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2009 J. Phys.: Condens. Matter 21 385405

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High-pressure polymorphs of Li_2BeH_4 predicted by first-principles calculations

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Received 4 June 2009, in final form 12 August 2009

Published 27 August 2009

Online at stacks.iop.org/JPhysCM/21/385405

Abstract

We report two orthorhombic high-pressure polymorphs of $\beta\text{-Na}_2\text{SO}_4$ - and La_2NiO_4 -type structures for lithium beryllium hydrides (Li_2BeH_4) predicted by first-principles calculations. The $\beta\text{-Na}_2\text{SO}_4$ -type structure possesses BeH_4 tetrahedra, similar to the zero-pressure $\alpha\text{-Li}_2\text{BeH}_4$ structure, but in dramatic contrast to the peculiar BeH_4 octahedral layer in the La_2NiO_4 -type structure. The $\beta\text{-Na}_2\text{SO}_4$ -type structure energetically surpasses the $\alpha\text{-Li}_2\text{BeH}_4$ structure for stability above 7.2 GPa, which is nicely correlated with the experimental transition pressure of 9.1 GPa. Further transformation to the La_2NiO_4 -type structure is predicted at 28.8 GPa. The two transitions are identified as first-order in nature with volume contractions of 3.32% and 5.17%, respectively. Our current discovery has ruled out the previously proposed Cs_2MgH_4 -type structure as the candidate for the high-pressure phase.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Light metal complex hydrides are promising materials for solid-state hydrogen storage due to their high gravimetric hydrogen density (GHD) [1–4]. For example, sodium alanate (NaAlH_4) [2] and lithium borohydride (LiBH_4) [4] have theoretical hydrogen capacities of 7.5 and 18.5 wt%, respectively. However, their stabilities with respect to thermal decomposition remain the major drawback for practical applications [5]. Recently, high-pressure research on these materials has attracted extensive attention [6–10]; one exciting discovery of the high-pressure $\beta\text{-LiBH}_4$ polymorph [10], revealing a square-planar coordination of the BH_4 subunit by Li atoms, has been proposed as a step towards destabilization of LiBH_4 . This indicates that high-pressure phases of complex hydrides might serve as targets for obtaining improved hydrogen-storage materials. Therefore, exploration of the high-pressure polymorphs of the complex lithium beryllium hydrides is of fundamental interest and has attracted much attention.

Lithium beryllium hydride, Li_2BeH_4 (GHD 15.0 wt%), exhibits a monoclinic distorted perovskite-type structure,

$\alpha\text{-Li}_2\text{BeH}_4$ (space group $P2_1/c$), under ambient conditions [11, 12]. Recently, Lipinska-Kalita *et al* [13] investigated its high-pressure behavior, and affirmed a pressure-induced structure transition at 9.1 GPa. But due to the lack of sufficient x-ray diffraction data, structural information about the new high-pressure polymorph is still missing. Shortly afterwards, Hu *et al* [14] theoretically predicted a Cs_2MgH_4 -type structure, which energetically surpassed $\alpha\text{-Li}_2\text{BeH}_4$ for stability above 18.1 GPa. Since the proposed Cs_2MgH_4 -type structure was based on an educated guess from structures known for other materials, there is a possibility that hitherto unsuspected structures are also stable instead, and hence may advance our understanding of the high-pressure behavior of Li_2BeH_4 . Therefore, using a newly developed *ab initio* evolutionary algorithm for crystal structure prediction [15–17], we have extensively explored the crystal structures of Li_2BeH_4 over a wide range of pressures (0–40 GPa). This method has been very successful in predicting the unknown structures from only the information about *chemical compositions* [18–23]. Two novel high-pressure orthorhombic polymorphs of $\beta\text{-Na}_2\text{SO}_4$ -type (space group $Fddd$, hereafter denoted $\beta\text{-Li}_2\text{BeH}_4$), and La_2NiO_4 -type (space group $Cmca$, hereafter denoted $\gamma\text{-Li}_2\text{BeH}_4$), are reported here for the first time.

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2. Computational details

Evolutionary variable-cell simulations were performed at 10, 20, and 30 GPa with systems containing 1, 2, 3, and 4 formula units in the simulation cell using the USPEX code [15–17]. In the evolutionary search process, the first generation of structures is produced randomly. All structures are relaxed at constant pressures, and the enthalpy was used as a fitness function. Discarding the worst (i.e. highest-enthalpy) structures, the new generation was produced from the best 60% of the structures in the given generation. New structures are created by (1) heredity (combining spatially coherent slabs cut from two parent structures in a random direction at random positions and with random thickness) and (2) lattice mutation. In addition, the best structure of a generation is carried over into the next generation. The underlying *ab initio* calculations were carried out using density functional theory within the generalized gradient approximation (GGA) [24] as implemented in the Vienna *ab initio* simulation package (VASP) [25]. The all-electron projector augmented wave (PAW) [26, 27] method was adopted. To reduce the errors, the cut-off energy for the expansion of the wavefunction into plane waves was set to 330 eV in all calculations, and the Monkhorst–Pack grid with a maximum spacing of 0.03 \AA^{-1} was individually adjusted in reciprocal space to the size of each computational cell. During the structural optimizations, all forces on atoms were converged to be less than 0.01 eV \AA^{-1} , and the external stresses were reduced to the order of 0.01 GPa. The theoretical equilibrium properties and equation of state (EOS) are determined by fitting the total energies as a function of volume to the Murnahan EOS [28]. The phonon frequencies were calculated by the direct approach [29, 30], which is based on first-principles calculations of total energy, Hellman–Feynman forces, and the dynamical matrix as implemented in the VASP and PHONON packages [29]. Two supercells of $1 \times 2 \times 1$ and $1 \times 2 \times 2$ unit cells both containing 112 atoms were adopted in the calculations for β -Li₂BeH₄ and γ -Li₂BeH₄, respectively. The Mulliken charges and bond overlap populations are calculated according to the formalism described by Segall *et al* using the CASTEP code [31]².

3. Results and discussion

We find the first phase transition at 7.2 GPa from the ambient pressure α -Li₂BeH₄ to β -Li₂BeH₄ (figure 1(a)). The transition pressure is in good agreement with the experimental data of 9.1 GPa. The second transformation, from β -Li₂BeH₄ to γ -Li₂BeH₄ (see below for structural information for β -Li₂BeH₄ and γ -Li₂BeH₄), occurs at 28.8 GPa. There is no energetically stable region for the previously proposed Cs₂MgH₄-type structure (figure 1(a)). At zero temperature a stable crystalline structure requires all phonon frequencies to be positive. The phonon dispersion relations were calculated

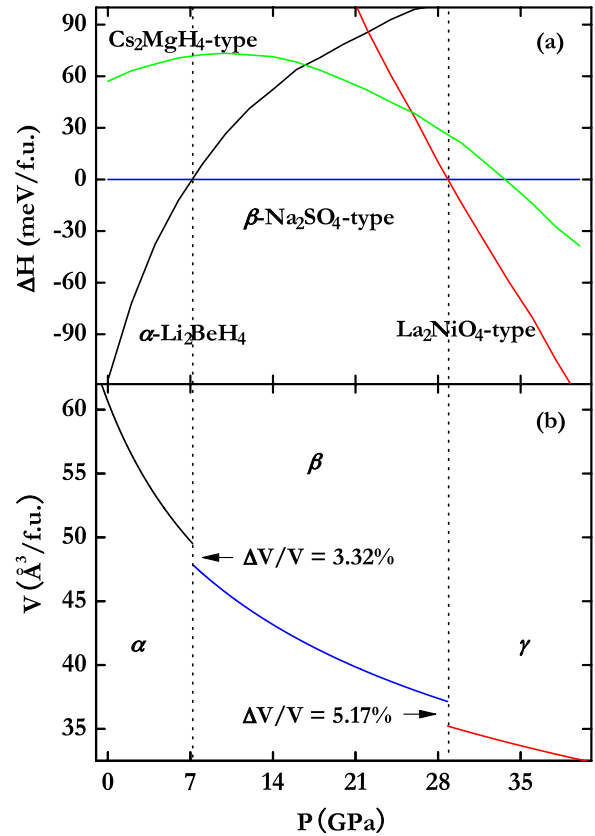


Figure 1. (a) Enthalpies for various structures relative to β -Li₂BeH₄ as a function of pressure. (b) The calculated equations of state for α -, β -, and γ -Li₂BeH₄. Vertical lines represent phase transitions.

for β -Li₂BeH₄ and γ -Li₂BeH₄ in the pressure ranges of 7.2–28.8 GPa and 28.8–40 GPa, respectively. No imaginary phonon frequency was observed in the whole Brillouin zones of the two high-pressure polymorphs, indicating dynamical stability. Evidently, the first ($\alpha \rightarrow \beta$) and second ($\beta \rightarrow \gamma$) transitions are of the first order, and show volume collapses of 3.32% and 5.17% (figure 1(b)), respectively. Such an obvious volume reduction at the transition is easy to detect in a high-pressure x-ray powder diffraction experiment. For example, volume drops of 6.6% and 2.9% have been experimentally observed in LiBH₄ [10] for the first and second transitions, respectively.

The optimized structural parameters for the three modifications of Li₂BeH₄ together with experimental and previously theoretical data [14] for α -Li₂BeH₄ are listed in table 1. It is clear that the current results for α -Li₂BeH₄ are in good agreement with experiment [11] and previous calculation [14]. Note that both the present work and [14] have obtained slightly smaller lattice constants (less than 2%) than the experimental values. This is mainly attributed to the neglect of zero-point fluctuations in the calculations. The zero-point effect has been demonstrated to efficiently enhance the lattice constants, and particularly for materials containing a substantial fraction of light elements such as metal hydrides [32, 33]. The bulk modulus B_0 derived from the Murnahan EOS is 25.2 GPa for α -Li₂BeH₄, which is in satisfactory agreement with that (28.4 GPa) in the

² The $5 \times 5 \times 4$, $9 \times 9 \times 9$, and $9 \times 9 \times 9$ Monkhorst–Pack meshes of k points in the primitive Brillouin zones were adopted for α -Li₂BeH₄, β -Li₂BeH₄, and γ -Li₂BeH₄, respectively, to give good convergence of the electronic densities of the three phases. Pseudo-atomic calculations were performed for H 1s1, Li 1s2 2s1, and Be 2s2.

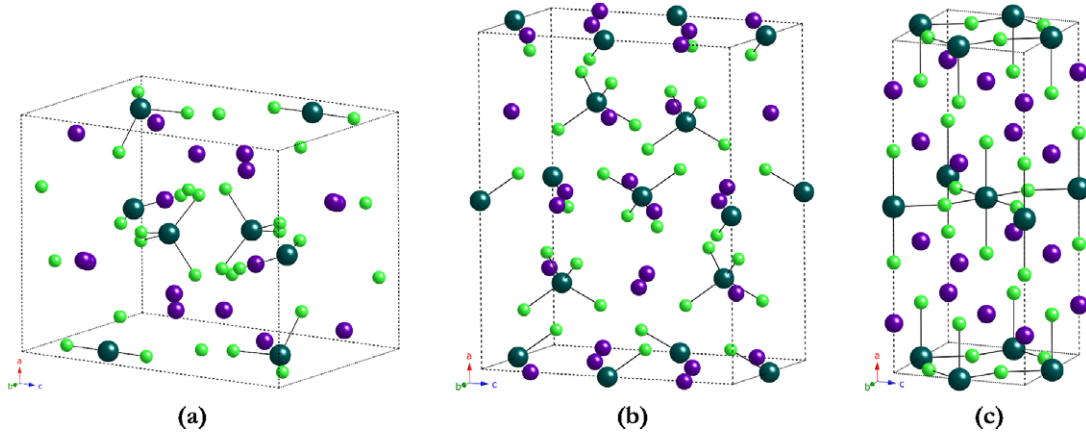


Figure 2. Crystal structures of α -Li₂BeH₄ (a) at 0 GPa, β -Li₂BeH₄ (b) at 7.2 GPa, and γ -Li₂BeH₄ (c) at 28.8 GPa. The small, middle, and large spheres represent H, Li, and Be atoms, respectively. The dark dotted lines denote the unit cells, and the short dark lines represent the Be–H bonds.

Table 1. Optimized structural parameters, a (Å), b (Å), c (Å), and β (deg), atomic position in fractional coordinates, bulk modulus B_0 (GPa), and energy gap E_g (eV) for α -Li₂BeH₄ at 0 GPa, β -Li₂BeH₄ at 7.2 GPa, and γ -Li₂BeH₄ at 28.8 GPa, respectively.

Structure	Lattice constant			B_0	E_g
	Calculation		Experiment ^a		
α -Li ₂ BeH ₄	$a = 7.024$	$a = 7.017^b$	$a = 7.097$	25.2	4.30
	$b = 8.264$	$b = 8.178^b$	$b = 8.374$		
	$c = 8.352$	$c = 8.259^b$	$c = 8.384$		
	$\beta = 93.789$	$\beta = 93.593^b$	$\beta = 93.577$		
	Lattice constant		Internal atomic position		
β -Li ₂ BeH ₄	$a = 9.880$		Li: 0.000, 0.000, 0.188	33.2	2.84
	$b = 4.886$		Be: 0.000, 0.000, 0.500		
	$c = 7.923$		H: 0.175, 0.416, 0.640		
γ -Li ₂ BeH ₄	$a = 9.353$		Li: 0.850, 0.000, 0.000	61.2	1.73
	$b = 3.888$		Be: 0.500, 0.000, 0.000		
	$c = 3.887$		H1: 0.000, 0.312, 0.312		
			H2: 0.667, 0.000, 0.000		

^a Reference [12].

^b Reference [14].

previous work [14]. It is suggested that the compressibility of Li₂BeH₄ is slightly lower than that ($B_0 = 13$ –26 GPa) of LiBH₄ [10] and LiAlH₄ [34], but higher than that of rare-earth hydrides [35] ($B_0 = 70$ –145 GPa) and transition-metal hydrides (FeH_x [36], $B_0 = 120$ –180 GPa).

β -Li₂BeH₄ has a β -Na₂SO₄-type structure as shown in figure 2(b). The BeH₄ unit forms a perfect tetrahedron with a Be–H bond length of 1.408 Å, in contrast to the slightly distorted tetrahedron in α -Li₂BeH₄ (figure 2(a)) in which the Be–H bond lengths vary from 1.429 to 1.447 Å. The BeH₄ tetrahedron reveals a γ -Pu-type substructure, while Li atoms form planar zigzag chains distributed in the voids of the BeH₄ network. γ -Li₂BeH₄ exhibits a La₂NiO₄-type structure (figure 2(c)), and consists of alternately stacked BeH₄ layers of vertex-sharing octahedra. Each octahedron apex sits between four apexes of the next layer. The bond angle at the bridging H atom of the Be–H–Be zigzag chain is 152°. The Li atoms just fit into the hollow between four H atoms of the non-bridging octahedron apexes. It is noteworthy that the peculiar BeH₄ octahedral layer allows a denser packing than the BeH₄

tetrahedron. This results in a larger volume collapse of 5.17% for the $\beta \rightarrow \gamma$ transition than for the $\alpha \rightarrow \beta$ transition.

The coordination number of Be changes from 4 to 6 at the $\beta \rightarrow \gamma$ transition, which is consistent with the expected general trend of increasing coordination number with pressure. Interestingly, γ -Li₂BeH₄ reveals a strikingly longer Be–H bond length (e.g. 1.562 Å at 28.8 GPa versus 1.408 Å for β -Li₂BeH₄ at 7.2 GPa), which is likely to reduce the activation energy for hydrogen desorption. Therefore, γ -Li₂BeH₄ is suggested to be a promising hydrogen-storage material with lower hydrogen decomposition temperature than that of α -Li₂BeH₄ if stabilized at ambient pressure. However, the β -Li₂BeH₄ \rightarrow γ -Li₂BeH₄ transition occurs at very high pressure (above 28.8 GPa). This suggests that γ -Li₂BeH₄ is unlikely to be stabilized at ambient conditions [37, 38]. Phonon calculations give a criterion for the crystal stability and indicate, through soft modes, structural instability. Therefore, we have optimized the γ -Li₂BeH₄ to zero pressure and performed the full phonon dispersion calculation. We found severe imaginary phonon frequencies to exclude the stability of γ -Li₂BeH₄ under ambient conditions.

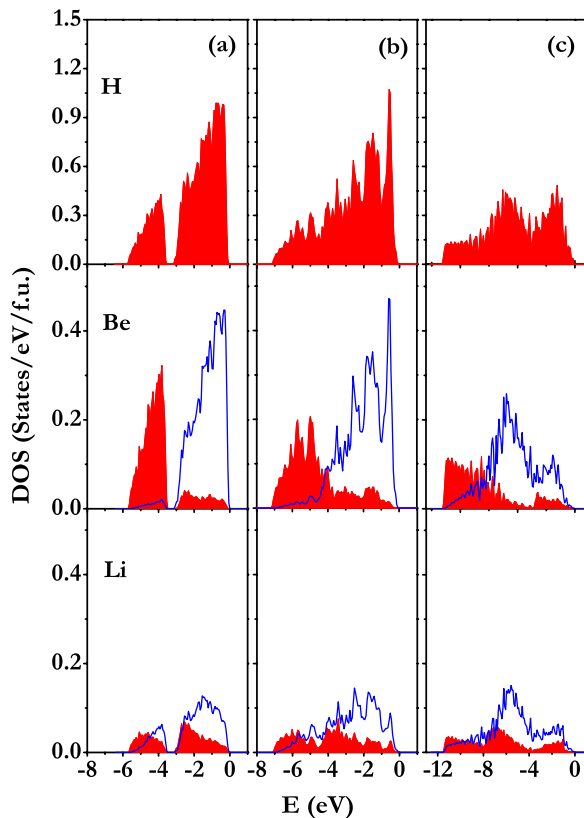


Figure 3. Partial densities of states for valence electrons in α - Li_2BeH_4 (a) at 0 GPa, β - Li_2BeH_4 (b) at 7.2 GPa, and γ - Li_2BeH_4 (c) at 28.8 GPa. The Fermi level is set to be zero, and s states are depicted as shaded-red curves, while p states are blue curves.

Analysis of the calculated electronic density of states (DOS) (figure 3) reveals that the two high-pressure phases exhibit a common insulating feature with a finite energy gap (table 1). The occupied valence bands are plotted in figure 3. For α - Li_2BeH_4 , the valence bands split into two peaks whose positions and widths agree well with those in [14], and the splitting features are similar to those in NaBH_4 [6, 39] and $\text{Ca}(\text{AlH}_4)_2$ [40]. The two peaks merge into one broad peak in β - Li_2BeH_4 and γ - Li_2BeH_4 resulting from the broadening of valence bands under high pressure originating from the shortened interatomic distance upon squeezing. For all three phases, the Be s, p and H s orbitals are energetically degenerate, implying strong Be–H hybridization and thus the formation of directional covalent bonds within the BeH_4 tetrahedron or BeH_4 octahedron layers.

The Mulliken charges and the bond overlap populations (BOPs) were studied to quantify the nature of the chemical bonding in Li_2BeH_4 . Average charge transfers from the Li^+ cation to the $[\text{BeH}_4]^-$ anion are calculated to be $1.0e$ in α - Li_2BeH_4 (0 GPa), $0.95e$ in β - Li_2BeH_4 (7.2 GPa), and $0.99e$ in γ - Li_2BeH_4 (28.8 GPa), respectively. This manifests an ionic interaction between Li atoms and the BeH_4 tetrahedron or BeH_4 octahedral layers. The Be–H and Li–H BOPs with the variation of bond lengths for the three phases are plotted in figure 4. It is found that the Be–H bonds possess very large overlap populations, e.g. 0.84 for β - Li_2BeH_4 , indicating

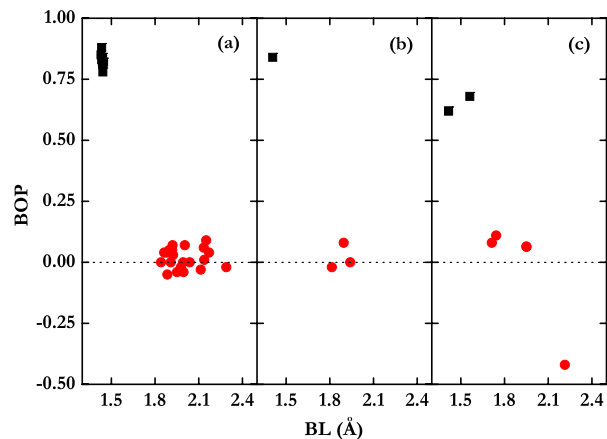


Figure 4. Bond overlap populations (BOP) of α - Li_2BeH_4 (a), β - Li_2BeH_4 (b), and γ - Li_2BeH_4 (c) over their bond lengths (BL) at 0 GPa, 7.2 GPa, and 28.8 GPa, respectively. Different symbols for different bonds: \blacksquare (Be–H), \bullet (Li–H).

a strong covalent nature. It is notable that the BOPs of Be–H bonds decrease from 0.84 in β - Li_2BeH_4 to 0.64 in γ - Li_2BeH_4 as the coordination numbers of Be change from 4 to 6 at the $\beta \rightarrow \gamma$ transition. However, the Li–H bonding behaviors are more complicated. In the three phases, a few Li–H bonds are found to reveal a mixed ionic and weak covalent character with BOPs of about 0.1, while a majority of Li–H bonds exhibit an ionic nature with BOPs close to zero or a negative value (anti-bonding states). For example, in γ - Li_2BeH_4 , the Li atom forms two kinds of bonds with the four nearest bridging H atoms in the Be–H–Be zigzag chains: one is the mixed ionic and weak covalent Li–H bond (bond length 1.743 Å) with a BOP of 0.11, the other one is a Li–H anti-bonding bond (bond length, 2.214 Å) with a BOP of -0.42 . The two different Li–H bonds lead to the H atoms in Be–H–Be chain deviating from the $\text{Be} \cdots \text{Be}$ line, and hold up the zigzag network of the BeH_6 octahedra. Moreover, previous studies [14] have shown that the average BOP of a complex hydride might serve as an indicator for its hydrogen desorption ability, i.e. the smaller the BOP is, the lower the hydrogen desorption kinetic energy. From this point of view, the current study suggests that the activation energy of β - Li_2BeH_4 for hydrogen desorption is similar to that of α - Li_2BeH_4 originating from the similar bonding behavior in the two phases.

4. Concluding remarks

We have preformed a systematic exploration of the high-pressure crystal structures of Li_2BeH_4 using an *ab initio* evolutionary algorithm. Two orthorhombic structures of β - Li_2BeH_4 and γ - Li_2BeH_4 were reported for the first time. The β - Li_2BeH_4 energetically surpasses the ground state α - Li_2BeH_4 for stability above 7.2 GPa, while it is less favorable than γ - Li_2BeH_4 above 28.8 GPa. The electronic density of states supports a nonmetallic character for the three phases. The Mulliken charges reveal an ionic picture for the interaction between Li atoms and the BeH_4 tetrahedron or BeH_4 octahedral layers. The BOP analysis shows that

the bonding properties of β -Li₂BeH₄ are similar to that of α -Li₂BeH₄, indicating similar hydrogen decomposition abilities. Nevertheless, γ -Li₂BeH₄ possesses BeH₄ octahedral layers that might decrease the activation energy for hydrogen desorption. However, γ -Li₂BeH₄ is unlikely to be stabilized at ambient pressure in view of the high transition pressure and the existence of imaginary phonons at zero pressure. The present simulation thus does not support superior destabilization in the high-pressure polymorphisms of Li₂BeH₄. We expect that the two high-pressure polymorphs can be detected by the x-ray diffraction measurements in view of the obvious volume collapses of 3.32% and 5.17% at the transitions.

Acknowledgments

This work is supported by the China 973 Program under grant no. 2005CB724400, the NSAF of China under grant no. 10676011, the National Natural Science Foundation of China under grant no. 10874054, the Program for 2005 New Century Excellent Talents in University, and the 2007 Cheung Kong Scholars Program of China. H Wang thanks L J Zhang, A R Oganov, C H Hu and Y Filinchuk for helpful discussions and technical supports.

References

- [1] Schlapbach L and Züttel A 2001 *Nature* **414** 353
- [2] Bogdanovi B and Schwickardi M 1997 *J. Alloys. Compounds* **253** 1
- [3] Schwarz M, Haiduc A, Stil H, Paulus P and Geerlings H 2005 *J. Alloys. Compounds* **404** 762
- [4] Zütel A, Wenger P, Rentsch S, Sudan P, Mauron P and Emmenegger C 2003 *J. Power Sources* **118** 1
- [5] Grochala W and Edwards P P 2004 *Chem. Rev.* **104** 1283
- [6] Araujo C M, Ahuja R, Talyzin A V and Sundqvist B 2005 *Phys. Rev. B* **72** 054125
- [7] Talyzin A V and Sundqvist B 2006 *High Pressure Res.* **26** 165
- [8] Talyzin A V, Andersson O, Sundqvist B, Kurnosov A and Dubrovinsky L 2007 *J. Solid State Chem.* **180** 510
- [9] Filinchuk Y, Talyzin A V, Chernyshov D and Dmitriev V 2007 *Phys. Rev. B* **76** 092104
- [10] Filinchuk Y, Chernyshov D, Nevidomskyy A and Dmitriev V 2008 *Angew. Chem. Int. Edn* **47** 529
- [11] Bell A and Coates G E 1968 *J. Chem. Soc. A* **1968** 628
- [12] Bulychev B M, Shpanchenko R V, Antipov E V, Sheptyakov D V, Bushmeleva S N and Balagurov A M 2004 *Inorg. Chem.* **43** 6371
- [13] Lipinska-Kalita Y D K E, Song Y, Lin J, Somayazulu M, Dera P, Yarger J, Mao H K and Hemley R J 2004 *First Annual SSAAP Symp. (Albuquerque, NM)* unpublished
- [14] Hu C H, Chen D M, Wang Y M, Xu D S and Yang K 2007 *Phys. Rev. B* **75** 224108
- [15] Glass C W, Oganov A R and Hansen N 2006 *Comput. Phys. Commun.* **175** 713
- [16] Oganov A R, Glass C W and Ono S 2006 *Earth Planet. Sci. Lett.* **241** 95
- [17] Oganov A R, Ma Y M, Glass C W and Valle M 2007 *Psi-k Newsletter* **84** 1
- [18] Ma Y M, Oganov A R and Glass C W 2007 *Phys. Rev. B* **76** 064101
- [19] Gao G Y, Oganov A R, Bergara A, Martinez-Canales M, Cui T, Iitaka T, Ma Y M and Zou G T 2008 *Phys. Rev. Lett.* **101** 107002
- [20] Ma Y M, Oganov A R and Xie Y 2008 *Phys. Rev. B* **78** 014102
- [21] Ma Y, Oganov A R, Li Z, Xie Y and Kotakoski J 2009 *Phys. Rev. Lett.* **102** 065501
- [22] Oganov A R, Chen J, Gatti C, Ma Y, Ma Y, Glass C W, Liu Z, Yu T, Kurakevych O O and Solozhenko V L 2009 *Nature* **457** 863
- [23] Ma Y, Eremets M, Oganov A R, Xie Y, Trojan I, Medvedev S, Lyakhov A O, Valle M and Prakapenka V 2009 *Nature* **458** 182
- [24] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [25] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [26] Blöchl P E 1994 *Phys. Rev. B* **50** 17953
- [27] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
- [28] Murnaghan F D 1944 *Proc. Natl Acad. Sci.* **30** 244
- [29] Parlinski K, Li Z Q and Kawazoe Y 1997 *Phys. Rev. Lett.* **78** 4063
- [30] Parlinski K 1999 in *Neutrons and Numerical Methods—N₂M* (New York: AIP) p 121
- [31] Segall M D, Lindan P J D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys.: Condens. Matter* **14** 2717
- [32] Herbst J F and Hector J L G 2005 *Phys. Rev. B* **72** 125120
- [33] Stephens D R and Lilley E M 1968 *J. Appl. Phys.* **39** 177
- [34] Vajeeston P, Ravindran P, Vidya R, Fjellvag H and Kjekshus A 2003 *Phys. Rev. B* **68** 212101
- [35] Palasyuk T and Tkacz M 2007 *Solid State Commun.* **141** 302
- [36] Hirao N, Kondo T, Ohtani E, Takemura K and Kikegawa T 2004 *Geophys. Res. Lett.* **31** L06616
- [37] Brazhkin V V and Lyapin A G 2004 *Nat. Mater.* **3** 497
- [38] Grochala W, Hoffmann R, Feng J and Ashcroft N 2007 *Angew. Chem. Int. Edn* **46** 3620
- [39] Vajeeston P, Ravindran P, Kjekshus A and Fjellvag H 2005 *J. Alloys Compounds* **387** 97
- [40] Miwa K, Aoki M, Noritake T, Ohba N, Nakamori Y, Towata S-I, Züttel A and Orimo S-I 2006 *Phys. Rev. B* **74** 155122