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Intrinsic localized modes in the one-dimensional zinc-blende structure: two-body potential versus anharmonic force constant model

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Abstract. In this paper we examine the existence of anharmonic localized modes using a full two-body potential to describe all interactions between particles in a zinc-blende-structure material, and we make a comparison with the results obtained with a nearest-neighbour force constant model that includes interactions up to quartic anharmonicity. We show that for amplitude up to a maximum displacement of the order of 0.25 Å there are no appreciable differences between the two approaches, while for the largest amplitudes the force constant model gives unphysical results.

1. Introduction

The study of anharmonicity in crystals has revealed the existence of a new class of localized modes called intrinsic localized modes (ILMs), which exist in infinite translationally invariant lattices [1–4]. The first studies showed the existence of ILMs above the top of the harmonic phonon branch for one-dimensional lattices [5–7]. These modes were obtained by using a force constant approach based on quartic anharmonicity. Subsequent studies revealed that the inclusion of cubic anharmonicity, which makes the potential softer, reduces the frequency of the ILMs [8, 9]. In particular, in a diatomic chain, if the cubic term is sufficiently large, the modes are confined in the gap region [10]. More recently, calculations based on the use of two-body potentials, which include anharmonicity to all orders, demonstrate that ILMs exist only in the gap [11, 12]. They are a general feature of one-dimensional diatomic lattices. Molecular dynamics simulations verify that these modes do not depend on dimensionality and are also present in diatomic three-dimensional crystals. These calculations show that ILMs exist for a very large range of amplitude of the displacements up to one nanometre. Recently, ILMs due to anharmonicity have been observed in crystalline arrays of charged linear chains of PtCl with resonant Raman scattering [13].

In the present work we consider a diatomic chain, with two alternating masses which represent a row of atoms along the ⟨111⟩ direction of a zinc-blende structure. The study of simple one-dimensional systems is of particular significance because they provide an interpretative framework for understanding the results of the more complex three-dimensional molecular dynamics simulations. In a previous paper [14] we investigated a row of GaN which has a relatively large phonon gap. We use a force constant model that includes harmonic, cubic and quartic anharmonicity (K_2, K_3, K_4). We show that ILMs are present in the gap for small

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maximum values of the displacement amplitude, up to 0.3–0.4 Å. The aim of the present paper is twofold. First, to examine the existence of anharmonic localized modes when a two-body potential is used to describe the interactions among all particles in the zinc-blende-structure material GaN and, second, to make a comparison with the results obtained with a nearest-neighbour force constant model that includes interactions up to quartic anharmonicity. We investigate at what amplitude the frequencies of the ILMs obtained with the force constant model start to differ from the results given by the full potential. We treat the problem numerically as discussed in the previous papers, by solving the equations of motion for a chain containing a large number of atoms, so that the results are independent of the chosen number of atoms.

The paper is organized as follows. In section 2 we first introduce the two-body potential for a $\langle 111 \rangle$ row of GaN atoms and the force constant model. Then we discuss the equations of motion in the rotating-wave approximation (RWA) for the localized modes. In section 3 we discuss the results from both models for localized modes in the interior of the chain. In section 4 we discuss surface modes with a pair of end atoms weakly bound. An end atom can be connected to its interior neighbour by either a strong or a weak interaction. The case of a pair of atoms strongly bound is also discussed. Finally, in section 5 we present the conclusions of the paper.

2. Potential and equations of motion

We consider a one-dimensional diatomic lattice with two different alternating masses. The unit cell is taken to have the light atom at the origin. This atom is strongly bonded to the heavy atom of the basis, which in turn is weakly bonded to the next neighbouring light atom. For the strong interaction in our one-dimensional system we use the potential of Zapol *et al* [15], containing a repulsive exponential part and an attractive Coulombic part, constructed to match bulk properties, such as the total energy and bulk modulus of the three-dimensional GaN. To describe the weak interaction for our one-dimensional system we use the same form of the potential, but we change the parameters of the long-range Coulomb part to fit the phonon branches in the $\langle 111 \rangle$ direction. Harmonic, cubic and quartic strong and weak force constants are derived from these potentials. In this case the equations of motion take a simple form. Considering nearest-neighbour interactions, the equation of motion of the particle at lattice site n can be written as

$$m_n \ddot{u}_n = V'_{n+1}(u_{n+1} - u_n) - V'_n(u_n - u_{n-1}) \tag{1}$$

where u_n is the displacement of atom n and $V_n(u_{n+1} - u_n)$ is the interaction potential of neighbouring atoms. For n even, $V_n(u_{n+1} - u_n)$ is the potential relative to the strong interaction and m_n is the mass of the light atom. For n odd, $V_n(u_{n+1} - u_n)$ is the weak potential and m_n is the mass of the heavy atom. The prime means the spatial derivative. To solve equation (1) we use the rotating-wave approximation, so the equations of motion represent oscillators which oscillate periodically in time with frequency ω. To apply the RWA we Fourier transform the potential, retaining the zero-order term and the first-order term in $\cos(\omega t)$. The details of the time Fourier transform are given in the paper of Kiselev *et al* [11].

We seek stationary solutions of the type

$$u_n = A(\xi_n \cos(\omega t) + \phi_n) \tag{2}$$

so that the normalized vibrational amplitude ξ_n and the static displacement ϕ_n related to the local expansion of the anharmonic lattice are independent of time. A is the maximum amplitude of the mode. Substituting equation (2) in equation (1) and making the RWA we obtain a system

of coupled equations for the static and dynamical displacements. To solve this system we use a routine based on the Newton scaled gradient method. We start with three atoms and an initial guess for the displacements ($\xi_0 = 1, \phi_0 = 0, \xi_{-1} = \xi_1 = 0, \phi_{-1} = \phi_1 = 0$). The routine then determines the solution through an iterative procedure. One atom is then added to each end of the chain and the calculation of the displacements is repeated. The iterative procedure is continued up to 200 atoms. The addition at step n of two atoms acts as a perturbation on the chain. If the iterative perturbation does not destroy the mode, we consider the mode to be a stable solution.

3. Bulk modes

The linear chain of zinc-blende structure we are considering has no centre of inversion, so that we cannot classify the modes as even or odd as done in the case of the diamond structure [16] or the alkali halide chains [10]. However, the modes can be classified as quasi-even and quasi-odd to indicate the relation to the corresponding modes when the centre of inversion is present. Here the modes are classified considering the displacement pattern of the light mobile atoms. We start by studying the ILMs in the interior of the chain by using the full potential previously described and by performing the calculations also for the force constant model. We consider displacements with maximum amplitude A up to 0.5–0.6 Å. Results obtained for the frequencies of the modes both for the full-potential model and the force constant model are presented in figure 1. One notes that the frequencies obtained with the full potential lie inside the gap for any value of the amplitude, whereas with the force constant model the modes lie inside the gap for small amplitudes, but go above the top of the optical branch for large amplitudes. However, we show here that for amplitudes of 0.30 Å or less the two approaches give frequencies that are within 10% of each other. In both approaches we have found that the quasi-even and quasi-odd modes are nearly degenerate in frequency.

In figure 2 we present the displacement pattern for the quasi-odd mode for the full-potential case. The maximum amplitude is on the light atom. The loss of symmetry mainly affects the

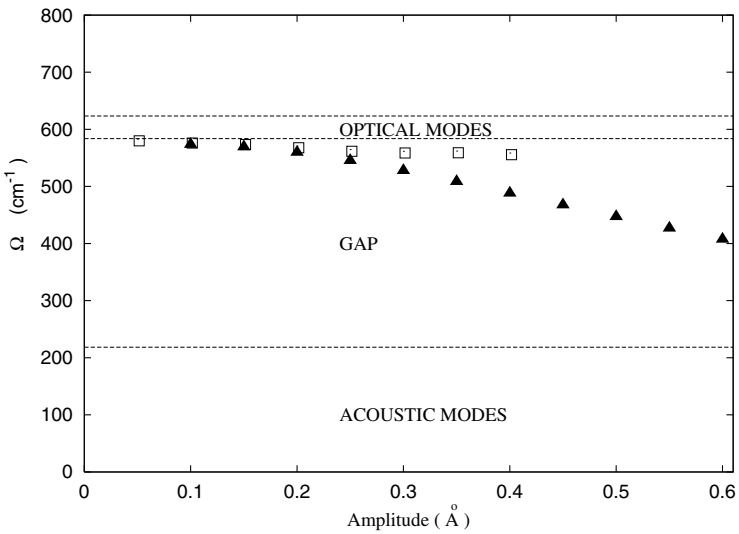

Figure 1. Frequency of bulk gap localized modes versus amplitude A for the full-potential model (▲) and the force constant model (□).

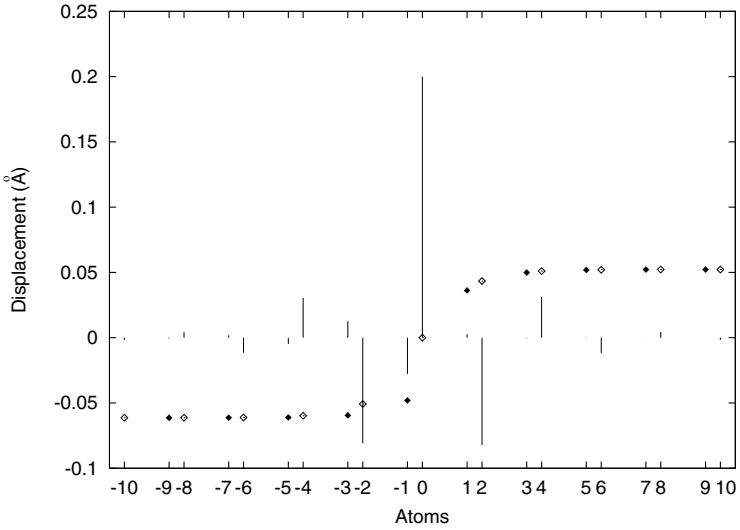

Figure 2. Normalized displacements ξ_n of the bulk 'quasi-odd' localized mode for amplitude $A = 0.20$ in the full-potential model. Only the central part of the chain is shown. The static displacements ϕ_n are shown as $\diamondsuit$. Open diamonds indicate the light atoms; full diamonds indicate the heavy atoms.

displacement of the heavy atom that is strongly bound to the light atom at the origin. The displacement pattern of the quasi-odd mode obtained using the force constant model for the same value of $A = 0.20$ Å is very similar to the one presented in figure 2 and is not presented. The displacement pattern of the quasi-even mode is shown in figure 3. Again up to $A = 0.25$ Å the displacement pattern obtained with the full-potential model and with the force constant model are very similar, so we present only the results obtained with the full potential. The

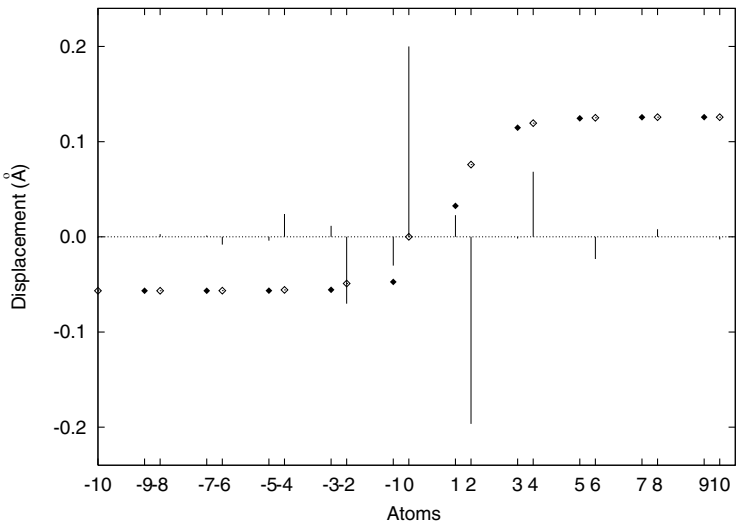

Figure 3. As figure 2, but for the bulk 'quasi-even' localized mode for amplitude $A = 0.20$ in the full-potential model. The static displacements ϕ_n are shown as $\diamondsuit$.

pattern of the quasi-even modes and of the quasi-odd modes becomes identical to the pattern of the purely even end purely odd modes shown [10] for diatomic chains with different masses and equal force constants and for diamond-like chains [16] with equal masses and different force constants.

4. Surface modes

We consider a chain of 200 atoms with free-end boundary conditions. The absence of inversion symmetry in the zinc-blende structure permits several types of surface mode which depend on the strength of the interaction potential of the end atom pair and on the mass of the surface atom. We found the existence of two types of mode, as in the case of the diatomic chain. One, called S_1, which exists also in the harmonic case, is related to the termination of the crystal with the light atom and the other, called S_2, entirely due to the anharmonicity, is related to the heavy end atom. For small amplitudes the frequency of the S_1 mode tends to the frequency of the harmonic surface mode, while the S_2 surface mode becomes a non-localized mode in the optical branch.

We start by discussing the case of a pair of end atoms weakly bound. For a light atom at the end of the chain the boundary condition is $\xi_0 = 1$. The S_1 mode has its maximum displacement on the end atom. It is derived from the bottom of the optical branch as in the harmonic case. The frequency as a function of the amplitude A is presented in figure 4 both for the full-potential case and for the force constant case. One notices that the two models give almost the same frequency for amplitudes up to 0.25 Å. For larger amplitudes the results for the force constant model become unphysical and the frequency rises over the top of the optical branch. The displacement pattern of the mode S_1, for the full potential, is plotted in figure 5 for $A = 0.20$ Å and is similar to that of the force constant model. The interior strongly bound pairs of atoms move as single entities. The asymmetry of the potential causes an expansion of the chain. For the heavy-end-atom case, the frequencies of the surface mode S_2 are presented

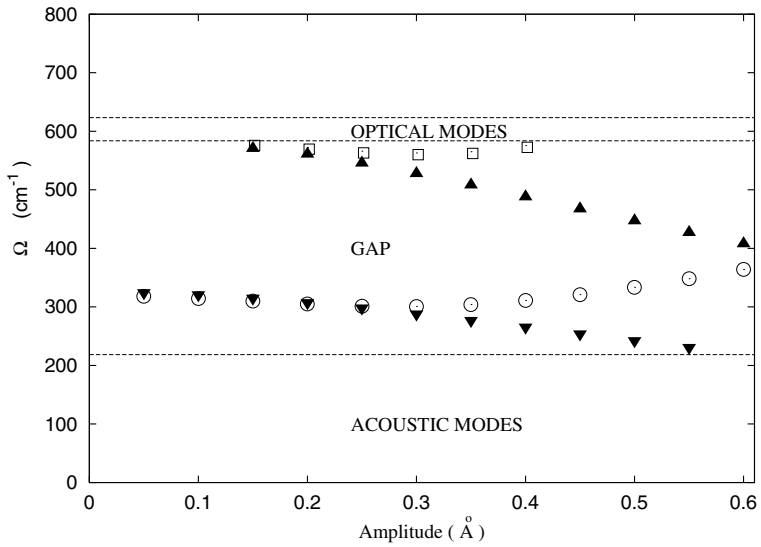

Figure 4. Frequency of surface gap modes S_1 and S_2 versus amplitude A for a chain with a weakly bound end atom for the full-potential model (▲ and ▼) and the force constant model (□ and ◯).

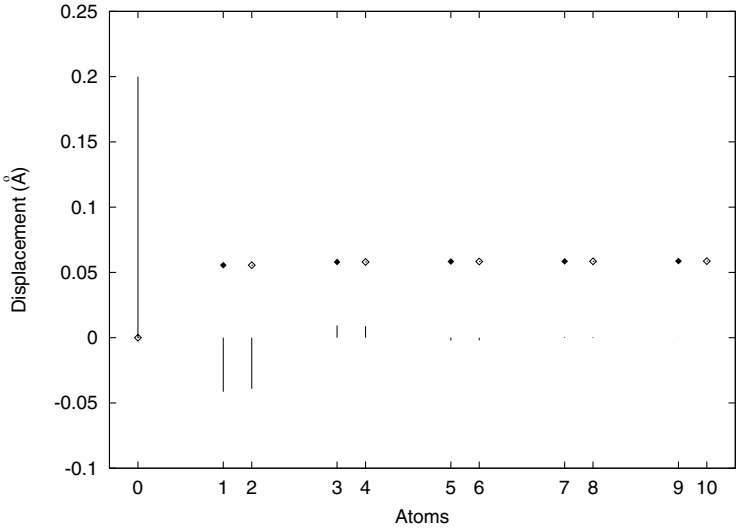

Figure 5. Normalized displacements ξ_n of the surface localized mode S_1 with a light end atom weakly bound for amplitude $A = 0.20$ in the full-potential model. The static displacements ϕ_n are shown as $\diamondsuit$.

in figure 4 both for the full-potential model and for the force constant model. The boundary condition for the displacement of the light atom next to the heavy end atom is $\xi_1 = 1$. The displacement patterns for the S_2 mode, very similar in the two cases, are illustrated in figure 6 for the full potential. The largest displacement occurs on the light atom next to the heavy end atom and there is a noticeable static expansion at the surface. The force constant model breaks down for $A > 0.3$–0.4 Å.

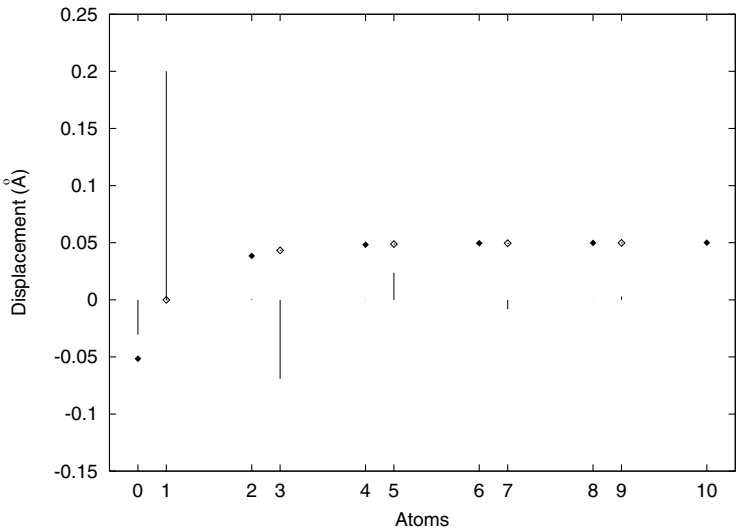

Figure 6. Normalized displacements ξ_n of the surface localized mode S_2 with a heavy end atom weakly bound for amplitude $A = 0.25$ in the (K_2, K_3, K_4) model. The static displacements ϕ_n are shown as $\diamondsuit$.

We pass now to the case of the end pair of atoms strongly bound. The frequencies of the S_1 and S_2 modes, both for the full-potential model and for the force constant model, are shown in figure 7. By comparing these results with those of the end pair weakly coupled, one sees that only the frequency of the S_1 mode is affected by the strength of the interaction with the first interior atom which enhances the frequency of this mode. The displacement patterns for $A = 0.2$ Å are very similar for the two models of interaction. For the S_2 mode we present in figure 8 the results relative to the full potential. The strong interaction between an end pair of atoms causes the displacement of the first interior atom to be larger than that of the second interior atom. The displacement pattern of the S_1 mode is given in figure 9 and is rather similar to that for a weakly bound end pair.

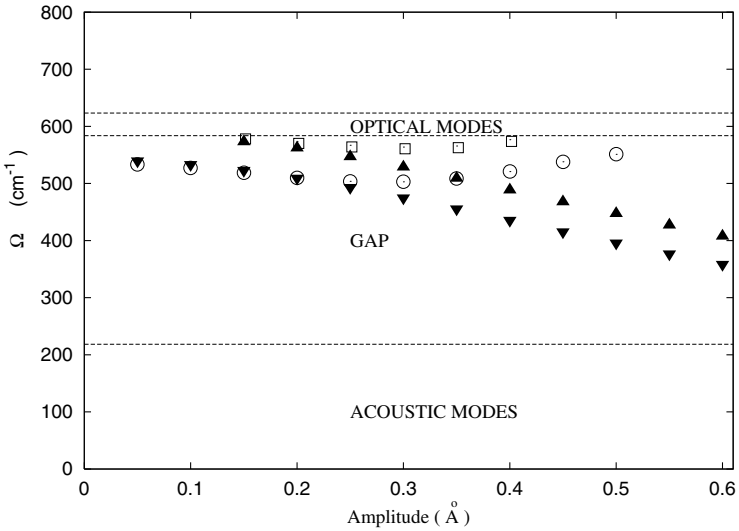

Figure 7. Frequency of surface localized modes S_1 and S_2 with the end atom strongly bound versus amplitude A for the full-potential model (▲ and ▼) and the force constant model (□ and ◯).

5. Conclusions

In this paper we have studied intrinsic localized modes of vibration in a finite diatomic chain with alternating interactions. We have used a realistic two-body potential to describe the interactions between the Ga–N pair of atoms of the basis and the Ga–N pair in adjoining bases. We compare these results with those obtained with a force constant model by expanding the potential up to the fourth order. We show that for the amplitude of the maximum displacement of the order of 0.25 Å there are no appreciable differences between the two approaches. For the largest amplitudes the force constant model becomes unphysical. The quartic anharmonicity force constants dominate and give a mode with frequency above the top of the optical branch. With the full potential, intrinsic localized modes are present in the gap for a very large range of amplitudes, up to 1.0 Å. Since the crystal considered here has no centre of inversion symmetry, the localized modes cannot be classified as having even or odd parity. In agreement with our previous analysis, we found two types of localized mode in the gap—one of quasi-odd symmetry and the other of quasi-even symmetry. Due to the presence of the two different nearest-neighbour interactions in the zinc-blende-structure chain, the crystal can be truncated to create a surface in several different ways. For all of the possibilities we found surface modes

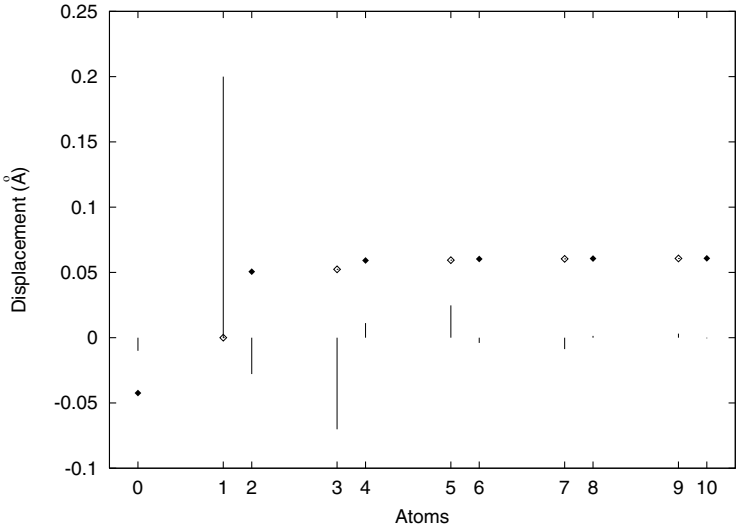

Figure 8. Normalized displacements ξ_n of the surface localized mode S_2 with a heavy end atom strongly bound for amplitude $A = 0.20$ in the full-potential model. The static displacements ϕ_n are shown as $\diamondsuit$.

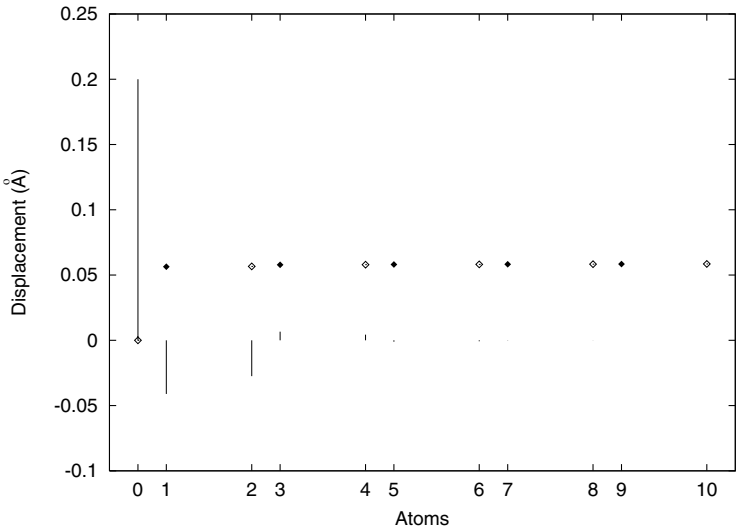

Figure 9. Normalized displacements ξ_n of the surface localized mode S_1 with a light end atom strongly bound for amplitude $A = 0.20$ in the full-potential model. The static displacements ϕ_n are shown as $\diamondsuit$.

with the maximum displacement on a light atom. In the case of a light end atom weakly bound to the next interior neighbour we have found a displacement pattern very close to that of the harmonic surface mode. For bulk and surface intrinsic localized modes we have shown that a force constant model which includes harmonic, cubic and quartic anharmonic force constants derived from a realistic potential is appropriate to the study of intrinsic localized modes for an amplitude not larger than 0.25 Å. Moreover, this is the range of the amplitude that should be detected experimentally without damaging the crystal, by introducing vacancies or melting.

The insight gained by the use of a simple one-dimensional force constant model can be very useful in the interpretation of more complex 3D molecular dynamics calculations. Because of its large gap, GaN seems to be a good material for use in an experimental investigation of localized modes.

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