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Structural and thermodynamic properties of AlB_2 compound*

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We employ a first-principles plane wave method with the relativistic analytic pseudopotential of Hartwigsen, Goedecker and Hutter (HGH) scheme in the frame of DFT to calculate the equilibrium lattice parameters and the thermodynamic properties of AlB_2 compound with hcp structure. The obtained lattice parameters are in good agreement with the available experimental data and those calculated by others. Through the quasi-harmonic Debye model, obtained successfully are the dependences of the normalized lattice parameters a/a_0 and c/c_0 on pressure P, the normalized primitive cell volume V/V_0 on pressure P, the variation of the thermal expansion α with pressure P and temperature T, as well as the Debye temperature $\Theta_{\rm D}$ and the heat capacity $C_{\rm V}$ on pressure P and temperature T.

Keywords: thermodynamic property, Local density approximation, AlB_2
PACC: 7115M, 6740K, 7470E

1. Introduction

The aluminium-richest phase of the binary aluminium–boron system has been known for a long time, and the corresponding structure type AlB_2 is one of those phases most frequently observed among intermetallic phases. The chemical variability and simplicity of the crystal structure with graphite-like nets of boron atoms separated by aluminium atoms in hexagonal prismatic voids (space group $P6/mmm$) make this structure type a very interesting one for the systematic investigation of crystal chemical and physical properties by using experimental and theoretical methods.

The discovery of superconductivity at $T_{\rm c} = 39$ K in MgB_2[1] has aroused a strong interest of all in $s-p$ diborides. The in-plane boron–boron bonding plays a crucial role in not only the electron–phonon coupling but also the electronic density of states near Fermi energy $E_{\rm F}$.[2]

The nature of bonding in boron layer depends crucially on the lattice constants a and c, and then the changes of a and c will greatly affect the electronic structures around the Fermi energy $E_{\rm F}$. Therefore, it is very important to optimize a and c theoretically when one investigates the behaviours of AlB_2 under a pressure. As a key thermodynamic property of a solid under a pressure, the equations of state (EOS) determine the solid behaviours with respect to the change in macroscopic variable, such as pressure (P) and temperature (T). The structural properties of materials under a pressure can help us understand the fundamental changes in bonding nature, and the pressure can influence the electronic band in different directions of Brillouin zone (BZ) and hence physical properties.

Our interest is aroused by the strongly varying data of simple phase AlB_2 theoretically and experimentally, including lattice dynamics properties,[3–11] electronic and optical properties,[12,13] high temperature and high pressure properties.[8,14]

In this work, we investigate the structural and the thermodynamic properties of AlB_2 by using a first-principles plane wave method with a relativistic analytic pseudopotential of Hartwigsen, Goedecker and Hutter (HGH) scheme[15] within density functional theory (DFT).[16,17] The results are consistent with the available experimental data and theoretical results obtained by others.

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2. Theoretical method

2.1. Total energy electronic structure calculations

In our calculations, we use the first-principles plane wave method with a relativistic analytic pseudopotential of HGH scheme[15] in the frame of DFT within a local density approximation (LDA). The HGH-type pseudopotential requires about ten parameters.[15] The kinetic energy cut-off criterion of 10 Hartree is applied to obtaining the convergence of 10^{-7} Hartree in energy. The total energy and the ground-state wave functions are calculated on a $10 \times 10 \times 10$ k-point mesh. For the exchange-correlation functional, the Perdew–Zunger–Ceperly–Alder functional[18] is employed. Applying this method, we have successfully investigated the properties of MgB_2.[19−21]

2.2. Thermodynamic properties

To investigate the thermodynamic properties, we employ the quasi-harmonic Debye model,[22] by which the thermodynamic properties of MgB_2[19−21] and GaAs[23] are successfully obtained. In the quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V;P,T)$ takes the form of

$$G^*(V;P,T) = E(V) + PV + A_{\rm Vib}(\Theta(V);T)\,, \quad (1)$$

where $\Theta(V)$ is the Debye temperature, and the vibrational term $A_{\rm Vib}$ can be written as[24,25]

$$A_{\rm Vib}(\Theta;T) = nKT\Big[\frac{9}{8}\frac{\Theta}{T} + 3\ln(1-{\rm e}^{-\Theta/T}) - D(\Theta/T)\Big]\,, \quad (2)$$

where $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. The non-equilibrium Gibbs function$G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume V

$$\Big(\frac{\partial G^*(V;P,T)}{\partial V}\Big)_{P,T} = 0\,. \quad (3)$$

By solving Eq.(3), one can have the thermal EOS $V(P,\,T)$. The isothermal bulk modulus B_T, the heat capacity C_v and the thermal expansion coefficient α are given by[26]

$$B_T(P,T) = V\Big(\frac{\partial^2 G^*(V;P,T)}{\partial V^2}\Big)_{P,T}, \quad (4)$$

$$C_V = 3nk\Big[4D(\Theta/T) - \frac{3\Theta/T}{{\rm e}^{\Theta/T}-1}\Big], \quad (5)$$

$$\alpha = \frac{\gamma C_V}{B_T V}\,. \quad (6)$$

Through the quasi-harmonic Debye model, one can calculate the thermodynamics quantities of any temperatures and pressures of AlB_2 compound from the calculated energy-volume data at $T = 0$ and $P = 0$.

3. Results and discussion

We firstly calculate the structural and thermodynamic properties of AlB_2 with hcp structure. Since the experimental c/a ratio of AlB_2 is 1.0827,[8] we thus calculate a series of different c/a ratios between 1.081 and 1.085. For each c/a ratio, a series of different lattice parameters a and c (corresponding to different primitive cell volumes V) are set to calculate the total energies E and V, and then an energy-volume $(E-V)$ curve can be obtained by fitting the calculated energy-volume $(E-V)$ data. It is found that the ratio c/a of 1.084 corresponds to the most stable hcp structure of AlB_2 at zero pressure (i.e. the normalized primitive cell volume $V_n = V/V_0 = 1.0$, where V_0 is the primitive cell volume at zero pressure). Through these calculations, we can obtain the equilibrium lattice parameters a and c as well as the corresponding equilibrium ratio c/a at any pressure.

In Table 1, we list the calculated lattice parameters a and c, and the available experimental data[2,8] and other theoretical results.[3−8] The agreement among them is good. The zero pressure bulk modulus B_0 and its first order pressure derivative are determined by fitting the calculated energy-volume data to the Birch–Murnaghan equation of state.[27] The results obtained are also shown in Table 1, which are close to the recently reported results by Loa *et al.*[8]

In Fig.1, we illustrate the normalized lattice parameters a/a_0 and c/c_0 (where a_0 and c_0 are the zero pressure equilibrium lattice constants) as well as the normalized primitive cell volume V_n as a function of pressure, together with the experimental data at the x-ray diffraction for pressures increasing up to 40 GPa.[8] Our results are consistent with the measurements. By fitting these data to second-order polynomials of the applied pressure, we obtain the following relationships at $T = 0$ K:

$$a/a_0 = 1.0000 - 0.00154P + 8.77268\times10^{-6}P^2\,, \quad (7)$$

$$c/c_0 = 1.0000 - 0.00227P + 1.84237\times10^{-5}P^2\,, \quad (8)$$

$$V/V_0 = 1.0000 - 0.00492P + 3.42566\times10^{-5}P^2\,. \quad (9)$$

Table 1. The calculated lattice parameters (Å), bulk modulus (GPa) and its pressure derivative, together with the experimental data and other theoretical results available from the literature.

	a	c	c/a	B_0	B_0'
present work	3.0078	3.2607	1.084	195	3.78
Ref.[2]	3.0050	3.2537	1.0828		
Ref.[3]	3.009	3.262	1.084		
Ref.[4]	3.005	3.257	1.084		
Ref.[5]	3.001	3.245	1.081		
Ref.[6]	3.003	3.251	1.083		
Ref.[7]	3.009	3.262	1.084		
Ref.[8]	2.9977	3.2855	1.0960	176.8	3.64
Ref.[8]	3.0062	3.2548	1.0827	170	4.81

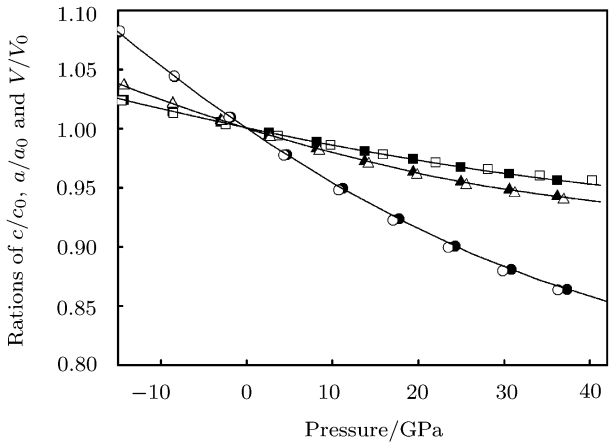


Fig.1. The lattice parameters a/a_0 and c/c_0, as well as the normalized volume V_n of AlB_2 as a function of pressure, where the solid rectangles, triangles and circles represent our calculated c/c_0, a/a_0 and V/V_0, respectively, and the blank ones represent the experimental data.[8]

It is obvious that, as the pressure increases, the equilibrium ratio c/a of hcp AlB_2 varies from 1.084 at zero pressure to 1.0715 at 20 GPa, i.e. decreases by about 1.13 %. The compression along the c axis is considerably larger than along the a axis in the basal plane. The interlayer linear compressibility, $\mathrm{d}\ln c/\mathrm{d}P = 0.00238$ GPa^{-1} is about 1.44 times the basal plane value, $\mathrm{d}\ln a/\mathrm{d}P = 0.00165$ GPa^{-1}(for MgB_2, $\mathrm{d}\ln c/\mathrm{d}P = 0.00353$ GPa^{-1}, $\mathrm{d}\ln a/\mathrm{d}P = 0.00196$ GPa^{-1}.[28]) These results consist with the comparatively weak Al-B bonds that determine the lattice constant c. Moreover, the closer the atoms in the interlayers, the stronger the interactions among them.

From the quasi-harmonic Debye model, we can determine the thermal expansion coefficient α of AlB_2 at simultaneous extreme pressure and temperature conditions, shown in Fig.2. It is noted that at zero pressure α increases exponentially with temperature at low temperatures and gradually turns to a linear increase at high temperatures. As the pressure increases, the increase of α with temperature becomes smaller, especially at higher temperatures. At a given temperature, α decreases strongly with increasing pressure, the thermal expansion coefficient α at 2000 K is just a little larger than at 1500 K, which means that the temperature dependence of α is very weak at higher temperatures and higher pressures.

In Table 2, we list the heat capacities and the Debye temperatures at various temperatures (300, 600, 900, 1300, and 1500 K) and pressures (0, 5, 10, 15, 20, 30, and 40 GPa). The heat capacity of AlB_2 at constant volume is plotted in Fig.3, which shows that when $T < 1500$ K, the heat capacity C_V is dependent on the temperature and pressure. This is due to the anharmonic approximations of the Debye model used

here. However, at higher temperatures, the anharmonic effect on C_V is suppressed, and C_V is very close to the Dulong–Pettit limit $3k_B(\approx 49.90$ J mol^{-1} K$^{-1})$.

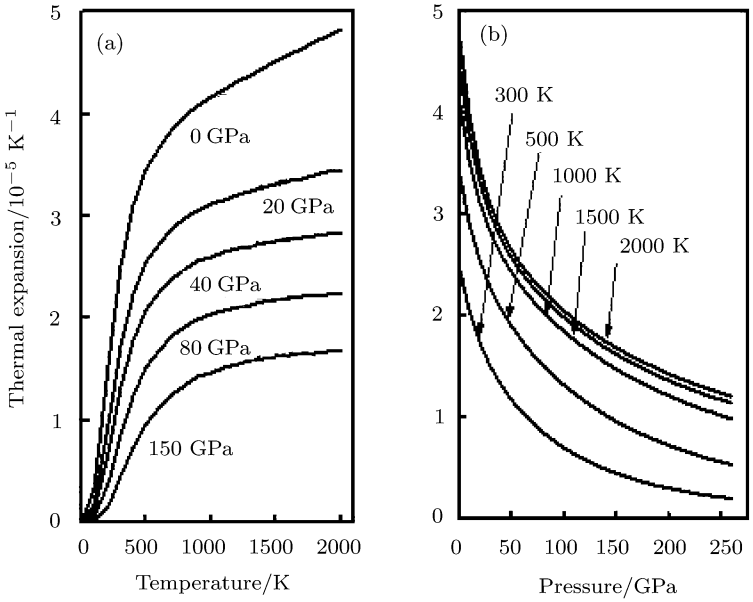


Fig.2. The thermal expansion versus temperature and pressure for AlB_2.

Table 2. The heat capacity C_V(Jmol^{-1} K^{-1}) and the Debye temperature Θ_D(K) of AlB_2 over a wide range of temperatures T (K) and pressures P (GPa).

T	P	0	5	10	15	20	30	40
300	C_V	34.39714	33.44917	32.54318	31.69017	30.87153	29.31417	27.85956
	Θ_D	964.60	1003.97	1041.22	1076.79	1111.05	1176.42	1238.56
600	C_V	45.29589	44.93599	44.58623	44.24415	43.90736	43.24581	42.59560
	Θ_D	949.05	989.45	1027.59	1063.92	1098.77	1164.95	1227.56
900	C_V	47.82020	47.64636	47.47632	47.30913	47.14402	46.81789	46.49447
	Θ_D	931.06	972.56	1011.50	1048.33	1083.49	1150.25	1213.22
1300	C_V	48.91545	48.82946	48.74489	48.66095	48.57919	48.41691	48.25538
	Θ_D	905.25	947.90	987.79	1025.48	1061.38	1129.07	1192.85
1500	C_V	49.16835	49.10269	49.03858	48.97571	48.91369	48.79074	48.66854
	Θ_D	892.04	935.54	975.73	1013.82	1050.29	1118.07	1181.87

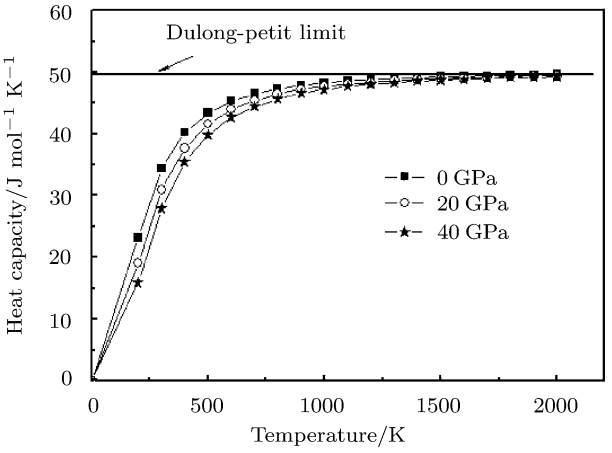


Fig.3. The heat capacity of AlB_2 at various pressures and temperatures.

It is found from Table 2 that as pressure increases, the heat capacity C_V decreases and the Debye temperature Θ_D increases. When the applied pressure increases from 0 to 40 GPa, the heat capacities decrease by 19.00 %, 5.96 %, 2.77 %, 1.35 %, 1.02%, and the Debye temperatures increase by 28.4 %, 29.35 %, 30.31 %, 31.77 %, 32.49 % at T=300 K, 600 K, 900 K, 1300 K, and 1500 K, respectively. The heat capacity C_V in this work is 34.39714 Jmol^{-1} K^{-1} at zero pressure and ambient temperature. As temperature increases, the heat capacity C_V nearly approaches the Dulong-Petit limit, which all solids follow at high temperatures.

References

[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63

[2] Burkhardt U, Gurin V, Haarmann F, Borrmann H, Schnelle W, Yaresko A and Grin Y 2004 *J. Solid State Chem.* **177** 389

[3] Mazin I I and Antropov V P 2003 *Physica* C **385** 49

[4] Vekshina N V, Markovskii L Ya, Kondrashev Yu D and Voevodskaya T K 1971 *J. Anal. Chem. USSR* **44** 970

[5] Hofmann W and Jäniche W 1936 *Z. Metall.* **1** 28

[6] Fjellstedt J, Jarfors A E W and Svendsen L 1999 *J. Alloys Compounds* **283** 192

[7] Nakao M 2003 *Physica* C **388–389** 137

[8] Loa I, Kunc K, Syassen K and Bouvier P 2002 *Phys. Rev.* B **66** 134101

[9] Parvin F, Islam A K M A, Islam F N, Wahed A F M A and Haque M E 2003 *Physica* C **390** 16

[10] Matkovich V I, Economy J and Griese R F 1964 *J. Am. Chem. Soc.* **84** 2337

[11] Parvin F, Islam A K M A and Islam F N 2004 *Solid State Commun.* **130** 567

[12] Kortus J, Mazin I I, Belashchenko K D, Andropov V P and Boyer L L 2001 *Phys. Rev. Lett.* **86** 4656

[13] Bohnen K P, Heid R and Renker B 2001 *Phys. Rev. Lett.* **86** 5771

[14] Fisher B, Chashka K B, Patlagan L and Reisner G M 2003 *Physica* C **384** 1

[15] Hartwigsen C, Goedecker S and Hutter J 1998 *Phys. Rev.* B **58** 3641

[16] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B 864
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133

[17] Meng X, Xu X G, Liu W, Sun Y and Chen G 2004 *Acta Phys. Sin.* **53** 3873 (in Chinese)
Shen Y W and Kang J Y 2002 *Acta Phys. Sin.* **51** 645 (in Chinese)

[18] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566

[19] Guo H Z, Chen X R, Zhu J, Cai L C and Gao J 2005 *Chin. Phys. Lett.* **22** 1764

[20] Chen X R, Guo H Z, Cai L C and Gao J 2005 *Chin. Phys. Lett.* **22** 1504

[21] Guo H Z, Chen X R, Cai L C, Zhu J and Gao J 2005 *Solid State Commun* **134** 787

[22] Blanco M A, Francisco E and Luana V 2004 *Comput. Phys. Commun.* **158** 57

[23] Lu L Y, Chen X R, Yu B R and Gou Q Q 2006 *Chin. Phys.* **15** 802

[24] Blanco M A, Martín Pendás A, Francisco E, Recio J M and Franco R 1996 *J. Mol. Struct.* (*Theochem.*) **368** 245

[25] Flórez M, Recio J M, Francisco E, Blanco M A and Martín Pendás A 2002 *Phys. Rev.* B **66** 144112

[26] Francisco E, Sanjurjo G and Blanco M A 2001 *Phys. Rev.* B **63** 094107

[27] Murnaghan F D 1944 *Proc. Natl. Acad. Sci. USA* **30** 244

[28] Wang H Y, Chen X R, Zhu W J and Cheng Y 2005 *Phys. Rev.* B **72** 172502