

## Theory of random alloy vibrations with account for cluster effects

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A theory of vibration spectra of solid solutions has been developed. In this theory, a cluster of  $n$  cells statistically filled with impurity atoms is used as a phonon scattering unit. The calculation of vibration spectra of a disordered linear chain in the generalized non-self-consistent approximation has demonstrated a strong dependence of the spectrum on the number  $n$  for  $n \leq 4$ . For  $n = 6$ , the calculated spectrum is in an excellent agreement with the result of the computer experiment performed by Dean for a chain of 8000 atoms. The maximum number of impurities in the cluster to be considered depends on the magnitude of the initial damping (due to anharmonicity). The spectrum of the linear chain has also been calculated in the usual and generalized self-consistent approximation. These calculations give smeared structureless curves, which absolutely does not agree either with the theoretical calculation in the non-self-consistent approximation or with the results obtained by Dean. This failure is related to the mean-field properties of self-consistent theories. The spectrum of a three-dimensional solid solution is calculated using a simple model of the crystal.

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### I. INTRODUCTION

A theory of vibration spectra of solid solutions, which was proposed in [1, 2], can explain the complex structure of the spectrum and has no disadvantages of the preceding theories (see reviews [3, 4]). The specific feature of the theory is that the impurity complex (cluster) rather than a single impurity is used as a phonon scattering unit. This permits taking into account the phase relationships in scattering by cluster impurities. Explicitly, the cluster is considered as a set of  $n$  lattice cells, each being filled by an impurity atom with the probability  $x$  ( $x$  is the fraction of impurity atoms in the lattice). It is assumed that the cluster is translated over the lattice as a whole and the origin of the coordinates of the cluster can be at any point of the lattice. When summing these clusters over the lattice, each lattice atom is taken into account  $n$  times. To avoid the mistake of repeated summation, the coefficients  $1/n$  are placed before the sum signs. The result of the theory is represented as a series for the Green's function, in which multiple scattering of phonons by clusters is taken into account and corrections of multiple occupations are included. After averaging over the cluster positions, the series can be summed. Physical quantities (response functions, spectrum) are expressed through the Green's functions. In the present work, as an extension of theory [1, 2], the following problems are considered. (1) The variation of the spectrum of a solid solution with an increase in the number of cells  $n$  in the cluster has been studied. (2) The number of cells  $n$  in a cluster, which is sufficient for a good description of the spectrum

of a solid solution for a given value of the damping parameter of vibration excitations, has been determined. (3) A comparison of the vibration spectra of solid solutions is made, which were calculated in the non-self-consistent and self-consistent approximations, both with each other and with the result of the computer experiment [5]. The aforementioned investigations have been performed predominantly using a one-dimensional model of a solid solution because it requires a shorter time for the calculation. Moreover, there is a computer experiment for this model, the result of which can be compared with it. (4) In order to draw conclusions about the dependence of the spectrum of a solid solution on its dimensionality, the spectrum has been calculated using a simple three-dimensional model.

## II. BASIC RELATIONSHIPS

To avoid a cumbersome notation, we will use the simplest model of a crystal lattice, namely, the lattice with one atom per unit cell. The relationships are easily generalized for the case of a more complex lattice. We assume that the replacement of a host atom by an impurity leads only to a change in the mass by  $\Delta m$ . The effect of this perturbation depends on the frequency  $\omega$ . It is convenient to transform it into the form independent of the frequency [1, 2, 6]. Then, the obtained relationships are easily transferred to the electronic systems. The equation for the Fourier component of the full Green's function  $F$  averaged over the positions of impurities has the form

$$\langle F(\mathbf{y}) \rangle = f(\mathbf{y}) + f(\mathbf{y}) \sum(\mathbf{y}) \langle F(\mathbf{y}) \rangle, \quad (1)$$

where  $f(\mathbf{y})$  is the Fourier component of the free Green's function,  $\sum(\mathbf{y})$  is the self-energy part, and  $\mathbf{y}$  is the wave vector. The relation of  $\langle F(\mathbf{y}) \rangle$  to the Green's function  $\langle F(l l') \rangle$  in real space is given by the formula

$$\langle F(l l') \rangle = N^{-1} \sum_{\mathbf{y}} \langle F(\mathbf{y}) \rangle \exp\left(2\pi i \mathbf{y} \cdot \mathbf{x}(l l')\right), \quad (2)$$

where  $l$  and  $l'$  characterize the positions of lattice cells and  $N$  is the number of cells in the periodically translated volume. The Fourier component of the free Green's function  $f(l l')$  has the form  $f(\mathbf{y}) = \omega(\mathbf{y})^2 / [\omega(\mathbf{y})^2 - \omega^2]$ , where  $\omega(\mathbf{y})$  is the dispersion law of phonons in the ideal lattice. Such an unusual form of the Green's function is explained by the perturbation transformation from the frequency-dependent form to the frequency-independent form. The conventional Green's function  $g(l l')$  differs from  $f(l l')$  in that the  $\omega(\mathbf{y})^2$  term is absent in the numerator of the expression for  $f(\mathbf{y})$ . The self-energy part  $\sum(\mathbf{y})$  is expressed through its matrix form  $\overline{\sum}(\mathbf{y})$  with the use of the relationship  $\sum(\mathbf{y}) = \overline{u}' \overline{\sum}(\mathbf{y}) \overline{u}$ ; where  $\overline{u}'$  and  $\overline{u}$  stand for a row and a column of  $n$  unities, respectively. Here, line bars above the symbols denote rows, vectors, and matrices in the index space of the cluster;  $\overline{\sum}(\mathbf{y})$  is the matrix of  $n \times n$  elements; and  $\overline{u}'$  and  $\overline{u}$  stand for a row and a column of  $n$  unities. In the non-self-consistent approximation, which is referred to in [1, 2] as ATAM- $n$  (the modified average

$t$ -matrix approximation),  $\overline{\Sigma}(\mathbf{y})$  has the form

$$\overline{\Sigma}(\mathbf{y}) = n^{-1} [\overline{I} + \overline{\tau}_\phi \overline{f}_\phi]^{-1} \overline{\tau}_\phi, \quad (3)$$

where  $\overline{f}_\phi \equiv f(i\mu | i\mu') \exp(-i\phi_{\mu\mu'})$ . Here, in the free Green's function, instead of the indices  $l$  or  $l'$ , the lattice points are numbered by pairs of the indices  $i, \mu$  or  $i, \mu'$ , where  $i$  denotes the position of the cluster as a whole, and  $\mu$  or  $\mu'$  is the position of the cell in the cluster ( $\mu, \mu' = 1, 2, \dots, n$ ). The function  $\phi_{\mu\mu'} = 2\pi\mathbf{y}\mathbf{R}_{\mu\mu'}$  determines the phase difference in phonon scattering by impurities  $\mu$  and  $\mu'$ , and  $\mathbf{R}_{\mu\mu'} = \mathbf{R}_\mu - \mathbf{R}_{\mu'}$  is the vector connecting the cells  $\mu$  and  $\mu'$  of the cluster. The matrix  $\overline{\tau}_\phi$  denotes the scattering matrix  $\overline{t}_\phi(i)$ , averaged over the impurity distribution. The averaging is given by the expression

$$\overline{\tau}_\phi = \sum_{\eta(i1)=0,1} \sum_{\eta(i2)=0,1} \cdots \sum_{\eta(in)=0,1} (1-x)^n \left[ x/(1-x) \right]^{(\eta(i1)+\eta(i2)+\cdots+\eta(in))} \overline{t}_\phi(i), \quad (4)$$

where  $x$  is the fraction of impurity atoms in the lattice ( $0 \leq x \leq 1$ ). The matrix  $\overline{t}_\phi(i)$  is given by the relationship  $\overline{t}_\phi(i) \equiv \Delta \overline{I}_\eta [\overline{I} - \Delta \overline{f}_{\eta\phi}(ii)]^{-1}$ , where  $\overline{I} \equiv \delta_{\mu\mu'}$ ,  $\overline{I}_\eta(i) \equiv \eta(i\mu)\delta_{\mu\mu'}$ ,  $\overline{f}_{\eta\phi}(ii) \equiv f(i\mu | i\mu')\eta(i\mu)\eta(i\mu') \exp(-i\phi_{\mu\mu'})$ ;  $\Delta = \Delta m/(m + \Delta m)$ , and  $\Delta m$  is the change in the mass of the atom with the mass  $m$  when it is substituted for an impurity. The result of the generalized self-consistent approximation, which is referred to in [1, 2] as CPAM- $n$  (modified coherent potential approximation) can be obtained if on the right-hand side of Eq. (3) (including the expression for  $\overline{\tau}_\phi$ ), we make the change  $\overline{f}_\phi \rightarrow \overline{F}_\phi$ , where

$$\overline{F}_\phi = \langle \overline{F}_\phi \rangle \left[ I + n \overline{\Sigma}(\mathbf{y}) \langle \overline{F}_\phi \rangle \right]^{-1}, \quad (5)$$

In contrast to relationship (3), where  $\overline{\Sigma}(\mathbf{y})$  is the function of  $\overline{f}_\phi$ , here  $\overline{\Sigma}(\mathbf{y})$  is the function of  $\overline{F}_\phi$ , i.e.,  $\overline{\Sigma}(\mathbf{y}) \equiv \overline{\Sigma}(\overline{F}_\phi)$ .

### III. VIBRATION SPECTRUM OF A DISORDERED LINEAR CHAIN AS A FUNCTION OF THE NUMBER OF CLUSTER CELLS TAKEN INTO ACCOUNT

The vibration spectrum is calculated according to the formula

$$\sigma(\nu) = (1/\pi) \int_0^\pi \Delta(\varphi, \nu) d\varphi, \quad (6)$$

where  $\Delta(\varphi, \nu) = (1/\pi)\omega_0^2 \mathbf{Im}[G(\varphi, \nu)]$ . Here,  $G(\varphi, \nu)$  is the Green's function with the frequency-dependent perturbation. This Green's function is related to the Green's function  $F$  by expression (6) from [1]. The quantity  $\nu$  is the dimensionless square of the frequency  $\nu = (\omega/\omega_0)^2$ , where  $\omega_0$  is the maximum frequency in the spectrum of the ideal linear chain  $\omega(\mathbf{y})^2 = (1/2)\omega_0^2(1 - \cos(\varphi))$ ,  $\varphi = 2\pi|\mathbf{y}|a$  is the dimensionless wave vector, and

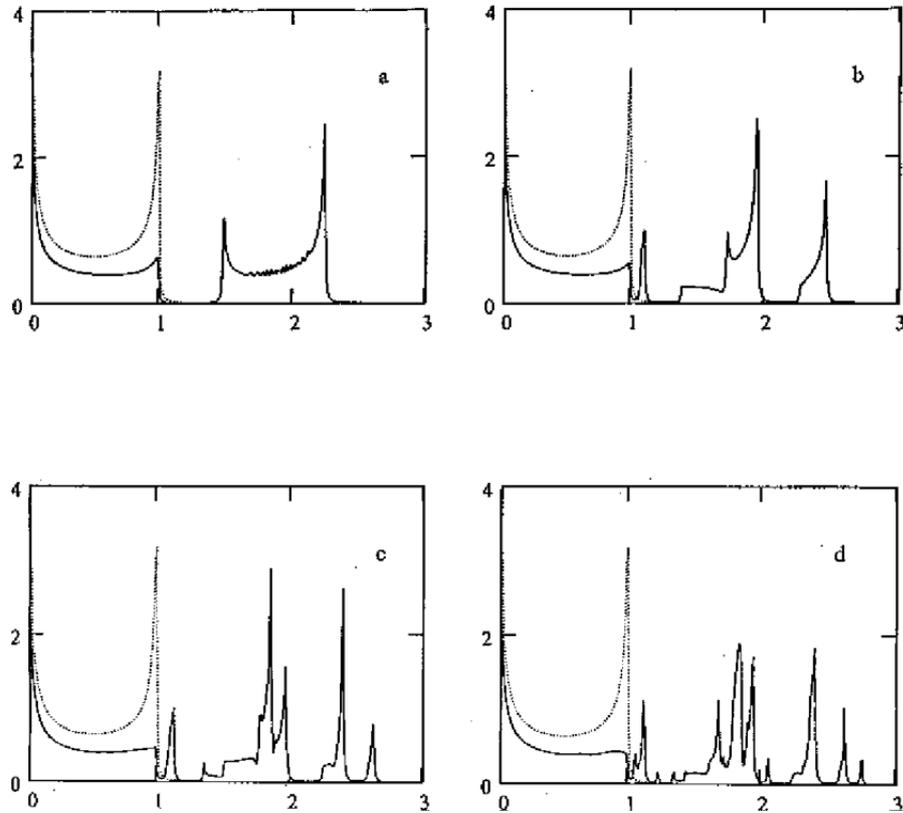


FIG. 1: Spectral function  $\sigma(\nu)$  of a linear disordered chain (in dimensionless units) calculated for clusters consisting of  $n =$  (a) 1, (b) 2, (c) 3, and (d) 4 cells for the mass ratio of the impurity and host atoms  $(m + \Delta m)/m = 1/3$  ( $\Delta = -2$ ), the fraction of impurity atoms  $x = 1/3$ , the damping parameter  $\varepsilon = 0.01$ , and  $\nu = (\omega/\omega_0)^2$ . The dotted line represents the spectrum of the lattice without impurities.

$a$  is the lattice constant. The function  $\sigma(\nu)$  is normalized so that  $\int_0^{\infty} \sigma(\nu) d\nu = 1$ . The initial damping  $\varepsilon$  was introduced through the change  $\nu \rightarrow \nu + (1/2)i\varepsilon$ . In real crystals, it corresponds to the damping due to anharmonicity.

FIG. 1 illustrates the variations in the vibration spectrum  $\sigma(\nu)$  of a linear chain when the number of cells  $n$  in the cluster is changed. The function  $\sigma(\nu)$  is calculated for clusters consisting of  $n = 1, 2, 3, 4$  neighboring cells,  $\Delta = -2$ ,  $x = 1/3$ , and  $\varepsilon = 0.01$ . For  $n = 1$  (FIG. 1a), in the region  $\nu \approx 1.5-2.2$ , only one impurity band is seen, which is related to vibrations of single impurities. When considering clusters with  $n = 2$  (FIG. 1b), two additional impurity bands appear at  $\nu \approx 1.1$  and  $\nu \approx 2.2-2.5$ . The first band is related to vibrations of the neighboring impurities in the phase, whereas the second band is associated with their out-of-phase vibrations. Because of the interaction of two-impurity and single-

impurity modes, the shape of single-impurity band ( $\nu \approx 1.5-2.2$ ) changes significantly. In the case  $n = 3$  (FIG. 1c) at  $\nu \approx 2.6$ , there appears a new peak attributed to vibrations of three impurities when the neighbors oscillate out-of-phase. In what follows, for brevity, these vibrations will be termed “out-of-phase vibrations.” The low-frequency edge of the two-impurity band at  $\nu \approx 2.2-2.5$  changes. In the single-impurity band, additional fine features appear. The spectrum for the case  $n = 4$  (FIG. 1d) in comparison with the spectrum for  $n = 3$  contains the following differences: the peak at  $\nu \approx 1.1$  is split into two components; in the gap  $\nu \approx 1.2-1.4$ , two weak peaks are present; in the single-impurity band, the third strong peak arises; and in the high-frequency range at  $\nu \approx 2.75$ , a peak related to the out-of-phase vibrations of four impurities appears. When the number of cells in the cluster further increases, beginning with  $n \sim 4$ , the large-scale structure of the spectrum remains almost unchanged and only small-scale features change. A weak splitting of the strongest peaks in the spectrum takes place with an intensity transfer between the components as the number  $n$  increases. With an increase in the damping  $\varepsilon$ , this splitting is smeared. The number of weak peaks in the gap  $\nu \approx 1.2-1.4$  increases, as well as the number of high-frequency peaks associated with the out-of-phase modes. Their intensity decreases as  $\sim x^n$ .

FIG. 2a shows the spectrum calculated for  $n = 6$  (the other parameters have the same values as for FIG. 1). FIG. 2b presents the spectrum obtained in the computer experiment by Dean [5] for a disordered linear chain of 8000 atoms. The parameters used are  $\Delta = -2, x = 0.26$ , and the value of  $\varepsilon$  is unknown. Also, the normalizing value for the curve in FIG. 2b is not known. The value of the abscissa 4 in FIG. 2b corresponds to value 1 in FIG. 2a. The theoretical curve in FIG. 2a agrees well with the “experimental” curve in FIG. 2b. Considering FIGs. 1 and 2, we can come to the conclusion that for a good description of the spectra of a disordered linear chain, it is necessary to take into account a sufficiently large number of cells in the impurity cluster. The question arises as to which number  $n$  is already enough. This problem can be conveniently solved by considering the spectrum in the region of high-frequency peaks. With an increase in  $n$ , the distance between the peaks with numbers  $n$  and  $(n - 1)$ ,  $\Delta\nu_n = \nu_n - \nu_{n-1}$ , decreases and reaches the value  $\varepsilon$  at a particular value of  $n = n_m$ . At this moment, the peak  $n$  is smeared, and it becomes indistinguishable from the background. Obviously, this value of  $n_m$  should be taken as the maximum number of cells in the cluster. It is a straightforward matter to derive the approximate dependence of  $\Delta\nu_n$  on  $n$  when it is considered that the spectrum of the cluster consisting of a sufficiently large number of neighboring impurities slightly differs from the spectrum of a linear chain entirely consisting of impurity atoms, which has the form  $\omega(\mathbf{y})^2 = (1/2)\omega_0^2(1 - \Delta)(1 - \cos(\varphi))$ . We will be interested in vibration modes that are the closest to the maximum of the spectrum and count the wave vector from this maximum. Then, we have  $\varphi = \pi - 2\pi|\mathbf{y}|a$ ,  $|\mathbf{y}| = 1/\lambda$ ,  $\lambda \sim 2na$ . We use the smallness of  $(1/n)$ , and obtain  $\Delta\nu_n \sim (1 - \Delta)(\pi^2/2)(1/n^3)$ . At  $\Delta = -2$  and  $n = 8$ ,  $\Delta\nu_8 \sim 0.03$ .

FIG. 3 shows the dependences  $\sigma(\nu)$  in the region of peaks 6 – 8 for the cases  $\Delta\nu_8 \gg \varepsilon$  ( $\varepsilon = 1/300$ , curve a) and  $\Delta\nu_8 \sim \varepsilon$  ( $\varepsilon = 0.02$ , curve b), which illustrate the aforementioned considerations.

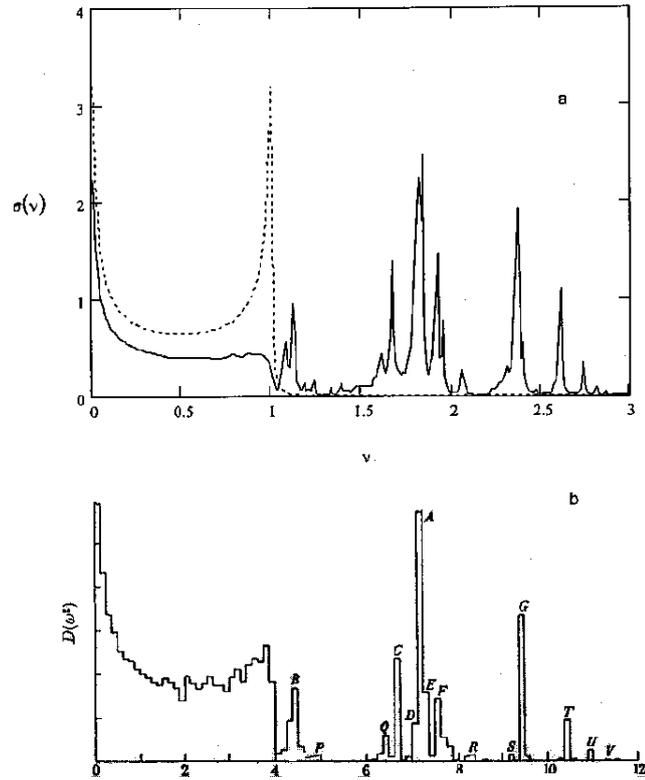


FIG. 2: (a) Spectral function  $\sigma(\nu)$  calculated for clusters of  $n = 6$  cells (the other parameters have the same values as for FIG. 1). (b) The spectrum obtained in the computer experiment by Dean [5] for a disordered linear chain of 8000 atoms with the parameters  $\Delta = -2$ ,  $x = 0.26$ , and the value of  $\varepsilon$  is unknown. The value of the abscissa 4 in panel (b) corresponds to the value 1 in panel (a).

#### IV. CALCULATION OF THE SPECTRUM OF A DISORDERED LINEAR CHAIN IN THE SELF-CONSISTENT APPROXIMATION

The generalized self-consistent approximation (CPAM- $n$ ) differs from the non-self-consistent approximation (ATAM- $n$ ) in that the propagation of excitation between the impurities of a particular cluster is described not by the free Green's function but by the Green's function  $F'$ , which takes into account the scattering by impurities of all clusters containing  $n$  cells, except for the cluster under consideration. The spectrum can be calculated in the self-consistent approximation by applying the iteration method to the related expressions (5), (1), and (3). On the right-hand side of Eq. (3), including the expression for  $\bar{\tau}_\phi$ , the quantity  $\bar{f}_\phi$  should be replaced by  $\bar{F}'_\phi$ . As the zeroth approximation, we take  $\bar{F}'_\phi = \bar{f}_\phi$  and  $\bar{\Sigma}(\mathbf{y}) = 0$ . In FIG. 4, the solid line (a) shows the spectrum of a linear chain for clusters of  $n = 6$  cells after performing 20 iterations of Eqs. (3) and (5). The following parameters are used:  $\Delta = -2$ ,  $x = 1/3$ , and  $\varepsilon = 0.01$ . By comparing curve (a) in FIG. 4 with FIG. 2a and 2b, we see that the function  $\sigma(\nu)$  calculated in the self-consistent

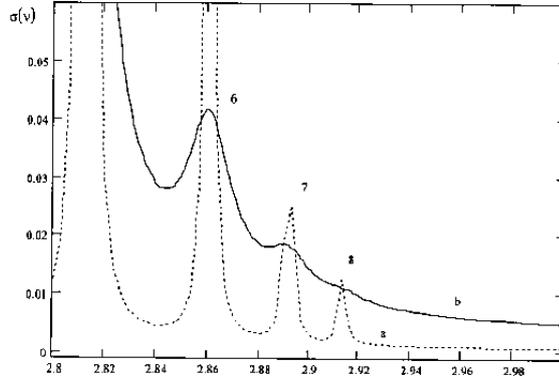


FIG. 3: Spectral function  $\sigma(\nu)$  in the region of high-frequency peaks 6–8 calculated for clusters of  $n = 8$  cells for two values of the damping parameter  $\varepsilon =$  (a)  $1/300$  and (b)  $0.02$ ;  $\Delta = -2$ ,  $x = 1/3$ .

approximation agrees neither with the “experimental” curve nor with the theoretical curve calculated in the approximation ATAM- $n$ . The curve also does not significantly deviate from the curve  $\sigma(\nu)$  calculated in the traditional approximation CPA-1 (curve b). This means that the approximation CPAM- $n$  overestimates the intensity of incoherent scattering processes, which leads to the averaging of the phases in scattering by impurities of the cluster under consideration. The failure of self-consistent theories in the description of linear chain vibration spectrum connected with the fact that CPA-1 and CPAM- $n$  are both the mean-field theories. A general statement exists that the mean-field theories work well only in the cases of large number of space dimensions, when  $d \geq 4$  [7, 8]. One should expect that in the case of  $d = 3$  CPA-1 and CPAM- $n$  give better results, but they will be not better than those of ATAM- $n$  ( $n \neq 1$ ).

## V. CALCULATION OF THE SPECTRUM OF A DISORDERED THREE-DIMENSIONAL LATTICE IN THE ATAM- $n$ APPROXIMATION

The purpose of this section is to demonstrate that the theory under consideration can be applied to the description of the spectra of disordered lattices of any dimensionality. In order to perform the calculation, it is necessary to know Green’s functions of the ideal lattice at the points corresponding to the distances between the cells of the impurity cluster at different frequencies and polarizations of the vibrations. The calculation of these Green’s functions is performed numerically and consumes a large amount of computer time. To avoid this disadvantage, we will use a simplified model of a three-dimensional lattice. We assume that the spectrum of the lattice is isotropic in all directions and coincides in the given direction with the above spectrum of the linear chain  $\omega(\mathbf{y})^2 = (1/2)\omega_0^2(1 - \cos(\varphi))$  and that the vibrations are polarized along the vector  $\mathbf{y}$ . Let us take a cluster of seven points: one point is at center, and the other six points are arranged symmetrically at distances  $x = \pm a$ ,  $y = \pm a$ , and  $z = \pm a$  from the center. FIG. 5 depicts the spectrum of this lattice,

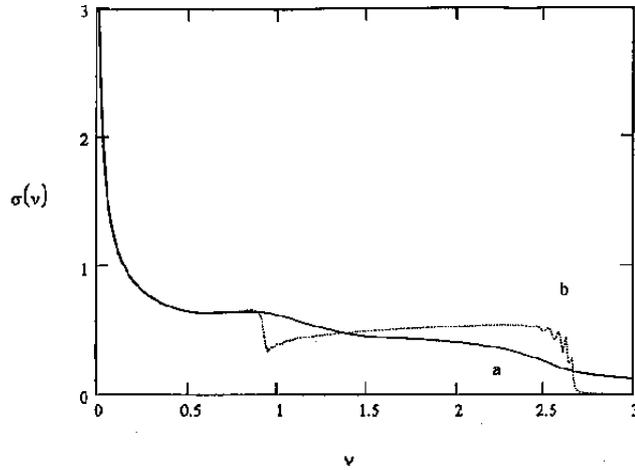


FIG. 4: Spectral function  $\sigma(\nu)$  calculated using (a) the generalized self-consistent approximation CPAM- $n$  ( $n = 6$ ) and (b) the conventional self-consistent approximation CPA-1. For both curves,  $\Delta = -2$ ,  $x = 1/3$ , and  $\varepsilon = 0.01$ .

which was calculated for the parameters  $\Delta = -2$ ,  $x = 0.2$ , and  $\varepsilon = 0.02$ . By comparing this spectrum with the spectrum of a one-dimensional chain (FIGs. 2a, 2b), we note the concentration of impurity peaks in a narrower frequency range and the shift of the whole group of peaks toward high frequencies.

## VI. CONCLUSIONS

The spectra of a disordered linear chain have been calculated by taking clusters with the number of cells  $n = 1, 2, \dots, 8$  into account in the non-self-consistent approximation (ATAM- $n$ ). With an increase of  $n$ , the spectrum changes significantly. For  $n = 6$ , the calculated spectrum is in an excellent agreement with the spectrum obtained in the computer experiment performed by Dean [5]. The maximum number of cells in the cluster  $n = n_m$ , which is to be taken into account within the ATAM- $n$  approximation, has been determined from a comparison of the distance between weak high-frequency peaks  $\nu_{n-1}$  and  $\nu_n$  in the spectrum with the magnitude of the damping parameter  $\varepsilon$  (anharmonic damping in real crystals). For  $\nu_n - \nu_{n-1} \sim \varepsilon$ , the "peak"  $\nu_n$  from the maximum changes into a gently sloping shoulder and becomes hardly distinguishable in the spectrum. For this reason, the inclusion of clusters with  $n > n_m$  is of no sense. The spectrum of a simple three-dimensional model of a solid solution has been calculated using the ATAM- $n$  ( $n = 7$ ) approximation and compared with the spectrum obtained in the computer experiment for a three-dimensional disordered crystal ([3], p. 498). Because of the differences in the models, the spectra differ significantly in the continuous region but are similar in the impurity region. Thus, the ATAM- $n$  approximation gives good results for the description of the vibration spectra of

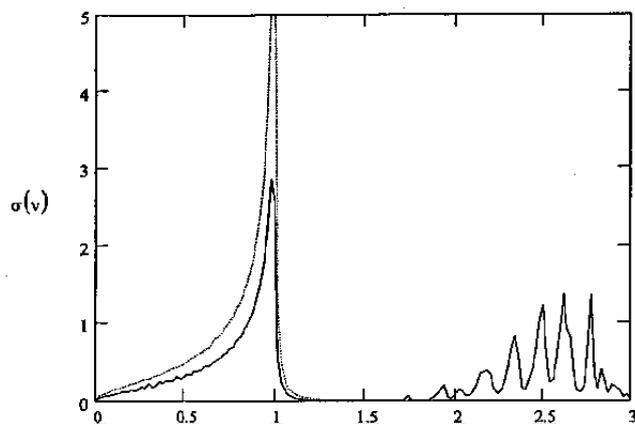


FIG. 5: Spectral function  $\sigma(\nu)$  for a simple three-dimensional lattice model calculated in the non-self-consistent approximation ATAM- $n$  ( $n = 7$ ) for the parameters  $\Delta = -2$ ,  $x = 0.2$ , and  $\varepsilon = 0.02$ . The dotted line represents the function  $\sigma(\nu)$  for the lattice without impurities.

solid solutions of any dimensionality.

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