------ Raf. J. Sci., Vol. 27, No.1, pp. 184-189, 2018------

Evaluation of Spinodal Pressure for Gallium nitride in the Zinc-blend and Wurtzite Structures by Using Different Equations of State (EOS_s)

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(Received 24/ 2 / 2014 ; Accepted 5 / 5 / 2014)

ABSTRACT

According to the definition of spinodal pressure as the negative pressure at which bulk modulus (of a substance) go to zero. Extrapolation of variation of bulk modulus results with pressure has been used to evaluate spinodal pressure for GaN in zinc-blende and wurtzite structures using different equations of state (EOS) (Birch-Murnaghan, Bardeen, Libby and Libby, and Born-Mie). Result obtained in the present work for GaN in the zinc-blende structure using Born-Mie equation of state shows a good agreement with literature. While results for wurtzite structure, obtained by using Birch-Murnaghan and Bardeen EOSs are in a good agreement with literature. Present results and many literature show that (Jiuxun, 2005) approach for evaluation of spinodal pressure yield results in less agreement with other works.

Keywords: EOS, GaN, Spinodal pressure, Negative pressure, bulk modulus.

حساب ضغط السبينودال (ضغط التمدد) لنتريد الكاليوم، في كل من بنية كبريتيد الخارصين وبنية التركيب السداسي، باستخدام معادلات حالة مختلفة

الملخص

استناداً لتعريف ضغط السبينودال، بأنه الضغط السالب الذي يصبح عنده معامل المرونة الحجمي للمادة صفراً. تمت الاستعانة بالأستكمال الرياضي لنتائج تغير معامل المرونة الحجمي مع الضغط لحساب ضغط السبينودال (ضغط التمدد) لنتريد الكاليوم GaN ذي بنية كبريتيد الخارصين وذي بنية التركيب السداسي وذلك بأستخدام معادلات حالة مختلفة (برخ–مرنكهان، باردين، ليبي و ليبي ، بورن–ماي). بينت نتائج GaN، ذو بنية كبريتيد الخارصين، باستخدام معادلة الحالة بورن–ماي، توافقا جيدا مع نتائج الابحاث العلمية المنشورة. في حين بينت النتائج الخاصة ببنية التركيب السداسي لـ GaN، باستخدام معادلتي الحالة برخ–مرنكهان وباردين توافقاً جيدا مع نتائج الابحاث العلمية المنشورة. ان النتائج التي تم الحصول عليها، فضلاً عن العديد من نتائج الابحاث العلمية المنشورة، تظهر ان معالجة (Jiuxun, 2005) لحساب ضغط السبينودال تعطي نتائج متفاوتة مع نتائج الابحاث العلمية.

الكلمات الدالة: معادلة حالة، نتريد الكاليوم، ضغط السبينودال، الضغط السالب، معامل المرونة الحجمي

INTRODUCTION

The calculation of the properties such as enthalpy, entropy, internal energy, compression volume, etc for different substances requires knowledge of the PVT (pressure-volume-temperature) behavior of the substance. This can be given in the form of a table, graphs, or analytically, an analytical expression to express PVT behavior which is called an equation of state. The correct equation of state (EOS) is the gateway to obtaining spinodal and other derived properties, which are then used to develop corresponding states correlations. It is sufficient to consider the PVT equation of state (Shamsundar and Lienhard, 1993).

There are at least two conditions which should be satisfied by an equation of state in order to be physically acceptable, these conditions are (Singh and Gajendra, 2011):

(i) The pressure derivative of bulk modulus (dB/dP) in the limit of extreme compression (V→0 and P→∞) must be greater than 5/3.

(ii) Real and reasonable values of properties should be obtained for the entire range of compressions.

In the following we write out the EOS considered in this work, which they have these merits and also satisfy the following spinodal condition (Jiuxun, 2005).

$$B \propto (P - P_{sp})^{\frac{1}{2}} \qquad with \qquad B(P - P_{sp}) = 0$$

where P: pressure. P_{sp}: spinodal pressure. B: the bulk modulus.

- Birch-Murnaghan EOS (Birch, 1952)

$$P_{BM} = \frac{3B_o}{2}\left(\eta^{-\frac{7}{3}} - \eta^{-\frac{5}{3}}\right)\left[1 + \frac{3}{4}(B_o' - 4)\left(\eta^{-\frac{2}{3}} - 1\right)\right] \quad \ldots\ldots\ldots\ldots\ldots(1)$$

- Bardeen EOS (Bardeen, 1938)

$$P_B = 3B_o\left(\eta^{-\frac{5}{3}} - \eta^{-\frac{4}{3}}\right)\left[1 + \frac{3}{2}(B_o' - 3)\left(\eta^{-\frac{1}{3}} - 1\right)\right] \quad \ldots\ldots\ldots\ldots\ldots(2)$$

- Libby and Libby EOS (Libby and Libby, 1972)

$$P_{LL} = 3B_o\left(\eta^{-\frac{5}{3}} - \eta^{-\frac{4}{3}}\right) \quad \ldots\ldots\ldots\ldots\ldots(3)$$

- Born-Mie EOS (Anderson, 1995)

$$P_{B-Mi} = \frac{3B_o}{3B_o'-8}\left(\eta^{-(B_o'-\frac{4}{3})} - \eta^{-\frac{4}{3}}\right) \quad \ldots\ldots\ldots\ldots\ldots(4)$$

where $\eta = \frac{V_p}{V_o}$, B_o *and* B_o' are the bulk modulus and its first derivative at zero pressure, V_o is the volume at zero pressure, V_p is the volume at applied pressure (P).

THEORITICAL DETAILS AND RESULTS

(1) Bulk modulus under high pressure.

The bulk modulus (B) of a substance measure the substance's resistance to uniform compression. It is defined as the ratio of the infinitesimal pressure increase to the resulting relative decrease of the volume, formally expressed by the equation:

$$B = -V\frac{dP}{dV} \quad \ldots\ldots\ldots\ldots(5)$$

From above EOSs, we can express the isothermal bulk modulus (B_T) at pressure (P) as follows.

- Birch-Murnaghan EOS

$$B_T(BM) = \frac{3B_o}{2}\left[\frac{7}{3}\eta^{-\frac{7}{3}} - \frac{5}{3}\eta^{-\frac{5}{3}} + \frac{9}{4}(B_o' - 4)\eta^{-3} - \frac{7}{2}(B_o' - 4)\eta^{-\frac{7}{3}} + \frac{5}{4}(B_o' - 4)\eta^{-\frac{7}{3}}\right] \ldots(6)$$

- Bardeen EOS

$$B_T(B) = 3B_o\left[\frac{5}{3}\eta^{-\frac{5}{3}} - \frac{4}{3}\eta^{-\frac{4}{3}} + 3(B_o' - 3)\eta^{-2} - 5(B_o' - 3)\eta^{-\frac{5}{3}} + 2(B_o' - 3)\eta^{-\frac{4}{3}}\right] \ldots\ldots(7)$$

- Libby and Libby EOS

$$B_T(L - L) = 3B_o\left[\frac{5}{3}\eta^{-\frac{5}{3}} - \frac{4}{3}\eta^{-\frac{4}{3}}\right] \quad \ldots\ldots\ldots\ldots(8)$$

- Born-Mie EOS

$$B_T(B - Mi) = \frac{B_o}{3B_o'-8}\left[(3B_o' - 4)\eta^{-(B_o'-\frac{4}{3})} - 4\eta^{-\frac{4}{3}}\right] \quad \ldots\ldots\ldots\ldots(9)$$

Fig. (1) and Fig. (2) show the results of variation of thermal bulk modulus (B_T) at different values of applied pressure calculated by using equations (6, 7, 8 and 9) for GaN in zinc-blende structure and in wurtzite structure respectively. The values of B_o and B'_o which have been used in the calculations are tabulated in Table (1).

Table 1: values of B_o and B'_o for GaN (Christensen and Gorczyca, 1994)

material	B_o (Gpa)	B'_o
GaN (zinc-blende structure)	184	4.6
GaN (wurtzite structure)	200	3.8

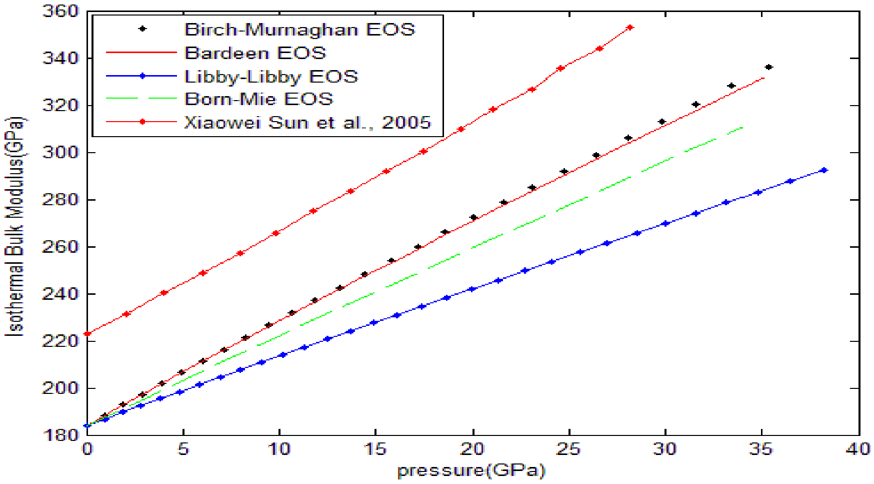


Fig. 1 : Variation if isothermal (B_T) bulk modulus with pressure (P) using different EOS for GaN (zinc-blende structure).

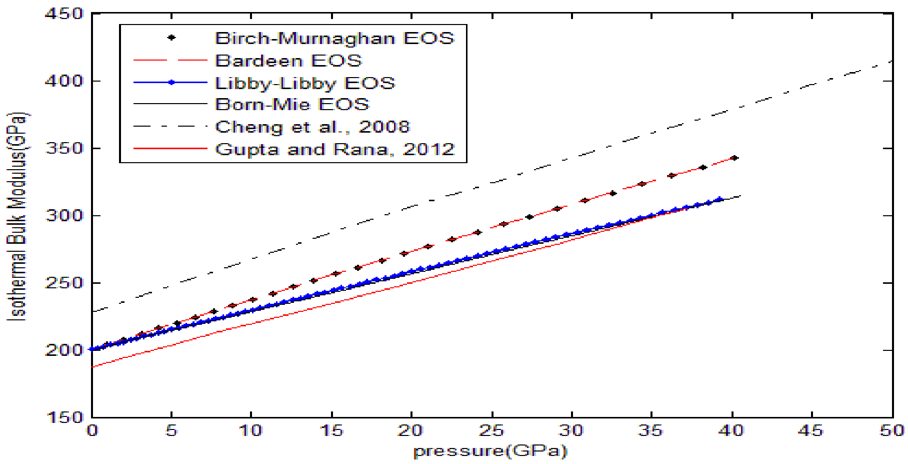


Fig. 2 : Variation of isothermal bulk (B_T) modulus with pressure (P) using different EOS for GaN (wurtzite structure).

(2) The spinodal pressure.

Since the spinodal pressure for material represents the negative pressure at which the bulk modulus of the material goes to zero (Al-sheikh *et al*., 2013), which whatever its values decreased or in other words its negative values increased no additional expansion occur in material (Stixrude, 2002). By using extrapolating results shown in Fig. (1) and Fig. (2), one can obtain the spinodal pressure from the following expression (Al-Sheikh and Mohammed, 2012; Al-Saqa and Al-Sheikh, 2013):

$$P_{sp} = -B_o \frac{dP}{dB} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ldots (10)$$

The values of P_{sp} for GaN (zinc-blende and wurtzite structures) are shown in Fig.(3), Fig. (4) and in Table (II), in comparison with values calculated by equation 11 which was given by (Jiuxun, 2005):

$$P_{sp} = -\frac{B_o}{4n}, \text{ where } n = -\frac{1}{3}B_o' \quad \therefore \; P_{sp} = -0.75\frac{B_o}{B_o'} \ldots\ldots\ldots\ldots (11)$$

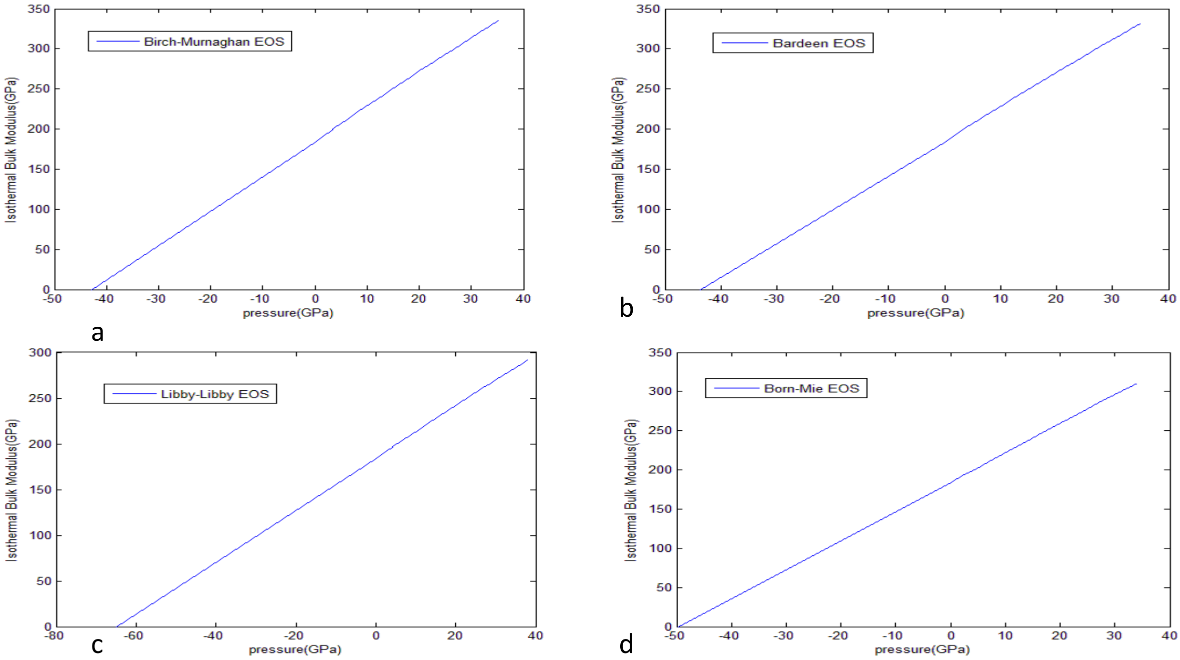
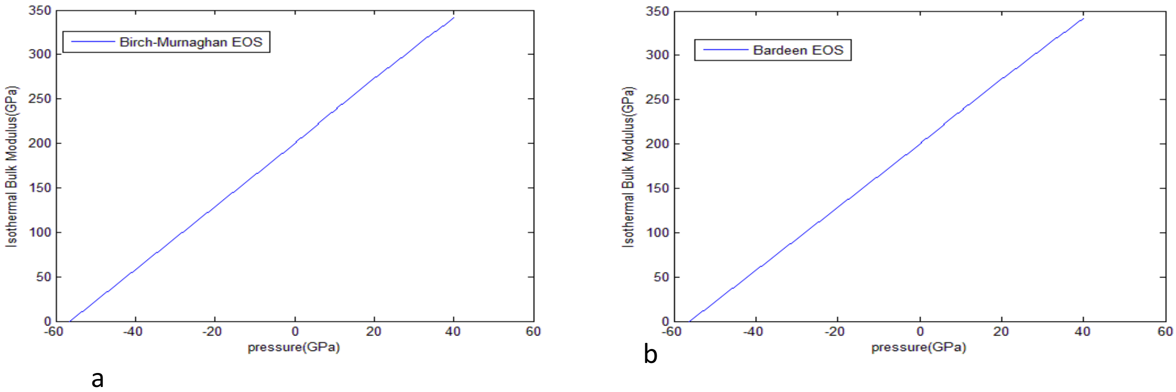


Fig. 3: Spinodal pressure for GaN (zinc-blende structure) by using (a) Birch-Murnaghan EOS (b) Bardeen EOS (c) Libby and Libby EOS (d) Born-Mie EOS



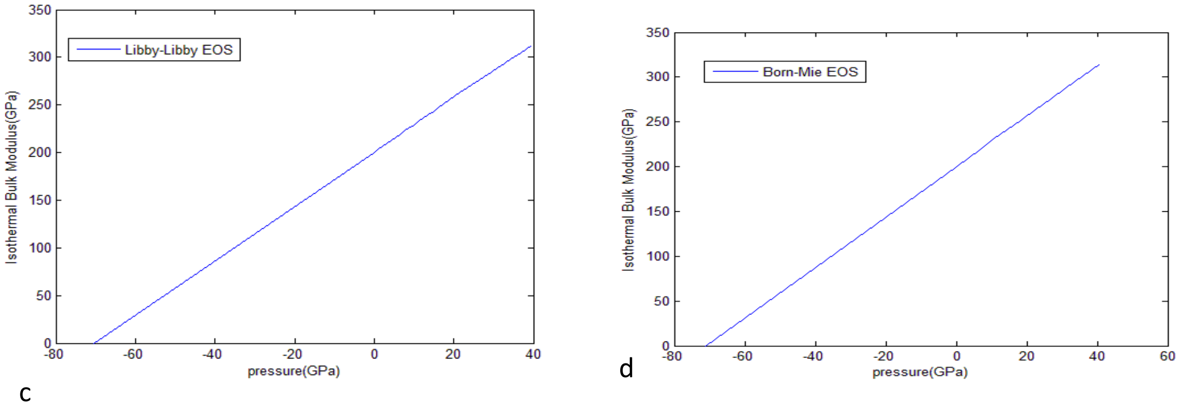


Fig. 4: Spinodal pressure for GaN (wurtzite structure) by using (a) Birch-Murnaghan EOS (b) Bardeen EOS (c) Libby and Libby EOS (d) Born-Mie EOS

Table 2: Spinodal pressure values in comparison with results given in literatures

material	Present work		Jiuxun, 2005	Xiaowei *et al.*, 2005	Gupta and Rana, 2012	Cheng *et al.*, 2008
	EOS	Psp(Gpa)	Psp(Gpa)	Psp(Gpa)	Psp(Gpa)	Psp(Gpa)
Zinc-blende GaN	Birch-Murnaghan Bardeen Libby and Libby Born-Mie	-42.847 -43.766 -64.943 -49.6975	-30	-48.3564		
Wurtzite GaN	Birch-Murnaghan Bardeen Libby and Libby Born-Mie	-56.4775 -56.36 -70.4523 -71.053	-39.4737		-59.0739	-60.9647

DISCUSSION

Experimental results are meager and quite hard to obtain particularly in the neighborhood of spinodal limit, because spinodal is the limit of metastability of substance with respect to phase transition, therefore we used extrapolation of bulk modulus data under high pressure shown in Fig. (1) and Fig. (2), combining these data with equation 5, and (depending on) the definition of spinodal pressure as the negative pressure at which bulk modulus value go to zero. Equation 10 represent a new approach for evaluating spinodal pressure. By using different EOSs which satisfy spinodal condition. The spinodal pressure values for GaN obtained in present work is close together with results obtained from works of (Cheng *et al*., 2008), and (Gupta and Rana, 2012), but differ from that obtained by (Jiuxun, 2005), this may be attributed to the fact that our present work used first principle approach in evaluation of P_{sp} for material obtained within the metastable state, while (jiuxun, 2005) work didn't consider that (Psp) for the material obtained within the metastable state. Present work show that P_{sp} value obtained by Born-Mie EOS is in a good agreement with values given by (Xiaowei *et al.*, 2005) for GaN in zinc-blende structure. While using, either Birch-Muranghan or Bardeen EOS, in the present work, in evaluating P_{sp} value for GaN in wurtzite structure, reveal a good agreement with the values given by (Gupta and Rana, 2012) and (Cheng *et al.*, 2008).

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