Phonons in a medium with correlated substitutional disorder: a one-dimensional study

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Abstract. 1D lattice dynamics are considered for a pseudo-binary atomic chain in order to investigate the effects of thermodynamical clustering due to non-ideality of the solid solution $A_x B_{1-x} C$ on the phonon density of states (DOS). Using an exact dimensional distribution function for impurity clusters, phonon spectra are calculated numerically for 1D models of (Cd,Hg)Te and (Al,Ga)As of different compositions and temperatures of alloy preparation. The phonon DOS is also obtained analytically near the limits of the frequency range, and in the vicinity of the local mode. It is shown that clustering strongly suppresses the local mode. Moreover, for the decaying alloy where impurity clusters can be quite long, the DOS looks like a superposition of the phonon DOSs of pure materials, and positions of the maxima of the alloy DOS with respect to those in pure materials are sensitive to the degree of clustering.

1. Introduction

The vibrational properties of pseudo-binary solid solutions $A_x B_{1-x} C$ have been studied extensively both theoretically and experimentally [1]. A basic result of the experimental study by means of far-infrared (FIR) and Raman spectroscopy is that these alloys can display two (the so-called 'one-mode' and 'two-mode') types of optical spectrum. In the latter case, two separate optical modes are observed, which approximately correspond to those of the pure materials. It turned out that just this type of spectrum was detected for the most important semiconductor solid solutions of the $A_3 B_5$ and $A_2 B_6$ groups [1]. Apart from the two fundamental modes, an additional feature between the two fundamental modes was observed in the FIR and Raman spectra of Ga(As,P), (Cd,Hg)Te and (Cd,Zn)Te [2–6]. This mode is often referred to as a 'cluster mode' since it was speculatively prescribed to some specific realization of the five-atom elementary tetrahedron in the zincblende structure [2, 3].

At the same time, it was shown in different ways that isovalent semiconductor alloys are not perfectly random. Some tendency to clustering in the bulk (Cd,Hg)Te and (Cd,Zn)Te was pointed out by Zamir *et al* [7] from their nuclear magnetic resonance (NMR) study and was confirmed by measuring the mixing enthalpy [8] of these compounds. However, so far it has been difficult to predict the existence of some short-range order with respect to a particular method and conditions of sample preparation. In this situation, the non-destructive methods of FIR and Raman spectroscopy, if the data are interpreted properly, can supply some useful information concerning correlated clustering in the isovalent semiconductor alloys [5, 6, 9].

From the theoretical point of view, the effect of clustering on phonons in (Cd,Hg)Te was treated in [3] in the framework of the random-element isodisplacement approach. The five kinds of elementary tetrahedron mentioned above, with a Te atom in the centre and four cations, were considered. Accordingly, they obtained five different modes, one of which was identified as the 'cluster mode'. More recently, similar results were presented by Wu and Dow [10], who used a recursion method [11] of calculation for the local density of states (DOS) in real space at the central site of a large cluster. They averaged the DOS over the five kinds of elementary tetrahedron in the centre of their crystallite.

A local DOS can be measured as the chemical shift in NMR experiments, as was shown in [7], since this shift is sensitive only to the local environment of the atom, but not through FIR or Raman spectra, because the optical probe averages over a volume containing a large number of unit cells. Unfortunately, these results [10] strengthened the opinion in the literature that the 'cluster mode' is connected with some particular type of five-atom tetrahedron. This point of view neglects the environment of the microcluster.

It seems reasonable to begin a study of the correlated disorder effects on phonons with a 1D model. Because of their simplicity and clear interpretation of results, 1D models have been studied extensively (see [12, 13] and references therein; see also [14]). Moreover, such a model can be compared somewhat with experimental data since 1D lattice dynamics give a good quantitative description of phonons propagating along the (100) direction of short-period GaAs/AlAs superlattices [9, 15]. Thus, we studied the phonon DOS of a pseudo-binary atomic chain with nearest-neighbour (NN) interaction, modelling the thermodynamical clustering in the decaying 1D alloy.

2. Model of disorder

An exact expression for the dimensional distribution function of impurity microclusters was obtained in [16] for the 1D Ising model of a substitutional solid solution $A_x B_{1-x}$ of any concentration x. In this model, disorder is characterized only by the parameter

$$E_m = \tfrac{1}{2}(\epsilon_{11} + \epsilon_{22}) - \epsilon_{12} \tag{1}$$

where ϵ_{ij} are the pairwise interaction energies. The model can be applied to our case of the pseudo-binary atomic chain $A_x B_{1-x} C$ if we put

$$\epsilon_{11} = 2\epsilon_{AC} \qquad \epsilon_{12} = \epsilon_{AC} + \epsilon_{BC} \qquad \epsilon_{22} = 2\epsilon_{BC}.$$

Thus, we reproduce some results of [16] which are relevant here.

The dimensional distribution function for impurity clusters (either A or B atoms can be considered as the impurity) is given by the following formula:

$$W(n) = (p/x)(1 - p/x)^{n-1} \tag{2}$$

where n is the number of unit cells in the cluster, and p obeys the equation

$$(1 - x - p)(x - p)/p^2 = \exp(-2E_m/kT). \tag{3}$$

In (3), T is the temperature of sample preparation.

These results can also be expressed in terms of the pair correlation function

$$\Gamma(j) = x(\xi - x)\xi^{j-1} \tag{4}$$

where j is the dimensionless distance (for simplicity, let us put the lattice constant equal to unity), and $\xi = 1 - (p/x)$.

3. Phonon DOS: some analytical results

The equation of motion for an isotopic linear chain of $2N$ atoms (N unit cells) with NN interactions can be written as

$$\mathbf{B}U = \omega^2 U \tag{5}$$

where U is the displacement vector, and $\mathbf{B}$ is the dynamical matrix

$$\mathbf{B} = \begin{pmatrix} \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots; & -\frac{f}{m_i}; & \frac{2f}{m_i}; & -\frac{f}{m_i}; & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}. \tag{6}$$

In (6) m_i is the mass of the ith atom, and f is the strength constant.

Even in this simplest model, the average phonon DOS can be obtained analytically only for some regions of the frequency spectrum. An expansion of the DOS near $\omega^2 = 0$ was adduced in [17].

Near the upper boundary ω_{max} of each optical subband (say , GaAs like and AlAs like for (Ga,Al)As), the vibrations are produced by long sequences of like unit cells, which occur fluctuatingly. Accordingly, these boundaries of spectrum are called 'fluctuational' [18].

The number of states can be written as follows [18]:

$$\ln N(\omega^2) \sim \ln \left\{ \sum_{s=1}^{N} s W\left(\left[\frac{\pi s}{k}\right]\right) \right\} \tag{7}$$

where

$$k = \cos^{-1}(2\omega^2/\omega_{max}^2 - 1) \tag{8}$$

and $[z]$ denotes the integer part of z. If $k \to 0$, we keep only the leading term in the sum in (7). Using (2) we obtain for the DOS

$$\rho(\omega^2) \sim \omega_{max}^{-2} \exp(-\pi|\ln \xi|/k) \, (\pi|\ln \xi|/k^3). \tag{9}$$

For a strongly clustered alloy ($\xi \to 1$) the DOS given by equation (9) peaks at

$$k_0 = (\pi/3)|\ln \xi|. \tag{10}$$

If $k \gg k_0$ but $k \ll \epsilon = 1 - m_2/m_1$ still (this is a condition for the validity of (7); m_1 and m_2 are host and impurity cation atomic masses), the sum in (7) can be replaced by an integral. Bearing in mind that

$$\int_0^\infty y W(y) \, dy \simeq x$$

we have

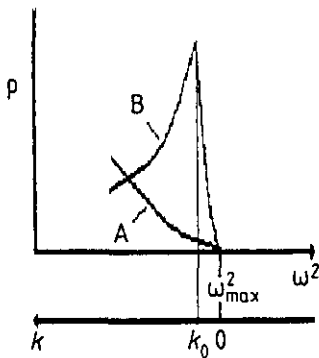$$\rho(\omega^2) \simeq \omega_{max}^{-2} x/2\pi k. \tag{11}$$

Figure 1. DOS near the fluctuational boundary of the frequency spectrum: curve A, random alloy; curve B, clustered alloy.
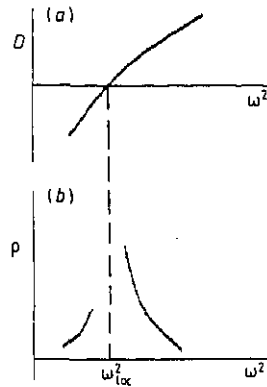
Figure 2. (b) DOS near the local mode. (a) The local mode obeys equation (14).

Note that (11) is not valid for a perfectly random alloy, and equation (9) describes simply the exponential decrease in the DOS as $\omega^2 \rightarrow \omega^2_{max}$. The DOS near the fluctuational boundary is shown schematically in figure 1 for the cases of random and strongly clustered alloys.

It is also possible to obtain some analytical results in the proximity of the local impurity mode by using the renormalized expansion in powers of impurity concentration [18]. An average (over all configurations) Green function of phonons can be written in the form

$$\langle G_{kk} \rangle = 1/[E - \omega^2(k) - \Sigma(k)] \tag{12}$$

where $\Sigma(k) = \langle R_k \rangle$ and, for R_k, one can obtain the following expansion up to the second order in x [18]:

$$R_k = \frac{1}{N} \sum_n \frac{\tau_n}{1 - l_n} + \frac{1}{N} \sum_{\substack{n \\ m \neq n}} \frac{\tau_n \tau_m \exp[-ik(n - m)]}{1 - l_n} F_{n-m}(E) \tag{13}$$

where

$$\tau_n = \frac{u_n}{[1 - u_n f(E)]} \qquad f(E) = F_0(E) \qquad u_n = \epsilon E c_n = u c_n$$

$$l_n = \sum_{m \neq n} \tau_n \tau_m F_{n-m}(E) F_{m-n}(E) \qquad F_n = \frac{1}{N} \sum_k \frac{\exp(ikn)}{E - \omega^2(k) - R_k}$$

$$c_n = \begin{cases} 1 & \text{if unit cell } n \text{ contains atom 1} \\ 0 & \text{if unit cell } n \text{ contains atom 2} \end{cases}$$

and $\omega^2(k)$ is the dispersion relation of the unperturbed binary chain. In the linear approximation

$$\Sigma(k) = xu/[1 - uf(E)]$$

and the equation

$$D(E) \equiv 1 - uf(E) = 1 - (\epsilon/2)\sqrt{E/(E - \omega_{max}^2)} = 0 \tag{14}$$

determines the local impurity mode. Keeping quadratic terms also, averaging (13) gives

$$\langle R_k \rangle = x\frac{u}{D} + \frac{u}{D}\sum_{r\neq 0}\frac{\langle c_0 c_r \rangle[A_r A_{-r} + A_r \exp(-ikr)]}{1 - A_r A_{-r}} \tag{15}$$

where $A_r = (u/D)F_r$. Calculating the integrals in (15), we obtain

$$\text{Im } \Sigma(k) = (\pi/2)u\{[1 + \cos(kr_0)\,\text{sgn }D(E)]/\alpha D(E)\}\langle c_0 c_{r_0}\rangle \tag{16}$$

where

$$\alpha^2 = (E - \omega_{max}^2)/\Omega^2 \qquad \Omega^2 = \omega_1^2\omega_2^2/\omega_{max}^2 \qquad \omega_i^2 = f/M_i \qquad i = 1,2$$

$$r_0 = (1/\alpha)\ln(u/2\Omega|D|\sqrt{E - \omega_{max}^2}). \tag{17}$$

Thus, the average phonon DOS is given by the expression

$$\rho(\omega^2) = \frac{1}{\pi N}\sum_k \frac{\text{Im } \Sigma(k)}{E^2 - \omega^2(k)} = \frac{[x^2 + \Gamma(r_0)]\epsilon\omega^2}{4(\omega^2 - \omega^2 max)}$$

$$\times \left[\frac{1}{|D(\omega^2)|} + \text{sgn } D(\omega^2)\ln\left(\frac{\epsilon\omega^2}{2\Omega|D|\sqrt{\omega^2 - \omega_{max}^2}}\right)\right]. \tag{18}$$

As shown schematically in figure 2, the DOS decreases asymmetrically with respect to the local mode because of the logarithmic term in (18). Clustering gives rise to the term containing the correlation function Γ (given by formula (4)). Since the 'cut-off length' r_0 depends on ω^2 (see equation (17)), it leads to additional asymmetry of the DOS in the vicinity of the local mode.

4. Numerical calculation of the DOS

The 1D phonon DOS was calculated as follows. Some (xN) impurity atoms were distributed over the binary chain BC (substituting B atoms) by means of the Monte Carlo procedure. Considering the decaying alloy $(E_m < 0)$, equations (2) and (3) were used to calculate the probability of formation of a cluster consisting of n adjacent unit cells containing impurity atoms. Then randomly selected $(AC)_n$ clusters were distributed randomly over the chain until all impurity atoms were settled. The criterion of proper settlement was

$$N_{12} - \sigma \leqslant L_{12} \leqslant N_{12} + \sigma$$

where L_{12} is the actual number of pairs of different NN atoms in the cation sublattice, $N_{12} = 2pN$ and σ is the standard deviation (for a long chain, $\sigma = \sqrt{N_{12}}$
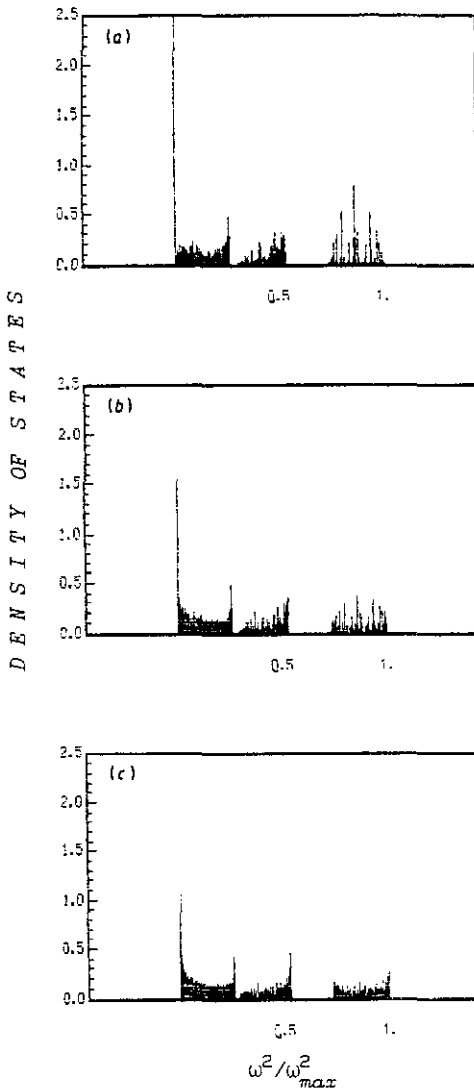
Figure 3. Calculated DOS versus ω^2/ω_{max}^2 for $Al_{0.5}Ga_{0.5}As$: (a) $E_m = 0$; (b) $E_m = -kT$; (c) $E_m = -2kT$. The histograms are scaled by 1000 for a chain of 10 000 atoms.
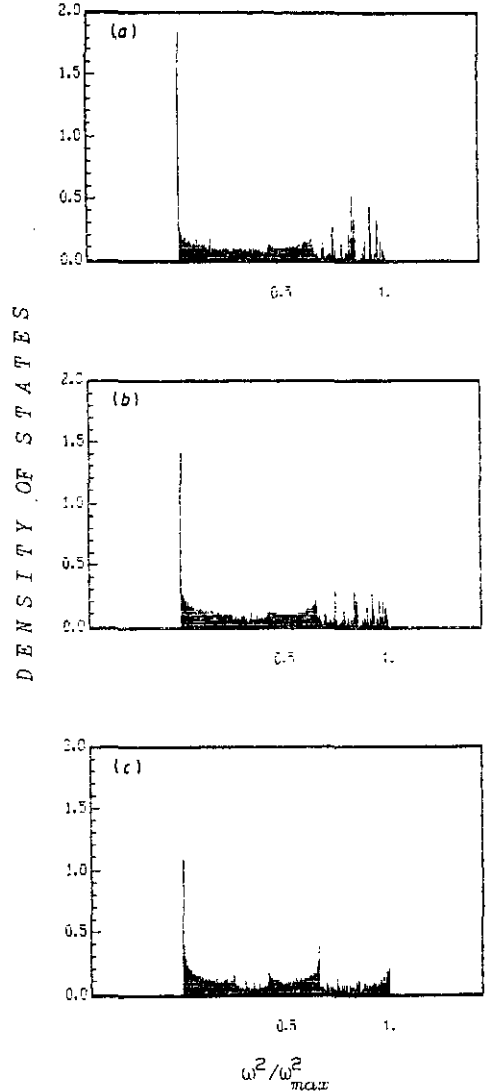
Figure 4. Same as for figure 3, but for $Cd_{0.5}Hg_{0.5}Te$.

[16]). Secondly, the DOS was calculated using the procedure for calculation of the eigenvalues of a tridiagonal matrix of Wilkinson and Reinch [19]. According to this procedure which is based on the negative-eigenvalue theorem [13], one finds the number of eigenvalues of the matrix (6) below some value of ω^2.

Histograms of the DOS for $Al_{0.5}Ga_{0.5}As$ and $Cd_{0.5}Hg_{0.5}Te$ calculated for different values of the mixing energy are presented in figures 3 and 4, respectively, and figure 5 shows the DOS for $Cd_{0.2}Hg_{0.8}Te$.

As well as the total DOS, we calculated the spectral DOS at the Brillouin zone

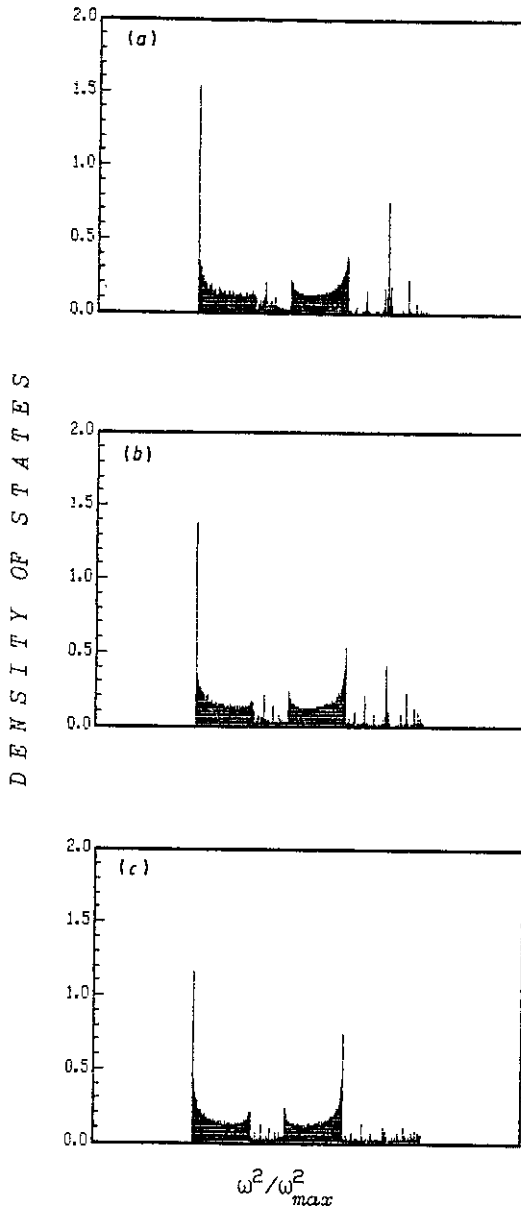**Figure 5.** Same as for figure 3, but for $Cd_{0.2}Hg_{0.8}Te$.

centre:

$$\rho(\omega^2, k = 0) = \sum_\nu \delta(\omega^2 - \omega_\nu^2)|\langle u_\nu|\Psi(k = 0)\rangle|^2 \tag{19}$$

where ν numbers the eigenvectors and eigenvalues of the dynamical matrix (6), and Ψ denotes the plane wave of the virtual-crystal chain (expressions for the acoustic and optical plane waves in the binary chain can be found, for example, in [20]). In contrast with the total DOS, the spectral DOS depends on the boundary conditions. We treated the chain with rigidly fixed ends.
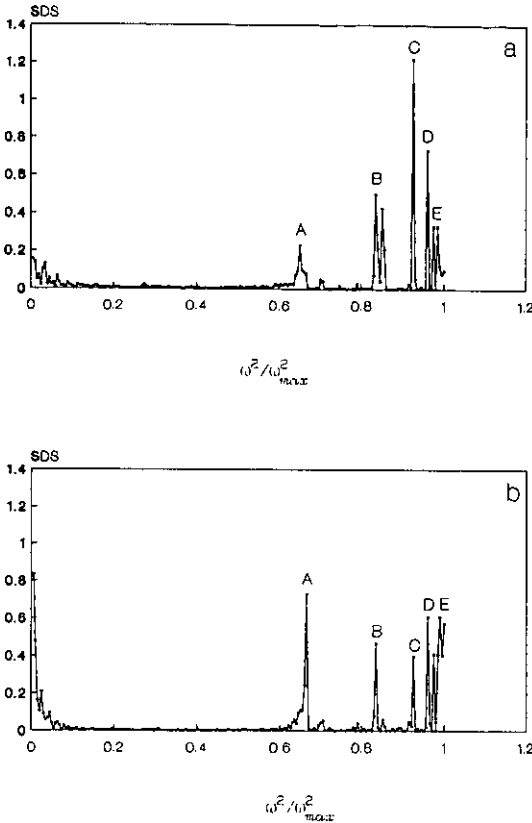
Figure 6. Spectral DOS at $k = 0$ versus ω^2/ω_{max}^2 for $Cd_{0.5}Hg_{0.5}Te$: (a) $E_m = 0$; (b) $E_m = -kT$. As above, it is scaled by $2N/10$. $2N = 1000$ in this calculation.

The results of the spectral DOS calculation for $Cd_{0.5}Hg_{0.5}Te$ are presented in figure 6 for $E_m = 0, -kT$. The principal features labelled by letters in figure 6 were identified through analysis of the corresponding eigenvectors. B is the local mode, and C and D are due to groups of two and three NN light atoms, respectively, surrounded by heavy neighbouring atoms in the cation sublattice. Modes A and E are not connected with any specific configurations since the corresponding eigenvectors have a considerable amplitude in all the clusters of HgTe or CdTe, respectively, which are sufficiently long ($n \geqslant 5$). Accordingly, these modes should be called HgTe like (A) and CdTe like (E).

5. Discussion and conclusion

It can be seen from figures 3–5 that the 'exact' DOS contains some 'eliminated' frequencies, (gaps), which is a characteristic feature of any discrete 1D system [12].

For an absolutely random infinite chain the gaps of the DOS should be infinitely narrow. However, the modes just above the eliminated frequencies are produced by the 'islands' of light atoms separated by long segments of heavy atoms. Since the probability of finding a long cluster of light atoms is very low for the random

finite chain, the gaps of the DOS are sufficiently broad (see, e.g., [12, 13] for further discussion). As the degree of clustering increases, the gaps are filled in, resulting in quite smooth histograms (see figures 3 and 4). At the same time the $Cd_{0.2}Hg_{0.8}Te$ DOS displays rather discontinuous behaviour even for $E_m = -2kT$ (figure 5). This is in accordance with the 'island' interpretation. The increase in $|E_m|$ causes the DOS to tend to a superposition of $\rho(\omega^2)$ functions for binary chains of pure substances (which are readily seen in figures 3(c) and 4(c)), and all the features are smoothed out.

Analytical approximation methods where the disorder is averaged by some recipe lead to the DOS for an effective medium without disorder. Thus, they do not reproduce features such as the discontinuities. This average DOS is what is measured experimentally through light scattering, because even in the case of the resonant Raman scattering technique the averaging volume defined by the electron–phonon interaction range is about $(50 \text{ Å})^3$ [21]. Our 'exact' DOS is automatically averaged over the chain (in contrast with the local DOS calculated in [3, 10, 11]). Consequently, an envelope function of the DOS calculated numerically for a sufficiently long chain must follow the theoretical predictions made in section 3. The behaviour of the envelope function near the upper boundary frequencies of two optical subbands for the same alloy (e.g. of the CdTe-like and HgTe-like modes) can be seen from figures 3–5. Both these maxima of the DOS move upwards with an increase in the degree of clustering (compare with figure 1).

Most of the peaks in the proximity of the local mode (except the local mode itself and those closest to it) are due to pairs of impurity atoms separated by different distances [13]. It can be seen that the envelope function of the histogram is asymmetrical with respect to the local mode and becomes more asymmetrical on increase in $|E_m|$ (compare with figure 2). However, the most dramatic effect is how strongly this local mode is suppressed as a result of clustering. The reason is obvious; the stronger the clustering, the lower is the probability of finding a solitary impurity atom. The same effect of clustering on the local mode can be seen from figure 6. In contrast, the intensity of the two fundamental modes increases significantly because of clustering. At the same time their positions in the spectral DOS do not change.

Looking at the histograms as a whole, it can be seen from figures 4 and 5 that the same alloy can display a phonon DOS of the 'persistence' type as well as of the 'amalgamation' type (terminology of [14]) depending on the composition and the temperature of preparation.

Thus, for instance, raising the temperature of (Cd,Hg)Te crystal growth, one can pass from one type of optical behaviour to the other. On the other hand, in (Al,Ga)As, two well separated optical subbands exist, even in the perfectly random case (figure 3).

As follows from equations (9) and (10) and is confirmed by our numerical calculation, the shift in the maxima of total DOS in the alloy with respect to those in the pure materials contains some information about clustering. We wish to draw attention to the functional compositional dependence of the shift. For example, in our model in the case of strong clustering it is proportional to $\sqrt{(1-x)/x}$ for $x > \frac{1}{2}$.

Our calculations do not show any particular 'cluster mode' below the HgTe like mode, which was observed experimentally near 133–135 cm^{-1} [5, 6, 22]. Either this mode has some origin other than clustering [22], or our 1D model is unable to produce it. At the same time, it is most likely that the 'cluster' mode observed by Kozyrev *et al* [3] is just the local mode of Cd atoms. Another mode which one can expect to

observe in the CdTe reststrahl band is due to pairs of Cd atoms which are the NNs in the cation sublattice.

In conclusion, we have shown (both analytically and numerically) that clustering in semiconductor solid solutions (if it really occurs) must be taken into account in the calculation of the phonon DOS, since it changes the spectrum significantly. No particular clustering mode appears because of the decaying character of the alloy, but the shifts in the maxima of the alloy DOS with respect to those of the pure materials are sensitive to the degree of clustering. In this paper, we wished to draw attention to the problem. The results of similar calculations for more realistic 2D and 3D lattices will be published elsewhere.

Acknowledgments

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