ORIGINAL PAPER

physica status solidi b

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Bain Deformation Mechanism and Lifshitz Transition in Magnesium under High Pressure

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HPSTAR 1155-2021

The body-centered cubic (bcc) to face-centered cubic (fcc) phase transition of magnesium is explained by Bain deformation using first-principles calculations. It is shown that the bcc structure transforms into the fcc structure at a pressure of 489 GPa. The electronic band structure of the bcc structure exhibits the Lifshitz transition. The projected density of states of the bcc structure displays the s–d hybridization near the Fermi energy under high pressure. This remarkable structural feature shows the unique pathway leading to a common bcc–fcc Bain deformation mechanism among alkaline-earth metals.

1. Introduction

The phase transitions of alkaline-earth metals (AEMs) under extreme pressure have revealed orbital electron transfer from low- to high-pressure phases.[1] The electrons are anticipated to play an important role in describing the electronic structures of AEMs. Calculations in terms of structural energy differences have revealed a hexagonal close-packed (hcp) structure of magnesium (Mg).[1] The crystal structure of Mg has been observed at high pressure by using energy-dispersive X-ray diffraction (XRD) at room temperature, with it transforming into the body-centered cubic (bcc) structure at ≈50 GPa.[2]

Moriarty and McMahan[3] predicted the conditions with which the hcp structure of Mg transformed into the bcc structure and then transformed into the face-centered cubic (fcc) structure by linear muffin-tin orbital calculations. In addition, Errandonea et al.[4] revealed the behavior of Mg using in situ energy-dispersive XRD in a multianvil apparatus. The results of the experimental observations indicated that the hcp structure transformed to a double hexagonal close-packed (dhcp) structure above 9.6 GPa, with no hcp to bcc transition found. Moreover, Li et al.[5] extensively explored crystal prediction evidence of the fcc structure for Mg at 456 GPa. To investigate the possibility of the stabilized fcc structure, the high-pressure phase transitions of Mg were considered by Yao and Klug,[6] who explored the characterized phase-transition mechanisms of the dhcp transition, as well as the stabilized fcc structure, by first-principles calculations. The calculations indicated that the bcc structure transformed into the fcc structure above 450 GPa.

Recently, the phase diagram of Mg has been investigated using a combination of XRD and resistive and laser heating[7] at high temperatures and pressures ranging from 211 GPa at 300 K to 105 GPa at 4500 K. It was also reported that the hcp structure transformed to the bcc structure at ≈45 GPa.[7] The melting of Mg has been investigated in the bcc structure by density functional theory.[8] The calculations predicted that the maximum melting temperature and pressure of the bcc structure are ≈4500 K and 300 GPa, respectively.

Several AMEs have been investigated under high pressure for metallization, including Ca, Sr, and Ba. Ca possesses a high superconductivity temperature of 29 K under a pressure of 216 GPa[9] and also has the highest superconducting critical temperature among metal elements. In the case of Mg, the high-pressure phase of Mg has revealed that the fcc structure remained metallic[5] and it is thus anticipated that Mg could transform to a superconducting phase at very high pressure.

The structural phase transitions in AEMs have been previously investigated. A theoretical study of Sr,[10] as indicated by the screened exchange local density approximation, was able to predict the transition nature of Sr and in turn reported agreement with experimental observations. Moreover, the structures in

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DOI: 10.1002/pssb.202000279

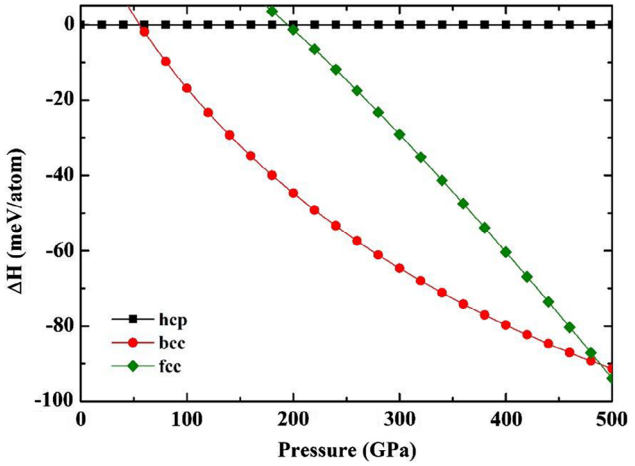

Figure 1. Calculated enthalpies for Mg in the pressure range of 0–500 GPa. The enthalpies of the hcp structure are taken as references.

AEMs can be attributed to the possibility of being able to examine the stable structure through the energy of valence states. The stable structure of Ca[11] has been examined by the full-potential linear muffin-tin orbital method. It was shown that the reduced volume of the simple cubic structure gradually tends to render the valence states increasingly inhabited. The Burgers mechanism and Bain deformation in AEMs have been investigated for structural phase transitions,[12] where a simple structural transformation was found through an intermediate structure. For Bain deformation, the fcc–bcc reverse Bain deformation referred to the fcc structure transformed into the bcc structure through the body-centered tetragonal (bct) structure. In addition, Sr was examined in terms of the fcc–bcc transition by the fcc–bcc reverse Bain deformation mechanism at 3.5 GPa through the bct structure. Notably, the phase transition of Ba possesses the hcp–bcc transition.[13] The transformation is described through the Burgers mechanism, where the hcp structure transformed into bcc structure by the Cmcm intermediate Burgers path.

Accordingly, Mg has been reported to undergo a bcc to fcc transformation above 450 GPa. There are several questions for investigations for Mg under extreme compression, namely, could it be transformed through the Bain deformation mechanism under high pressure? And how does the electronic topological transition (ETT) evolve after applying pressure? In this work, we attempt to address these questions. Moreover, we also report a theoretical investigation of the bcc to fcc transformation by considering Bain deformation and the ETT under high pressure.

2. Computational Details

We present calculation details that successfully work for metals.[14–16] Phase stabilities were determined by the enthalpy. This is because the calculations were considered at 0 K, indicating that the entropy contributions were neglected. Electronic structures were performed by the generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA-PBE) of the exchange-correlation functional.[17] We used the projector augmented wave (PAW) method,[18] as implemented in the Vienna ab initio simulation package (VASP).[19] The PAW potential with ten electrons ($2s^2 2p^6 3s^2$) for Mg was used. Plane waves

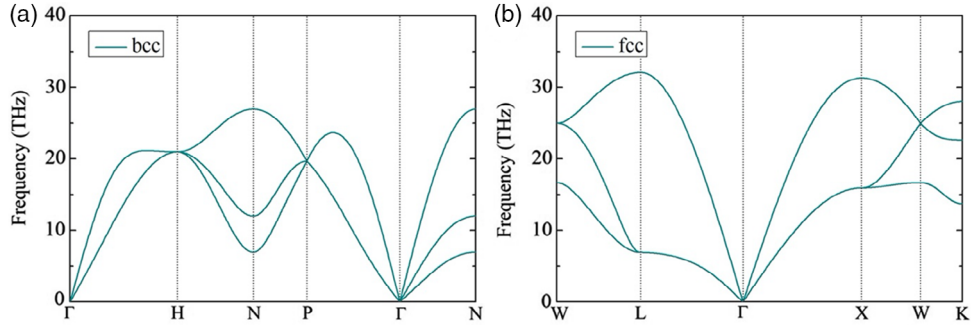

Figure 2. Calculated phonon dispersions of a) bcc structure at 300 GPa and b) fcc structure at 500 GPa.

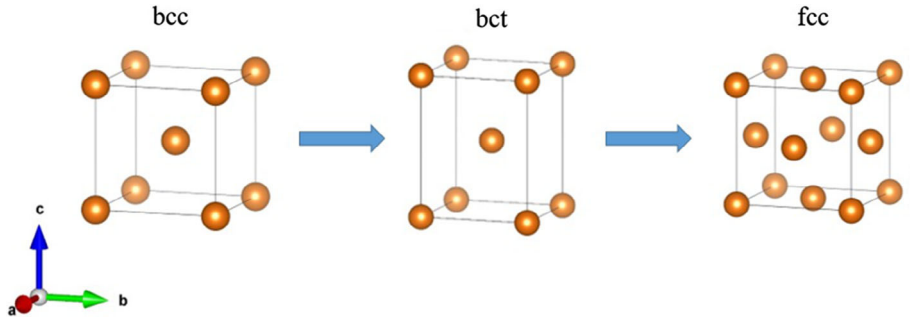

Figure 3. Structural relation for the bcc–fcc transition path through the bct structure.

with a cutoff energy of 600 eV were used. A pseudocore radius of 1.70 bohr was used, which is small enough to ensure that the overlap of spheres does not occur. An $18 \times 18 \times 10$ k-point mesh was used for the hcp structure and an $18 \times 18 \times 18$ k-point mesh for the bcc and fcc structures. All the structural parameters were fully relaxed using the Methfessel–Paxton smearing method. All structures were relaxed using a conjugate gradient scheme. All the considered structures were relaxed at each pressure until the Hellman–Feynman forces became less than 10^{-3} eV Å^{-1}. The phonon calculations were performed by the PHONOPY code.[20] All structures were relaxed and their equations of state were obtained by fitting the calculated energy–volume data to the third-order Birch–Murnaghan equation. The bcc structure for the electronic band structure and density of states (DOS) calculations were accomplished using the GGA-PBE method. The DOS calculations of the bcc structure were performed by the tetrahedron method.

3. Results and Discussion

The structural phase transformation is calculated by the static enthalpies ($T = 0$ K). The enthalpies of the most energetically competitive structures are compared over the pressure range up to 500 GPa. According to our calculations, the transition sequence with increasing pressure displayed the ambient phase, which in turn transformed into the high-pressure phases. At this point, the hcp structure transformed into the bcc structure at 55 GPa and transformed into the fcc structure at 489 GPa, as shown in **Figure 1**.

Regarding phonon calculations of the bcc and fcc structures, we found that the bcc structure is dynamically stable at 300 GPa because it has no imaginary frequency modes (**Figure 2**a). In addition, we computed the phonons of the fcc structure at 500 GPa. The remarkable result displayed that the fcc structure is dynamically stable (Figure 2b). It is noteworthy that the fcc structure is the stable phase of Mg at very high pressures.

The important feature of the Bain deformation mechanism is duly explained. Henceforth, our calculations examined the bct structure for an explanation regarding the Bain deformation (**Figure 3**). The bcc structure transformed into the fcc structure through the bct structure because it is the intermediate structure. The results manifest that the Bain deformation of Mg has a similarity in appearance to Ca and Sr[12] but the nature of the pathway is slightly different. The pathway of Ca and Sr is the fcc–bcc reverse Bain deformation mechanism and they are identified from the fcc-Ca to bcc-Ca transition and also the fcc-Sr to bcc-Sr transition under high pressure. Here, the case of Mg is represented by the bcc–fcc Bain deformation mechanism. Likewise, the calculation has shown that the bcc structure transformed into the fcc structure through the bct structure using a specific ratio c/a of the lattice parameters.[12] At this point, the lattice parameters c/a as a function of the pressure are explained by Bain deformation. There is a continuous increase of c/a as a function of pressure of the bcc structure ($c/a = 1$) to the fcc structure ($c/a = 1.41$) and the bcc–fcc Bain deformation mechanism of Mg is compressed up to 500 GPa, as shown in **Figure 4**.

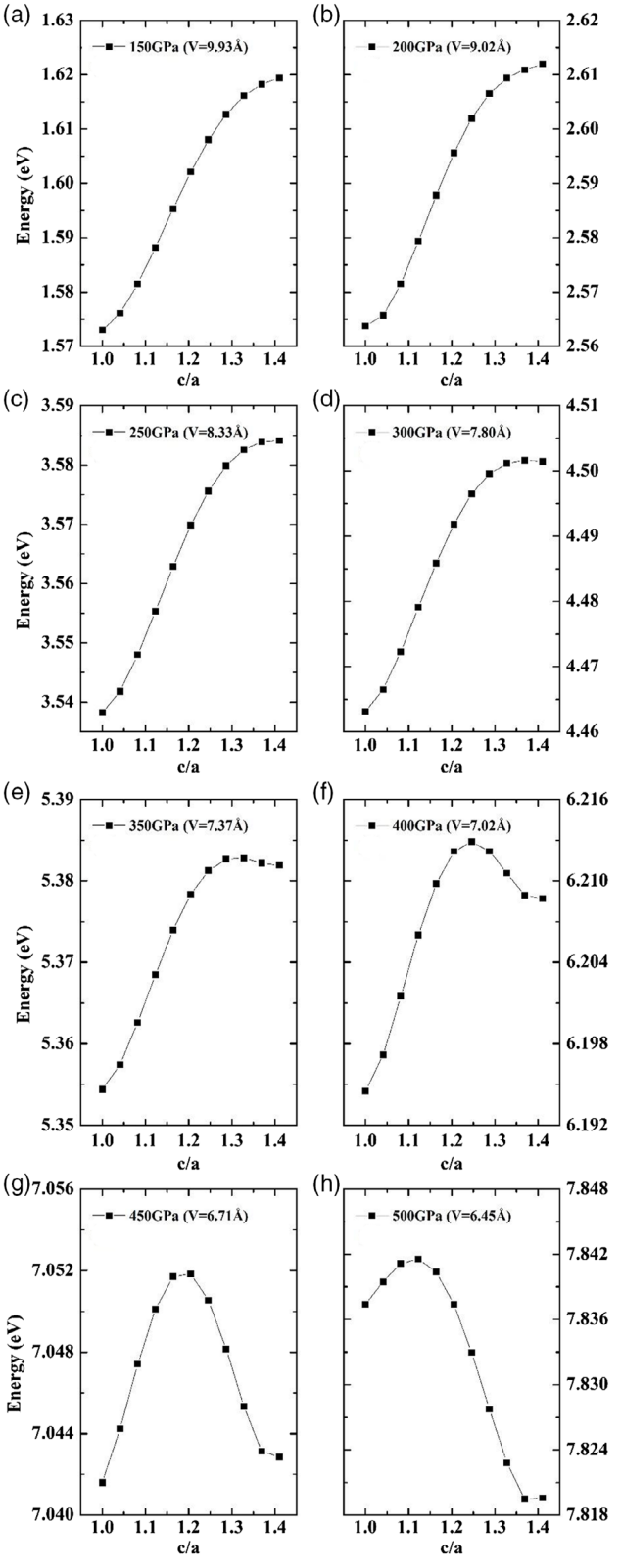

Figure 4. bcc–fcc transition paths through the bct structure and the calculated barriers at a) 150, b) 200, c) 250, d) 300, e) 350, f) 400, g) 450, and h) 500 GPa, respectively.

The transition barriers from the bcc to fcc structure at each pressure are shown in Figure 4. The barriers are 0.046 eV at 150 GPa, 0.048 eV at 200 GPa, 0.045 eV at 250 GPa, 0.038 eV at 300 GPa, 0.028 eV at 350 GPa, 0.018 eV at 400 GPa, 0.010 eV at 450 GPa, and 0.004 eV at 500 GPa. A significant observation is that the calculated barrier decreases from more than 0.010 eV at 450 GPa to ≈0.004 eV at 500 GPa. This suggests that the observation of the bcc–fcc transition can proceed more easily in Bain deformation because the fcc structure is favored at 500 GPa.

The calculated band structure of the bcc structure is shown in **Figure 5**. Accordingly, the band structure along the Γ–H–N is presented on the conduction band. The characterized band shape at the H-point (≈3.63 eV) decreased from 150 to 200 GPa.

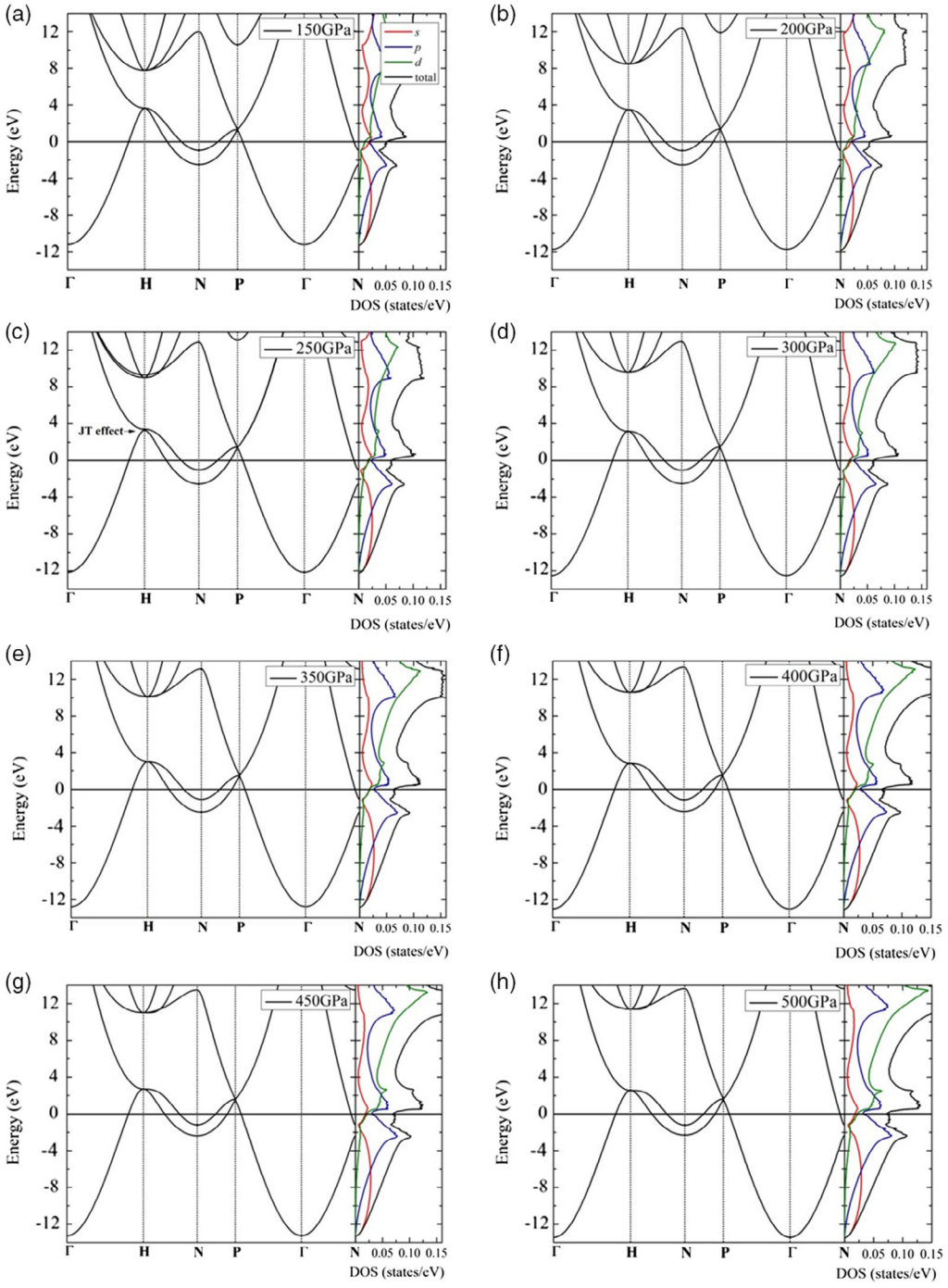

Figure 5. Electronic band structure and projected DOS of bcc structure at a) 150, b) 200, c) 250, d) 300, e) 350, f) 400, g) 450, and h) 500 GPa, respectively.

The remarkable result at 250 GPa revealed that the characterized conduction band exhibited a degenerate band of ≈3.25 eV at the H-point. Typically, this would lead to a Jahn–Teller effect.[21,22] At this point, we believe that it led to the nature of a second-order isostructural phase transition.[23–25] Moreover, the ETT is displayed under high pressure through the characterized band shape. This ETT is called the Lifshitz transition.[26] Thus, the second-order isostructural phase transition is revealed through the Lifshitz transition. Upon an increase in pressure, our results revealed that the characterized conduction band at the H-point displayed a nondegenerate of the band of ≈3.14 eV at 300 GPa. Interestingly, the Lifshitz transition results in the evolution of the conduction band at an H-point at 300 GPa being slightly decreased (increased) from 3.14 eV (9.59 eV) to 2.50 eV (11.40 eV) at 500 GPa.

As shown in Figure 5, we computed the projected density of states (pDOS) of the bcc structure. We found that the characteristic of the pDOS changed with increasing pressure. The analysis of the pDOS showed that there are electrons transferred near the Fermi level with increasing pressure. This indicated that the bcc structure is likely to be expected in the s–d hybridization. It is worth noting that the bcc structure displayed the s-electron transferred into the d-electron from 250 to 500 GPa, leading to the s–d hybridization.[27]

4. Conclusion

In summary, we have studied the structural phase transformation of Mg under high pressure. The calculations revealed the bcc structure transformed into the fcc structure at 489 GPa. We have explored the transition path of the bcc–fcc transformation through the Bain deformation mechanism. The fcc structure is energetically more favorable than the bcc structure at 500 GPa. The electronic band structure has been manifested to exhibit the Jahn–Teller effect at 250 GPa. This phenomenon displays the second-order isostructural phase transformation and it is concluded that the Lifshitz transition is significant for the bcc structure. The DOS of the bcc structure shows that it exhibits s–d hybridization near the Fermi level.

Acknowledgements

The authors gratefully acknowledge the NSC (National Computer Center, Linköping, Sweden) in Sweden for providing computing time and the Thailand Center of Excellence in Physics (ThEP). This research was supported by the Ratchadapisek Somphot Fund for Postdoctoral Fellowships, Chulalongkorn University. This work was partially supported by a Sci Super-IV research grant, Faculty of Science. This research is funded by a Chulalongkorn University Grant for Research and National Research Council of Thailand (NRCT): (NRCT5-RSA63001-04). R.A. and W.L. thank the Swedish Research Council and Swedish Research Links for financial support. The authors are also greatly indebted to the proofreader of this manuscript, Dr. Malay Kumar Das.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

Bain deformation, high pressure, Lifshitz transition, magnesium

Received: May 22, 2020
Revised: October 20, 2020
Published online: November 17, 2020

[1] H. L. Skriver, *Phys. Rev. Lett.* **1982**, *49*, 1768.
[2] H. Olijnyk, W. B. Holzapfel, *Phys. Rev. B* **1985**, *31*, 4682.
[3] J. A. Moriarty, A. K. McMahan, *Phys. Rev. Lett.* **1982**, *48*, 809
[4] D. Errandonea, Y. Meng, D. Häusermann, T. Uchida, *J. Phys.: Condens. Matter* **2003**, *15*, 1277.
[5] P. Li, G. Gao, Y. Wang, Y. Ma, *J. Phys. Chem. C* **2010**, *114*, 21745.
[6] Y. Yao, D. D. Klug, *J. Phys.: Condens. Matter* **2012**, *26*, 26540.
[7] G. W. Stinton, S. G. MacLeod, H. Cynn, D. Errandonea, W. J. Evans, J. E. Proctor, Y. Meng, M. I. McMahon, *Phys. Rev. B* **2014**, *90*, 13410.
[8] Q. J. Hong, A. van de Walle, *Phys. Rev. B* **2019**, *100*, 140102.
[9] M. Sakata, Y. Nakamoto, K. Shimizu, T. Matsuoka, Y. Ohishi, *Phys. Rev. B* **2011**, *83*, 22051.
[10] P. Tsuppayakorn-aek, W. Chaimayo, U. Pinsook, T. Bovornratanaraks, *AIP Adv.* **2015**, *5*, 097202.
[11] R. Ahuja, O. Eriksson, J. M. Wills, B. Johansson, *Phys. Rev. Lett.* **1995**, *75*, 3473.
[12] H. Katzke, P. Tolédano, *Phys. Rev. B* **2007**, *75*, 174103.
[13] T. Kenichi, *Phys. Rev. B* **1994**, *50*, 16238.
[14] C. Cazorla, S. G. MacLeod, D. Errandonea, K. A. Munro, M. I. McMahon, C. Popescu, *J. Phys.: Condens. Matter* **2016**, *28*, 445401.
[15] P. Tsuppayakorn-aek, W. Luo, R. Ahuja, T. Bovornratanaraks, *Sci. Rep.* **2018**, *8*, 3026.
[16] P. Tsuppayakorn-aek, W. Luo, T. Watcharatharapong, R. Ahuja, T. Bovornratanaraks, *Sci. Rep.* **2018**, *8*, 5278.
[17] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
[18] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953.
[19] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.
[20] A. Togo, F. Oba, I. Tanaka, *Phys. Rev. B* **2008**, *78*, 134106.
[21] J. B. Neaton, N. W. Ashcroft, *Nature* **1999**, *400*, 141.
[22] S. Lee, R. Hoffmann, *J. Am. Chem. Soc.* **2002**, *124*, 4811.
[23] L. Bellaiche, K. Kunc, J. M. Besson, *Phys. Rev. B* **1996**, *54*, 8945.
[24] A. L. J. Pereira, J. A. Sans, R. Vilaplana, O. Gomis, F. J. Manjón, P. Rodríguez-Hernández, A. Muñoz, C. Popescu, A. Beltrán, *J. Phys. Chem. C* **2014**, *118*, 23189.
[25] A. L. J. Pereira, O. Gomis, J. A. Sans, J. Contreras-García, F. J. Manjón, P. Rodríguez-Hernández, A. Muñoz, A. Beltrán, *Phys. Rev. B* **2016**, *93*, 224111.
[26] I. M. Lifshitz, *Sov. Phys. JEPT* **1960**, *11*, 1130.
[27] U. Häussermann, K. Söderberg, R. Norrestam, *J. Am. Chem. Soc.* **2002**, *124*, 15359.