Effects of the local configuration on the lattice dynamics of group-IV semiconductors

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The relative importance of short-range order and local topology versus long-range order in determining the vibrational properties of group-IV semiconductors is investigated. We have developed a cluster–Bethe-lattice method which treats a cluster of atoms with the short-range order and local topology therein exactly. The rest of the system is treated within the Bethe-Peierls approximation which retains the short-range tetrahedral order. We have studied the lattice vibration spectra corresponding to clusters of different sizes in the diamond structure. We find that the presence of rings of bonds have clear and discernible effects not found previously. The main feature of the perfect-crystal density of states is already present in small (~ 30 atoms) clusters. We can conclude that, as in the electronic case, the density of vibrational states is governed by the local configurations.

I. INTRODUCTION

The problem of whether or not the short-range order and local topology determine the spectrum of vibrations of group-IV semiconductors (Si, Ge) is still an open question.[1] It is known experimentally that in amorphous semiconductors the short-range order is kept,[2] i.e., the perfect tetrahedral arrangement of atoms almost remains in the amorphous phase. In addition, it is also known experimentally that the vibrational densities of states of the crystalline and amorphous phases are similar.[3] Thus, one can conclude that the local bonding character between the nearest neighbors determines the basic properties of solids.[4] This conclusion, however, is an oversimplification of the problem as we know from our knowledge of the electronic properties of amorphous semiconductors: small deviations from the perfect tetrahedral arrangement can give notable differences in the density of electronic states.[5] As a consequence, it is only by a detailed study of the interplay of the long-range order versus short-range order and local topology that we can hope to understand the vibrational properties of amorphous semiconductors.

In the past, there have been several approaches to the study of the vibrational properties of amorphous materials: (i) calculation of the spectrum of a finite cluster of atoms[6]; (ii) study of clusters of atoms with quasiperiodic boundary conditions[7]; (iii) study of molecular units interacting weakly[8]; (iv) calculation of the density of phonon states by statistically averaging the crystalline density of states[9]; and (v) application of the Bethe-Peierls approximation.[10]

None of these methods is completely satisfactory for the study of group-IV semiconductors. Method (i) requires very large clusters to yield results independent of the boundary condition; even with clusters of about 500 atoms, the boundary condition is very important.[6] Method (ii) shares some of the drawbacks of method (i); in addition, the periodicity can introduce spurious features in the density of states. Despite their drawbacks, both methods (i) and (ii) take into account the local configuration exactly. Method (iii) is not acceptable to study group-IV semiconductors since a continuous random network structure is currently being accepted to describe the structure of these semiconductors. Method (iv) is not very useful since it does not deal with a real structure and consequently neither the short-range order nor the local topology can be taken into account properly. Finally, although method (v) treats the short-range order exactly, it cannot distinguish between different topological arrangements of atoms.

In this paper we introduce a technique which allows us to study, for the first time, the effect of both the short-range order and local topology on the density of lattice vibrations in group-IV semiconductors. To this end we consider an infinite connected network of atoms with any desired topological configuration. We focus our attention on a particular atom of such system; then, the local environment around it (i.e., a cluster of atoms) is treated exactly and the rest of the system is approximated by the Bethe-Peierls approximation.[11] Finally the local density of states associated with this atom is calculated. The technique is essentially equivalent to the cluster–Bethe-lattice method intended originally to study electronic densities of states.[5,12] The Bethe-Peierls

approximation provides us with a boundary to the
cluster of atoms we are dealing with such that
the desired short-range order is present in both
the cluster and the boundary condition. This tech-
nique allows us to study the effects of the sys-
tematic variation of bond angles and short-range-
order topologies.

This paper is organized as follows. In Sec. II
we discuss the application of the Bethe-Peierls
approximation to study lattice vibrations in the
diamond structure. We use the transfer matrix
technique which yields identical results to those
reported by Thorpe using mean-field techniques.[10]
The Weaire-Alben transformation,[13] valid in the
limit in which only central forces are present, is
recovered. In Sec. III the extension of the cluster–
Bethe-lattice method to study lattice vibrations
is made. We study clusters of different sizes in
the diamond lattice structure. The structure we
obtain in the density of states is analyzed. Fin-
ally, in Sec. IV, some conclusions are drawn.

II. BETHE-PEIERLS APPROXIMATION IN DIAMOND STRUCTURE

To study the vibrational properties of group-IV
semiconductors we will consider the Born model[14]
where forces are restricted to nearest neighbors
only as in the Keating model.[15] The potential en-
ergy in the Born model is given by[7]

FIG. 1. Tetrahedral unit of the diamond structure.

$$\tfrac{3}{4}\beta \sum_{l\Delta}[(\overline{U}_l - \overline{U}_{l\Delta})\cdot \hat{r}_\Delta(l)]^2 + \tfrac{1}{4}(\alpha - \beta)\sum_{l\Delta}(\overline{U}_l - \overline{U}_{l\Delta})^2.$$

$$(1)$$

The sums are on atoms l and their nearest neigh-
bors Δ. $\hat{r}_\Delta(l)$ is the unit vector from the equili-
brium position of atom l to that of its neighbor Δ.
$\overline{U}_l$ and $\overline{U}_{l\Delta}$ are the displacement vectors of these
atoms. In the Born model we can distinguish a
central force given by $(2\beta + \alpha)$ and a noncentral
one given by $(\alpha - \beta)$.

The four nearest neighbors of an atom in the
diamond structure are drawn in Fig. 1. This
tetrahedral unit repeats itself periodically to gen-
erate the diamond structure. These are only four
different bond directions in the diamond lattice
and then there are only four different dynamical
matrices[16] between nearest-neighboring atoms.
These matrices for the Born model are

$$\underline{D}_{0,1} \equiv \underline{D}_1 = \begin{pmatrix} -\alpha & -\beta & -\beta \\ -\beta & -\alpha & -\beta \\ -\beta & -\beta & -\alpha \end{pmatrix}; \quad \underline{D}_{0,2} \equiv \underline{D}_2 = \begin{pmatrix} -\alpha & \beta & \beta \\ \beta & -\alpha & -\beta \\ \beta & -\beta & -\alpha \end{pmatrix};$$

$$\underline{D}_{0,3} \equiv \underline{D}_3 = \begin{pmatrix} -\alpha & -\beta & \beta \\ -\beta & -\alpha & \beta \\ \beta & \beta & -\alpha \end{pmatrix}; \quad \underline{D}_{0,4} \equiv \underline{D}_4 = \begin{pmatrix} -\alpha & \beta & -\beta \\ \beta & -\alpha & \beta \\ -\beta & \beta & -\alpha \end{pmatrix}.$$

$$(2a)$$

The diagonal term is

$$\underline{D}_{ii} \equiv \underline{D}_0 = \begin{pmatrix} 4\alpha & 0 & 0 \\ 0 & 4\alpha & 0 \\ 0 & 0 & 4\alpha \end{pmatrix},$$

$$(2b)$$

where the first, second, and third columns (rows)
correspond to the x, y, and z components of the
vibrations, respectively. The matrix $\underline{D}_{ij}$ in (2)
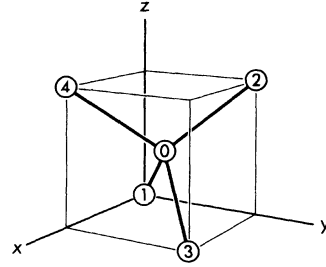contains the dynamical matrix elements between

the three different vibrations of atoms i and j.

In order to calculate the density of states we
first calculate the Green's function G, which is
given by

$$\underline{G} = (m\omega^2 \underline{1} - \underline{D})^{-1},$$

$$(3)$$

where m is the mass of the atoms, ω is the fre-
quency and D is the full dynamical matrix.

Using a standard procedure[5,12] we can write
for the matrix elements of the Green's function
the following infinite set of linear equations:

$$m\omega^2 \underline{G}_{0,0} = \underline{1} + \sum_{i=0}^{4} \underline{D}_i \cdot \underline{G}_{i,0} \,,$$

$$m\omega^2 \underline{G}_{1,0} = \underline{D}_1 \cdot \underline{G}_{0,0} + \underline{D}_0 \cdot \underline{G}_{1,0} + \underline{D}_2 \cdot \underline{G}_{2,0}^1 + \underline{D}_3 \cdot \underline{G}_{3,0}^1 + \underline{D}_4 \cdot \underline{G}_{4,0}^1 \,,$$

$$m\omega^2 \underline{G}_{2,0} = \underline{D}_2 \cdot \underline{G}_{0,0} + \underline{D}_0 \cdot \underline{G}_{2,0} + \underline{D}_1 \cdot \underline{G}_{1,0}^2 + \underline{D}_3 \cdot \underline{G}_{3,0}^2 + \underline{D}_4 \cdot \underline{G}_{4,0}^2 \,,$$

$$m\omega^2 \underline{G}_{3,0} = \underline{D}_3 \cdot \underline{G}_{0,0} + \underline{D}_0 \cdot \underline{G}_{3,0} + \underline{D}_1 \cdot \underline{G}_{1,0}^3 + \underline{D}_2 \cdot \underline{G}_{2,0}^3 + \underline{D}_4 \cdot \underline{G}_{4,0}^2 \,,\qquad (4)$$

$$m\omega^2 \underline{G}_{4,0} = \underline{D}_4 \cdot \underline{G}_{0,0} + \underline{D}_0 \cdot \underline{G}_{4,0} + \underline{D}_1 \cdot \underline{G}_{1,0}^4 + \underline{D}_2 \cdot \underline{G}_{2,0}^4 + \underline{D}_3 \cdot \underline{G}_{3,0}^4 \,,$$

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$$\cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot$$
$$\cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot$$

where the 3×3 matrix $\underline{G}_{j,0}$ is formed by the matrix elements of the Green's function (3) between the three vibrational modes of atoms j and 0. The matrix $\underline{G}_{j,0}^i$ involves the matrix elements of the Green's function (3) between the vibrations of atom 0, and the vibrations of the atom nearest neighbor of atom i along the same direction as bond 0-j in Fig. 1.

Equation (4) forms an infinite set of equations. We seek the solution of $\underline{G}_{0,0}$ which gives the local density of states $n_{0,0}$ at atom 0

$$n_{0,0}(\omega) = (1/\pi)\, \mathrm{Im}\, \mathrm{Tr}[\,\underline{G}_{0,0}(\omega)]\,. \qquad (5)$$

In order to solve for $\underline{G}_{0,0}$ in (4), we use the Bethe-Peierls approximation.[17] In this approximation each atom is surrounded by four nearest neighbors in a perfect tetrahedral orientation but the coherence due to the presence of closed rings of bonds is neglected. This is equivalent to dealing with a Bethe lattice[17] instead of a perfect diamond structure. Within this approximation the infinite set of Eqs. (4) is such that the sequence of four consecutive equations repeats itself up to infinity and we can define the following four 3×3 transfer matrices[5,12]:

$$\underline{T}_i \cdot \underline{G}_{n-1,0}^i = \underline{G}_{n,0}^i\,, \quad i = 1,2,3,4, \; n \geqslant 1\,, \qquad (6)$$

where $i = 1,2,3,$ and 4 corresponds to the directions of the bonds 0-1, 0-2, 0-3, and 0-4 in Fig. 1, respectively, and $\underline{G}_{n,0}^i$, $\underline{G}_{n-1,0}^i$ corresponds to *any* pair of nearest-neighboring atoms forming a bond along the direction of bond 0-i in Fig. 1.

If we insert (6) into the four generic equations in (4), we get

$$m\omega^2 \underline{T}_1 = \underline{D}_0 \cdot \underline{T}_1 + \underline{D}_1 + \underline{D}_2 \cdot \underline{T}_2 \cdot \underline{T}_1 + \underline{D}_3 \cdot \underline{T}_3 \cdot \underline{T}_1 + \underline{D}_4 \cdot \underline{T}_4 \cdot \underline{T}_1 \,,$$

$$m\omega^2 \underline{T}_2 = \underline{D}_0 \cdot \underline{T}_2 + \underline{D}_2 + \underline{D}_1 \cdot \underline{T}_1 \cdot \underline{T}_2 + \underline{D}_3 \cdot \underline{T}_3 \cdot \underline{T}_2 + \underline{D}_4 \cdot \underline{T}_4 \cdot \underline{T}_2 \,,$$

$$m\omega^2 \underline{T}_3 = \underline{D}_0 \cdot \underline{T}_3 + \underline{D}_3 + \underline{D}_1 \cdot \underline{T}_1 \cdot \underline{T}_3 + \underline{D}_2 \cdot \underline{T}_2 \cdot \underline{T}_3 + \underline{D}_4 \cdot \underline{T}_4 \cdot \underline{T}_3 \,,\qquad (7)$$

$$m\omega^2 \underline{T}_4 = \underline{D}_0 \cdot \underline{T}_4 + \underline{D}_4 + \underline{D}_1 \cdot \underline{T}_1 \cdot \underline{T}_4 + \underline{D}_2 \cdot \underline{T}_2 \cdot \underline{T}_4 + \underline{D}_3 \cdot \underline{T}_3 \cdot \underline{T}_4 \,.$$

The Green's function $\underline{G}_{0,0}$ is now given by

$$m\omega^2 \underline{G}_{0,0} = \underline{1} + \underline{D}_0 \cdot \underline{G}_{0,0} + \sum_{i=1}^{4} \underline{D}_i \cdot \underline{T}_i \cdot \underline{G}_{0,0} \,. \qquad (8)$$

In order to solve for the $\underline{T}$'s in (7) we use the following operators which transform the $\underline{T}$ matrices into each other:

$$\underline{S}_1 \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\,; \quad \underline{S}_2 \equiv \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\,;$$

$$\underline{S}_3 \equiv \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\,, \quad \underline{S}_4 \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\,. \qquad (9)$$

It is obvious that

$$\underline{T}_2 = \underline{S}_2 \cdot \underline{T}_1 \cdot \underline{S}_2\,, \quad \underline{T}_3 = \underline{S}_3 \cdot \underline{T}_1 \cdot \underline{S}_3\,,$$
$$\underline{T}_4 = \underline{S}_4 \cdot \underline{T}_1 \cdot \underline{S}_4\,. \qquad (10)$$

Using these relations, the problem of solving (7) has been reduced to obtain the solution of

$$m\omega^2 \underline{T}_1 = \underline{D}_1 + \underline{D}_0 \cdot \underline{T}_1 + \sum_{i=2}^{4} \underline{D}_i \cdot \underline{S}_i \cdot \underline{T}_1 \cdot \underline{S}_i \cdot \underline{T}_1\,. \qquad (11)$$

Even more; it is straightforward to prove that $\underline{T}_1$ has to be of the following form:

$$\underline{T}_1 = \begin{pmatrix} t_0 & t_1 & t_1 \\ t_1 & t_0 & t_1 \\ t_1 & t_1 & t_0 \end{pmatrix}\,. \qquad (12)$$

If we now insert (12) into (11), we find

$$(m\omega^2 - 4\alpha)t_0 = -\alpha - 3\alpha t_0^2 - 4\beta t_0 t_1 + 2(\alpha + \beta)t_1^2,$$

$$(m\omega^2 - 4\alpha)t_1 = -\beta - 2(\alpha - \beta)t_0 t_1 \qquad (13)$$

$$+ (\alpha - 5\beta)t_1^2 + \beta t_0^2.$$

The solution of (13) to get t_0 and t_1 entails the solution of a quartic equation, that can be easily obtained numerically.

Finally, the local density of states at atom 0 is given by

$$n_{0,0} = -\pi^{-1} \text{Im Tr}(\underline{G}_{0,0})$$

$$= -\pi^{-1} \text{Im}[3(m\omega^2 - 4\alpha + 4\alpha t_0 + 8\beta t_1)^{-1}]. \qquad (14)$$

If we call

$$m\omega^2 - 4\alpha = \epsilon, \qquad (15)$$

we can see that there are some interesting relations between the lattice vibrations density of states and the electronic density of states of a simple s-state Hamiltonian[5,12] with interaction between nearest neighbors only.

In the limit of only central forces[7,10] $\alpha = \beta$ and t_0 is identical to t_1. Then (13) becomes

$$\epsilon t_0 = -\alpha - 3\alpha t_0^2. \qquad (16)$$

t_0 is nothing but the transfer matrix for the electronic case.[5,12] Once we insert t_0 in Eq. (14) we see that we obtain a continuous density of states identical to the electronic density of states for the Bethe lattice and two δ functions at $\epsilon = \pm 4\alpha$, with weight equal to 1. They correspond to the acoustic and optical transverse modes, respectively. This result is nothing but the Weaire-Alben theorem.[13]

In the limit in which the central and noncentral forces are equal, i.e., $\beta = 0$, it is easy to see that $t_1 = 0$ and t_0 is again given by (16). The density of states now is *identical* to the electronic density of states. The transverse-modes merge into the longitudinal-modes region.

Although our derivation of the density of states is different from the Thorpe's derivation,[10] the results are identical. In Fig. 2 we have drawn the density of states as a function of the reduced frequency, ω/ω_{max}, in the diamond lattice for $\beta/\alpha = 0.6$ which is a ratio of the parameters appropriate to Si or Ge. In Fig. 2(a) we show the density of states using the Bethe-Peierls approximation and in Fig. 2(b) we show exact density of states of the perfect infinite diamond structure.[10] As pointed out in Ref. 10, the crystal transverse-optical and acoustical modes are well approximated by the Bethe-Peierls approximation. However, the peaks corresponding to longitudinal modes at the values of 0.66 and 0.76 reduced fre-
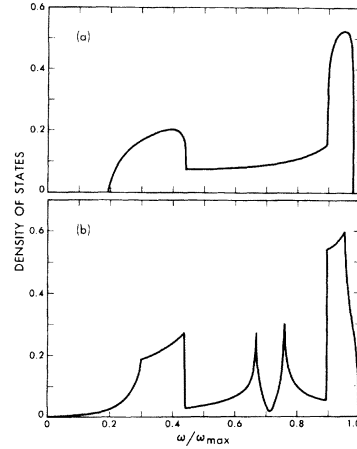

FIG. 2. Density of vibrational states in the diamond structure for the Born model with $\beta/\alpha = 0.6$ vs the reduced frequency ω/ω_{max}. $\omega_{max}^2 = 8\alpha/m$. (a) Bethe-Peierls approximation. (b) Exact (Ref. 10).

quency do not appear in the Bethe-Peierls approximation.

It has been argued that the peaks in the spectrum corresponding to the longitudinal modes in the crystal are coming from long-range correlations since a small cluster calculation by Thorpe did not give any noticeable feature in that part of the spectrum.[18] In order to elucidate the origin of these peaks we study different clusters of atoms using the cluster—Bethe-lattice method.[5,12] This is done in Sec. III.

III. STUDY OF CLUSTERS OF DIFFERENT SIZE

Once we know the solution for the Bethe-Peierls approximation, the study of any structure using
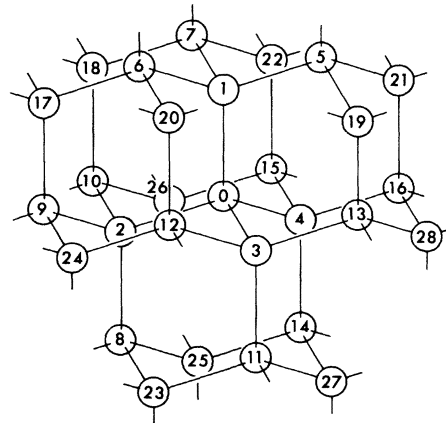

FIG. 3. Twenty-nine-atom cluster in the diamond structure.

the cluster−Bethe-lattice method is rather straightforward. In this section, we focus our attention on the diamond structure.

Let us take a cluster of 29 atoms as in Fig. 3 and saturate the dangling bonds of atoms labelled 5−28 with the diamond lattice treated within the Bethe-Peierls approximation. We are aiming to calculate the density of states at the central atom labelled 0. To do this we can write a finite system of linear equations as in Ref. 5. Using the symmetry of the diamond structure we can write

$$\epsilon \underline{G}_{0,0} = \underline{1} + \underline{D}_1 \cdot \underline{G}_{1,0} + \sum_{i=2}^{4} \underline{D}_i \cdot \underline{S}_i \cdot \underline{G}_{1,0} \cdot \underline{S}_i ,$$

$$\epsilon \underline{G}_{1,0} = \underline{D}_1 \cdot \underline{G}_{0,0} + \underline{D}_3 \cdot \underline{G}_{7,0} + \underline{D}_2 \cdot \underline{M}_1^{-1} \cdot \underline{G}_{7,0} \cdot \underline{M}_1$$
$$+ \underline{D}_4 \cdot M_3^{-1} \cdot \underline{G}_{7,0} \cdot \underline{M}_3 ,$$

$$\epsilon \underline{G}_{7,0} = \underline{D}_3 \cdot \underline{G}_{1,0} + \underline{D}_2 \cdot \underline{G}_{18,0} + \underline{D}_4 \cdot \underline{M}_1^{-1} \cdot \underline{G}_{18,0} \cdot \underline{M}_1$$
$$+ \underline{D}_1 \cdot \underline{T}_1 \cdot \underline{G}_{7,0} , \tag{17}$$

$$\epsilon \underline{G}_{18,0} = \underline{D}_2 \cdot \underline{G}_{7,0} + \underline{D}_1 \cdot \underline{S}_2 \cdot \underline{M}_3^{-1} \cdot \underline{G}_{7,0} \cdot \underline{M}_3 \cdot \underline{S}_2$$
$$+ (\underline{D}_3 \cdot \underline{T}_3 + \underline{D}_4 \cdot \underline{T}_4) \cdot) \cdot \underline{G}_{18,0} .$$

The M's are nothing but the operators of the mirror symmetry operations of the cluster

$$\underline{M}_1 \equiv \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad \underline{M}_2 \equiv \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}; \quad \underline{M}_3 \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

$$\tag{18}$$

Owing to the symmetry of the cluster the matrix elements of the matrices $G_{n,0}$ in (17) have special relations. We can write

$$\underline{G}_{0,0} \equiv \begin{pmatrix} g^0 & 0 & 0 \\ 0 & g^0 & 0 \\ 0 & 0 & g^0 \end{pmatrix}; \quad \underline{G}_{1,0} \equiv \begin{pmatrix} g_0^1 & g_1^1 & g_1^1 \\ g_1^1 & g_0^1 & g_1^1 \\ g_1^1 & g_1^1 & g_0^1 \end{pmatrix};$$

$$\underline{G}_{7,0} \equiv \begin{pmatrix} g_{00}^7 & g_{01}^7 & g_{02}^7 \\ g_{01}^7 & g_{00}^7 & g_{02}^7 \\ g_{20}^7 & g_{20}^7 & g_{11}^7 \end{pmatrix}; \quad \underline{G}_{18,0} \equiv \begin{pmatrix} g_{00}^{18} & g_{01}^{18} & -g_{01}^{18} \\ g_{10}^{18} & g_{11}^{18} & g_{12}^{18} \\ -g_{10}^{18} & g_{12}^{18} & g_{11}^{18} \end{pmatrix}.$$

$$\tag{19}$$

If we now insert these matrices in (17), we end up with a system of 13 linear equations with 13 unknowns which can be readily solved numerically in the computer to get $\mathrm{Tr}(G_{0,0})$. We have then reduced the problem of solving 87 (29 atoms in the cluster × three directions of vibrations per atom) linear equations.

The solution for the local density of states at the central atom for $\beta/\alpha = 0.6$ is given in Fig. 4(a). We notice immediately that there are two peaks in the

density of states spectrum at around 0.62 and 0.80, which can be identified with the two peaks on the crystal spectrum [Fig. 2(b)] at 0.66 and 0.76, respectively. Although the peaks in the cluster are not as sharp as in the crystal case [see Fig. 2(b)] they are clearly noticeable. Another feature of the density of states curve of Fig. 4(a) is that the transverse modes peaks that were already present in the Bethe-Peierls approximation become more pronounced in the cluster. The two peaks at the edges of the spectrum (dotted line) are, of course, spurious.

The structure in the density of states is rather stable against changes in the boundary condition. We have taken different values of α and β in the boundary of the cluster and the structure of the density of states remains almost unchanged except for the two peaks at the edge of the spectrum which, since they are due to the boundary condition, are extremely sensitive to the values of α and β.
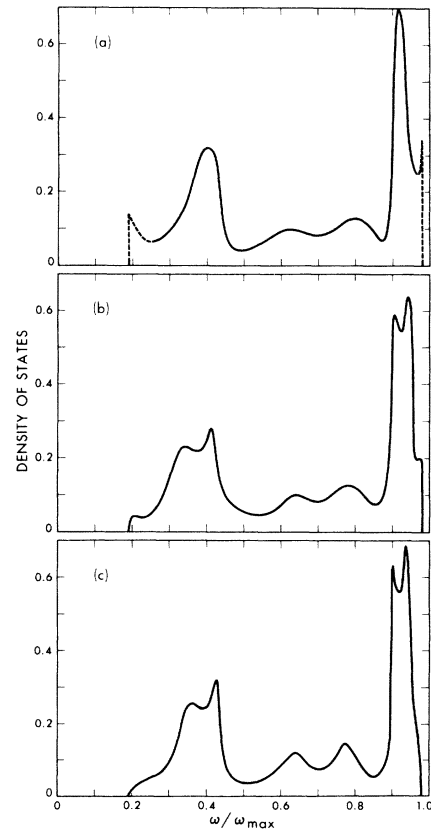
A direct comparison of Fig. 4(a) with Figs. 2(a)

FIG. 4. Density of vibrational states for the diamond structure treated within the cluster−Bethe-lattice approximation. $\beta/\alpha = 0.6$. (a) Local density of states at atom labelled 0 of the 29-atom cluster of Fig. 3. (b) The same for the 35-atom cluster. (c) The same for the 59-atom cluster.

and 2(b) reveals that the two peaks in the middle region of the spectrum are due to the topology of the cluster, in particular, to the presence of 12 sixfold rings of bonds passing through the central atom.

In order to check the above discussed results, we have studied the density of states of clusters of different sizes. In particular we calculate the density of states of 35- and 59-atom clusters in the diamond structure. The cluster of 35 atoms can be obtained from the cluster of 29 atoms by saturating atoms labelled 17 and 18 in Fig. 3 with a new atom (and the same for the five equivalent pairs of atoms). The 59-atom cluster can be obtained from the 35-atom cluster by saturating atoms labelled 5, 6, and 7 in Fig. 3 with six new atoms (and the same for the 4 equivalent sets of three atoms). This cluster contains up to the fourth-nearest-neighbor atom of the central atom. The densities of states corresponding to these clusters are drawn in Figs. 4(b) and 4(c). If we compare Fig. 2 with Fig. 4 we see how the cluster calculation converges to the crystal density of states as the size of clusters increases. We notice that not only the position and the shape of the longitudinal peaks is improved with respect to the crystal density of states, as the size of the cluster increases, but also the structure of the transverse part of the spectrum is fairly well approximated by the clusters of 35 and 59 atoms. In addition, the spurious peaks at the edges of the spectrum of the 29-atom cluster are no longer present in the spectrum of the 59-atom cluster. One can be tempted to associate the long-itudinal peaks in Fig. 4(a) with the eigenvalues of isolated sixfold rings of bonds as in the electronic case.[5] To check this we have calculated the eigen-values of an isolated sixfold ring of bonds in the diamond structure. The eigenvalues we have obtained by no means can be identified with the structure in the spectrum of Fig. 4(a). This identification of the structure in the density of states with the presence of rings of bonds in the structure is to some extent meaningless in the case of lattice vibrations. Since the potential (1) depends on both bond angle and bond length, it is possible to build clusters of atoms with the same number and kind of rings of bonds but with different topologies, i.e., different bond angles and bond lengths, and consequently the corresponding densities of states are different. Another reason why the identifica-tion of the peaks in the spectrum with the eigen-values of isolated rings of bonds is useless is be-cause the lattice vibrations of the small unit are extremely sensitive to the boundary condition at the surface of such unit. To show this we have calculated the density of states at the central atom of the bare 29-atom cluster of Fig. 3. To do this
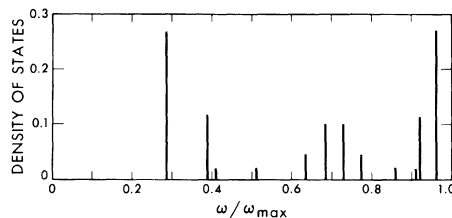

FIG. 5. Local density of states at atom labelled 0 of the bare 29-atom cluster of Fig. 3. The straight lines represent δ functions. The height of the straight lines is proportional to the weight of the corresponding δ function.

we just take $t_0 = t_1 = 0$ in Eq. (17). The result is shown in Fig. 5. If we now compare this spectrum with the spectrum in Fig. 4(a), we notice that they are very different. We cannot find any correlation between them. The two δ functions close to 0.7 in Fig. 5 are too close to support the existence of two well-separated peaks in the actual density of states of the diamond structure, whereas the den-sity of the cluster−Bethe-lattice system [Fig. 4(a)] gives two well-separated peaks. This stresses again the need of a good boundary condition when dealing with not very large clusters of atoms.

As a consequence, although we cannot identify the longitudinal peaks with rings of bonds, as in the electronic case,[5] we can however assess that they are due to *short-range* topologies and not to longer range structural correlations as it has been suggested.[10,18]

IV. CONCLUSIONS

The main conclusion that can be drawn from the above discussed results is that the salient features of the vibrational density of states of crystalline diamondlike semiconductors are due to short-range order. In particular, we can assess that the peaks in the spectrum corresponding to trans-verse modes are due to the tetrahedral coordina-tion of these semiconductors. On the other hand, the peaks corresponding to the longitudinal modes are due to short-range correlations such as the presence of closed rings of bonds.

The results of our calculations show clearly that when dealing with clusters of atoms, the boundary condition at the surface of the cluster is very im-portant in order to get a reliable spectrum of the lattice vibrations. The Bethe-Peierls approxima-tion provides us with a good *physical* boundary condition.

The method we have developed can be easily ex-tended to study densities of states of noncrystalline phases of group-IV semiconductors. A systemmat-ic study of the density of states of continuous ran-dom networds is underway and will be reported in a future publication. At the moment, we have

studied the effects of bond angle variations in the density of states of the Bethe lattice only. The shape of the transverse peaks [see Fig. 2(a)] is rather sensitive to bond angle variation, whereas the changes of the featureless longitudinal part of the spectrum are of the order of 10% for deviations of the perfect tetrahedral angle of the order of 10°. Since the peaks corresponding to longitudinal modes in Fig. 4 are not very pronounced and a perfect coherence in the phase of the wave func-

tion is needed to see the effects of the presence of rings of bonds,[19] we expect that in the amorphous phase the dip between the two peaks might be filled up, giving rise to a single peak structure.

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[1]See, for instance, AIP Conf. Proc. 20 (1974), edited by M. H. Brodsky, S. Kirkpatrick, and D. Weaire; and A. S. Baker, Jr., and A. J. Sievers, Rev. Mod. Phys. Suppl. 2, 47 (1975).

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