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Surface and gap intrinsic localized modes in one-dimensional III–V semiconductors

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Abstract. A theoretical investigation has been made of intrinsic localized vibrational modes in an anharmonic one-dimensional diatomic lattice with alternating force constants coupling successive neighbours. This system simulates a row of atoms in the ⟨111⟩ direction of a III–V semiconductor. Specific calculations have been carried out for GaN, because it has a large gap between acoustic and optical branches. We study small-amplitude atom vibrations (up to 0.4 Å), accessible to experimental detection, in order to legitimize the expansion of the full potential to include cubic and quartic terms. We consider then nearest-neighbour interactions through harmonic as well as cubic and quartic anharmonic interactions to study the interplay between cubic and quartic terms in the frequencies of the localized modes. The force constants were determined empirically by fitting the longitudinal branches in the Γ–L direction of GaN. We have studied both gap and surface intrinsic localized modes. Zinc-blende-structure chains are of particular interest, because the lack of inversion symmetry prevents the classification of the modes as even or odd parity. Nevertheless, modes were found that closely resemble the even- or odd-parity modes of an NaCl-structure chain. Their frequencies lie inside the gap for GaN. The absence of inversion symmetry permits a variety of surface modes to exist, depending on whether the bond at the surface is strong or weak and the atom at the surface is light or heavy. All surface mode frequencies for GaN lie inside the gap as found with the use of the full potential.

1. Introduction

It has been known for some time [1–4] that anharmonicity in translationally invariant lattices can produce localized vibrational modes that travel at constant speed through the crystal. The studies of Sievers and Takeno [5, 6] on one-dimensional monatomic chains with quartic anharmonicity revealed the existence of odd-parity localized modes with frequency above that at the zone boundary. Subsequent work by Page [7] showed that even-parity localized modes also exist. The inclusion of a cubic term [8] of negative sign in the (K_2, K_3, K_4) interaction potential decreases the frequency of the localized mode. With increasing magnitude of the cubic coefficient the frequency of the localized mode drops into the continuum of harmonic modes thereby causing the localized mode to become unstable.

Analyses of one-dimensional lattices with realistic potentials [9] that include anharmonicity to all orders demonstrate that intrinsic localized modes do not appear above the top of the harmonic band, but do appear in the gap between the acoustic and optical branches. These calculations show that intrinsic localized modes exist for a very large range of amplitudes up to 1 Å. Recently it has been shown for 3D diatomic systems that the use of the full potential gives rise to modes localized inside the gap between the acoustic and optical branches [10].

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Even in this case the localized modes can occur for very large amplitudes. The molecular dynamics simulations [10] indicate that the lifetime of the ILM modes is about 100–200 vibrational periods for large amplitudes. In a recent investigation [11] of diatomic chains with the (K_2, K_3, K_4) potential, localized modes were found with frequencies both above the top of the optical branch and within the gap. The mode above the top of the optical branch appears for larger values of the amplitude of the mode. In this case the positive quartic K_4-contribution of the potential dominates the interactions between neighbouring atoms increasing the frequency of the mode. For this system two types of surface modes have been found: one related to the surface mode of a harmonic diatomic chain [12] and the other entirely due to the anharmonicity. A number of other investigations of surface modes in anharmonic linear chains have been reported [13–18]. Recently ILM due to anharmonicity have been observed in crystalline arrays of charged linear chains of PtCl with resonant Raman scattering [19]. For III–V compounds up to now no measurements are available. In principle they could be made for superlattices where minigaps are present at the minizone boundaries [20].

In this paper we restrict ourselves to the study stationary modes of small amplitudes up to 0.4 Å. These amplitudes are accessible to experiments and on the other hand allow us to expand with sufficient accuracy the potential up to fourth order. The advantage of using a force-constant model is that we can study the interplay of the cubic and quartic interactions in the value of the frequencies of the localized modes.

Of particular interest to the present work is a study [21] of anharmonic localized modes in a linear chain with atoms of equal mass bonded by two different force constants that alternate from one bond to the next. This simulates a row of atoms in the ⟨111⟩ direction of a diamond-structure crystal. Localized modes of both even and odd parity can occur. Whether these modes have frequencies in the gap or above the top of the optical branch is related to the balance between the cubic and quartic anharmonic interactions. Surface modes of an anharmonic character were also found.

In the present work we consider a diatomic chain with alternating force constants between nearest neighbours, which models a row of atoms in the ⟨111⟩ direction of a zinc-blende-structure crystal. This system differs from both the diatomic chain with a single force constant and a diamond-structure chain in that there is no centre of inversion and hence no classification of the modes as even or odd parity. Furthermore, surface modes are possible in the harmonic limit.

We treat the problem numerically [13] by solving the equations of motion of a chain containing a large number of atoms so that the results do not depend on the number of atoms chosen. As a specific case, we investigate GaN which has a relatively large gap. The interatomic potentials are discussed in section 2, where we also present the results for localized modes in the interior of the chain. In section 3 we discuss surface modes with a light atom at the end of the chain. The end atom can be connected to its interior neighbour by either a strong bond or a weak bond. The case of a heavy atom at the end of the chain is treated in section 4. Here the end pair of atoms can be connected to the interior by either a strong bond or a weak bond. The conclusions are presented in section 5.

2. Intrinsic localized modes in the gap

We consider a diatomic chain of alternating light and heavy atoms, of masses m and M respectively. The unit cell is taken to have the light atom at the origin. This atom is bonded with a strong force constant to the heavy atom of the basis, which in turn is weakly bonded to the next-neighbour light atom. The atoms interact via nearest neighbours with harmonic, cubic and quartic interactions. Since the cubic terms introduce static displacements, we express the

displacement u_n of the nth atom in the form

$$u_n = a_0 A(\xi_n \cos(\omega t) + \phi_n) \tag{1}$$

where a_0 is a unit length whose value has been taken equal to 1 Å, the ξ_n are the relative time-independent displacements of the atoms, the ϕ_n are the static displacements, A is the dimensionless maximum amplitude and ω is the frequency. The rotating-wave approximation is employed to study stationary modes.

We do not present the equations of motion, since they are easily constructed from those for a diamond-structure chain [21] by a simple replacement of the masses. The strong force constants are denoted by k_2, k_3 and k_4 for the harmonic, cubic and quartic interactions, respectively. The weak force constants are denoted by $\overline{k_2}$, $\overline{k_3}$ and $\overline{k_4}$. The force constants for GaN were determined from the potential used by Zapol *et al* [22] by matching the bulk phonon frequencies of GaN. For our one-dimensional system we represent the short-range part by a Born–Mayer potential. The parameters were fitted to the acoustic and optical branches in the $\langle 111 \rangle$ direction at the zone boundary.

We introduce dimensionless quantities defined by

$$\Omega^2 = m\omega^2/k_2 \qquad K_3 = k_3 a_0/k_2 \qquad K_4 = k_4 a_0^2/k_2$$
$$\overline{K_2} = \overline{k_2}/k_2 \qquad \overline{K_3} = \overline{k_3} a_0/k_2 \qquad \overline{K_4} = \overline{k_4} a_0^2/k_2.$$

The values of the dimensionless force constants were found to be

$$\overline{K_2} = 0.32$$
$$K_3 = -1.75 \qquad \overline{K_3} = -0.63$$
$$K_4 = 1.44 \qquad \overline{K_4} = 0.53.$$

To solve the system of coupled equations of motion we use a routine based on the Newton scaled gradient method. We start with a few atoms and an initial guess of the displacements. The routine then determines the solution through an iterative procedure. One atom is then added to each end of the chain and the iterative procedure is continued up to a total of about 200 atoms. The addition of atoms at step n acts as a perturbation on the atomic displacements pattern of step $n-1$. If the perturbation does not destroy the mode, we say that the mode is a stable solution. The stable mode that we obtain has a large displacement amplitude on the atom at the centre of the chain and a rapidly decaying amplitude on the neighbouring atoms. ILM can also be obtained with the maximum displacement off-centre. When the maximum displacement occurs at a surface atom, one has a surface ILM.

To study the relative effects of cubic anharmonicity, which lowers the frequency of the modes, and of the quartic anharmonicity, which raises them, we have made calculations in which $\overline{K_2}$, K_4, and $\overline{K_4}$ are fixed, but K_3 and $\overline{K_3}$ are varied. In additional calculations only K_4 and $\overline{K_4}$ are varied. Results obtained for the frequencies of the localized modes for several values of the cubic anharmonic force constants are presented in figure 1. The (K_2, K_4) model has a localized mode with frequency above the top of the optical branch, as it is known [8, 11]. The introduction of cubic terms lowers the frequency until finally, for the full (K_2, K_3, K_4) model, the frequency drops into the gap. The effect of reducing K_4 and $\overline{K_4}$ is to cause the localized mode frequency to move lower into the gap as shown with full symbols in figure 1.

The displacement pattern for the localized mode associated with the (K_2, K_4) model is given in figure 2. The maximum relative displacement of the central light atom was fixed by setting $\xi_0 = 1$. This mode has neither odd nor even parity as a consequence of the lack of a centre of inversion in the GaN crystal. If the mass of the heavy atom is reduced, displacements of the heavy atoms are increased.

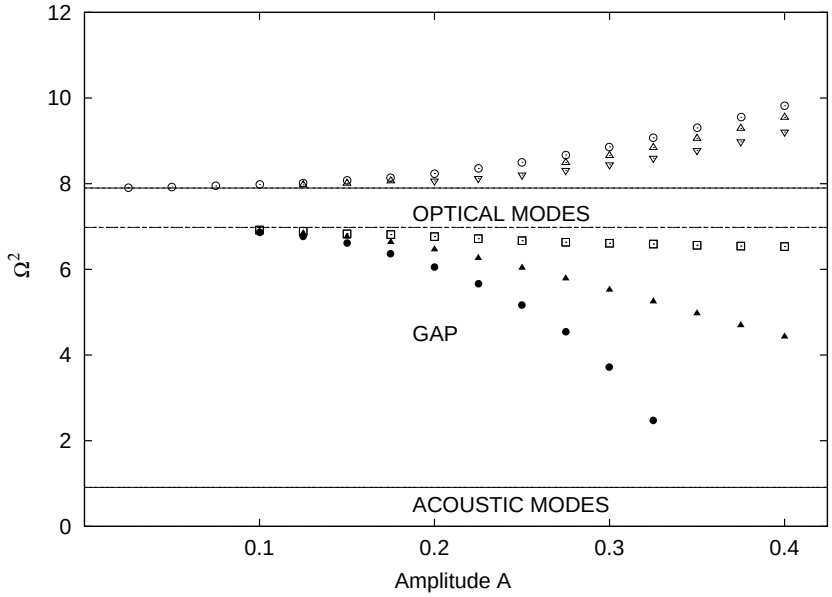

Figure 1. Frequency squared for gap localized modes versus amplitude A for different values of the cubic terms. The curves refer to: ◯: the (K_2, K_4) model; △ and ▽: the (K_2, $K_3/2$, K_4) model (upward-pointing and downward-pointing triangles refer to 'quasi-odd' and 'quasi-even' modes); □: the (K_2, K_3, K_4) full model; •: the (K_2, K_3) model; ▲: the (K_2, K_3, $K_4/2$) model.

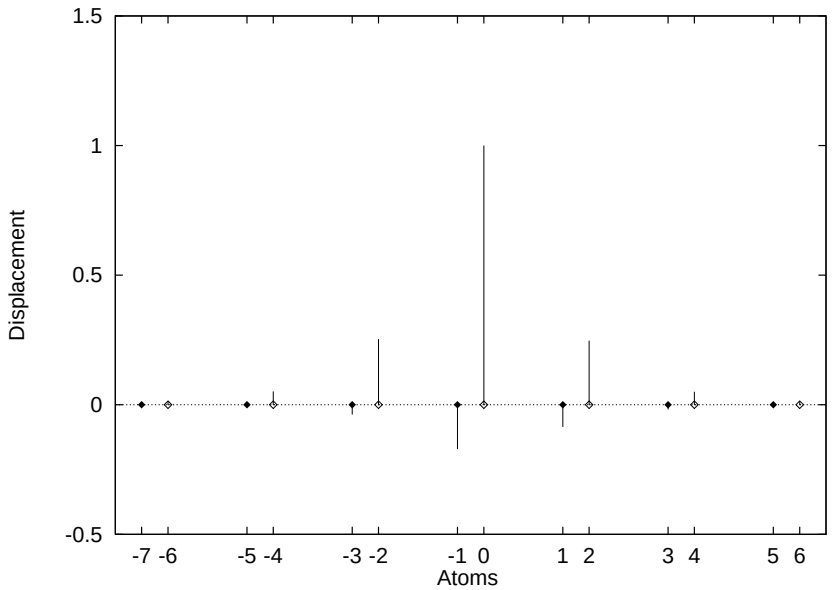

Figure 2. Normalized displacements ξ_n of the localized mode for amplitude $A = 0.25$ in the (K_2, K_4) model. Only the central part of the chain is shown. Open diamonds indicate the light atoms; full diamonds indicate the heavy atoms.

When cubic anharmonicity is added to the potential, the situation changes considerably. For the case of half-maximum cubic anharmonicity with force constants $K_3/2$ and $\overline{K_3}/2$, two

localized modes with distinct frequencies were found, shown at upward-pointing triangles and downward-pointing triangles in figure 1. With full cubic anharmonicity the frequencies of these two modes become quasidegenerate and are within 1% of each other. In figure 3 the displacement pattern for one of these modes is presented. The maximum amplitude is on a light atom and the frequency is inside the gap as shown in figure 1. This mode closely resembles the even-parity gap localized mode present in a diatomic chain [11]. The loss of inversion symmetry produced by the two different force constants mainly affects the displacement of the heavy atom that is strongly bound to the light atom at the origin.

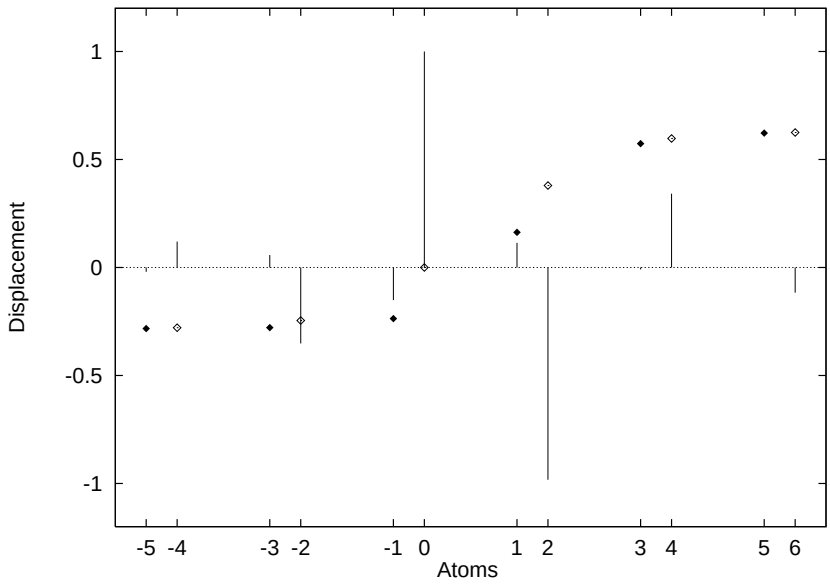

Figure 3. As figure 2, but for the 'quasi-even' gap localized mode for amplitude $A = 0.225$ in the (K_2, K_3, K_4) model. The static displacements ϕ_n are shown as $\diamondsuit$.

The displacement pattern of the second mode, which strongly resembles that of an odd-parity mode, is shown in figure 4. The presence of full cubic anharmonicity causes the frequency to lie in the gap.

3. Surface modes with a light end atom

The lack of inversion symmetry in the zinc-blende structure permits two inequivalent semi-infinite chains: one with the end pair of atoms strongly bound and the other with the end atom pair weakly bound. We first discuss the case of a strong bond with a light atom at the end of the chain. The boundary condition is $\xi_0 = 1$, where ξ_0 is the relative displacement of the end atom. The surface mode has its maximum displacement on the end atom and is the anharmonic analogue of the surface mode that exists in a semi-infinite diatomic harmonic chain. It is derived from the bottom of the optical branch as a result of the creation of the surface.

The frequency of the surface mode as a function of the amplitude A is presented in figure 5 for several sets of force constants. The (K_2, K_4) potential gives a mode with frequency in the gap for small amplitudes. Increasing A causes the mode to rise into the continuum of the optical branch and become a broad resonance. For sufficiently large amplitudes A, the mode

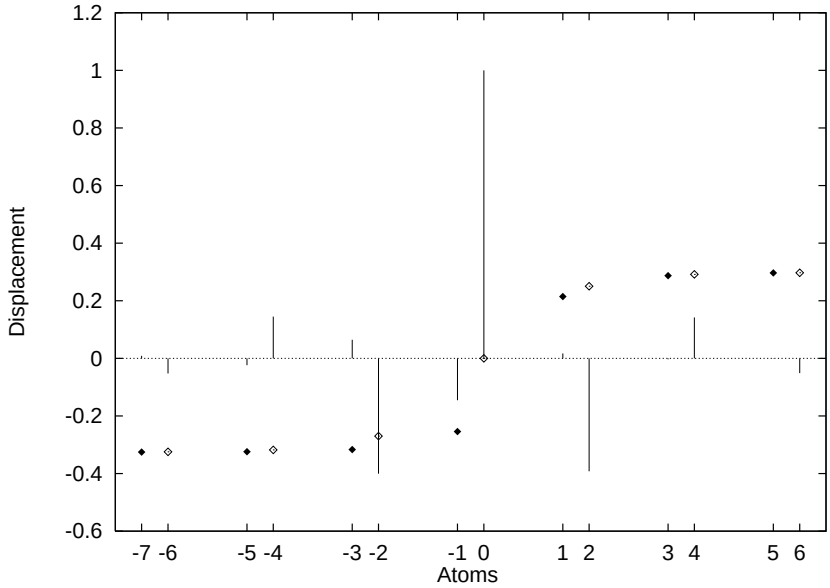

Figure 4. As figure 2, but for the 'quasi-odd' gap localized mode for amplitude $A = 0.25$ in the (K_2, K_3, K_4) model.

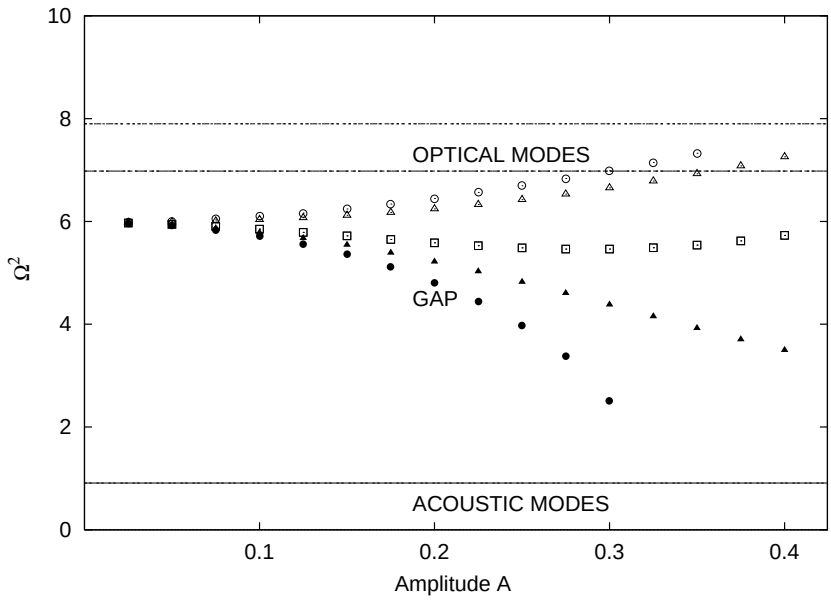

Figure 5. Frequency squared for surface localized modes with a light end atom strongly bound versus amplitude A for different values of the cubic terms. The curves refer to: ◯: the (K_2, K_4) model; △: the (K_2, $K_3/2$, K_4) model; □: the (K_2, K_3, K_4) full model; ●: the (K_2, K_3) model; ▲: the (K_2, K_3, $K_4/2$) model.

becomes localized again with frequency above the top of the optical branch.

Introducing cubic anharmonicity into the potential leads to a lower mode frequency. For the full (K_2, K_3, K_4) potential the frequency is inside the gap for all values of the amplitude

considered. For the (K_2, K_3) model the frequency decreases with increasing A and merges into the acoustic continuum for $A > 0.2$. In figure 6 the displacement pattern of the surface mode for the (K_2, K_3, K_4) model is plotted. The strong bond coupling the end pair of atoms causes the displacement of the first interior atom to be larger than that of the second interior atom. We recall that these two displacements are equal in the case of a harmonic diatomic chain with a single set of force constants. Note that the static displacements produce an expansion at the surface.

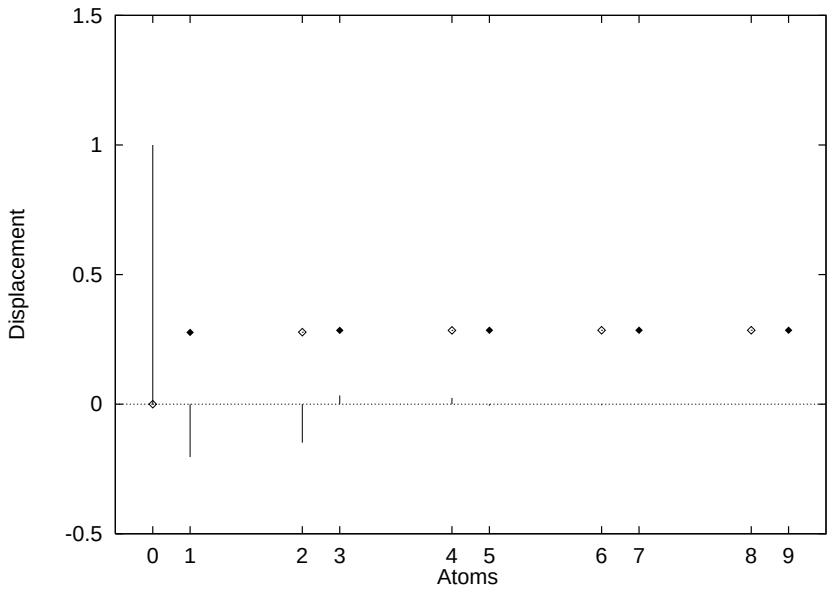

Figure 6. Normalized displacements ξ_n of surface localized modes with a light end atom strongly bound for amplitude $A = 0.25$ in the (K_2, K_3, K_4) model. The static displacements ϕ_n are shown as $\diamondsuit$.

In the case of a weak bond at the end of the chain we find that the frequency remains in the gap for several models of the potential as displayed in figure 7. Only for the (K_2, K_3) model does the surface mode enter the acoustic branch. The displacement pattern, illustrated in figure 8, is similar to that of the harmonic surface mode of a diatomic chain with a single set of force constants for all amplitudes up to $A = 0.4$. The interior strongly bound pairs of atoms move as single entities. One also notices that cubic anharmonicity causes an expansion of the chain through the static displacements. In the case of a diamond-structure chain nonlinear surface modes arise from either the top of the acoustic branch or the top of the optical branch. In the present case (GaN) the nonlinear surface mode emerges only from the bottom of the optical branch. However, for zinc-blende-structure materials with smaller mass ratio such as GaAs, nonlinear surface modes can arise from the top of the optical branch.

4. Surface modes with a heavy end atom

Just as in the case of a light end atom we find two types of surface mode. The boundary condition for the displacement of the light atom next to the heavy end atom is $\xi_1 = 1$. When the end pair of atoms is strongly bound, the frequency is found to depend on amplitude as shown in figure 9 for several sets of values for the force constants. For the (K_2, K_4) model the

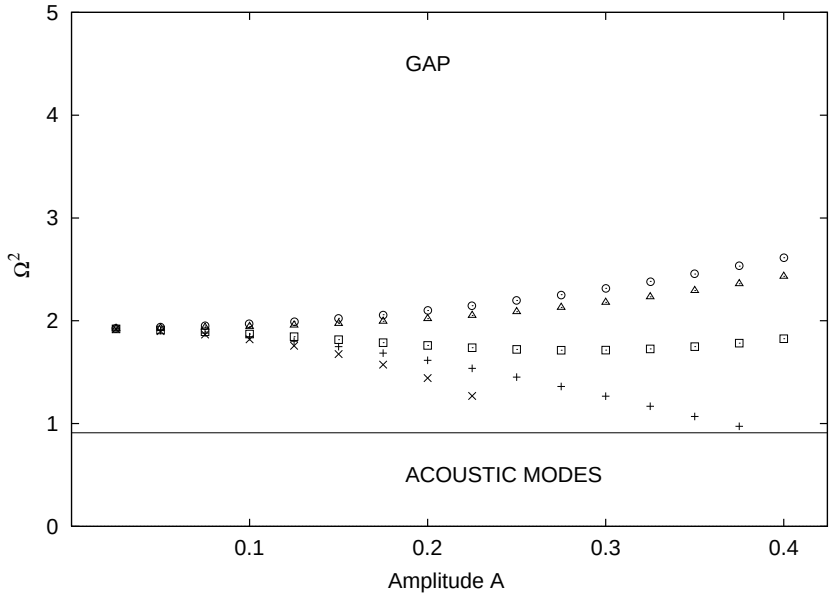

Figure 7. Frequency squared for surface localized modes with a light end atom and weak bond versus amplitude A for different values of the anharmonic terms. The curves refer to: ◯: the (K_2, K_4) model; △: the (K_2, $K_3/2$, K_4) model; □: the (K_2, K_3, K_4) full model; +: the (K_2, K_3, $K_4/2$) model; ×: the (K_2, K_3) model.

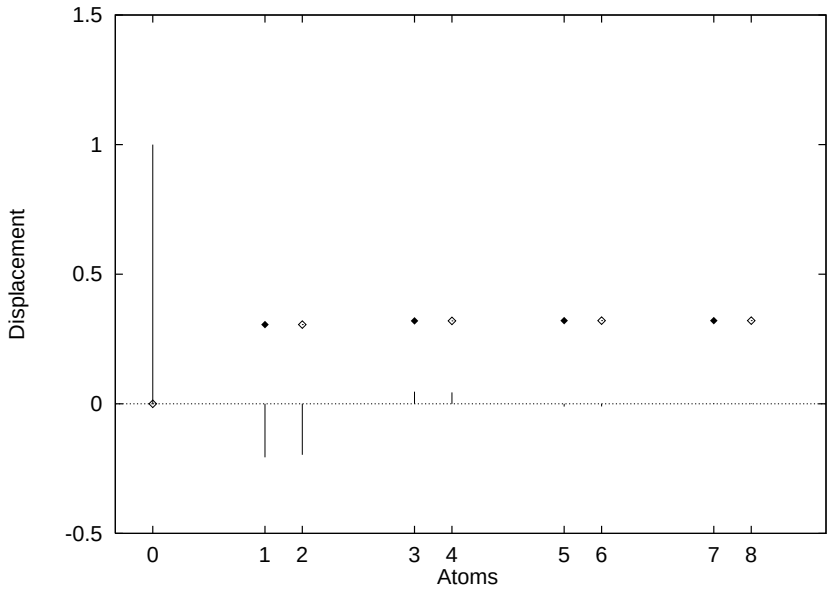

Figure 8. Normalized displacements ξ_n of surface localized modes with a light end atom weakly bound for amplitude $A = 0.25$ in the (K_2, K_3, K_4) model. The static displacements ϕ_n are shown as ◇.

frequency lies above the top of the optical branch. Introduction of cubic anharmonicity lowers the frequency. For the full (K_2, K_3, K_4) model the frequency emerges from the bottom of the

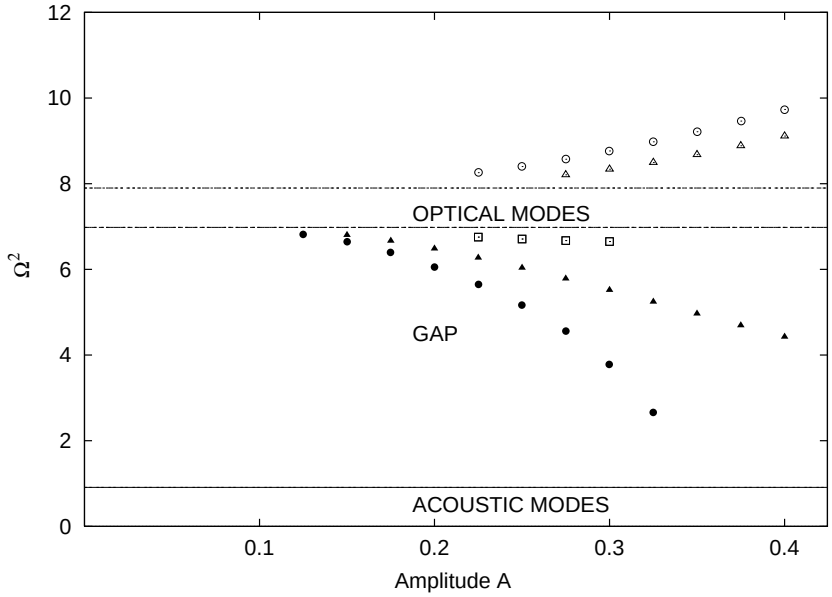

Figure 9. Frequency squared for surface localized modes with a heavy end atom strongly bound versus amplitude A for different values of the cubic terms. The curves refer to: ◯: the (K_2, K_4) model; △: the (K_2, $K_3/2$, K_4) model; □: the (K_2, K_3, K_4) full model; •: the (K_2, K_3) model; ▲: the (K_2, K_3, $K_4/2$) model.

optical branch and exists in the gap for a limited range of amplitudes. The (K_2, K_3) model produces a surface mode whose frequency approaches the acoustic branch at large amplitudes, $A > 0.3$. The displacement pattern for the surface mode in the full (K_2, K_3, K_4) model is shown in figure 10. The largest displacement occurs on the light atom next to the heavy end atom and there is a noticeable static expansion at the surface. Only the first two heavy atoms close to the surface have appreciable displacements. A similar displacement pattern is found for the (K_2, $K_3/2$, K_4) model.

When the end pair of atoms is weakly bound, a surface mode occurs for the full (K_2, K_3, K_4) model whose displacement pattern is given in figure 11. It is rather similar to that for a strongly bound end pair (figure 10). The principal differences are that the heavy end atom has a smaller displacement in the weakly bound case, but the heavy-atom displacements are significant more deeply into the interior of the chain. The frequency of this surface mode is almost degenerate with that of the surface mode associated with a strong bond.

5. Summary and conclusions

In this article we report the results of a theoretical investigation of stationary intrinsic localized modes of vibration in a diatomic chain with alternating force constants. We focus our attention on small, but physical displacements in order to expand with accuracy the full potential up to fourth order. The use of a force-constant model makes more transparent the role played by the cubic and quartic anharmonicity terms. The model considered simulates a row of atoms in the ⟨111⟩ direction of a III–V semiconductor such as GaN. Cubic and quartic anharmonic interactions are included in the interaction potential. A rich spectrum of intrinsic localized modes has been found. These modes are stable with respect to perturbations produced by

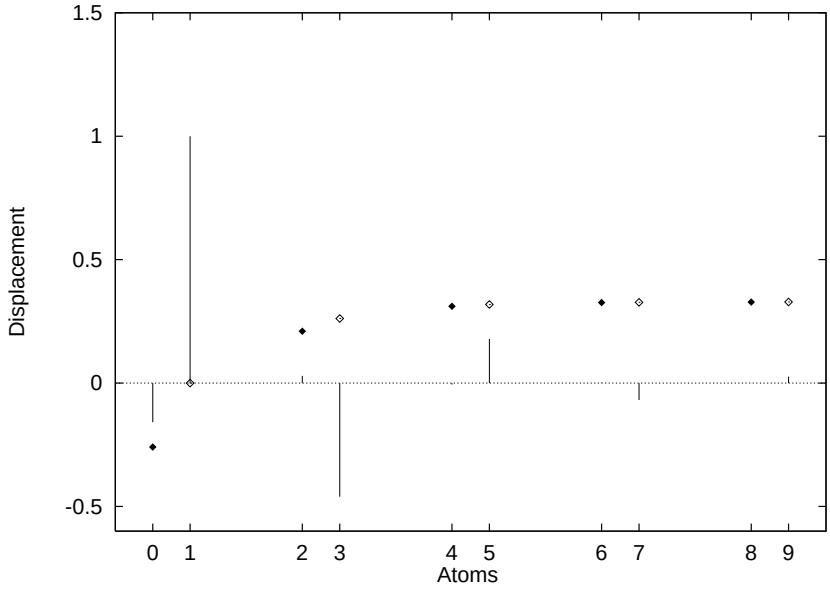

Figure 10. Normalized displacements ξ_n of surface localized modes with a heavy end atom strongly bound for amplitude $A = 0.25$ in the (K_2, K_3, K_4) model. The static displacements ϕ_n are shown as $\diamondsuit$.

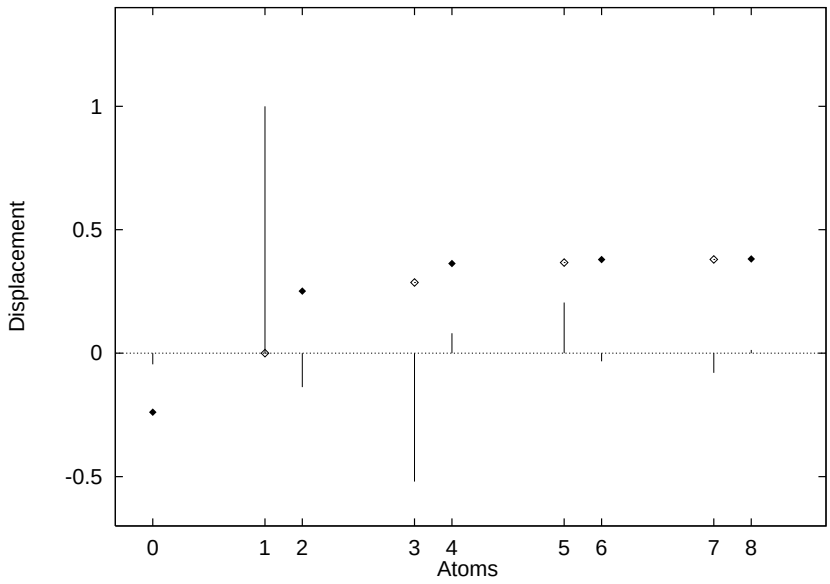

Figure 11. As figure 10, but for a surface localized mode with a heavy end atom weakly bound for amplitude $A = 0.25$ in the (K_2, K_3, K_4) model.

adding extra pairs of atoms to a chain of n atoms. Since the crystal considered has no centre of inversion symmetry, the localized modes cannot be classified as having even or odd parity. Our analysis, however, reveals the existence of two different types of localized mode in the gap. One type closely resembles an odd-parity mode in a diamond-structure chain, while the other

type resembles an even-parity mode. However, the displacement amplitude of a light atom is larger than that of a closest-neighbour heavy atom by roughly the ratio of the two masses.

The quartic term in our interaction potential strengthens the potential, whereas the cubic term weakens it. To understand the interplay between the cubic and quartic terms we have performed several calculations in which we reduce the cubic or the quartic term with respect to the values that we have determined for GaN. In contrast to the case for the Si chain, the full (K_2, K_3, K_4) potential gives the frequency of all the localized modes inside the gap for the range of amplitudes considered. This difference can be attributed to the larger value of the K_3/K_4 ratio in GaN.

Due to the presence of two different nearest-neighbour bonds in the zinc-blende-structure chain, the crystal can be truncated to create a surface in several different ways: an end light atom can be strongly or weakly bound to the next-neighbour heavy atom in the interior of the crystal or an end heavy atom can be strongly or weakly bound to the next-neighbour light atom. For all these possibilities we found surface modes with the maximum displacement on a light atom. In the case of a light end atom weakly bound to its interior neighbour we have found a displacement pattern very close to that of the harmonic surface mode. Because of its large gap, GaN seems to be a good candidate for experimental studies of intrinsic localized modes.

Acknowledgments

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