [1].

This defect of the CPA becomes pronounced if for example with increasing impurity concentration the mode frequencies change in such a way that the corresponding spectral densities penetrate each other. Let us consider as the simplest example the case of light substitutional impurities (mass changes only) in a linear chain of atoms with nearest-neighbour interaction. For one impurity with a mass defect $\varepsilon = -\Delta M/M > 0$, there exists an acoustic branch given by $\omega^2 = \omega^2_{\max} \frac{1}{2}[1 - \cos(ka)]$ and a mode which is localized at the impurity at $\omega^2_{\text{loc}} = \omega^2_{\max}/(1 - \varepsilon^2)$ [3]. Both branches are shown in figure 1. The significance of the wavevector for the local mode branch is given by the Fourier transform of the local wavefunction, which contains all k-values. On increase in the number of impurities, the mode positions, their intensities and half-widths have to change in such a way that, for $c = 1$, c being the concentration of light impurities, one acoustic branch with $\omega^2 = \omega^2_{\max}[1/(1 - \varepsilon)] \frac{1}{2}[1 - \cos(ka)]$ results (figure 1).

It is the aim of this paper to determine how the spectral densities of the initial two modes (for $c \simeq 0$) rearrange with increasing $c \to 1$. The result of the CPA for this case is shown in figure 2. The spectral density of the impurity mode shows all the defects mentioned above.

Here we show that the exact knowledge of the Green function in the two limits $c \simeq 0$ and $c \simeq 1$ (one-impurity problems) can be exploited in order to obtain an interpolation

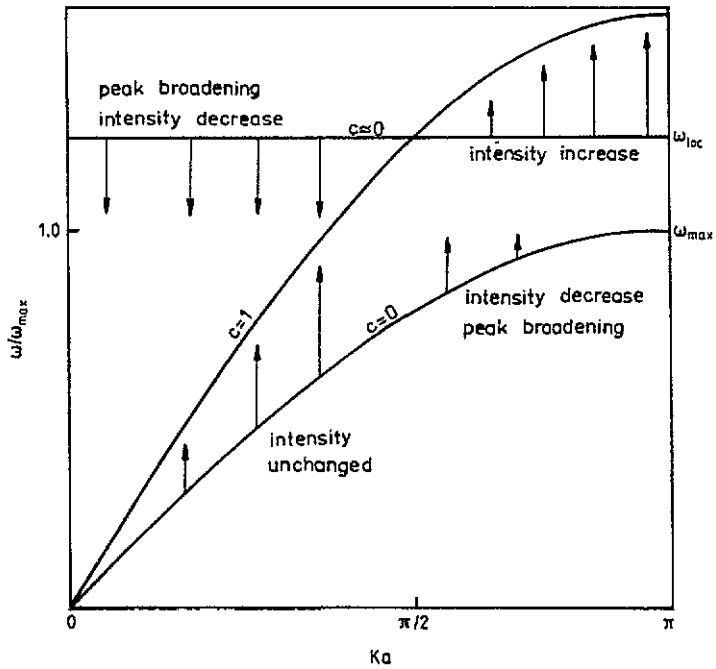

Figure 1. Acoustic and localized mode branches for $c \approx 0$ and acoustic mode branch for $c = 1$ for a mass defect of $\varepsilon = -\Delta M/M = 0.6$. The arrows indicate the rearrangements with increasing c within the present approximation.

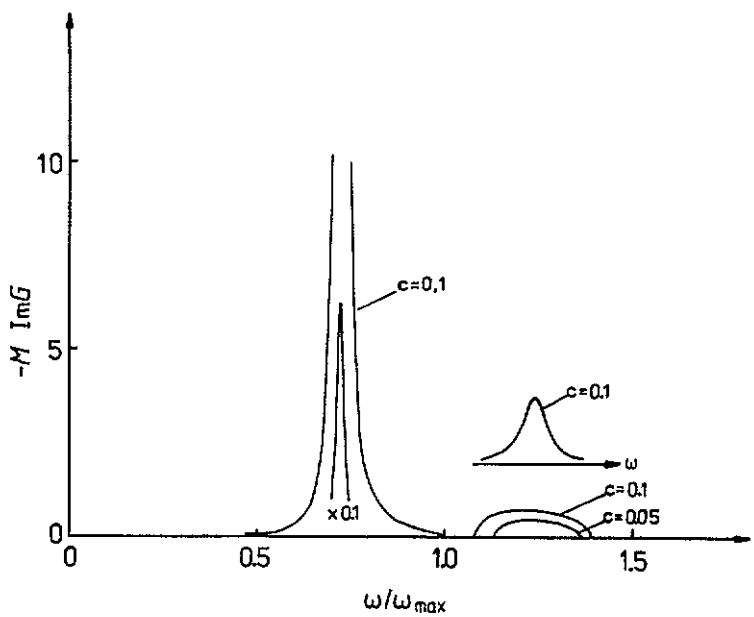

Figure 2. Spectral weights at $ka = \pi/2$ for a mass defect ε of 0.6 with concentrations $c = 0.1$ and $c = 0.05$ within the CPA, and $c = 0.1$ within the present approximation (inset).

scheme for all c. This scheme is applied to the linear-chain model. It is demonstrated that the result is free of the shortcomings of the CPA and that the rearrangements of the phonon modes with c can be determined.

2. The limiting cases $c \simeq 0$ and $c \simeq 1$

Our aim is to calculate the retarded displacement–displacement Green function $G_{ll'} = \langle\langle u_l, u_{l'}; \omega \rangle\rangle$ for a linear chain of A atoms of mass M with substitutional light impurities B of mass $M + \Delta M$, $\varepsilon = -\Delta M/M > 0$, for all impurity concentrations. u_l is the displacement of the atom in the lth unit cell, containing one atom only. For simplicity we assume a nearest-neighbour interaction which is independent of the types of atom. The Green function obeys the equation of motion

$$\sum_{l'} (M\omega^2 \delta_{ll'} - \varphi_{ll'} - V_{ll'}) G_{l'l''} = \delta_{ll''} \tag{1}$$

where

$$\varphi_{ll'} = \begin{cases} 2f & \text{if } l = l' \\ -f & \text{if } |l - l'| = 1 \\ 0 & \text{else} \end{cases}$$

and $V_{ll'} = M\varepsilon\omega^2 \delta_{ll'}$ if l is occupied by an impurity (B atom), $V_{ll'}$ being zero otherwise (A atoms).

Introducing the Green function $P_{ll'}$ of the unperturbed ($c = 0$) chain as a solution of (1) with $V_{ll'} = 0$ we obtain

$$G_{ll'} = P_{ll'} + \sum_{l'',l'''} P_{ll''} V_{l''l'''} G_{l'''l'}. \tag{2}$$

The averaged Green function $\bar{G}_{ll'}$ is defined as

$$\bar{G}_{ll'} = \frac{1}{N} \sum_i G_{i+l,i+l'} \tag{3}$$

and obeys the equation ($\bar{P}_{ll'} = P_{ll'}$)

$$\bar{G}_{ll'} = P_{ll'} + \sum_{l'',l'''} P_{ll''} \overline{V_{l''l'''} G_{l'''l'}}. \tag{4}$$

Introducing a single-site self-energy Σ as

$$\overline{G_{ll'}} = P_{ll'} + \sum_{l''} P_{ll''} \Sigma \overline{G_{l''l'}} \tag{5}$$

we get

$$\Sigma \overline{G_{ll'}} = \frac{1}{N} \sum_{i,l''} V_{i+l,i+l''} G_{i+l'',i+l'}$$

or

$$\Sigma \overline{G_0} = \Sigma \overline{G_{ll}} = \frac{1}{N} \sum_i V_{ii} G_{ii}. \tag{6}$$

On the other hand we can write

$$\overline{G_0} = \frac{1}{N} \sum_i G_{ii} = (1 - c) G_{\mathrm{A}} + c G_{\mathrm{B}} \tag{7}$$

with

$$G_A = \frac{1}{N_A} \sum_{i \in A} G_{ii}$$

and

$$G_B = \frac{1}{N_B} \sum_{i \in B} G_{ii}$$

where N_A and N_B are the numbers of lattice sites occupied by A atoms and B atoms, respectively, and the sums are restricted to these sites.

In a similar way we obtain

$$\frac{1}{N} \sum_i V_{ii} G_{ii} = (1 - c) V_A G_A + c V_B G_B \tag{8}$$

with $V_A = 0$ and $V_B = M\varepsilon\omega^2$, and from (6) the exact result for the self-energy

$$\Sigma = (cM\varepsilon\omega^2 G_B/G_A)/[(1 - c) + cG_B/G_A]. \tag{9}$$

The ratio G_B/G_A is a still unknown function of c. G_A and G_B, however, are exactly known in the limits $c \simeq 0$ and $c \simeq 1$ from the solutions of the corresponding one-impurity problems. For one light impurity at the origin we obtain

$$G_A = \frac{1}{N - 1} \sum_{i \neq 0} G_{ii}. \tag{10}$$

Now, $G_{ii} = P_{ii}$ for all lattice sites except for a few in the neighbourhood of $i = 0$. Therefore we obtain $G_A = P_{ii} = P_0$ for the infinite chain $N \to \infty$.

$$G_B = \frac{1}{N_B} \sum_{i \in B} G_{ii} = G_0$$

is given by the equation

$$G_0 = P_0 + P_0 M\varepsilon\omega^2 G_0$$

which can be solved to give

$$G_B = P_0/(1 - M\varepsilon\omega^2 P_0). \tag{11}$$

From (9)–(11) we obtain

$$\Sigma = cM\varepsilon\omega^2/[1 - (1 - c)M\varepsilon\omega^2 P_0] \tag{12}$$

which is identical with the result of the averaged **t**-matrix approximation (ATA) at $c \simeq 0$† [4].

† The abbreviation ATA is not uniquely used in the literature; see [5].

P_0 in (12) for the linear-chain model is given by

$$P_0 = \frac{1}{N}\sum_k \frac{1}{M\{\omega^2 - \frac{1}{2}\omega_{\max}^2[1 - \cos(ka)]\}} \tag{13}$$

where k varies between $-\pi/a$ and $+\pi/a$. Equation (13) can be integrated with the result that

$$P_0 = (1/M)(1/\sqrt{\omega^4 - \omega_{\max}^2\omega^2}) \tag{14}$$

where $\omega_{\max} = \sqrt{4f/M}$ [3].

The whole analysis can be repeated near the limit $c = 1$. The result for the self-energy then is

$$\Sigma = \varepsilon\omega^2 M - (1 - c)\varepsilon\omega^2 M/(1 + c\varepsilon\omega^2 M Q_0) \tag{15}$$

where

$$Q_0 = P_0(M + \Delta M). \tag{16}$$

3. Interpolation scheme for intermediate c

From (12) and (15) the self-energy Σ and its first derivative $\mathrm{d}\Sigma/\mathrm{d}c$ are exactly known in the limits $c = 0$ and $c = 1$ and are given by

$$\begin{aligned} &\Sigma|_0 = 0 \qquad \Sigma|_1 = \varepsilon\omega^2 M \\ &(\mathrm{d}\Sigma/\mathrm{d}c)|_0 = \Sigma'|_0 = \varepsilon\omega^2 M/(1 - \varepsilon\omega^2 M P_0) \\ &(\mathrm{d}\Sigma/\mathrm{d}c)|_1 = \Sigma'|_1 = \varepsilon\omega^2 M/(1 + \varepsilon\omega^2 M Q_0). \end{aligned} \tag{17}$$

The higher derivatives $\mathrm{d}^2\Sigma/\mathrm{d}c^2$, $\mathrm{d}^3\Sigma/\mathrm{d}c^3$, . . . at $c = 0$ and $c = 1$ are not known. Their knowledge would correspond to the solution of infinite two-, three-, . . . impurity problems with different impurity distances.

The easiest way to obtain Σ at all c is, therefore, to look for a fourth-order differential equation, which has to be solved under the boundary conditions (17). Such a differential equation, of course, never can be exact. Otherwise the mixed-crystal problem could be solved exactly.

As in [6–8] we use the exact forms Σ = numerator/denominator = $(a + bc + \ldots)/(d + ec + \ldots)$ of the self-energy, obtained in section 2, in order to obtain the higher derivatives $\mathrm{d}^2\Sigma/\mathrm{d}c^2$, $\mathrm{d}^3\Sigma/\mathrm{d}c^3$ and $\mathrm{d}^4\Sigma/\mathrm{d}c^4$. These are found to be coupled by

$$\mathrm{d}^4\Sigma/\mathrm{d}c^4 = \tfrac{4}{3}(\mathrm{d}^3\Sigma/\mathrm{d}c^3)^2/(\mathrm{d}^2\Sigma/\mathrm{d}c^2) \tag{18}$$

which is exact near $c = 0$ (from (12)) and near $c = 1$ (from (15)).

As in [6–8] we now propose (18) to be valid not only near $c = 0$ and $c = 1$ but for all c. Equation (18) can be solved under the boundary conditions (17) analytically with the result that

$$\Sigma(c) = \alpha + \beta c + \gamma/(1 + \delta c) \tag{19}$$

where

$$\begin{aligned}
\alpha &= \Sigma|_0 - \gamma \\
\beta &= \gamma\delta + \Sigma'|_0 \\
\gamma &= [(1+\delta)/\delta^2](\Sigma|_1 - \Sigma|_0 - \Sigma'|_0) \\
\delta &= (\Sigma'|_0 - \Sigma'|_1)/(\Sigma|_1 - \Sigma|_0 - \Sigma'|_1) - 2.
\end{aligned} \tag{20}$$

Equations (19) and (20) constitute an interpolation scheme for the self-energy which uses maximally all the exact knowledge that we have—the numerator-over-denominator form of the self-energy as well as the expansions of both in c and $1 - c$ up to first order—hence correctly reproducing the limits $c \to 0$ and $c \to 1$.

The new interpolation scheme presented here is based on the single-site approximations (12) and (15), respectively. It is often stated in the literature that the best single-site approximation is the self-consistent CPA. This statement, however, is a misunderstanding of the original reasoning of Velický *et al* [1]: there exists an infinite number of single-site theories differing in the infinite possible choices of initial mean self-energies. It was shown in [1] that all these theories would give identical results if the underlying single-site approximation were correct. The best single-site theory, hence, would be that which minimizes the difference to the exact result. This, however, has never been proved for the self-consistent single-site approximation, the CPA [6].

4. Results and discussion

The Fourier transform of the averaged Green function (5) is

$$\overline{G(k,\omega)} = 1/\{M\omega^2 - (M/2)\omega_{\max}^2[1 - \cos(ka)] - \Sigma(\omega)\}. \tag{21}$$

The spectral weight of (21) is given (up to a factor $-1/\pi$) by its imaginary part which can easily be calculated using (19) and (20) together with (17). The results for different concentrations are given in figure 3 for a mass defect ε of 0.6 (and in the inset of figure 2).

For small concentrations ($c = 0.1$) (figure 1(a)) we obtain Lorentzian-shaped spectral weights near the expected positions, the acoustic and the localized phonon branches. The finite half-widths of these spectral weights indicate that the wavevector k is no longer a good quantum number in mixed crystals. With increasing concentration the localized phonon branch for small wavevectors $k < \pi/2a$ decreases in intensity, broadens and moves to smaller energies down to $\omega_{\max}$ of the acoustic branch at $c = 0$. For $k > \pi/2a$ this branch increases in intensity; it first broadens, then narrows and moves up in energy in order to transform into the acoustic mode branch at $c = 1$. Correspondingly the acoustic mode branch for $k < \pi/2a$ transforms to that at $c = 1$ whereas the acoustic mode branch for $k > \pi/2a$ broadens, moves upwards in energy up to $\omega_{\max}$ and vanishes in intensity. Thus the upper part of the localized phonon branch ($k > \pi/2a$) and the lower part ($k < \pi/2a$) of the acoustic branch at $c = 0$ transform with increasing c to the new acoustic branch; the remaining mode parts vanish. This behaviour is indicated schematically in figure 1.

We would like to recall that the normalized spectral density $\rho(\omega)$ cannot be obtained in the phonon case from a k-summation of the imaginary part of the Fourier transform (21) of the displacement–displacement Green function; $\rho(\omega)$ is connected with a different Green function (see, e.g., [4] and [9]). Because most numerical results for disordered linear chains are obtained for $\rho(\omega)$ (see, e.g., [5]) a direct comparison of our

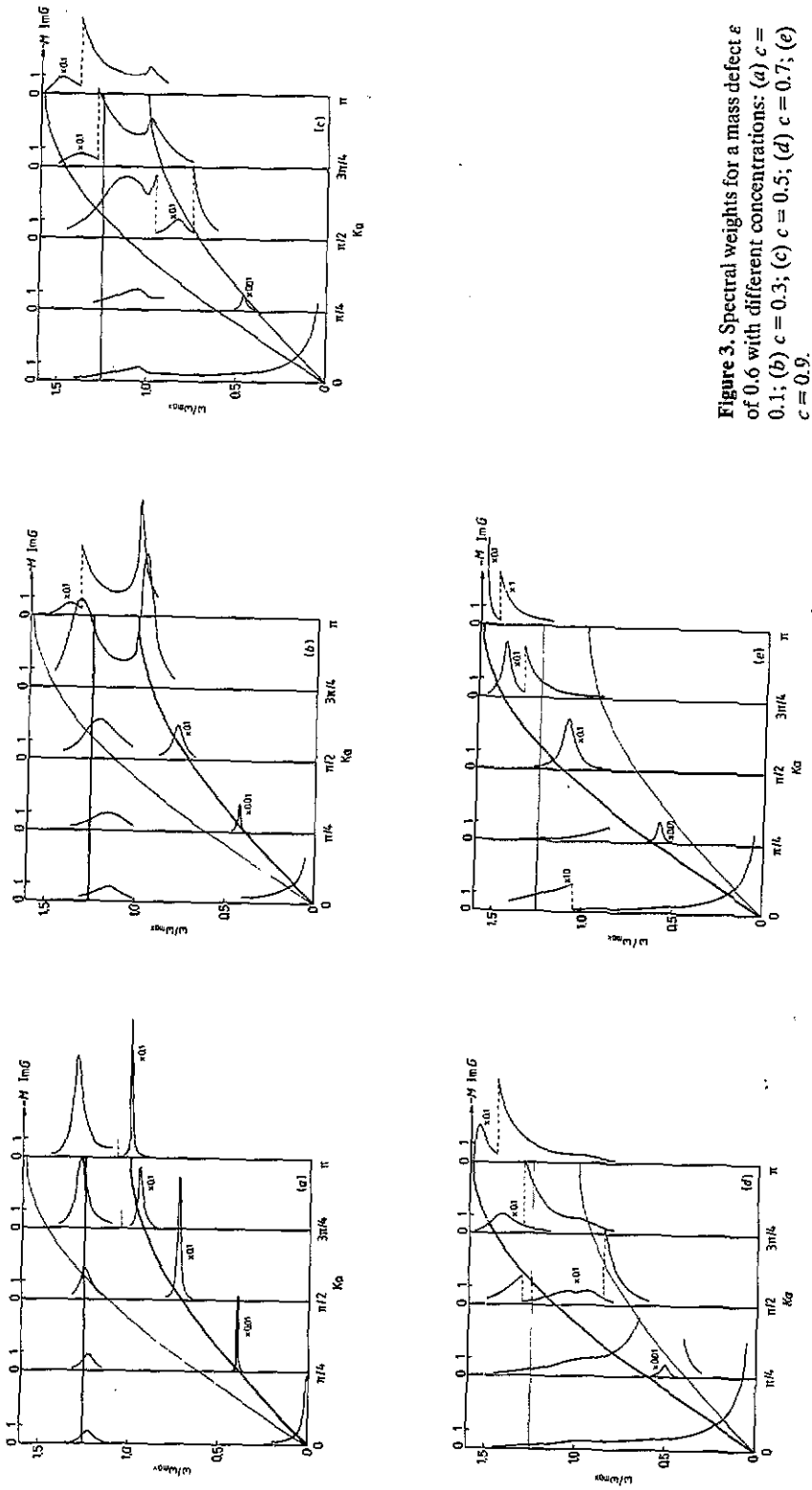

Figure 3. Spectral weights for a mass defect ε of 0.6 with different concentrations: (*a*) $c = 0.1$; (*b*) $c = 0.3$; (*c*) $c = 0.5$; (*d*) $c = 0.7$; (*e*) $c = 0.9$.

theory with such results is not possible. There is, however, no doubt in the presence of band tails in the numerically obtained spectra. On the other hand, some sharp structures within the impurity bands can be explained only by cluster formations and can never be obtained with a single-site theory [10].

In this paper we have given an interpolation scheme for diagonal perturbations only. Force constant changes, for example, have not been considered. The generalization to non-diagonal perturbations can easily be performed as in the case of electronic properties of alloys [11].

In conclusion it can be stated that the interpolation scheme presented here results in spectral weights which do not show the shortcomings of those of the CPA and, hence, is able to describe the rearrangements of elementary excitation branches even in the case of their mutual penetration. The reason is that we have exploited all the exact knowledge about the self-energy: the numerator-over-denominator form of it given by the definition (6) together with the exact equations (7) and (8) as well as the first terms of the series expansions of the numerator and of the denominator in c and $1 - c$, respectively, known from the exactly solvable one-impurity problems. It was demonstrated by the present author that the same interpolation scheme can also be successfully applied to electronic excitations [6] and to the classical electrodynamics of heterogeneous media [7, 8].

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