

High-pressure modulated structures in beryllium chalcogenidesXiaolei Feng,^{1,2,3,*} Pengyue Gao,^{1,*} Xue Li,¹ Min Wu,⁴ Hui Wang,¹ Jian Lv,^{1,†}
Simon A. T. Redfern,^{2,3,5,†} Hanyu Liu,^{1,†} and Yanming Ma^{1,6}HPSTAR
790-2019¹*Innovation Center of Computational Physics Methods and Software & State Key Laboratory for Superhard Materials,
College of Physics, Jilin University, Changchun, 130012, China*²*Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai, 201203, China*³*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom*⁴*College of Materials sciences and Engineering, Zhejiang University of Technology, 310014, China*⁵*Asian School of the Environment, Nanyang Technological University, Singapore 639798*⁶*International Center of Future Science, Jilin University, Changchun 130012, China*

(Received 18 April 2019; revised manuscript received 1 June 2019; published 8 July 2019)

Structure searches of beryllium chalcogenides (BeS, BeSe, and BeTe) at high pressures using a swarm intelligence algorithm, in conjunction with density functional theory, reveal modulated polymorphs, unusual for such simple binary compounds. Apart from the well-known cubic (space group $F\bar{4}3m$, zinc-blende structure) to hexagonal closed-packed (space group $P6_3/mmc$, nickel-arsenide structure) structural transition, a further transition at higher pressure to an orthorhombic structure is predicted for BeS and BeSe. The orthorhombic phase is space group $Cmca$ in BeS and $Pnma$ before finally adopting $Cmca$ in BeSe, each accompanied by the onset of modulation of the atomic arrangement. The amplitude of displacements associated with the modulation increases with increasing pressure and molecular dynamics simulations show the modulated structure to become stable at least to 300 GPa and 2000 K. This unusual structural modulation is not seen, however, in BeTe, which instead transforms to a $C2/m$ phase. Links are drawn between the modulated phases of BeS and BeSe and the high-pressure modulated phases of their parent chalcogens. Our results provide key insights into understanding the modulation in binary compounds at high pressure.

DOI: [10.1103/PhysRevB.100.014102](https://doi.org/10.1103/PhysRevB.100.014102)**I. INTRODUCTION**

Modulated structures are of particular interest because they typically reflect competing processes that give rise to long-range interactions resulting in the modulation. The first recognition of a modulated structure was from the breakdown of the “law of rational indices” in the mineral calaverite ($\text{Au}_{1-p}\text{Ag}_p\text{Te}_2$, $p < 0.15$) in 1931 by Victor Goldschmidt [1]. Later, in Cambridge in 1940, Bradley observed satellite reflections in the x-ray diffraction patterns of copper-iron-nickel alloys [2] and after three years’ work it was realized that such satellite reflections corresponded to structural modulation [3,4]. Since then, evidence of structural modulation in solids has been relatively widely reported, including incommensurate and long-range modulation in a number of structurally complex compounds, such as the high- T_c superconductors of the Bi-Sr-Ca-Cu-O system, $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_6\text{O}_x$, and $\text{Bi}_4\text{Sr}_3\text{Ca}_2\text{Cu}_4\text{O}_y$ [5]. Many naturally occurring minerals, including åkermanite [6], mullite [7], pyrrhotite [8], quartz [9–11], feldspar [12], nepheline [13], and sodium carbonate [14], also exhibit modulated structures. Apart from these complex crystal structures, many elemental solids, interestingly, also display structural modulation at high pressure [15,16], such as Cl_2 [17], Br_2 [18], I_2 [19], S [20,21], Se [21–24],

and Te [23–25]. However, pressure-induced modulation is significantly less common in simple compounds. Indeed, a previously known AB compound showing pressure-induced structural modulation, to our knowledge, is NiBi [26], although high-pressure magnetic incommensuration has been reported in some AB materials, for example that in MnGe [27]. In another recent case, the structure of superconducting H_2S is interpreted as modulated phases at high pressure [28–31].

Among the II-VI AB compounds, the BeX ($X = \text{S}, \text{Se}, \text{and Te}$) compounds are of particular note. Elemental S, Se, and Te display structural modulation on increasing pressure [20–25], and it is interesting to consider whether AB compounds based on these elements may, therefore, inherit such modulation. Structural modifications of these materials are of intrinsic interest because they may drive changes in physical properties and other characteristics. Furthermore, only these BeX phases among the II-VI AB compounds, crystallize in the cubic-close-packed structure at ambient pressure, before transforming to a hexagonal-close-packed structure at higher pressure [32–35]. Most of the other II-VI compounds adopt the rock-salt structure [36–38] except for BeO [39,40] and MgTe [41], which adopt the wurtzite and NiAs structures, respectively. Finally, several previous theoretical studies have investigated the structures and physical properties of BeX materials at pressures of lower than 100 GPa, assuming the structures of ZB, NiAs, or NaCl [42–45].

Experimental investigations of BeX compounds have been hampered by their toxic nature, but the few studies that

*These authors contributed equally to this work.

†Authors to whom correspondence should be addressed: lvjian@calypso.cn; satr@cam.ac.uk; hanyuliu@jlu.edu.cn

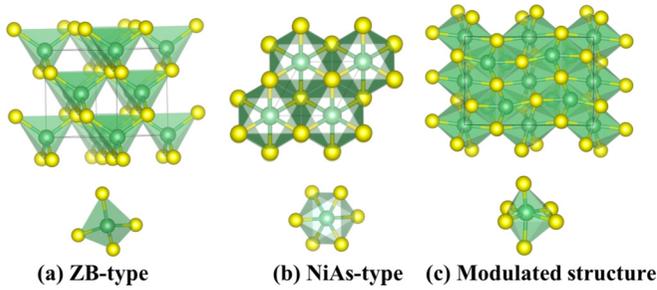


FIG. 1. Variation of structure of BeS with pressure, showing the structural response in terms of variation in coordination environment of Be by S and S by Be from tetrahedral in zinc blende to distorted octahedral in the $Cmca$ structure. Green and yellow spheres represent Be and S/Se.

have been conducted have not suggested the existence of any modulated structure. The pioneering work by Staritzky and Goldschmidt *et al.* gave the lattice parameters of BeX [46,47]. Later, Yim *et al.* confirmed that these compounds crystallize in the zinc-blende structure with space group symmetry $F\bar{4}3m$ at ambient pressure [48]. At higher pressures, they undergo a phase transition to the nickel-arsenide structure with space group symmetry $P6_3/mmc$ [28]. For BeS, for example, there are reports of a reversible first-order phase transition at 51 GPa from the $F\bar{4}3m$ structure to the $P6_3/mmc$ structure [33–35]. This $P6_3/mmc$ phase was found to remain stable up to at least 96 GPa.

In view of the disparity between the observed modulations seen in elemental S, Se, and Te and the lack of any discovered to date in their AB compounds, we have carried out density functional theory calculations of beryllium chalcogenides to higher pressures, with the aim of investigating the possible occurrence of such pressure-induced structural modulation phenomena. Computational studies of these materials provide an especially important tool in understanding their stabilities and structures at such extreme conditions. We report on the structures and physical properties of the BeX compounds as a function of pressure up to 300 GPa, using the swarm-intelligence based CALYPSO code for structure prediction in combination with the first-principles total energy calculations [49,50]. Apart from the well-known first-order phase transition from the $F\bar{4}3m$ zinc-blende structure to the $P6_3/mmc$

nickel-arsenide structure, a further phase transition at higher pressures is revealed from our calculations, and is characterized by the onset of high-pressure structural modulation. We find unusual pressure-induced modulation in both BeS and BeSe, rarely reported in the AB compound, e.g., Refs. [42–45]. In contrast, our investigation of BeTe suggests that, for this composition, no such modulated phase occurs.

II. COMPUTATIONAL DETAILS

Our search for low-energy high-pressure crystalline structures of BeX phases was performed using the swarm-intelligence based CALYPSO structure prediction method and its same-name code [49,50]. Recent successful applications of this method include several examples of structure predictions for various crystalline systems, ranging from elemental solids to binary and ternary compounds [51–54]. Structural optimizations, enthalpies, electronic structures, and phonons were calculated using a first-principles implementation of density-functional theory. The underlying optimizations were performed using the Vienna *ab initio* simulation (VASP) program [55,56] and projector-augmented plane-wave potentials [57] with an energy cutoff of 650 eV. The Be, S, Se, and Te potentials have $2s^22p^1$, $3s^23p^4$, $4s^24p^4$, and $5s^25p^4$ as valence states, respectively, employing the Perdew-Burke-Ernzerhof functional [58]. The phonon simulations have been performed using the pseudopotential plane-wave method and density functional perturbation theory as implemented in the QUANTUM ESPRESSO package [59]. An ultrasoft pseudopotential was used for Be and S with the choices of electronic configurations of $2s^22p^1$ and $3s^23p^4$. Convergence tests gave the use of kinetic energy cutoff 80 Ry. Structure searching calculations were performed at 0, 50, 100, 150, 200, 250, and 300 GPa, respectively. We have performed a supercell with 32 Be and 32 S atoms for the $Cmca$ -BeS phase at 300 GPa and 300 and 2000 K using the NVT (N -number of particle, V -volume, T -temperature) ensemble. The results indicate that the predicted $Cmca$ -BeS phase is stable up to 2000 K at 300 GPa.

III. RESULTS AND DISCUSSIONS

Our structure predictions with simulation cell up to eight BeX formula units (f.u.) were performed over a pressure range

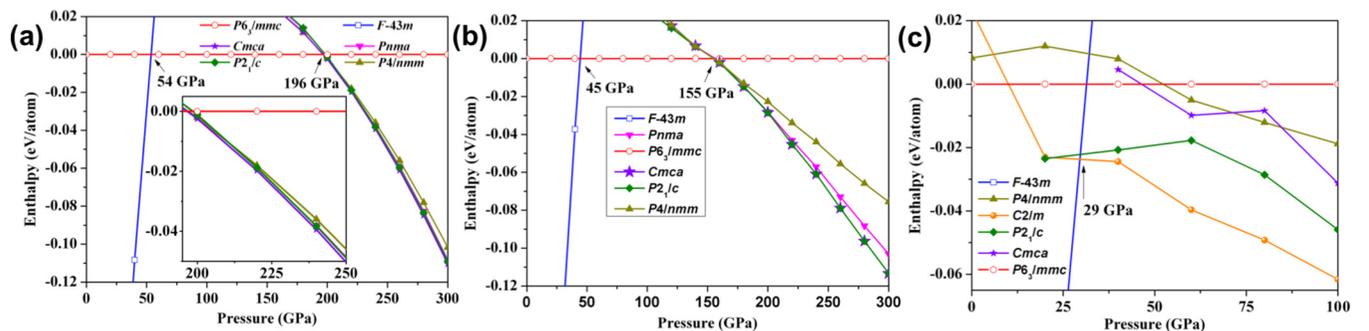


FIG. 2. Enthalpies of candidate phases of BeX as a function of pressure, plotted with respect to the NiAs $P6_3/mmc$ phase. Closed symbols represent modulated phases whereas open symbols correspond to nonmodulated structures. The similarity between BeS and BeSe is apparent, whereas the highest-pressure phase of BeTe adopts the unmodulated $C2/m$ structure, but at much lower pressure.

TABLE I. Calculated structural parameters of various BeS, BeSe, and BeTe phases at high pressures.

	Space group	Lattice parameters (\AA , $^\circ$)	Atoms	Atomic coordinates (Fractional)		
BeS (180 GPa)	$P2_1/c$	$a = 3.78, b = 7.72, c = 5.33$ $\alpha = 90, \beta = 134.97, \gamma = 90$	Be	0.487	0	0.757
			Be	0.039	0.799	0.760
			S	0.979	0.038	0.744
			S	0.462	0.25	0.740
			Be	0	0.75	0.718
BeS (220 GPa)	$Pnma$	$a = 7.58, b = 3.68, c = 3.69$ $\alpha = \beta = \gamma = 90$	Be	0.307	0.75	0.208
			S	0.455	0.25	0.724
			S	0.25	0.25	0.208
			Be	0	0	0.5
			Be	0.5	0	0.132
BeS (240 GPa)	$P4/nmm$	$a = b = 3.64, c = 3.79$ $\alpha = \beta = \gamma = 90$	S	0.5	0	0.607
			S	0	0	0
			Be	0.599	0.599	0.75
			S	0.927	0.927	0.25
			Be	0.788	0.213	0
BeS (260 GPa)	$C2/m$	$a = b = 2.61, c = 5.08, \alpha = \beta = 122.12,$ $\gamma = 87.88$	Be	0.707	0.708	0.779
			S	0.282	0.282	0.056
			S	0.294	0.794	0.25
			Be	0.785	0.216	0.5
			Be	0.293	0.293	0.804
BeS (300 GPa)	$Cmca$	$a = b = 3.54, c = 7.37$ $\alpha = \beta = 90, \gamma = 89.03$	Se	0.724	0.724	0.461
			Se	0.209	0.709	0.25
			Be	0.865	0.865	0.75
			Te	0.557	0.557	0.25
			BeSe (200 GPa)	$Cmca$	$a = b = 3.92, c = 8.04, \alpha = \beta = 90$ $\gamma = 88.81$	Be
BeTe (40 GPa)	$C2/m$	$a = b = 3.62, c = 6.98, \alpha = \beta = 126.39$ $\gamma = 81.43$	Be	0.293	0.293	0.804
			Se	0.724	0.724	0.461
			Se	0.209	0.709	0.25

of 0–300 GPa for BeS and BeSe, and 0–100 GPa for BeTe, respectively. The experimentally observed structures shared by BeX compounds were successfully reproduced over the appropriate pressure ranges, validating the reliability of our computational scheme. At ambient pressure, simulations readily found the zinc-blende structure [Fig. 1(a)], which is composed of corner-sharing $X\text{Be}_4/\text{BeX}_4$ tetrahedra. At 50 GPa, our simulations successfully reproduced the NiAs structure [Fig. 1(b)] in which each chalcogen atom is coordinated to six Be atoms forming a triangular prism and each Be atom is coordinated to six chalcogen atoms forming an octahedron.

The structural search of BeX compounds at higher pressure uncovered several structures with competitive enthalpies. The most stable structures over each pressure range are shown in Fig. 2. The enthalpies of these predicted structures with respect to the NiAs structure of BeX are plotted as a function of pressure in Fig. 2.

In BeS, three energetically competitive structures with very similar geometries are predicted at 250 and 300 GPa: a monoclinic $P2_1/c$ phase (Table I), and two orthorhombic structures ($Pnma$ and $Cmca$), among which the $Cmca$ structure is energetically most favorable. All of the low-enthalpy structures consist of face-sharing distorted $\text{BeS}_6/\text{SBe}_6$ octahedra with each Be and S atom sixfold coordinated to each other. The most intriguing finding in these high-pressure phases is the emergence of structure modulations (Fig. 3). As depicted in Fig. 1, all the three structures can be described as a distortion of an unmodulated tetragonal $P4/nmm$ structure. The basic tetragonal structure is composed of two interpenetrating distorted face-centered tetragonal sublattices formed by Be and

S, respectively. The modulated distortion occurs with varying atomic displacement along the z axis and with periodicity that is commensurate with a doubling of the underlying cell of the basic tetragonal phase, corresponding to a wave vector of $(0\ 0\ 0.5)$. The distortions lead to highly distorted body-centered orthorhombic sublattices for both Be and S in the modulated structures, in which all S atoms are displaced along the y axis, while corner and body-centered Be atoms are displaced along the x and y axes, respectively. It should note that, although elemental chalcogen has long been known to exhibit structure modulations at high pressure, the current findings represent a unique example of a simple AB compound showing a structure modulation.

The enthalpy curves relative to the NiAs structure for various structures of BeS are shown in Fig. 2(a). The phase transition pressure of the zinc-blende structure to the

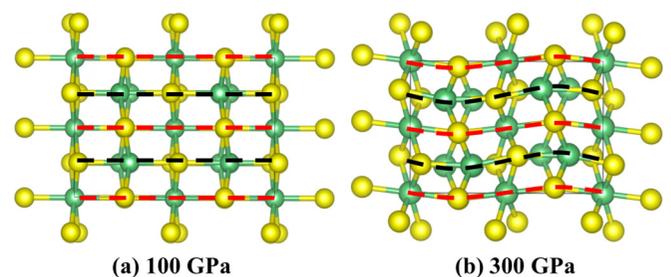


FIG. 3. The modulation amplitude of the $Cmca$ phase of BeS increases upon compression.

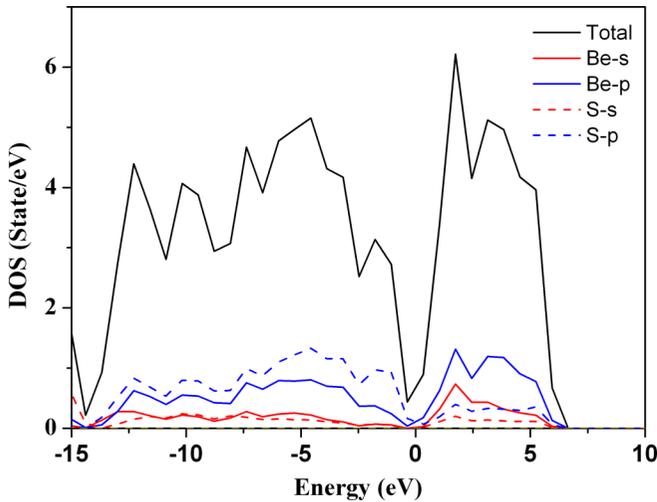


FIG. 4. Calculate partial density of states of *Cmca*-BeS at 200 GPa.

nickel-arsenide structure is 54 GPa, in good agreement with previous experimental reports of a transition at ~ 51 GPa. The experimental nickel-arsenide structure has the lowest-enthalpy up to 200 GPa, beyond which the predicted $P2_1/c$, $Pnma$ and $Cmca$ structures, as well as the unmodulated $P4/nmm$ structure become more favorable, with nearly degenerate enthalpies [the differences of enthalpy among different structures are of the same order of magnitude as the precision (or error) in the calculations, namely ~ 1 meV/atom]. Given the existence of several energetically competitive and

geometrically similar structures, the potential energy surface is expected to be flat with many shallow local minima and the system can be significantly frustrated by competing interactions. In experiment at finite temperature, it is not impossible to observe incommensurately modulated structures. As pressure increases, the modulated structures ($P2_1/c$, $Pnma$ and $Cmca$) become marginally more stable than the unmodulated $P4/nmm$ phase, up to the highest pressure of 300 GPa considered here. This suggests that pressure promotes the structure modulation.

Furthermore, we have investigated the electronic properties of *Cmca* BeS at 200 GPa. We find a charge transfer of $1.36 e$ from Be to S, indicating that Be has $2+$ valence at 200 GPa, as performed from Bader simulations. The electronic density of states calculations suggest that *Cmca* BeS is metallic at 200 GPa. These results suggest the possible hybridization between Be-*p* and S-*p* below Fermi-energy level, as shown in Fig. 4.

The behavior of BeSe was investigated by the same methodology as adopted for BeS and extraordinarily similar results were obtained. The calculated enthalpy curves indicate transformations from the zinc-blende structure to the nickel-arsenide structure at 44 GPa and from the nickel-arsenide structure to the modulated structure at 160 GPa [Fig. 5(b)]. The replacement of S by the heavier Se atom leads to each phase transition occurring at a lower pressure, which is consistently observed in elements and compounds under compression as atoms are substituted by same-group heavier congeners. Among modulated structures, the $Pnma$ structure is marginally most stable in the pressure range of 160–200 GPa, beyond which the final $Cmca$ structure becomes most stable

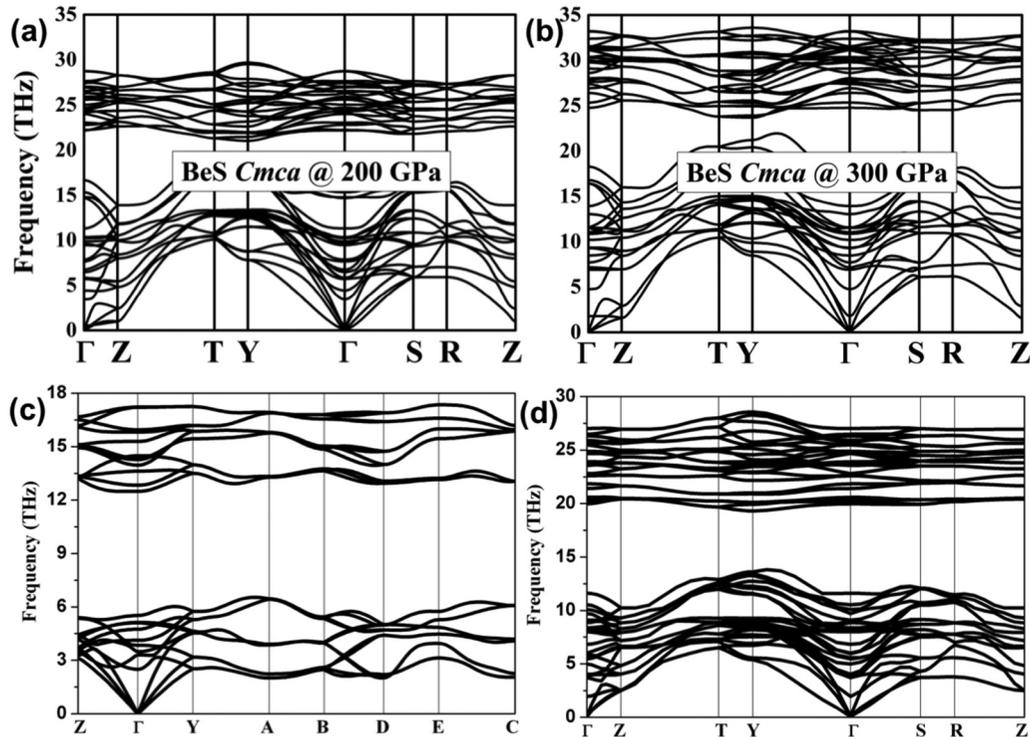


FIG. 5. Phonon dispersion curves for candidate high-pressure structures of (a),(b) *Cmca*-BeS, (c) *Cmca*-BeSe at 200 GPa, and (d) $C2/m$ -BeTe at 40 GPa

up to at least 300 GPa. This is different from BeS where $Cmca$ structure is always the most favorable in the stability field of the modulated structures.

In the case of BeTe, the pressure-dependent behavior is distinct from that of BeS and BeSe. Upon compression, the structure transforms from zinc-blende to an unmodulated monoclinic $C2/m$ structure at 29 GPa, rather than showing a transition to modulated structure up to the highest pressure of 100 GPa considered in the current work [Fig. 2(c)]. Within the $C2/m$ structure, each Be and Te are sixfold coordinated with each forming a high distorted octahedron similar to those in the modulated structures of BeS and BeSe, but the octahedra connect each other via edge sharing. We have calculated phonon dispersion curves of $Cmca$ -BeSe at 200 GPa and $C2/m$ -BeTe at 40 GPa, as shown in Fig. 5. There is no imaginary mode in the phonon dispersion curves of these predicted structures, indicating they are dynamically stable at the pressure we considered in this work.

IV. CONCLUSION

In summary, we have performed systematic structure searches of beryllium chalcogenides using a global swarm structure search method as a function of pressure. For BeS, above 200 GPa, a series of low-enthalpy candidate structures has been identified, and the dynamically stable phase (Fig. 5) with lowest enthalpy is a previously unreported $Cmca$ modulated structure. The same structure occurs in BeSe at pressures above 164 GPa. We have found that these are simple AB compounds that transform to a modulated structure upon compression.

Interestingly, BeTe shows contrasting behavior. Although the $P2_1/c$ phase of BeTe is one of the lowest-enthalpy high-pressure candidate structures for BeTe, it instead transforms to an alternative structure with $C2/m$ symmetry, at a much lower pressure than seen for the $P2_1/c$ transition in BeS and BeSe. This may point to the fact that extreme pressure is an important driver for the formation of the modulated monoclinic structure, and that in BeTe this transition is averted by

the earlier transformation to the unmodulated $C2/m$ structure. Indeed, the remarkable transition to a high-pressure modulated structure in such a simple AB compound may be related to the previously noted modulated high-pressure phases of their parent chalcogen elements. These occur at 102, 46, and 8.5 GPa in S, Se, and Te, respectively. We note that the transitions in S and Se occur in, or very near to, the stability field of the NiAs polymorph of BeS and BeSe, respectively, while the transition in Te (at 8.5 GPa) falls well below the stability field of the NiAs phase of BeTe, but squarely in that of the cubic zinc-blende-type polymorph. It seems that the transformation to a modulated structure in the Be chalcogenides only occurs from the nickel-arsenide phase, and is suppressed or less favored when the zinc-blende-structure type is compressed, instead favoring the alternative nonmodulated $C2/m$ structure.

We note that the transition from the intermediate pressure nickel-arsenide phase to the high pressure $Cmca$ structure in both BeS and BeSe is accompanied by only a very small volume change, unlike the strongly first-order transition from zinc-blende to nickel-arsenide structures at lower pressure. This is consistent with the fact that the zinc-blende to nickel-arsenide structural phase transition involves a drastic change in coordination from fourfold to sixfold, while the transition from the nickel-arsenide structure to the $P2_1/c$ modulated phase does not change the primary coordination number of either element.

ACKNOWLEDGMENTS

We acknowledge funding from the National Natural Science Foundation of China (Grant No. 11534003), Science Challenge Project No. TZ2016001, National Science Associated Funding (NSAF, No. U1530124). This work is supported by the Program for JLU Science and Technology Innovative Research Team (JLUSTIRT). We utilized computing facilities at the High Performance Computing Centre of Jilin University and Tianhe2-JK at the Beijing Computational Science Research Centre. S.A.T.R. is grateful for support from NERC (NE/P012167/1). X.F. acknowledges the China Scholarship Council (CSC) funding.

-
- [1] V. Goldschmidt, C Palache, and M. Peacock, *Neu. Jb. Mineral.* **63**, 1 (1931).
 - [2] A. J. Bradley, *Proc. Phys. Soc. (London)* **52**, 80 (1940).
 - [3] V. Daniel and H. Lipson, *Proc. R. Soc. A* **181**, 368 (1943).
 - [4] V. Daniel and H. Lipson, *R. Soc. London Proc.* **182**, 378 (1944).
 - [5] M. Yoshio, M. Hiroshi, T. Yoshiaki, and H. Shigeo, *Jpn. J. Appl. Phys.* **27**, L361 (1988).
 - [6] M. Riester and H. Böhm, *Z. Kristallgr.* **212**, 506 (1997).
 - [7] R. J. Angel, R. K. McMullan, and C. T. Prewitt, *Am. Mineral.* **76**, 332 (1991).
 - [8] A. Yamamoto and H. Nakazawa, *Acta Crystallogr.* **38**, 79 (1982).
 - [9] A. K. A. Pryde and V. Heine, *Phys. Chem. Miner.* **25**, 603 (1998).
 - [10] Z. Peng, S. Y. Chien, and S. A. Redfern, *J. Phys.: Condens. Matter* **24**, 5826 (2012).
 - [11] R. J. Hemley, A. P. Jephcoat, H. K. Mao, L. C. Ming, and M. H. Manghnani, *Nature (London)* **334**, 52 (1988).
 - [12] N. Morimoto, *Acta Crystallogr.* **53**, 299 (1979).
 - [13] R. J. Angel, *Amer. Miner.* **92**, 408–411 (2007).
 - [14] E. Brouns, J. W. Visser, and P. M. D. Wolff, *Acta Crystallogr.* **17**, 614 (1964).
 - [15] M. I. McMahon and R. J. Nelmes, *Chem. Soc. Rev.* **35**, 943 (2006).
 - [16] H. Nagara, K. Mukose, T. Ishikawa, M. Geshi, and N. Suzuki, *J. Phys.: Conf. Ser.* **215**, 012107 (2010).
 - [17] P. Li, G. Gao, and Y. Ma, *J. Chem. Phys.* **137**, 2840 (2012).
 - [18] D. Duan, Y. Liu, Y. Ma, Z. Liu, T. Cui, B. Liu, and G. Zou, *Phys. Rev. B* **76**, 104113 (2007).
 - [19] T. Kenichi, S. Kyoko, F. Hiroshi, and O. Mitsuko, *Nature (London)* **423**, 971 (2003).

- [20] C. Hejny, L. F. Lundegaard, S. Falconi, M. I. McMahon, and M. Hanfland, *Phys. Rev. B* **71**, 020101(R) (2005).
- [21] O. Degtyareva, E. Gregoryanz, H. K. Mao, and R. J. Hemley, *High Press. Res.* **25**, 17 (2005).
- [22] M. I. McMahon, C. Hejny, J. S. Loveday, L. F. Lundegaard, and M. Hanfland, *Phys. Rev. B* **70**, 054101 (2004).
- [23] C. Hejny and M. I. McMahon, *Phys. Rev. B* **70**, 184109 (2004).
- [24] C. Hejny and M. I. McMahon, *Phys. Rev. Lett.* **91**, 215502 (2003).
- [25] I. Loa, M. I. McMahon, and A. Bosak, *Phys. Rev. Lett.* **102**, 035501 (2009).
- [26] S. Lidin, V. Petricek, L. Stenberg, S. Furuseth, H. Fjellvåg, and A. K. Larsson, *Acta Crystallogr.* **45**, 33 (1989).
- [27] U. K. Rößler, *J. Phys.: Conf. Ser.* **391**, 012104 (2012).
- [28] A. Majumdar, J. S. Tse, and Y. Yao, *Angew. Chem., Int. Ed.* **56**, 11390 (2017).
- [29] Y. Yao and J. S. Tse, *Chem.: Eur. J. A* **24**, 1769 (2018).
- [30] R. Akashi, W. Sano, R. Arita, and S. Tsuneyuki, *Phys. Rev. Lett.* **117**, 075503 (2016).
- [31] E. E. Gordon, K. Xu, H. Xiang, A. Bussmann-Holder, R. K. Kremer, A. Simon J. Köhler, and M. Whangbo, *Angew. Chem., Int. Ed.* **55**, 3682 (2016).
- [32] H. Luo, K. Ghandehari, R. G. Greene, A. L. Ruoff, S. S. Trail, and F. J. Disalvo, *Phys. Rev. B* **52**, 7058 (1995).
- [33] C. Narayana, V. J. Nesamony, and A. L. Ruoff, *Phys. Rev. B* **56**, 14338 (1997).
- [34] C. Narayana, V. J. Nesamony, and A. L. Ruoff, in American Physical Society, Annual March Meeting, March 17-21, 1997, abstract id. R26.03.
- [35] C. Narayana, V. Nesamony, and A. L. Ruoff, *Rev. High Press. Sci. Technol.* **7**, 322 (1998).
- [36] C. Bocchi, A. Catellani, F. Germini, L. Nasi, J. K. Morrod, K. A. Prior, and G. Calestani, *Phys. Rev. B* **79**, 235310 (2009).
- [37] R. W. G. Wyckoff, American Chemical Society Monograph Series, 2nd edition (Chemical Catalog Co., New York, 1931), p. 497.
- [38] C. M. I. Okoye, *J. Phys.: Condens. Matter* **39**, 5 (2004).
- [39] G. A. Jeffrey, G. S. Parry, and R. L. Mozzi, *J. Chem. Phys.* **25**, 1024 (1956).
- [40] R. M. Hazen and L. W. Finger, *J. Appl. Phys.* **59**, 3728 (1986).
- [41] Y. Li, Y. Ma, T. Cui, Y. Yan, and G. Zou, *Appl. Phys. Lett.* **92**, 101907 (2008).
- [42] A. Muñoz, P. Rodríguez-Hernández, and A. Mujica, *Phys. Status Solidi(b)* **198**, 439 (1996).
- [43] G. P. Srivastava, H. M. Tütüncü, and N. Günhan, *Phys. Rev. B* **70**, 085206 (2004).
- [44] A. Munoz, P. Rodriguez-Hernandez, and A. Mujica, *Phys. Rev. B* **54**, 11861 (1996).
- [45] S. Dabhi, V. Mankad, and P. K. Jha, *J. Alloys Compd.* **617**, 905 (2014).
- [46] E. Staritzky, *Anal. Chem.* **28**, 915 (1956).
- [47] V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente* (J. Dybwad, Oslo, 1927).
- [48] W. M. Yim, J. P. Dismukes, E. J. Stofko, and R. J. Paff, *J. Phys. Chem. Solids* **33**, 501 (1972).
- [49] Y. Wang, J. Lv, L. Zhu, and Y. Ma, *Phys. Rev. B* **82**, 094116 (2010).
- [50] Y. Wang, J. Lv, Z. Li, and Y. Ma, *Comput. Phys. Commun.* **183**, 2063 (2012).
- [51] J. Lv, Y. Wang, L. Zhu, and Y. Ma, *Phys. Rev. Lett.* **106**, 015503 (2011).
- [52] X. Feng, S. Lu, C. J. Pickard, H. Liu, S. A. T. Redfern, and Y. Ma, *Commun. Chem.* **1**, 85 (2018).
- [53] Y. Li, X. Feng, H. Liu, J. Hao, S. A. T. Redfern, W. Lei, D. Liu, and Y. Ma, *Nat. Commun.* **9**, 722 (2018).
- [54] J. Zhang, J. Lv, H. Li, X. Feng, C. Lu, S. A. T. Redfern, H. Liu, C. Chen, and Y. Ma, *Phys. Rev. Lett.* **121**, 255703 (2018).
- [55] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [56] W. Dong, G. Kresse, J. Furthmüller, and J. Hafner, *Phys. Rev. B: Condens. Matter* **54**, 2157 (1996).
- [57] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [58] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [59] P. Giannozzi, *J. Phys.: Condens. Matter* **21**, 395502 (2009).