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Isosymmetric phase transitions, ultrahigh ductility, and topological nodal lines in α -Ag₂S

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We report two reversible pressure-induced isosymmetric phase transitions in α -Ag₂S that are accompanied by two compressive anomalies at 7.5 and 16 GPa, respectively. The first transition arises from a sudden and drastic puckering of the wrinkled Ag-S layers, which leads to an anomalous structural softening at high pressure and gives rise to the ultrahigh compressive ductility in α -Ag₂S. The second transition stems from a pressure-driven electronic state crossover from a conventional semiconductor to a topological metal. The band-crossing points near the Fermi energy form a nodal-line structure due to the preservation of the time-reversal and space-inversion symmetries under pressure. Our findings not only reveal the underlying mechanism responsible for the ultrahigh ductility in this class of inorganic semiconductors, but also provide a distinctive member to the growing family of topological metals and semimetals.

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Ductility is one of the hallmark properties of metals arising from the itinerant nature of metallic bonds. In striking contrast to ductile metals that can sustain high plastic strains typically in the range of 5%–100% [1–3], inorganic semiconductors are often brittle as manifested by small deformation strains of 0.1%–0.2% [4,5]. It is therefore rather unexpected that metal-like ductility is observed in α -Ag₂S [6], one of the widely used inorganic semiconductors in a variety of resistance switches [7,8], memory devices [9,10], photocatalysts [11,12], photochemical cells [13,14], and infrared detectors [15,16]. The fracture strains under tension and compression are more than 4% and 50% [6], respectively, marking it as the first known ductile inorganic semiconductor at room temperature. A possible explanation for the observed high ductility was recently proposed, resulting from its structural and chemical bonding features [6,17]. However, it is still puzzling why the plastic strain is so much greater under compression than that under tension, and it is likely that an unidentified mechanism is responsible for such ultrahigh compressive ductility.

In fact, Ag₂S belongs to a large family of silver chalcogenides Ag₂M ($M = S, Se, \text{ and } Te$) that were actively investigated for novel topological properties. For example,

β -Ag₂Te was identified as a topological insulator with gapless Dirac-type surface states [18]. The orthorhombic $Cmce$ – Ag₂S was predicted to be a topological nodal-line semimetal with a single glide symmetry-protected nodal loop [19]. Unfortunately, this phase is yet to be synthesized and the stable α -Ag₂S is just a conventional semiconductor at ambient pressure. Previous works reported that pressure can tune the lattice and electronic structures of different Ag₂S phases away from the pristine states [20,21], and thus it is worth studying whether α -Ag₂S can transform into a topological state at pressures. However, the crystal structures of those high-pressure (HP) phases are still under debate because of the difficulties in structural solutions based on HP diffraction data, calling for more accurate experiments toward this issue.

In this Rapid Communication, we present a comprehensive and multifaceted investigation of the HP behaviors of α -Ag₂S. Our combined experimental and theoretical study reveals that α -Ag₂S undergoes two reversible isosymmetric phase transitions under HP. The first transition results from a sudden and drastic puckering of the zigzagging Ag-S layers, which produces an anomalous structural softening at HP and induces the ultrahigh ductility in α -Ag₂S. At higher pressure, we identify a second transition of completely different origin, which stems from an electronic state crossover from a conventional semiconductor to a topological metal. We report that pressure-induced isosymmetric phase transitions may be correlated with seemingly unrelated properties such as

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FIG. 1. (a) Refined high-pressure XRD patterns for three phases (i.e., I, II, and III) of α -Ag₂S collected at different pressures. The inset of each panel is the crystal structure of the corresponding phase. (b) Refined lattice parameters a , b , c , and β of α -Ag₂S vs pressure. (b) Pressure-volume data of α -Ag₂S fitted to the second Birch-Murnaghan equation of states. The inset is the normalized pressure (F) vs Eulerian strain (f).

ultrahigh ductility and topological nodal-line structures in a single semiconductor.

We performed *in situ* HP synchrotron x-ray diffraction (XRD) measurements for α -Ag₂S to examine its structural evolution under pressures. Experimental details are described in the Supplemental Material (SM) [22] (see also Refs. [23–25] therein). At ambient condition, it adopts a monoclinic $P2_1/c$ structure with refined lattice parameters $a_0 = 4.228$ Å, $b_0 = 6.929$ Å, $c_0 = 9.534$ Å, and $\beta = 125.57^\circ$ (denoted by phase I), in excellent agreement with previous reports [26,27]. As the pressure increases gradually, the phase I transforms into two HP phases (denoted by phase II and III) around 7.5 and 16.0 GPa, respectively (also see Fig. S1 in SM [22]). We attempt to index these XRD patterns using different space groups (e.g., $P2_1/c$, $P2_12_12_1$, and $Pnma$) [20,21], but the best refinements for all these phases are achieved using the same $P2_1/c$ symmetry, suggesting two isosymmetric phase transitions.

The refined lattice parameters (i.e., a , b , c , and β) and cell volume (V) of α -Ag₂S at pressures are presented in Figs. 1(b) and 1(c), respectively. Three distinct compressive

regimes are separated by two lattice anomalies at 7.5 and 16 GPa, respectively. At 7.5 GPa, the anomaly corresponds to a first-order I $\rightarrow$ II phase transition as suggested by the discontinuous jumps in the lattice parameters. At 16 GPa, the II $\rightarrow$ III phase transition is of second-order nature with no indication of discontinuity in the lattice parameters. Upon close inspection, the V , b , and β display a slight but convincing change in their slopes below and above 16 GPa. Moreover, fitting the volume-pressure data to the second-order Birch-Murnaghan equation of states gives distinct bulk moduli of 47(2), 70(6), and 124(9) GPa for the I, II, and III phases, respectively, further confirming the two phase transitions. Interestingly, these structural transitions are reversible and the high-pressure phases cannot exist at ambient pressure (see Fig. S1 in SM [22]). We would like to mention that these transitions in α -Ag₂S are also evidenced by our high-pressure Raman measurements (see Figs. S2–S4 in SM [22]).

To verify these experimental findings, we performed detailed density functional theory (DFT) calculations to explore the structural response of α -Ag₂S under pressure. Computational details are described in the Supplemental Material [22]

FIG. 2. (a) Calculated normalized lattice parameters (a/a_0 , b/b_0 , c/c_0 , and β/β_0) of α -Ag₂S as a function of pressure. Here, V , a , b , c , and β (V_0 , a_0 , b_0 , c_0 , and β_0) are the corresponding values at specific pressures (at zero pressure). The vertical dashed lines mark the transition pressures. (b) Calculated Pugh's modulus ratio vs shear modulus for α -Ag₂S, Cu₂S, Au₂S, and other common materials. The blue and red symbols represent metals and the semiconductor, respectively. (c) Calculated bulk modulus (black) and shear modulus (red) of α -Ag₂S as a function of pressure. (d) Calculated Pugh's modulus ratio (blue) and hardness (green) of α -Ag₂S as a function of pressure.

(see also Refs. [28–33] therein). As shown in Fig. 2(a), our optimized lattice parameters of α -Ag₂S well reproduce the two experimentally identified anomalies at pressures. A more careful analysis of the symmetry indicates that the relaxed α -Ag₂S structures retain the $P2_1/c$ space group across the whole pressure range. Moreover, the relaxed atomic positions also agree with the values obtained from the XRD data (see Table S1 and Fig. S5 in SM [22]). Therefore, our theoretical results completely support the experimentally observed isosymmetric phase transitions.

Applying HP to α -Ag₂S brings about large atomic displacements and volume contractions. However, it is rather surprising that such enormous structural changes are reversible upon decompression. This naturally raises two fundamental questions: (i) Are the phase transitions related to the ultrahigh compressive ductility? (ii) Can the phase transitions lead to novel electronic properties or even the much sought after topological states? Answering both questions requires an in-depth understanding of the pressure-dependent mechanical and electronic properties of the system.

We first investigate the mechanical properties of α -Ag₂S at ambient pressure. Its calculated bulk modulus (96 GPa) is comparable with that of well-known semiconductors such as Si (66 GPa) [34]. However, its shear modulus (26 GPa) is much lower than that of Si (98 GPa), but is very close to that of soft metals such as Ag (29 GPa), Au (49 GPa), and

Cu (27 GPa) [34]. The shear stiffness alone cannot provide a full picture of the highly unusual mechanical properties of this system. The classic Pugh's modulus ratio k (i.e., the ratio of bulk modulus to shear modulus) has been applied extensively to measure the brittle or ductile behavior of materials [35]. Usually, a high (low) k suggests that a material is ductile (brittle) and the widely used critical value is $k = 1.75$, a value that separates typical metals from semiconductors. Figure 2(b) compares the k value of α -Ag₂S with those of various metals and semiconductors [34]. The k of α -Ag₂S at ambient pressure is predicted to be 4.14, which is much larger than those of other semiconductors, but falls well in the typical range of metals. This supports the recent experimental observation that α -Ag₂S exhibits extraordinary metal-like ductility [6]. Therefore, even at ambient pressure, α -Ag₂S already displays highly unusual mechanical properties.

We further evaluate the effect of pressure on the mechanical properties of α -Ag₂S. Calculated bulk and shear moduli at pressures are displayed in Fig. 2(c). As expected, the bulk modulus increases continuously with rising pressures. Small but noticeable variations in the slope of the curve can be observed across the phase transitions. Intriguingly, the shear modulus exhibits an unexpected reduction from 31 to 25 GPa across the I→II phase transition. Because of the strong correlation between shear modulus and hardness [36], the hardness of α -Ag₂S also exhibits an anomalously large dip

FIG. 3. (a) Calculated bulk modulus (black) and shear modulus (red) of Cu₂S as a function of pressure. (b) Calculated Pugh's modulus ratio (blue) and hardness (green) of Cu₂S as a function of pressure. (c) Calculated bulk modulus (black) and shear modulus (red) of Au₂S as a function of pressure. (d) Calculated Pugh's modulus ratio (blue) and hardness (green) of Au₂S as a function of pressure.

around the transition pressure of 7.5 GPa, as shown in Fig. 2(d). Such an anomalous reduction in shear stiffness and hardness ultimately yields the ultrahigh compressive ductility of α -Ag₂S. This is also supported by our calculated k curve that corresponds to an abrupt increase across the I $\rightarrow$ II transition in Fig. 2(d). Therefore, we conclude that the I $\rightarrow$ II phase transition, which triggers the unusual structural softening, in particular the softening of shear stiffness, is responsible for the ultrahigh compressive ductility of α -Ag₂S.

Since Cu and Au are isovalent with Ag, Cu₂S, and Au₂S are expected to exhibit a similar high ductility. In Fig. 2(b), the k values of Cu₂S and Au₂S at ambient pressure are evaluated to be 2.36 and 3.72, respectively, confirming that both possess a metal-like ductility. Recent experiments indicate that Cu₂S undergoes two phase transitions at 3.1 and 7.1 GPa, respectively [37], and we thus predict its HP mechanical properties. As illustrated in Fig. 3(a), the bulk modulus increases continuously from 130 to 190 GPa with pressure rising from 0 to 10 GPa, but the shear modulus shows two softening anomalies across the phase transitions. Such softening in the shear modulus leads to a drastic reduction in the hardness and a sharp rise in the Pugh's modulus ratio, as shown in Fig. 3(b). That is to say, the abrupt softening in shear stiffness and hardness creates the ultrahigh compressive ductility of Cu₂S. Unlike Cu₂S, the experiment shows the absence of a phase transition in Au₂S [38], but it also displays different HP mechanical behaviors. In Fig. 3(c), its bulk modulus increases with rising pressure whereas its shear modulus exhibits an unexpected reduction. This naturally induces an unusual softening in its hardness and thus the ultrahigh ductility under pressures, as shown in Fig. 3(d). In addition, our calculations of elastic constants indicate that Au₂S becomes mechanically unstable above 3 GPa. This well

explains the experimental observation that Au₂S undergoes a pressure-induced amorphization [38].

Although we have established that the I $\rightarrow$ II phase transition is closely related to the ultrahigh ductility of α -Ag₂S through a lattice softening mechanism, a microscopic understanding remains elusive, which we address now. As illustrated by insets in Fig. 1(a), α -Ag₂S can be viewed as a wrinkled layered structure. Two Ag1, two Ag2, and four S atoms constitute the eight-atomic ring fragment. These fragments are linked by Ag-S bonds to form zigzag-shaped layers stacked along the a axis. Obviously, these wrinkled layers can fold easily along the b axis under pressure. As confirmed by our experiment and theory, the b axis is more compressible than the a and c axis. At 7.5 GPa, the wrinkled layers pucker abruptly without changing the underlying symmetry of the structure. As a result, the b axis collapses and becomes significantly more compressible. The collapse of the b axis results in a sudden release of stress, which in turn leads to the lengthening and stiffening of the a and c axis. Therefore, the first transition arises from the sudden puckering of the wrinkled Ag-S layers at 7.5 GPa and is solely structural in nature.

With the above results at hand, the anomalous softening and ultrahigh ductility of α -Ag₂S can be fully understood. At low pressures, the Ag-S wrinkled layers form weak gliding systems with a low barrier against interlayer slippage; thus, it has low shear stiffness. As the pressure is increased, the bulk modulus normally increases monotonically. The shear modulus, however, depends sensitively on the interlayer binding, which is more susceptible to subtle changes to the bonding. The transition at 7.5 GPa increases the interlayer distances and significantly weakens their interaction. This allows the layers to glide more easily, resulting in a sudden decrease in the shear stiffness, and therefore the anomalous structural softening

FIG. 4. Band structures of α -Ag₂S at the pressures of (a) 0 GPa, (b) 10 GPa, and (c) 20 GPa. The Fermi levels are set at 0 eV and shown as horizontal dashed lines. It can be clearly seen that, as the pressure increases, the band gap decreases gradually and then forms an energy-inverted band structure. Two inverted bands, labeled as Γ_1^- and Γ_1^+ , form a band-crossing point near the Fermi energy. The zoomed inset in (c) indicates the two bands do not cross. (d) The nodal points in the three-dimensional Brillouin and its projection on the $k_x = 0$, $k_y = 0$, and $k_z = 0$ planes for α -Ag₂S at a pressure of 20 GPa. (e) Measured electrical resistance of α -Ag₂S as a function of pressure. The vertical dashed lines mark the transition pressures.

and ultrahigh compressive ductility. The II $\rightarrow$ III transition at 16 GPa, however, does not cause significant changes in the mechanical properties of α -Ag₂S. Moreover, the kink at 16 GPa is relatively small [see Fig. 2(a)]. Therefore, the second phase transition likely originates from changes in the electronic structures.

We turn our attention to the effect of pressure on the electronic properties of α -Ag₂S. Figure 4(a) displays its band structure at zero pressure (also see Figs. S6 and S7 in SM [22]), which shows a direct band gap of 0.6 eV at the Γ point. This value is in agreement with available first-principles results [39–42] but smaller than the experimental data (1.03 ± 0.1 eV) [6]. This is expected since the DFT calculations typically underestimate the band gap of semiconductors. We then examine the evolution of the band structure of α -Ag₂S under pressure, which may offer insight into the second phase transition under compression. Figures 4(b) and 4(c) show the band structures of α -Ag₂S calculated at 10 and 20 GPa, respectively. With increasing pressure, the band

structure broadens and the gap decreases gradually. The gap closes at about 14 GPa and the system becomes a metal with an inverted band structure around the Γ point.

We use the band structure calculated at 20 GPa to illustrate the pressure-induced band inversion in α -Ag₂S. The two energy-inverted bands, characterized by Γ_1^- and Γ_1^+ symmetry at the Γ point near the Fermi level, are shown in Fig. 4(c), where the superscripts indicate the opposite parity of the two bands. As the compressed crystal preserves the time-reversal and space-inversion symmetries, the energy-inverted bands with opposite parities form continuous band-crossing points (i.e., nodal lines) in the three-dimensional Brillouin zone [43–45]. Here, we adopt the Wannier-function method [46] to construct a tight-binding model, which is used to search the band-crossing points and to reveal the shape of the nodal lines in α -Ag₂S. Figure 4(d) plots the so-obtained nodal lines for the Γ_1^- and Γ_1^+ bands, which are mainly composed of three closed loops and four separated small rings. The band inversion and the node lines indicate that the topologically

nontrivial surface states can exist on the surface of α -Ag₂S. The details of the nodal lines and surface states are described in the Supplemental Material [22] (see also Ref. [47] therein). It is this electronic state crossover from a conventional semiconductor to a topological metal that is responsible for the second phase transition of α -Ag₂S.

To better probe the electronic response to pressure, we measured the *in situ* electrical resistance of α -Ag₂S up to 32 GPa. The electrical resistance as a function of pressure is shown in Fig. 4(e). As the pressure increases, the electrical resistance decreases. At 7.5 GPa, a discontinuous change in the slope of electrical resistance is observed, which corresponds to the first phase transition. At about 19 GPa, the electrical resistance falls sharply, suggesting that metallization occurs.

In summary, two reversible pressure-induced isosymmetric phase transitions have been identified at 7.5 and 16 GPa, respectively. The first transition arises from an abrupt puckering of the Ag-S layers, which induces an unexpected structural softening and is ultimately responsible for the ultrahigh ductility. The second transition is a manifestation of an electronic state crossover from a conventional semiconductor to a topological metal. In contrast to other semiconductors that are typically brittle, α -Ag₂S exhibits coexisting properties of ultrahigh ductility and sizable semiconducting gap, providing

a promising material for applications in the next-generation flexible and stretchable devices.

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- [1] J. Schiøtz, F. D. Tolla, and K. W. Jacobsen, *Nature (London)* **391**, 561 (1998).
 - [2] L. Lu, X. Chen, X. Huang, and K. Lu, *Science* **323**, 607 (2009).
 - [3] G. I. Taylor, *Proc. R. Soc. London, Ser. A* **145**, 362 (1934).
 - [4] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Materials Properties* (Springer, New York, 2010).
 - [5] D. J. Green, *An Introduction to the Mechanical Properties of Ceramics* (Cambridge University Press, Cambridge, UK, 1998).
 - [6] X. Shi, H. Chen, F. Hao, R. Liu, T. Wang, P. Qiu, U. Burkhardt, Y. Grin, and L. Chen, *Nat. Mater.* **17**, 421 (2018).
 - [7] C. H. Liang, K. Terabe, T. Hasegawa, and M. Aono, *Nanotechnology* **18**, 485202 (2007).
 - [8] Z. Xu, Y. Bando, W. Wang, X. Bai, and D. Golberg, *ACS Nano* **4**, 2515 (2010).
 - [9] A. N. Belov, O. V. Pyatilova, and M. I. Vorobiev, *Adv. Nanopart.* **3**, 1 (2014).
 - [10] R. Peng, Y. Ma, Z. He, B. Huang, L. Kou, and Y. Dai, *Nano Lett.* **19**, 1227 (2019).
 - [11] Y. Xie, S. H. Heo, Y. N. Kim, S. H. Yoo, and S. O. Cho, *Nanotechnology* **21**, 015703 (2010).
 - [12] A. Pourahmad, *Superlattices Microstruct.* **52**, 276 (2012).
 - [13] C. D. Lokhande and S. H. Pawar, *Phys. Status Solidi A* **111**, 17 (1989).
 - [14] X. F. Qian, J. Yin, S. Feng, S. H. Liu, and Z. K. Zhu, *J. Mater. Chem.* **11**, 2504 (2001).
 - [15] Y. Zhang, G. Hong, Y. Zhang, G. Chen, F. Li, H. Dai, and Q. Wan, *ACS Nano* **6**, 3695 (2012).
 - [16] Y. Du, B. Xu, T. Fu, M. Cai, F. Li, Y. Zhang, and Q. Wang, *J. Am. Chem. Soc.* **132**, 1470 (2010).
 - [17] G. Li, Q. An, S. I. Morozov, B. Duan, W. A. Goddard, Q. Zhang, P. Zhai, and G. J. Snyder, *npj Comput. Mater.* **4**, 44 (2018).
 - [18] W. Zhang, R. Yu, W. Feng, Y. Yao, H. Weng, X. Dai, and Z. Fang, *Phys. Rev. Lett.* **106**, 156808 (2011).
 - [19] H. Huang, K. H. Jin, and F. Liu, *Phys. Rev. B* **96**, 115106 (2017).
 - [20] Z. Zhao, H. Wei, and W. L. Mao, *Appl. Phys. Lett.* **108**, 261902 (2016).
 - [21] D. Santamaria-Perez, M. Marques, R. Chulia-Jordan, J. M. Menendez, O. Gomis, J. Ruiz-Fuertes, J. A. Sans, D. Errandonea, and J. M. Recio, *Inorg. Chem.* **51**, 5289 (2012).
 - [22] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.102.140101> for experimental and computational details of α -Ag₂S.
 - [23] H. M. Rietveld, *Acta Cryst.* **22**, 151 (1967).
 - [24] A. C. Larson and R. B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report No. LAUR 86-748 (2004).
 - [25] A. Dewaele, M. Torrent, P. Loubeyre, and M. Mezouar, *Phys. Rev. B* **78**, 104102 (2008).
 - [26] R. Sadanaga and S. Sueno, *Miner. J.* **5**, 124 (1967).
 - [27] S. I. Sadovnikov, A. I. Gusev, A. V. Chukin, and A. A. Rempel, *Phys. Chem. Chem. Phys.* **18**, 4617 (2016).
 - [28] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
 - [29] P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).
 - [30] R. Hill, *Proc. Phys. Soc. A* **65**, 349 (1952).
 - [31] X. Q. Chen, H. Niu, D. Li, and Y. Li, *Intermetallics* **19**, 1275 (2011).
 - [32] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [33] J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
 - [34] H. Niu, X. Q. Chen, P. Liu, W. Xing, X. Cheng, D. Li, and Y. Li, *Sci. Rep.* **2**, 718 (2012).
 - [35] S. F. Pugh, *Philos. Mag.* **45**, 823 (1954).
 - [36] S. H. Jhi, J. Ihm, S. G. Louie, and M. L. Cohen, *Nature (London)* **399**, 132 (1999).

- [37] D. Zimmer, J. Ruiz-Fuertes, W. Morgenroth, A. Friedrich, L. Bayarjargal, E. Haussuhl, D. Santamaria-Perez, S. Frischkorn, V. Milman, and B. Winkler, *Phys. Rev. B* **97**, 134111 (2018).
- [38] D. Santamaria-Perez, D. Daisenberger, J. Ruiz-Fuertes, T. Marqueno, R. Chulia-Jordan, C. Muehle, M. Jansen, P. Rodriguez-Hernandez, A. Munoz, E. R. Johnson, and A. Otero-de-la-Roza, *Chem. Sci.* **10**, 6467 (2019).
- [39] O. Alekperov, Z. Jahangirli, and R. Paucar, *Phys. Status Solidi B* **253**, 2049 (2016).
- [40] O. Alekperov, Z. Jahangirli, R. Paucar, S. Huseynova, N. Abdulzade, A. Nakhmedov, K. Wakita, and N. Mamedov, *Phys. Status Solidi C* **12**, 672 (2015).
- [41] T. B. Nasr, H. Maghraoui-Meherzi, H. B. Abdallah, and R. Bennaceur, *Solid State Sci.* **26**, 65 (2013).
- [42] S. Kashida, N. Watanabe, T. Hasegawa, H. Iida, M. Mori, and S. Savrasov, *Solid State Ionics* **158**, 167 (2003).
- [43] H. Weng, Y. Liang, Q. Xu, R. Yu, Z. Fang, X. Dai, and Y. Kawazoe, *Phys. Rev. B* **92**, 045108 (2015).
- [44] Y. Kim, B. J. Wieder, C. L. Kane, and A. M. Rappe, *Phys. Rev. Lett.* **115**, 036806 (2015).
- [45] R. Yu, H. M. Weng, Z. Fang, X. Dai, and X. Hu, *Phys. Rev. Lett.* **115**, 036807 (2015).
- [46] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, *Rev. Mod. Phys.* **84**, 1419 (2012).
- [47] S. Ryu and Y. Hatsugai, *Phys. Rev. Lett.* **89**, 077002 (2002).