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Vibrational properties of cubic group-III nitrides: Force constants study

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ABSTRACT

We study the lattice dynamics of the zinc-blende (ZB) allotropic form of bulk group-III nitrides using an approach based on the linear chain model. Supported by the fact that the longitudinal oscillations and the transverse oscillations are effectively decoupled, the relationship between the three dimensional (3D) and linear chain (1D) force constants has been reported. It is possible then to fit the 3D bulk force constants (and consequently the whole dynamical matrix) from the information related to few points, either experimental or theoretical. In particular, we derive the dispersion relation and the corresponding force constants of BN, AlN, GaN and InN. Our results are in good agreement with previous *ab initio* results.

1. Introduction

In recent years, the study of the group-III nitrides has become attractive because of their promising mechanical and electronic properties such as extreme hardness, high melting point, wide band gap and relatively low dielectric constants; with applications in high temperature, high power and high frequency electronics. It is a well established fact that most of those properties mentioned above are strongly dependent on the lattice dynamics. In the zinc-blende (ZB) phase of group-III nitrides this phenomenon has been studied theoretically using either the *ab initio* approach [1–3], the adiabatic bond charge model [4,5], and – experimentally – Raman spectroscopy techniques [6,7]. However, *ab initio* calculations are computationally very demanding while results using second order Raman scattering experiments (which provides information about phonon modes along the whole Brillouin zone) have not been reported. Therefore is not underrated to develop alternative methods to determine the dispersion relations on these materials, using a few number of free parameters with a clear physical meaning.

In the past the force constant model was the usual way to study the lattice dynamics of compounds in any crystal system, particularly in those which crystallize in the ZB structures [8–10]. Given the limited amount of experimental data available at that moment for the III–V compounds studied, the investigations cited above were carried out in a simplified way. However, nowadays the experimental phonon frequency values at the center and boundaries of the Brillouin zone of group-III nitrides with ZB structure are much better known. Taken this fact into account we propose using a force constant model once again, and to apply it to the study of the lattice dynamics in the ZB phase of BN, AlN, GaN and InN.

For that purpose, we consider harmonic interaction between a limited number of neighbors. The dynamical matrix is then constructed, taking into account the symmetry of the underlying lattice. Interesting properties of the equations of motion are found in this way. In particular, we check explicitly how the three-dimensional (3D) problem is reduced to decoupled linear chain equations for high symmetry directions, with the aim of obtaining the relation between the 3D and one-dimensional (1D) force constants. A partial study in this sense was previously reported in Ref. [11]. To the best of our knowledge, this relationship has not been explored so far. In consequence, our study helps to understand better the richness of the linear chain models. The numerical implementation of our model implies fitting the 3D bulk force constants (and consequently the whole dynamical matrix) from frequency values corresponding to very few points, either experimental or theoretically determined. We show the dispersion relation calculated for the mentioned materials and compare our results with Raman measurements and *ab initio* calculations. The paper is organized as follows. In Section 2 we describe briefly the theoretical method used. In Section 3 report and discuss our results. At the end in Section 4 our main conclusions are summarized.

2. Method

In our model we assume the harmonic and the adiabatic approximations. Within these approximations the equation of

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motion has the form [12]:

$$\omega^2(\vec{q})e_\alpha(\kappa)=\sum_{\kappa'\beta}D_{\alpha\beta}(\kappa\kappa',\vec{q})e_\beta(\kappa'). \quad (1)$$

In this equation and in the following we use the standard notation [12] for cells (n,n'), atoms (κ,κ'), components (α,β), polarization vectors (e_α,e_β), etc.; in particular, $D_{\alpha\beta}(\kappa\kappa',\vec{q})$ represents the dynamical matrix. It is given by

$$D_{\alpha\beta}(\kappa\kappa',\vec{q})=\frac{1}{\sqrt{m_\kappa m_{\kappa'}}}\sum_{n'}\Phi_{\alpha\beta}(n\kappa,n'\kappa')\times e^{-i\vec{q}\cdot(\vec{R}_n-\vec{R}_{n'})}+D^{LR}_{\alpha\beta}(\kappa\kappa',\vec{q}), \quad (2)$$

where $\Phi_{\alpha\beta}(n\kappa,n'\kappa')$ is the matrix of force constants defined as the second derivatives of the potential energy in the harmonic approximation. The second term, $D^{LR}_{\alpha\beta}(\kappa\kappa',\vec{q})$, is an expression modeling the long-range contribution needful to describe the splitting between longitudinal and transverse optical frequencies in the Brillouin zone center in partially ionic materials, and can be written as [13]

$$D^{LR}_{\alpha\beta}(\kappa\kappa',\vec{q})=\frac{4\pi e^2}{V\sqrt{m_\kappa m_{\kappa'}}}\left\{\frac{[\vec{q}\cdot\mathbf{Z}^*(\kappa)]_\alpha[\vec{q}\cdot\mathbf{Z}^*(\kappa')]_\beta}{|\vec{q}|^2}\right\}\times\exp\{-2\pi i\vec{g}\cdot[\vec{r}(\kappa)-\vec{r}(\kappa')]\}\times\frac{(1+\cos(\pi|\vec{q}|/|\vec{q}_{BZ}|)}{2}. \quad (3)$$

In this expression e is the elementary charge, $\mathbf{Z}^*$ represents the effective charge tensor, $\vec{q}$ is a wave vector within a Brillouin zone centered at the reciprocal lattice vector $\vec{g}$. V is the volume of the primitive unit cell, $(m_\kappa,m_{\kappa'})$ and $(\vec{r}(\kappa),\vec{r}(\kappa'))$ are atomic masses and positions, respectively. Additionally, $\vec{q}_{BZ}$ is a wave vector parallel to $\vec{q}$, with a length equals to the distance from Γ to the Brillouin zone surface. As a matter of convenience we define parameter Ω as

$$\Omega=\frac{4\pi e^2}{V\sqrt{m_1 m_2}}Z^2. \quad (4)$$

Notice that Ω is the limit of Eq. (3) as q tends to zero and is a measure of the importance of this term.

We consider the second neighbors interaction approximation and write the equation of motion in terms of the force constants matrices, given by $\Phi_{\alpha\beta}(n\kappa,n'\kappa')$ (2). The number of free parameters is reduced applying the symmetry invariance. The remaining parameters are determined fitting experimental and/or theoretical frequencies at the symmetry points Γ, L and X. The notation for the parameters representing force constants as well as the symmetry of each group of neighbors is listed in Table 1. A more detailed analysis is presented in Refs. [14,15].

Under such approximation the equations of motion along high symmetry directions ($\Gamma-X\rightarrow[1\,0\,0]$ and $\Gamma-L\rightarrow[1\,1\,1]$) are decoupled into one longitudinal and two degenerate transverse

Table 1
The matrix force constants elements are denoted by α_{ij} (cation-nitrogen) to first neighbors interaction and by β_{ij} (cation-cation) and γ_{ij} (nitrogen-nitrogen) to second neighbors interaction.

Neighbors	Force constants	Symmetry
First	α_{ij}	C_{3v}
Second	β_{ij}, γ_{ij}	C_{4v}

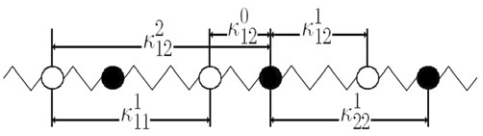

Fig. 1. Linear chain with second neighbors interaction.

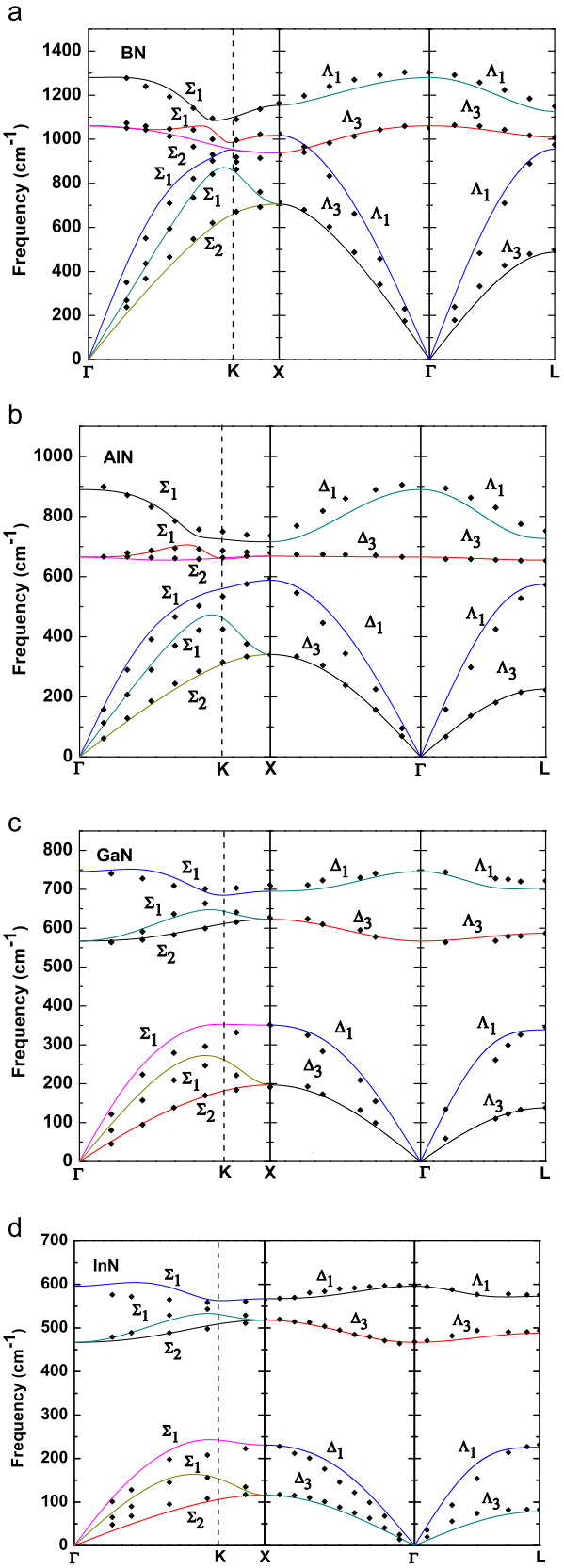

Fig. 2. Phonon dispersion curves for BN, AlN, GaN and InN in zinc-blende structure. Filled diamond are taken from *ab initio* calculations from Ref. [16] for BN, Refs. [1,2] for AlN and GaN, and Ref. [3] for InN.