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First Principles Investigation of Electronic Property and High Pressure Phase Stability of SmN

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An investigation of electronic property and high pressure phase stability of SmN has been conducted using first principles calculations based on density functional theory. The electronic properties of SmN show a striking feature of a half metal, the majority-spin electrons are metallic and the minority-spin electrons are semiconducting. It was found that SmN undergoes a pressure-induced phase transition from NaCl-type (B1) to CsCl-type structure (B2) at 117 GPa. The elastic constants of SmN satisfy Born conditions at ambient pressure, indicating that B1 phase of SmN is mechanically stable at 0 GPa. The result of phonon spectra shows that B1 structure is dynamically stable at ambient pressure, which agrees with the conclusion derived from the elastic constants.

Key words: First principles calculation, Electronic property, Phase stability, Elastic constants

I. INTRODUCTION

Anomalous physical properties of the rare-earth nitrides (RE-Ns) have attracted numerous attentions for several decades. The emergence of the spintronics field provides new interest in this class of materials because of their unique magnetic and electronic properties [1, 2].

There have been a lot of theoretical and experimental studies on the electronic structures of the RE-Ns. Aerts *et al.* systematically studied the electronic structures of the RE-Ns using *ab initio* self-interaction corrected local spin density approximation (LSDA), results showed that these materials had a broad range of electronic properties including forming a various class of half-metallic magnets [3]. Preston *et al.* investigated the electronic structures of DyN and SmN using LSDA+*U* method, results showed that the band gap of SmN was zero [4]. Larson *et al.* investigated the electronic structures of the RE-Ns in B1 structure using density functional theory calculations within the LSDA+*U* method and found that the early members of the RE-Ns before GdN (with the exception of NdN) are half-metals, while the later members after GdN have a small indirect gap [5].

SmN is reported to be antiferromagnetic with a very small net moment below 25 K, which is the earliest magnetic investigation of SmN [6]. Subsequently, a neutron scattering study suggested a ferromagnetic phase with near cancellation between the spin and orbital moment

[7]. Very recently, Anton *et al.* experimentally and theoretically investigated spin/orbit magnetic property. Their results show that SmN is ferromagnetic with its net magnetic moment of 0.03 μ_B per formula unit [8]. The near-zero moment is a result of the nearly equal and opposing spin and orbital moments in the ground state of Sm^{3+} ion.

The pressure-induced structure transition of the RE-Ns has been an interesting topic for the last two decades. Vaitheeswaran *et al.* investigated the structural phase stability of LaN, and it was predicted that LaN undergoes a transition from B1 to B2 structure at 27 GPa [9]. CeN was theoretically predicted to transform from B1 to B₂ structure at 62 GPa [10]. The structural and elastic properties of CeN and TbN under high pressure have been investigated using two body inter ionic potential theory, result showed that CeN and TbN exhibited a structural phase transition from B1 to B2 structure at 88 and 136 GPa, respectively [11]. The pressure-induced structure transformation of PmN was studied using first-principles tight-binding linear muffin-tin orbital method, and it was predicted a structural phase transformation from B1 to B2 structure at 3.4 GPa [12]. Jakobsen *et al.* experimentally and theoretically investigated high pressure behavior of TbN [13]. Ciftci *et al.* theoretically investigated the elastic and thermodynamic properties of LaN [14]. Hao *et al.* studied the elastic properties of NdN using first-principles calculations [15]. Elastic properties and hardness of lanthanide nitrides in B1 structure were investigated using first-principles calculations [16, 17]. The result reveals that the ligand field stabilization energy and lanthanide contraction play an important role in d-

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etermining the hardness of lanthanide nitrides in B1 structure.

To the best of our knowledge, the pressure-induced structure transition of SmN has not been investigated up to now. In this work, we discuss the electronic property and high pressure phase stability of SmN.

II. COMPUTATIONAL DETAILS

The calculations were performed using the plane-wave pseudopotential method as implemented in the CASTEP code [18]. For all calculations in the present work, the norm-conserving pseudopotential was employed to model the ion-electron interaction. The exchange-correlation functional was treated by the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [19]. The energy cutoff of the plane-wave basis was set to 770 eV. Integration in the Brillouin zone was performed using the Monkhorst method with $4 \times 4 \times 4$ [20]. The chosen plane-wave cutoff and numbers of k points were carefully checked to ensure good convergence.

The self-consistent convergence accuracy was set to be 5.0×10^{-6} eV/atom. The convergence criterion for the maximal force between atoms was 0.01 eV/Å. The maximum displacement was 5.0×10^{-4} Å, and the stress was set to be 0.02 GPa. For a given external hydrostatic pressure, lattice constants and internal coordination were fully relaxed.

III. RESULTS AND DISCUSSION

A. Electronic property

SmN is a strongly correlated system with 4f electrons. 4f bands are generally very narrow, which significantly differs from the bands dominated by s, p, and d states. Therefore there exist strong on-site Coulomb repulsions among the highly localized f electrons [21]. In the process of electronic structure calculations, the GGA+ U ($U=6.0$ eV) method is used to correct the strong on-site Coulomb repulsion of Sm 4f states.

We have carried out spin-polarized electronic structure calculations of SmN in B1 structure. The result is shown in Fig.1. It can be seen that an overlap of the majority-spin bands and an energy gap of 0.9 eV of the minority-spin bands coexist at Fermi level, indicating that SmN is a half metal. A striking feature of a half metal is that the minority-spin band structure has a semiconductor gap straddling the Fermi level, whereas the majority-spin band structure has metallic intersections [22]. Our results are in good agreement with those of Aerts *et al.* [3] and Larson *et al.* [5].

Figure 2 presents the partial density of states (DOS) of SmN in B1 structure. Just below the Fermi level E_F , the bands are predominantly due to N2p states with

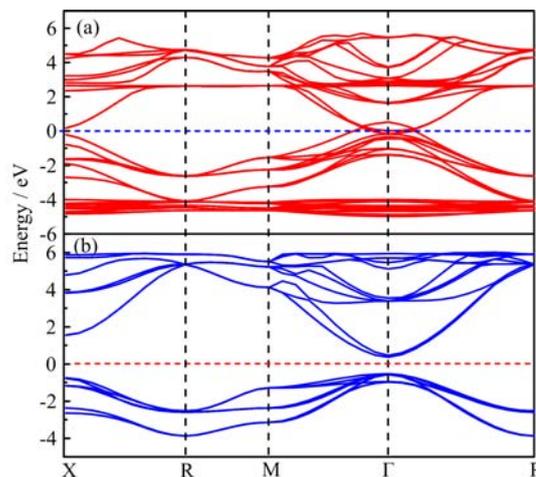


FIG. 1 Band structures of SmN in B1 structure. (a) Majority-spin states and (b) minority-spin states.

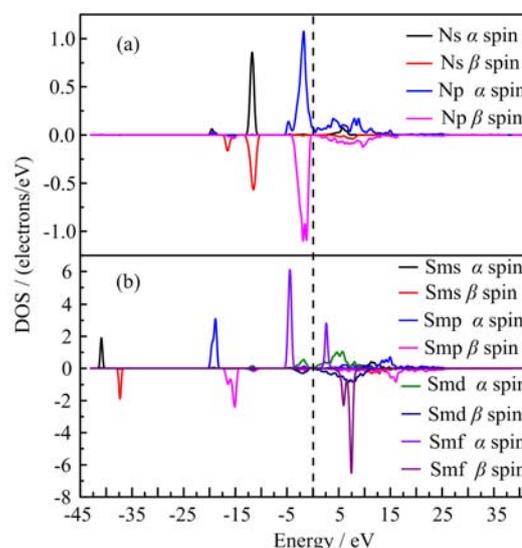


FIG. 2 Partial density of states of SmN in B1 structure. (a) N atom and (b) Sm atom. The vertical dash line at zero indicates Fermi level.

a substantial hybridization with Sm 5d and 4f states. Sm4f majority-spin electrons create an exchange field that leads to a N2p small spin splitting of 0.2 eV [23]. Above E_F are mainly Sm p-f states with a substantial hybridization with N s and p states. It was found that p-f hybridized states play a main role in the electronic bonding.

The occupied majority-spin f bands fall below N2p bands and push Sm5p bands lower in energy. The unoccupied majority-spin f bands sit just above E_F . There are two Sm f peaks between 5.0 and 8.0 eV, which are the unoccupied minority-spin bands.

A very large splitting of about 13.0 eV between Sm4f majority-spin and minority-spin states is responsible for the spin magnetic moments. A small spin splitting of

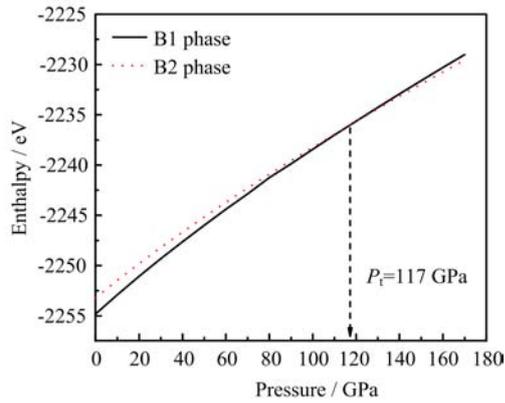


FIG. 3 Calculated enthalpies as a function of pressure for B1 and B2 phases of SmN.

Sm5d states implies that it has a weak contribution to the spin magnetic moments. It is the occupancy of the highly localized 4f states that determines the magnetic properties, while other electronic properties are principally determined by the itinerant s-d electrons [24].

B. High pressure phase stability

Here, we calculated the phase transition pressure of SmN. Our computational approach is based on constant-pressure static quantum mechanical calculations at $T=0$ K. The relative stability of different phases can be deduced from the pressure dependence of the enthalpy instead of the Gibbs free energy [25, 26]. The pressure corresponding to $\Delta H = H - H_{B1}$ approaching zero is the phase transition pressure (P_t). At a pressure higher than the predicted transition pressure, B1 phase becomes thermodynamically unstable while B2 phase becomes thermodynamically stable. The result shows that the transition pressure is 117 GPa, as shown in Fig.3.

C. Elastic constants and phonon spectra

To check the mechanical stability, we calculated the elastic constants of SmN at 0 GPa using the “volume-conserving technique”. The results are presented in Table I. As can be seen from Table I, our result is in reasonable agreement with the previous calculations [16].

The mechanical stability criteria (Born conditions) for a cubic crystal system are given by [27]:

$$C_{11} > 0, \quad C_{44} > 0, \quad C_{11} > |C_{12}|, \quad (C_{11} + 2C_{12}) > 0$$

From Table I, it can be seen that the elastic constants of SmN in B1 structure at 0 GPa satisfy Born conditions, indicating that B1 structure is mechanically stable at 0 GPa. While the elastic constants of B2 structure at

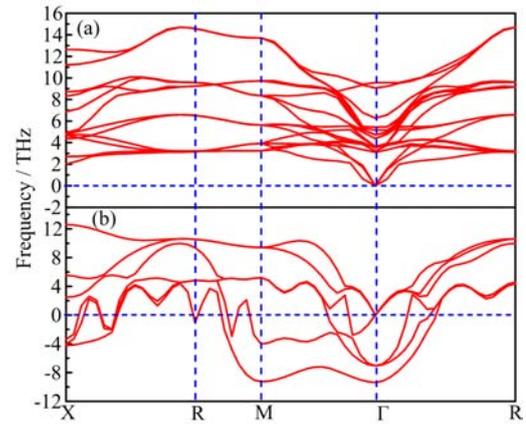


FIG. 4 The phonon spectra of SmN at 0 GPa. (a) B1 structure and (b) B2 structure.

TABLE I Calculated elastic constants C_{ij} (GPa), bulk modulus B (GPa) and shear modulus G (GPa) of SmN at 0 GPa, together with the previous result for comparison.

| Structure | C_{11} | C_{12} | C_{44} | B | G |
|-----------------|----------|----------|----------|-----|-----|
| B1 | 250 | 55 | 82 | 120 | 88 |
| B1 ^a | 216 | 83 | 77 | 127 | 73 |
| B2 | 293 | 15 | -49 | 107 | -41 |

^a These parameters were obtained from Ref.[16].

0 GPa do not satisfy Born conditions, indicating that B2 structure is not mechanically stable at 0 GPa.

To check the dynamic stability, we calculated the phonon spectra of SmN in B1 and B2 structures at 0 GPa. The result is shown in Fig.4. It can be seen from Fig.4(a) that there is not any imaginary frequency in the phonon spectra of SmN in B1 structure at 0 GPa. Therefore, our result shows that B1 structure is dynamically stable, which is in agreement with the result of elastic constants. From Fig.4(b), it can be seen that there are several imaginary frequencies in the phonon spectra of B2 structure, indicating that B2 structure is dynamically unstable at 0 GPa.

IV. CONCLUSION

A computational study of the electronic property and pressure-induced structure transition of SmN is reported. The result of electronic structure shows that an overlap of the majority-spin bands and an energy gap of 0.9 eV of the minority-spin bands coexist at Fermi level, indicating that SmN is a half metal. The result of relative enthalpy versus pressure indicates that SmN undergoes a pressure-induced phase transition from B1 to B2 structure. The transition pressure is determined to be 117 GPa. Our result reveals that the elastic constants of B1 structure satisfy Born conditions, indicating that B1 structure is mechanically stable at 0 GPa.

There is not any imaginary frequency in the phonon spectra of B1 structure, indicating that B1 structure is dynamically stable at 0 GPa. This conclusion is in agreement with that derived from elastic constants.

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- [1] H. Ohno, *Science* **291**, 840 (2001).
- [2] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. Von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, *Science* **294**, 1488 (2001).
- [3] C. M. Aerts, P. Strange, M. Horne, W. M. Temmerman, Z. Szotek, and A. Svane, *Phys. Rev. B* **69**, 045115 (2004).
- [4] A. R. H. Preston, S. Granville, D. H. Housden, B. Ludbrook, B. J. Ruck, H. J. Trodahl, A. Bittar, G. V. M. Williams, J. E. Downes, A. DeMasi, Y. Zhang, K. E. Smith, and W. R. L. Lambrecht, *Phys. Rev. B* **76**, 245120 (2007).
- [5] P. Larson, W. R. L. Lambrecht, A. Chantis, and M. van Schifgaarde, *Phys. Rev. B* **75**, 045114 (2007).
- [6] F. Hulliger, *Handbook on the Physics and Chemistry of Rare Earths*, New York: North-Holland, (1978).
- [7] R. Moon and W. Koehler, *J. Magn. Magn. Mater.* **14**, 265 (1979).
- [8] E. M. Anton, B. J. Ruck, C. Meyer, F. Natali, H. Warring, F. Wilhelm, A. Rogalev, V. N. Antonov, and H. J. Trodahl, *Phys. Rev. B* **87**, 134414 (2013).
- [9] G. Vaitheeswaran, V. Kanchana, and M. Rajagopalan, *Solid State Commun.* **124**, 97 (2002).
- [10] A. Svane, Z. Szotek, W. M. Temmerman, J. L. Lægsgaard, and H. Winter, *J. Phys.: Condens. Matter* **10**, 5309 (1998).
- [11] A. Rukmangad, M. Aynyas, and S. P. Sanyal, *Indian J. Pure Appl. Phys.* **47**, 114 (2009).
- [12] P. Pandit, V. Srivastava, M. Rajagopalan, and S. P. Sanyal, *Physica B* **403**, 4333 (2008).
- [13] J. M. Jakobsen, G. K. H. Madsen, J. E. Jørgensen, J. Staun Olsen, and L. Gerward, *Solid State Commun.* **121**, 447 (2002).
- [14] Y. O. Ciftci, K. Çolakoglu, E. Deligoz, and H. Ozisik, *Mater. Chem. Phys.* **108**, 120 (2008).
- [15] A. Hao, X. Yang, L. Zhang, and Y. Zhu, *J. Phys. Chem. Solid* **74**, 1504 (2013).
- [16] J. Yang, F. Gao, H. Wang, H. Gou, X. Hao, and Z. Li, *Mater. Chem. Phys.* **119**, 499 (2010).
- [17] J. Yang, *Ph.D. Dissertation*, Qinhuangdao: Yanshan University, (2010).
- [18] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne, *Z. Kristallogr.* **220**, 567 (2005).
- [19] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [20] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- [21] P. W. Anderson, *Rev. Mod. Phys.* **50**, 191 (1978).
- [22] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, *Phys. Rev. Lett.* **50**, 2024 (1983).
- [23] V. N. Antonov, B. N. Harmon, A. N. Yaresko, and A. P. Shpak, *Phys. Rev. B* **75**, 184422 (2007).
- [24] J. Jensen and A. R. Mackintosh, *Rare Earth Magnetism*. Oxford: Oxford Science, (1991).
- [25] A. Hao and Y. Zhu, *J. Appl. Phys.* **112**, 023519 (2012).
- [26] Y. Ma, A. R. Oganov, Z. Li, Y. Xie, and J. Kotakoski, *Phys. Rev. Lett.* **102**, 065501 (2009).
- [27] J. Hanies, J. M. Léger, and G. Bocquillon, *Annu. Rev. Mater. Res.* **31**, 1 (2001).