Vibrational properties of amorphous Si-N and Ge-N alloys

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Abstract. A theoretical study of the vibrational density of states of amorphous alloys was developed by applying a simple effective-medium theory with a Born Hamiltonian. This theory is equivalent to the coherent-potential approximation, with the advantage that it is set in real space in a very simple way. With this theory, one can observe the differences in the spectra of amorphous Si and Ge when several concentrations of N atoms are added. The predictions of the theory are compared with data from Raman scattering experiments.

1. Introduction

Amorphous semiconductors have acquired enormous importance in recent years, mainly because of their use in micro-electronics, image pick-up and solar energy conversion devices. They are also extremely interesting from the pure physics point of view, since they pose questions about basic notions which are, at present, far from well understood. Most of the studies reported so far, either theoretical or experimental, are concerned with the electronic properties of the amorphous semiconductors, which are directly connected with their immediate application in industry, such as ways to modulate the conductivity of devices. The most important compound in this field is, by far, the alloy of amorphous Si with hydrogen (a-Si : H), which is currently used in the micro-electronics industry, although basic knowledge of the conduction processes in this material is not well founded yet. One can say that experiment has surpassed theory in this field, and this is mainly because there are no mathematical developments powerful enough to deal with the complicated problem of an amorphous alloy, where the effects of disorder arise from the topological disarrangement of the Si matrix and from the very fact of alloying as well.

In solar cell applications, further developments have been made recently in order to improve the performance of a-Si : H solar cells. Some of these efforts are focused on the possibility of materials with a variable gap, which can be achieved by adding a further element such as C or N to the alloy. It is clear that adding a new element will affect the

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properties of various alloys differently; in particular, it has been reported that the inclusion of N in a-Si or in a-Ge modifies the network in substantially different ways, as is apparent from the Raman spectra obtained from these alloys.

A theory to simulate the effect of N in the vibrational properties of a-Si and a-Ge alloys is presented in § 2, and the results obtained are discussed in connection with the experimental data in § 3.

2. Theoretical method

In order to treat the vibrations of the atoms in the alloy, let us adopt a Born Hamiltonian

$$\mathcal{H} = \tfrac{1}{2} \sum_i \sum_j \{ (\alpha_i - \beta_i)[(\boldsymbol{u}_i - \boldsymbol{u}_j) \cdot \hat{\boldsymbol{r}}_{i,j}]^2 + \beta_i (\boldsymbol{u}_i - \boldsymbol{u}_i)^2 \} \tag{1}$$

where the summation is over nearest neighbours only, and α_i and β_i are the central and non-central parts of the force between atoms, linked in the direction $\hat{\boldsymbol{r}}_{i,j}$, when there are displacements u from the equilibrium positions of the atoms. There are bonds between Si atoms, between Ge atoms, between a Si atom and a N atom, and between a Ge atom and a N atom; in the latter two cases the force constants will be written with primes. The N–N bonds will not be considered here, because in infrared experiments (Chambouleyron *et al* 1985) there is no trace of N–N absorption, although they could be added to the theory without complications. Let us choose a site in the network and define it as zero; there is a probability $1 - x$ that this site is occupied by a Si (or a Ge) atom, i.e. it is in the centre of a tetrahedron formed by its first neighbours. Let us assume that there is certainly a Si (or a Ge) atom at site 0, where there is a frame of reference whose z axis lies along the direction of one of these four bonds (we shall call it direction 1). Then the conditional probability that the neighbour site along 1 is occupied by a N atom is $P_{SN} = 8x/(4 - x)$ (Castillo-Alvarado *et al* 1988), and the probability of Si (or Ge) occupancy is $P_{SS} = 1 - P_{SN}$. This gives $\tfrac{4}{9}$ as the maximum concentration x of N, because there are no N–N bonds and each N is bonded to three other atoms in a planar triangular configuration C_{3v}. In this geometry, one can write the equations of motion for the displacement–displacement Green function (Elliott *et al* 1974), using equation (1), in terms of 3×3 matrices. For instance, at a site in the pure lattice the equation is

$$(M\omega^2 \mathbf{I} - \mathbf{D}_0)\mathbf{G}_{00} = \sum_{i=1}^{4} \mathbf{S}_i^{-1} \mathbf{D}_1 \mathbf{G}_{01} \mathbf{S}_i \tag{2}$$

where M is the Si (or Ge) mass and $\mathbf{D}_1$ is a diagonal matrix with β in the first two diagonal elements and α in the last. $\mathbf{D}_0$ is the self-interaction due to the diagonal elements of equation (1), and it is obtained by summing the $\mathbf{D}_i$ matrices over the four bonds i arriving at site 0, which can be found from $\mathbf{D}_1$ by applying the tetrahedral rotations $\mathbf{S}_i$; it is found to be $\mathbf{I}(4\alpha + 8\beta)/3$, where $\mathbf{I}$ is the 3×3 identity matrix.

In the alloy there will be a probability that $\mathbf{D}_1$ in equation (2) is $\mathbf{D}_1'$ (which is exactly as $\mathbf{D}_1$, but with α' and β' instead of α and β), if a first neighbour is a N atom: this implies that the correlation $\mathbf{G}_{01}$ would be modified and all the equations in the chain with it. It is exactly here where the difficulty of solving the problem arises, even if one has a simple set of equations such as in the Bethe lattice. One can solve the problem numerically, constructing a large number of lattices with different random configurations, as has been done for a-Si:H (Vergés 1984), or one might prefer to define a simple effective medium in order to simulate the disorder. This effective medium can be defined by substituting

in the right-hand side of equation (2) an average interaction, as has been done by Kittler and Falicov (1976), although such a procedure can give rise to spurious features in some cases because of the artificial weakening of the interactions in the effective medium. Another way of defining an effective medium has been suggested by Vergés (1986), in which the average is taken in the Green functions and not in the transfer matrices or the interactions themselves. This theory has been applied successfully to the electronic problem in a-Si:H (Tagüeña *et al* 1987), where it was shown that this procedure is equivalent to the coherent-potential approximation (CPA). This picture differs from the well known 'cluster–Bethe lattice' method (Joannopoulos and Yndurain 1974) in an essential feature, since the effective medium is constructed in a self-consistent way here and not fixed as an averaged interaction. The basic equation to solve (Castillo-Alvarado *et al* 1988) can be written as

$$\langle \mathbf{G}_{00} \rangle = P_{\text{SS}} \langle \mathbf{G}_{00}^{\text{SS}} \rangle + P_{\text{SN}} \langle \mathbf{C}_{00}^{\text{SN}} \rangle \tag{3}$$

where the angular brackets mean a configurational average. The physical meaning of equation (3) can be represented pictorially as in figure 1. On the left-hand side of the
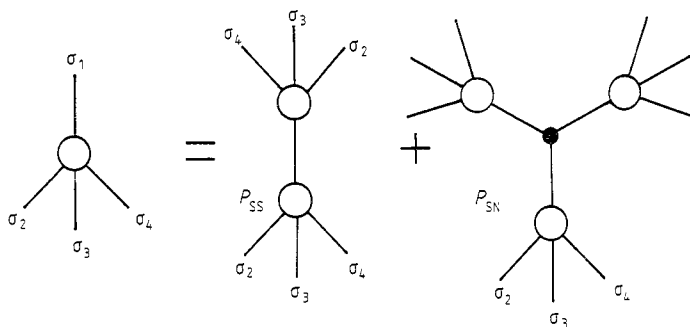
Figure 1. Representation of the effective-medium substitution in the alloy problem: ○, Si or Ge; ●, N.

figure, one has a Si (or a Ge) atom totally immersed in an effective medium, whose impedance is represented by a self-energy σ_j, attached to each bond j. The effective medium should be consistent with the right-hand situation, i.e. a configuration in which there is a probability P_{SS} of having a Si (or a Ge) neighbour along bond 1, and a probability P_{SN} of having a N neighbour. Note that all the three neighbours of the N site have to be Si (or Ge), owing to the absence of N–N bonds. One could relax this latter condition very easily, by introducing a new probability P_{NN} different from zero, as the case may be, or by introducing all the local surroundings which could arise from more complicated systems. Explicitly, from the equations of motion for the Green functions, one obtains

$$\langle \mathbf{G}_{00} \rangle = \left(M\omega^2 \mathbf{I} - \langle \mathbf{D}_0 \rangle - \sum_{j=1}^{4} \sigma_j \right)^{-1}, \tag{4}$$

$$\langle \mathbf{G}_{00}^{\text{SS}} \rangle = \left(M\omega^2 \mathbf{I} - \langle \mathbf{D}_{\text{SS}} \rangle - \sum_{j=2}^{4} \sigma_j - \Sigma_{\text{SS}} \right)^{-1} \tag{5}$$

$$\langle \mathbf{G}_{00}^{\text{SN}} \rangle = \left(M\omega^2 \mathbf{I} - \langle \mathbf{D}_{\text{SN}} \rangle - \sum_{j=2}^{4} \sigma_j - \Sigma_{\text{SN}} \right)^{-1} \tag{6}$$

where $\langle \mathbf{D}_{SS} \rangle$ and $\langle \mathbf{D}_{SN} \rangle$ are the averaged self-interactions, when there is definitely a Si–Si or Si–N bond, respectively, along bond 1, and they are given by

$$
\langle \mathbf{D}_{SS} \rangle = \begin{bmatrix} \gamma + P_{SN}(\beta - \beta') & 0 & 0 \\ 0 & \gamma + P_{SN}(\beta - \beta') & 0 \\ 0 & 0 & \gamma + P_{SN}(\alpha - \alpha') \end{bmatrix} \tag{7}
$$

$$
\langle \mathbf{D}_{SN} \rangle = \begin{bmatrix} \gamma - P_{SS}(\beta - \beta') & 0 & 0 \\ 0 & \gamma - P_{SS}(\beta - \beta') & 0 \\ 0 & 0 & \gamma - P_{SS}(\alpha - \alpha') \end{bmatrix} \tag{8}
$$

where $\gamma = 4[P_{SS}(\alpha + 2\beta) + P_{SN}(\alpha' + 2\beta')]/3$. The averaged self-interaction in the effective medium is $\langle \mathbf{D}_0 \rangle = \gamma \mathbf{I}$, and

$$
\Sigma_{SS} = \mathbf{D}_1 \left(M\omega^2 \mathbf{I} - \langle \mathbf{D}_{SS} \rangle - \sum_{i=2}^{4} \sigma_i \right)^{-1} \mathbf{D}_1 \tag{9}
$$

is the self-energy in the central site due to the Si–Si (or Ge–Ge) bond along direction 1. Therefore,

$$
\Sigma_{SN} = \mathbf{D}_1' \left[m\omega^2 \mathbf{I} - \mathbf{D}_N - \sum_{i=2}^{3} \mathbf{D}_i' \left(M\omega^2 \mathbf{I} - \langle \mathbf{D}_{SN} \rangle - \sum_{j=2}^{4} \sigma_j \right)^{-1} \mathbf{D}_i' \right]^{-1} \mathbf{D}_1' \tag{10}
$$

is the corresponding self-energy due to the Si–N (or Ge–N) bond, where m is the nitrogen mass and $\mathbf{D}_N$ is the self-interaction at a N site. It is in the calculation of this last term and in the summation over the three bonds in the trigonal site where problems arise because one has to decide about the orientation of the triangle of bonds with respect to the Si (or Ge) back bonds. It is seen that the stable configuration is attained when the triangle aligns with one of the back bonds; therefore one can perform an average over the three equivalent positions

$$
\sum_{i=2}^{3} \sigma_i = \tfrac{1}{3}[\sigma_2 + \sigma_3 + \varphi^{-1}(\sigma_2 + \sigma_3)\varphi + \varphi(\sigma_2 + \sigma_3)\varphi^{-1}] \tag{11}
$$

where φ is a rotation matrix of $2\pi/3$ around the z axis. This last average simplifies the problem tremendously, since all the matrices become diagonal and have the form of $\mathbf{D}_1$, explicitly

$$
\langle \mathbf{D}_N \rangle_\perp = \begin{bmatrix} \tfrac{3}{4}(3\beta' + \alpha') & 0 & 0 \\ 0 & \tfrac{3}{4}(3\beta' + \alpha') & 0 \\ 0 & 0 & \tfrac{3}{2}(\beta' + \alpha') \end{bmatrix}. \tag{12}
$$

Therefore, the self-consistent equations for σ become scalar, namely

$$
\sigma_\perp = E_\perp - A_\perp \tag{13a}
$$

$$
\sigma_\parallel = E_\parallel - A_\parallel \tag{13b}
$$

where

$$E_\perp = M\omega^2 - \gamma - \tfrac{1}{3}(4\sigma_\parallel + 5\sigma_\perp) \tag{14a}$$

$$E_\parallel = M\omega^2 - \gamma - \tfrac{1}{3}(\sigma_\parallel + 8\sigma_\perp) \tag{14b}$$

$$A_\perp = (P_{SS}/\langle G_{00}^{SS}\rangle_\perp + P_{SN}/\langle G_{00}^{SN}\rangle_\perp)^{-1} \tag{15a}$$

$$A_\parallel = (P_{SS}/\langle G_{00}^{SS}\rangle_\parallel + P_{SN}/\langle G_{00}^{SN}\rangle_\parallel)^{-1}. \tag{15b}$$

Here the symbols $\perp$ and $\parallel$ represent the directions perpendicular and parallel, respectively, to bond 1.

Equations (13) are solved iteratively, until a desired accuracy is attained. It is worth emphasising that the simplicity of the equations allows us to solve the problem with a minimum of computing efforts, and that no convergency problems, usually encountered in CPA calculations, were found. The averaged Green function at the N site is

$$\langle \mathbf{G}_{00}^N\rangle = \left(m\omega^2\mathbf{I} - \mathbf{D}_N - \sum_{i=1}^{3}\sigma_i\right)^{-1}. \tag{16}$$

The total density of states (DOS) is obtained from

$$\rho(\omega) = -(2/\pi)\omega\,\mathrm{Im}[mx(2\langle G_{00}^N\rangle_\perp + \langle G_{00}^N\rangle_\parallel) + M(1-x)(2\langle G_{00}\rangle_\perp + \langle G_{00}\rangle_\parallel)] \tag{17}$$

where $\langle G_{00}\rangle$ is given by equation (3).

3. Results and discussion

In order to illustrate the type of results obtained from the present theory the DOS was calculated for the Si–N and the Ge–N alloys, with various concentrations x of N. The values of the force constants for the Si–Si and Ge–Ge bonds were taken from the work of Barrio and Elliott (1982), previously adjusted to give the correct bands for the pure amorphous materials, the values for the Si–N bonds were fitted to the frequencies v_2 and v_3 of the particular normal modes reported for the stoichiometric a-Si$_3$N$_4$ alloy (Lucovsky 1983), and the values for the Ge–N bonds were fitted from the bending and stretching Ge–N localised modes measured by infrared absorption (Chambouleyron *et al* 1985). These values are given in table 1.

Table 1. Force constants used in the calculations (in units which give the frequency in units of 10^{-3} cm^{-1}, if the mass is in au).

System	α	β	α'	β'
Si–N	1.774	0.323	5.063	0.360
Ge–N	1.782	0.324	3.476	0.683

Figures 2(a) and 2(b) show the total DOSs (equation (17)) for the Si–N and the Ge–N alloys, respectively, for various values of x, ranging from the pure amorphous matrix ($x = 0$) to the stoichiometric alloy ($x = \tfrac{4}{7}$). The most important features to be noted are as follows.
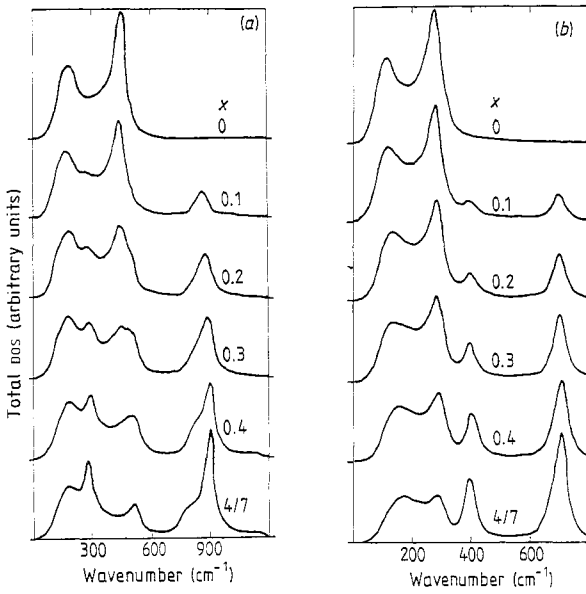
Figure 2. Total density of vibrational states for (*a*) the $Si_{1-x}N_x$ alloy and (*b*) the $Ge_{1-x}N_x$ alloy for various values of x.

(i) The optic modes (at about 480 cm^{-1} in Si and about 300 cm^{-1} in Ge) disappear completely in Si when N is added, and this is not so in Ge. However, it should be noted that an extra band, due to N, appears at about 500 cm^{-1} in the Si case, producing an apparent broadening and stiffening of the optic band.
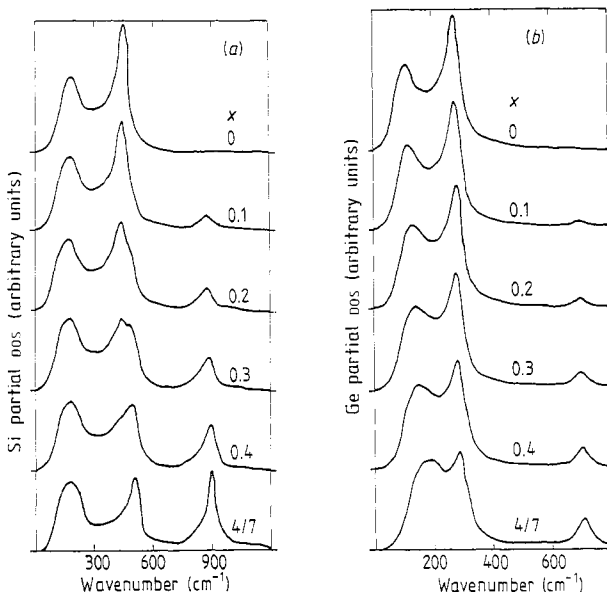
Figure 3. Partial local density of states (*a*) at a Si site in the Si–N alloy, and (*b*) at a Ge site in the Ge–N alloy.

(ii) The local stretching mode ν_3 in the N coordination plane (at about 900 cm^{-1} in Si and at about 700 cm^{-1} in Ge) shifts to higher frequencies with increasing x for both alloys.

(iii) The resonance due to the ν_2 off-plane vibrations of the N atom (at about 300 cm^{-1} in Si and at about 400 cm^{-1} in Ge) does not shift with x in either case.

In order to examine in more detail the characteristics of these spectra, in figures 3(a) and 3(b) the partial DOS at a Si site and a Ge site, respectively, are shown. The following features are apparent.

(iv) There is no resonance at 300 cm^{-1} in the Si spectrum, indicating that the modes are not coupled to the Si motion and explaining the small width of the resonance in the total DOS in figure 2(a).

(v) The weight ratio of the optic to the acoustic bands changes more with x for the Ge alloy than for the Si alloy.

(vi) The apparent broadening of the optic band width increasing x is larger for Si than for Ge.

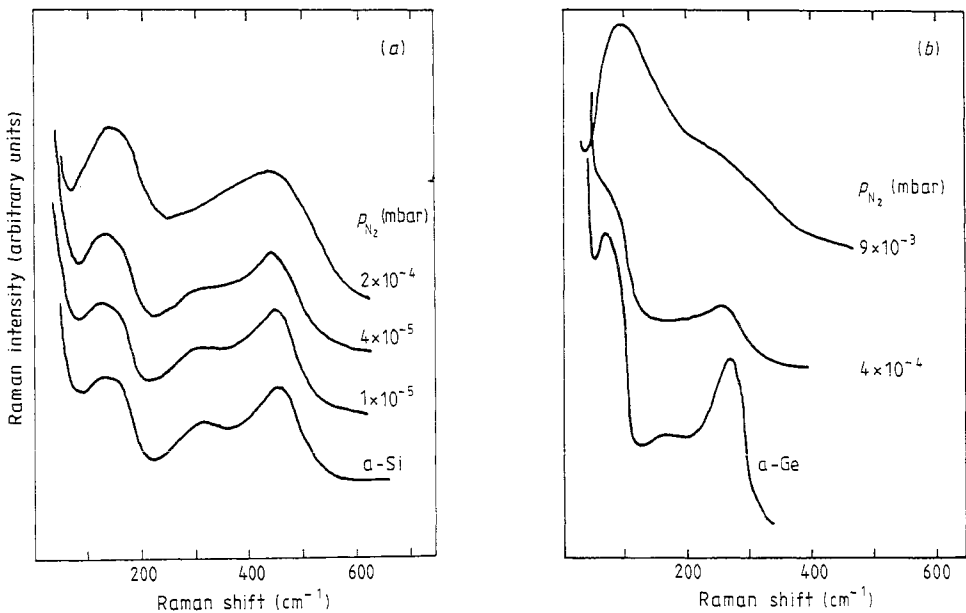(vii) There is a stiffening of the optic modes for Si and not so for Ge.

Figure 4. Raman spectra taken from (a) sputtered a-Si$_{1-x}$N$_x$ samples and (b) a-Ge$_{1-x}$N$_x$ alloys for various values of the partial nitrogen pressure.

Raman spectra from these alloys are shown in figure 4, and they seem to present the features predicted by the theory, particularly (iv)–(vi), although a better comparison with experiment would only be possible with data taken for the same concentrations of N in both alloys and with a more detailed analysis of the matrix element effects in the Raman experiments (Carriço *et al* 1986).
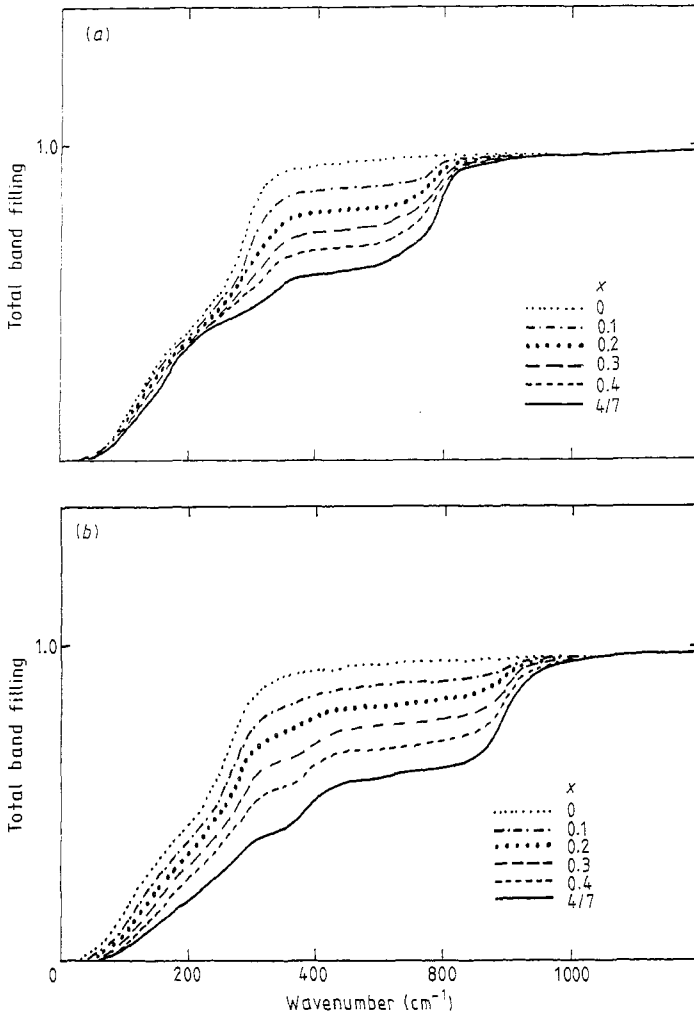
Figure 5. Total band-filling plots from the calculated densities of states for (*a*) the Si–N alloy and (*b*) the Ge–N alloy.

The main differences between the alloys can be seen clearly in figures 5 and 6, where the total and partial band fillings, which are the accumulated integrals under the curves in figures 2 and 3, are shown. It is worthwhile pointing out that for Si the weight of the N modes is taken almost exclusively from the optic band, leaving the acoustic band almost untouched, while in the Ge case this weight is taken equally from all the bands. It is also noticeable that the N modes take a considerable weight from the Si bands (about one-quarter), while they take only about one-tenth of the weight from the Ge bands, owing to the large mass of the Ge atoms, and therefore they do not vibrate easily at high frequencies.

The behaviour of these alloys is different from that obtained in a-Si : H (Barrio *et al* 1983), where a local picture of the bond configuration suffices to give a fair description of the alloy, owing to the extremely small mass of the H. It is clear that in the present case the results show that the N modes represent true bands, totally coupled to the alloy
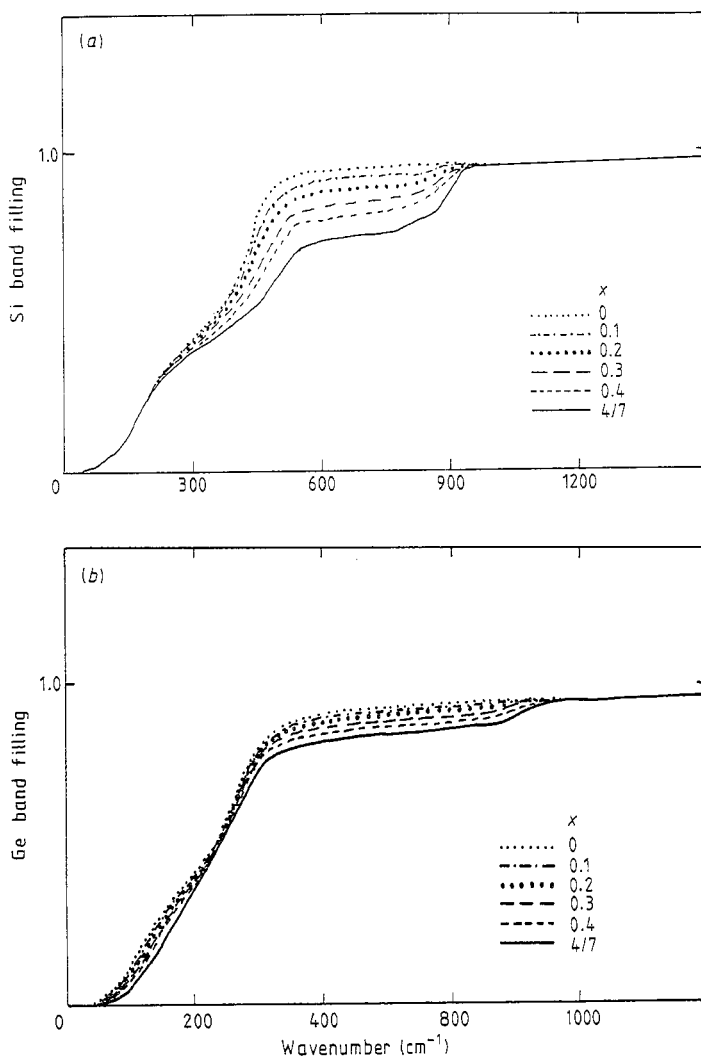
Figure 6. Partial filling of the bands at (a) a Si site and (b) a Ge site in the corresponding alloys.

modes, invalidating the local picture which is useful in a-Si : H. Other theories devoted to the Ge–N system (Schultz 1986) give a larger localisation of the N modes to the local nature of the effective medium used there. An interesting feature, obtained by Schultz, is that lowering the coordination of the Ge atoms gives more weight to the acoustic bands, a fact that seems to be reflected in the experiment (figure 4(a)). It is common to find a-Ge alloys which present a large percentage of low-coordinated atoms accumulated in voids (Contreras *et al* 1985), and therefore it would not be surprising if this were the case in the present alloy. It would be no problem to incorporate a low-coordinated component in the present treatment, although its inclusion here would only obscure the presentation of the concepts and it would be completely useless, since there are no accurate experiments yet in order to verify the theoretical predictions. At present, further experimental work is being carried out in order to test the theoretical results in

a more rigorous way. It is worthwhile pointing out that the present theory can be generalised to other systems with more complicated Hamiltonians which simulate the phonons in a more accurate way (with the inclusion of angular forces, for instance) or with more components, not necessarily tetravalent, since the only essential feature is to solve an equation such as (2), which can be written for more local configurations, arising for example from larger clusters to include further neighbour interactions. Obviously, in these more complicated systems the reduction to a scalar problem might not be feasible, and one would have to deal with the full matrix equations. These applications will be dealt with in future publications.

Acknowledgments

References

Barrio R A and Elliott R J 1982 *J. Phys. C: Solid State Phys.* **15** 4493
Barrio R A, Elliott R J and Thorpe M F 1983 *J. Phys. C: Solid State Phys.* **16** 3425
Carriço A S, Elliott R J and Barrio R A 1986 *J. Phys. C: Solid State Phys.* **19** 1113
Chambouleyron I, Marques F, Cisneros J, Alvarez F, Moehlecke S, Losch W and Pereyra I 1985 *J. Non-Cryst. Solids* **77–78** 1309
Contreras G, Tapfer L, Sood A K and Cardona M 1985 *Phys. Status Solidi* b **131** 475
Castillo-Alvarado F L, Contreras-Puente G S and Barrio R A 1988 *J. Phys. C: Solid State Phys.* **21** 1887
Elliott R J, Krumhansl J A and Leath P L 1974 *Rev. Mod. Phys.* **46** 465
Joannopoulos J D and Yndurain F 1974 *Phys. Rev.* B **10** 5164
Kittler R C and Falicov L M 1976 *J. Phys. C: Solid State Phys.* **9** 4259
Lucovsky G 1983 *Phys. Rev.* B **28** 3234
Schulz P 1986 *MSc Thesis* Universidade de Campinas
Tagüeña J, Barrio R A and Castillo-Alvarado F L 1987 *J. Phys. C: Solid State Phys.* **20** 1679
Vergés J A 1984 *Phys. Rev. Lett.* **53** 2270
——— 1986 unpublished