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Vibrational Properties Of Cubic And Wurtzite Phase Of Boron Nitride

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Abstract
The group-III nitrides are the most fascinating materials in these days due to their direct and wide band gap which make these materials exceptional candidate for applications in LDs, LEDs and optoelectronic devices. The significant features of these materials like short bond length, hardness, high thermal conductivity, low compressibility and high melting point makes them valuable for high frequency as well for high power electronic devices at extreme temperature. The BN has some special properties like hardness and confrontation to corrosion, which makes its useful to function at higher temperature and in radiative environment. In spite of remarkable technological achievements only modest effort has been made to examine the phonons of BN. The phonon mode study is important for dynamical, thermo dynamical and other structural properties. Furthermore excitations of phonons also affect the electron transport and non radiative electron relaxation process. So phonon properties are the most desired properties to study. Hence in this study it is decided to investigate the lattice dynamical properties of BN using de Launey angular force constant model. The results obtained at zone centre are in better agreement with experimental results. The phonon dispersion has been investigated throughout the Brillion zone and hence phonon density of states and variation of specific heat with temperature has been obtained for both phases i,e, cubic and wurtzite phase of BN.

1. Introduction

BN can be considered as the first member of group-III nitride family as the cation (Boron atom) has lowest mass as compared to mass of cation for other members of group-III nitrides. It have two crystallographic phases, cubic and wurtzite phase. Based on its prospective applications, this material has attracted a significant interest in these days. Along with hardness and confrontation to corrosion it can also function at higher temperature and in radiative environment. Because of these properties it has pleasing applications in microelectronic devices. It is of use for both at very low temperature and high-temperature lubricants and in situations where the chemical reactivity or electrical conductivity of graphite would be problematic. Due to high thermal stability of h-BN, it can be used in vacuum technology. It is also useful as a wear resistance lubricant and for x-ray lithography mask (Cappellini et al., 2001). Because of exceptional properties and applications of BN it is advantageous to study lattice dynamical properties of BN. As lattice dynamical properties of compounds provide us information about the nature of inter atomic forces in crystal, which leads to an understanding of bonding and structural properties of compounds. The physical properties of solid including optical, electrical and thermal properties depend upon phonon dispersion relation.

Recently, the phonon properties of the different phases of group-III nitrides has been studied using an adiabatic bond charge model (Nakamura 1999), the ab initio psuedo potential method (Tutuncu et al., 2005, Pandey et al., 2012) and local density approximation (LDA) and generalized gradient approximation (GGA) ((Zhang et al., 2013, Fu et al., 2015). But exact information regarding dynamical properties is still missing. Therefore in the this study phonon properties such as phonon dispersion curve, phonon density of states and specific heat of cubic and wurtzite phase of BN has been studied by using de Launey force constant model.

2. Methodology

In this study to obtain phonon dispersion curve and phonon density of state of BN, de Launey angular force constant model has been used. This model is based on assumption that atoms are oscillating with small amplitude and only elastic force is involved between these atoms. Amplitude of oscillation is enough small that Hooke's law is supposed to be obeyed. This model consider two types of interatomic interactions: Central force which acts on line joining their equilibrium position and angular force depends

upon angle made by the line joining the moving atoms and line joins their equilibrium position. This model has a benefit of incorporating interaction between many particles through angular force. The de Launey force constant model involves interactions with its neighbors but this interaction reduces suddenly as the distance between atoms increases. Hence Interatomic interaction up to second nearest neighbors is considered and hence two force constants are involved for both central and angular force. The two involved central force constants α_1 and α_2 represent central interaction between B-N (nearest neighbors) and B-B or N-N (second nearest neighbors) respectively while force constants α_1' and α_2' represent angular interaction between B-N (nearest neighbors) and B-B or N-N (second nearest neighbors) respectively. The non central restoring force acting on o due to i is given by,

$$F_i = -\alpha'(s_0 - s_i) - (\alpha - \alpha')\left[\hat{\zeta}_i X (s_0 - s_i)\right] X \hat{\zeta}_i$$

Using component form of the non central forces, a secular determinant is obtained and is given below.

$$\left[D_{ij}(q) - M\omega^2 I\right] = 0$$

Where D_{ij} are the elements of the dynamical matrix, i, j = 1, 2, 3 and I is the unit matrix.

Cubic structure have two atoms per unit cell hence a dynamical matrix of (6x6) has been established. The dynamical matrix is solved at zone centre (ZC) and along (q 0 0) to obtain the relation between force constants, frequency and elastic constants. The relations thus obtained are as given below.

$$\frac{4}{3}(\alpha_1 + 2\alpha_1') = \left[\frac{m_1 m_2}{(2m_1 + m_2)}\right]\omega_0^2$$

$$aC_{11} = \frac{1}{3}(\alpha_1 + 2\alpha_1') + 4(\alpha_2 + \alpha_2')$$

$$aC_{12} = \frac{1}{3}(\alpha_1 - 4\alpha_1') + 2(\alpha_2 - 5\alpha_2')$$

$$aC_{44} = \frac{1}{3}(\alpha_1 + 2\alpha_1') + 2(\alpha_2 + 3\alpha_2') - \frac{\left((\alpha_1 - \alpha_1')^2\right)}{\left(3(\alpha_2 + 2\alpha_1')\right)}$$

Here m_1 is the mass B atom and m_2 being mass of N atom. C_{11}, C_{12} and C_{44} are the elastic constants and a is the lattice parameter. By using ZC phonon frequency (Huan 2008; Alvesa 2002) experimental values of the elastic constants as given by (Shervin 1991; Marmalyuk 1998) and as input parameters the force constant has been calculated and are given in table I.

The wurtzite structure has four atoms per unit cell, hence a dynamical matrix of (12x12) has been established. The dynamical matrix of (12 x 12) thus established is solved at the zone center to obtain relation between some key vibrational frequencies and force constants. By solving the (12x12) dynamical matrix the following relations between force constants and some important vibrational frequencies are obtained.

$$\frac{4}{3}(\alpha_1 + 2\alpha_1') = \frac{m_1 m_2}{m_1 + m_2}\omega^2_{E_1(TO)}$$

$$\frac{4}{3}(\alpha_1 + 2\alpha_1') + 2(4\alpha_2 + 2\alpha_2') = m_2\omega^2_{A_1(TO)}$$

$$4(\alpha_2^2 + 25(\alpha_2')^2 + 10\alpha_2\alpha_2 - \alpha_1^2) + \frac{16}{3}(\alpha_1 + 2\alpha_1')(\alpha_2 + 5\alpha_2' + \alpha_1)$$

$$-\left(\frac{4}{3}(\alpha_1 + 2\alpha_1') + 2\alpha_1 + 10\alpha_2'\right)(m_1 + m_2)\omega^2_{E_2^h} + m_1 m_2 \omega^4_{E_2^h} = 0$$

$$\alpha_2 + 5\alpha_2' + \alpha_1' = \frac{m_1}{2}\omega^2_{E_2^l}$$

Here m_1 and m_2 are the mass of X (Al, Ga, B and In) and N atom respectively. By using the experimental values of the zone centre frequencies, m_1 and m_2 as the input parameter the above equations are solved to calculate force constants. The force constants thus obtained are given in table I.

Phase	Force constant (10^4 dyne cm^{-1})				Lattice constants (Å)	
	α_1	α_1'	α_2	α_2'	a	c
Cubic	23.78	3.225	4.335	0.55	3.62	-
Wurtzite	19.385	5.3716	6.3666	-1.7308	2.56	4.23

TableI Calculated force constants for cubic phase of BN

3. Results and Discussions

It is clear from the table II that the magnitude of force constant α_1 is largest among all for both the phases

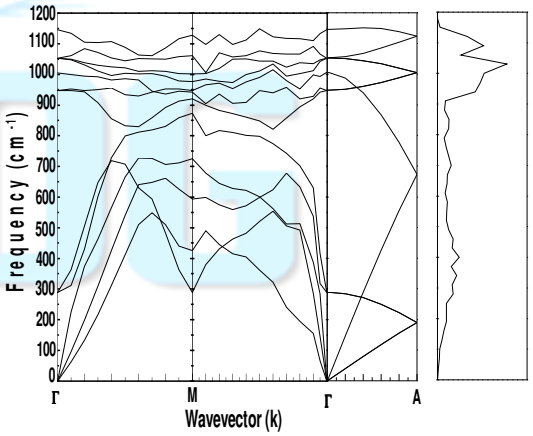
and it indicates that the interaction between B-N (central force) is strongest followed by α_2. The Interatomic interactions are stronger for cubic phase as compared to wurtzite phase.

With the use of FORTRAN programming the (6x6) dynamical matrix for cubic and (12x12) dynamical matrix for wurtzite phase has been diagonalized at zone centre (ZC) to obtain frequencies. Thus obtained phonon frequencies along with other theoretical results and few available experimental phonon frequencies at ZC are given in table I. For cubic phase the obtained frequency exactly matches with experimental frequency while for wurtzite structure A_1(TO) mode and E_1(TO) mode show no deviation from experimental results while a significant deviation is observed in case of the results obtained by other theoretical results. E_2(low) mode show deviation of 6.7% which is less than other theoretical results. The phonon dispersion relation consist three acoustical modes for both phases and three optical for cubic and nine optical modes for wurtzite phase. It is observed that doubly degenerate E_2 modes are Raman active while the A_1 and doubly degenerate E_1 modes are both Raman and infrared active while B_1 modes are the silent modes. It is observed that acoustical modes and optical modes are dispersive in nature and the acoustic and optical modes overlaps as one move along the symmetry directions. There is almost nil frequency gap between optical and acoustical modes due to very small difference of mass of B and N atom and same type of trends are observed by other studies (Lei et al., 2014, Zhang et al., 2013). The phonon density of states for BN shows two sharp peaks at 1030 cm^{-1} and 1090 cm^{-1} for wurtzite BN and while a sharp peak around 1055 cm^{-1} for cubic phase along with few small peaks. The two sharp peaks observed corresponds to optical modes which show dispersion is comparatively less in upper lying optical modes. From the phonon density of states, the specific heat at constant volume has been calculated. The specific heat curve thus obtained is in reasonable agreement with well known relation C_v = 3R, at high temperature (where R is the gas constant).

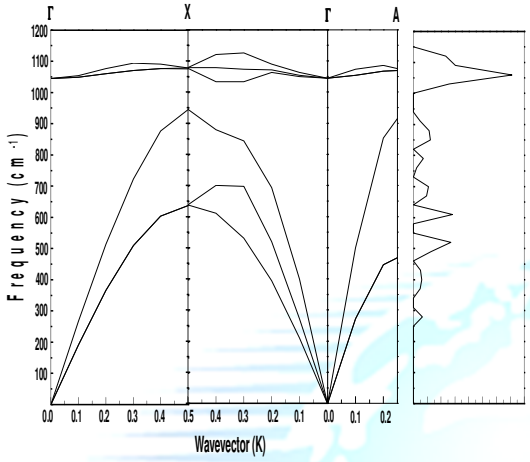
Table 2 Zone centre phonon frequencies (cm^{-1}) of wurtzite BN

Material	Phonon modes	This work	Other theoretical results[a,b]	Other theoretical results[c,d]	Experimental results[e,b]
Wurtzite	E_2(low)	289	459	482	310
	B_1(low)	1053	977	989	
	A_1(TO)	1006	1106	992	1006
	E_1(TO)	1053	1137	1024	1053
	E_2(high)	948	1041	1084	
	B_1(high)	1146	1142	1088	
Cubic	TO	1055	1060	1055	1055

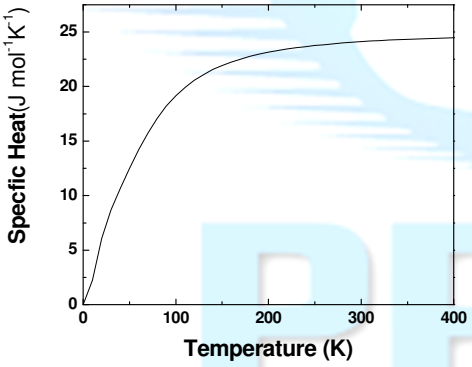
a = Zhang et al., (2013), ,c = Lei et al., (2014), b = Tutuncu et al., 2005, d = Karch et al., 1997, e = Tutuncu et al., (2000)



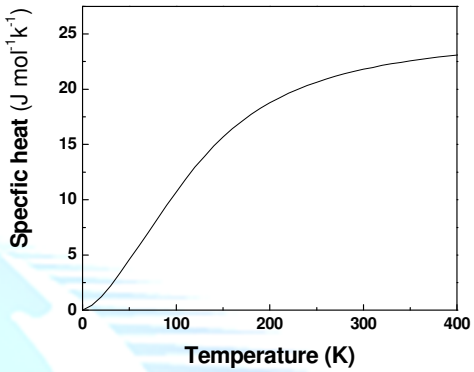
Graph 1. Phonon dispersion and phonon density of states of wurtzite BN



Graph 2. Phonon dispersion and phonon density of states of cubic BN



Graph 3 Variation of specific heat with temperature for wurtzite BN



Graph 4 Variation of specific heat with temperature for cubic BN

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