Novel triadius-like N₄ specie of iron nitride compounds under high pressure

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Various nitrogen species in nitrides are fascinating since they often appear with these nitride as superconductors, hard materials, and high-energy density. As a typical complex, though iron nitride has been intensively studied, nitrogen species in the iron–nitrogen (Fe-N) compounds only have been confined to single atom (N) or molecule nitrogen (N₂). Using a structure search method based on the CALYPSO methodology, unexpectedly, we here revealed two new stable high pressure (HP) states at 1:2 and 1:4 compositions with striking nitrogen species. The results show that the proposed FeN₂ stabilizes by a break up of molecule N₂ into a novel planar N₄ unit (P₆/mcm, >228 GPa) while FeN₄ stabilizes by a infinite 1D linear nitrogen chains N∞ (P₆/mcm, >50 GPa; Cmmm, >250 GPa). In the intriguing N₄ specie of P₆/mmc-FeN₄, we find that it possesses three equal N = N covalent bonds and forms a perfect triadius-like configuration being never reported before. This uniqueness gives rise to a set of remarkable properties for the crystal phase: it is identified to have a good mechanical property and a potential for phonon-mediated superconductivity with a Tc of 4–8 K. This discovery puts the Fe-N system into a new class of desirable materials combining advanced mechanical properties and superconductivity.

Nitrogen (N) is the most abundant element in the earth’s atmosphere and is one of the least studied elements regarding the composition of the Earth¹. At standard temperature and pressure (T = 298 K; P = 1 atm), elemental nitrogen is a gas, consisting of diatomic N₂ molecules that are bound by stiff covalent triple bonds. So the molecule is chemically inert and hardly dissociate and not many higher molecular or extended structures are known for nitrogen other than N₂ under normal conditions. Syntheses of useful nitrides with various nitrogen species rely on chemical methods via, e.g., photochemical reaction, electrochemical synthesis²–⁸. A few higher molecular units are known, such as photolytic cyclic N₃⁹–¹⁴, the tetrahedral N₄ molecule⁵, the N₅⁻ anion⁶, and the N₆³⁺ in a crystalline phase of N₆³⁺SbF₆⁻⁷,⁸. Note that, among these units, though the tetrahedral N₄ has been a form of the N₄ unit for synthesis, it is observed as a metastable species with a lifetime exceeding one microsecond.

Besides the chemical methods, in fact, adopting HP technology nitrogen also does form innumerable stable and metastable chemical compounds with various nitrogen species⁹–¹⁷. These nitrogen species have various structural forms ranging from single atom (N) to molecular (N₂, N₃, N₄, N₅, N₆) units and polynitrides¹⁸–²⁹. To note, these stable nitrides have a variety of intriguing properties, such as superconductivity (MoN)²³, high-energy density (LiN₃, NaN₃)²⁴, and high hardness (WN₃)²⁵, as well as extraordinary chemical and thermal stability (Xe-N)²⁶. These nitrides aroused our significant interest in the field of exploring new HP nitrogen species and their potential remarkable properties.

As a typical transition-metal nitride, the Fe-N system is extensively investigated to explore its compounds in the interior layers of earth following its first discovery since 19 century². A rich Fe-N chemistry exists, most synthesized compounds have a Fe/N ratio higher than unity, such as α₉⁻Fe₉₈N₂, α₄⁻Fe₄N, γ⁻Fe₄N, Fe₃N₁₂(x = 0.75–1.4), Fe₃N, Fe₄N, and Fe₅N₄⁴–⁶⁰. Among, the FeN compound is most nitrogen-rich iron nitride reported benign synthesized in a high pressure apparatus thus far⁶¹. This synthesis of FeN spurred the endeavors in search for Fe-N compounds with a more nitrogen content exceeding the FeN compound with other nitrogen species. However, in contrast to the Fe-rich compounds, there is little work on the N-rich iron nitrides, both from the experimental and theoretical sides. Only few theoretical investigations are available to report that an N-rich

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iron nitride (FeN$_2$) crystallizes in the space group $R\bar{3}m$ at 17 GPa (1000 K)$^{15}$ and transforms an orthorhombic $Pnnm$ structure up to 22 GPa$^{12}$ obtained by assuming the parent metal under pressure. All these known Fe–N compounds adapt single N atom or molecule N$_2$ configuration and keep iron 6-coordination.

In order to systematically explore the possibility of obtaining new stable N-rich iron nitrides, and especially to examine the possibility of attaining new nitrogen species at HP, we here present extensive structure searches of stoichiometric Fe–N compounds under various pressures ranging from 0 to 300 GPa, using an unbiased particle swarm optimization (PSO) algorithms for crystal structure predictions$^{18}$. This swarm-intelligence high-throughput searching has proven effective in revealing new compositions favorable to form in large sets of multicomponent Ca-H, Li-B, Xe-N, Cs-N systems$^{16,17,19,20}$. The effectiveness has been also demonstrated by recent successes in predicting high-pressure structures of various systems, and their several experimental confirmations$^{21–30}$. In this work, we proposed new N-rich iron nitrides at 1:4 and 1:2 compositions under HP. Identifying their nitrogen species, it is strikingly found that the nitrogen species evolve from a N$_2$ unit to a novel N$_4$ units, and eventually N\textsuperscript{∞} with the increase of N contents. In N$_i$ unit, we find that it possesses three N = N covalent bonds and one lone pair, which leads it to forms an unknown triadus-like configuration. Its structural uniqueness gives rise to a set of remarkable properties for the crystal $P6_3/mcm$ phase with an unexpectedly T$_c$ of 4–8 K and a good mechanical property.

**Methods**

The developed CALYPSO structure prediction method designed to search for the stable structures of given compounds has been employed for the investigation of phase stability of Fe–N systems in N-rich stoichiometry under HP. We performed structure predictions of stoichiometric Fe$_{1-i}$N$_i$ ($0 < i < 1$) compounds in a pressure range of 0 to 300 GPa. The local structural relaxations and electronic band structure calculations were performed in the framework of density functional theory within the generalized gradient approximation (GGA) and frozen-core all-electron projector-augmented wave (PAW) method$^{31,32}$, as implemented in the VASP code$^{33}$. The PAW pseudopotentials with 3$d^5$4$s^1$ and 2$s^2$$2p^2$ valence electrons were adopted for Fe and N, respectively. The kinetic energy cutoff for the plane-wave basis set is taken as 800 eV and a dense k-point grid with the spacing of $2\pi < 0.03$ Å$^{-1}$ was used to sample the Brillouin zone, which was shown to yield excellent convergence for total energies (within 1 meV/atom). The phonon calculations were carried out by using a finite displacement approach through the PHONOPY code$^{34}$. The electron-phonon coupling (EPC) of $P6_3/mcm$-FeN$_2$ was calculated within the framework of linear response theory through the Quantum-ESPRESSO code$^{35}$. A $2 \times 2 \times 2$ q mesh was used in the interpolation of the force constants for the phonon dispersion curve calculations. A MP grid of $12 \times 12 \times 12$ was used to ensure k-point sampling convergence, which approximates the zero-width limits in the calculations of EPC parameter. Elastic constants were calculated by the strain-stress method and the bulk modulus and shear modulus were thus derived from the Voigt-Reuss-Hill averaging scheme$^{36}$.

**Results and Discussions**

We focused our structure search on the phase stabilities of Fe–N systems in N-rich stoichiometry by calculating the formation enthalpy of various Fe$_{1-i}$N$_i$ ($0 < i < 1$) compounds in a pressure range of 0 to 300 GPa. The formation enthalpy was calculated with respect to the decomposition into FeN and N, as $\Delta h(Fe_{1-i}N_i) = h(Fe_{1-i}N_i) - (1 - i)h(FeN) - (2i - 1)h(N)$, where the enthalpies $h$ for Fe$_{1-i}$N$_i$ and FeN are obtained for the most stable structures as searched by the CALYPSO method at the desired pressures. The convex hulls are depicted in Fig. 1a for pressures at 0, 100, 200 and 300 GPa. The validity of using FeN instead of Fe in defining $\Delta h$ is ensured by the fact that
FeN is exceedingly stable with respect to the binary Fe-N system having a max nitrogen ratio below 50% (Fe₂N, Fe₃N, Fe₄N) under HP, as revealed by our study (Fig. S1) and relative experimental studies⁴⁻⁷,¹⁰. The stable structure of FeN below 50 GPa has space group \(F43m\) structure (Fig. S2, ref. 10). At 50 GPa, the FeN transforms into \(Pnma\) structure (Fig. S3), followed by a cubic \(P2_13\) structure above 150 GPa (Fig. S4). All these FeN structures takes on isolated N atomic sublattice and keeps six-fold coordinated by Fe forming edge-sharing FeN₆ octahedron in their corresponding stable pressure ranges.

Magnetism plays a central role in iron and its compounds. Therefore it is necessary to confirm the role of magnetism on the stability of these Fe-N structures. From our spin-polarized calculations, we find that every Fe atom of Fe-N compounds possesses a magnetic moment of 0.21–1.68 \(\mu_B\) under pressure (<50 GPa), which is substantially lower than that of the pure Fe solid (2.2 \(\mu_B\)). Meanwhile, the magnetic moment will decrease rapidly with increasing pressure and be completely quenched as pressure exceeds 50 GPa. As an example, we performed the energy calculations of FeN after considering magnetism and found that the magnetic effect did not change the phase transition sequence but slightly shifted the phase transition pressure. According to a model derived from a Slater-Pauling type behavior⁵⁻⁷, the magnetization with increasing amount of N becomes decrease in the Fe–N system. It thus is plausible to perform the structure search and enthalpy calculations without considering the magnetic effect under HP in the N-rich Fe–N compounds.

Analysis the convex hull for researching the thermodynamically stable in the Fig. 1a, we can get a main result as follows: at \(P = 0\) GPa, the \(\Delta h\) of all N-rich stoichiometry are positive, meaning that the nitrogen ratio above 50% Fe-N system are not stable. This is consistent with the experimental observation that no Fe-N compound whose the nitrogen content exceeds the iron content can form at ambient pressure; at 100 GPa, stable stoichiometries of FeN₂ and FeN₄ emerge on the convex hull as the most stable stoichiometry, this situation preserves up to 300 GPa. Detailed pressure-composition phase diagram for these two N-rich species is presented in Fig. 1b. Moreover, we performed phonon spectra calculations using the finite-displacement method to assess the dynamical structural stability of their structural phases at desired pressure. No imaginary frequency was found for their structures, which indicated that they are dynamically stable (Figs S5–10).

In the FeN₂ compound, the low pressure crystalline phase is a trigonal \(R-3m\) structure at approximately 22 GPa, above which an orthorhombic \(Pnma\) structure becomes more favorable, consistent with the previous reports¹¹,¹². These two structures both contain a dinitrogen unit and N-sharing six-fold FeN₆ octahedrons (Figs S11,12). Analysis of the dinitrogen unit indicating a strong N-N covalent bond and the dinitrogen unit can be formulated as \(\text{N}_2\) and \(\text{N}_2\) in the \(R-3m\) and \(Pnma\) structures, respectively¹¹,¹². Recently, these phases have been synthesized and verified by the experiment under high pressure and high temperature¹⁰. Upon to 228 GPa, an unknown energetically more favored hexagonal \(P6_3/mcm\) structure was firstly discovered (Fig. 2a). Tracing the volume change of the phase transition from \(Pnma\) to \(P6_3/mcm\), it is found that this transition is a first-order accompanied by a volume drop of 3.5%. Viewing the \(P6_3/mcm\) structure, it contains two types of N...
atoms occupying two different 2c Wyckoff sites as middle \( N_m \) and peripheral \( N_p \) (Fig. 2a): the \( N_m \) atom is shared by four Fe atoms forming a Fe\(_N\) octahedron with Fe-\( N_m \) distances of 1.76 Å, while the \( N_p \) atom bonds with three Fe atoms forming perfect \( N_p \) unit with a bond length of ~1.25 Å (at 300 GPa). These Fe-\( N_m \) distances are shorter than the sum (1.92 Å) of covalent radii of Fe and \( N_m \) atoms. In such 

In the Fe\(_N\) compound, the energetically favored structure of Fe\(_N\) (stable above 50 GPa) has a triclinic structure with a low \( P-1 \) symmetry (Fig. 2b). The nitrogen sublattice in this structure takes on a polyacetylene-like infinite linear chain structure with a closest NN separation (\( N\infty \)) in the range of 1.32 – 1.34 Å. Polyhedral view of the \( P-1 \) structure, it forms octahedrons linked together by the NN bonds of \( N\infty \), with Fe atoms sitting at the center of octahedrons and being 6-fold bonded to the N atoms of \( N\infty \). Up to 250 GPa, a surprising transition from such the 6-fold \( P-1 \) structure to a 8-fold structure takes place. This 8-fold structure adopts a high symmetric orthorhombic \( Cmmm \) structure, which have similar \( \infty \) structural character of the \( P-1 \) phase (Fig. 2c). Analysis of their ELF (Figs S15,16) suggests that the \( N \) atoms of \( N\infty \) are in \( sp^2 \) hybridization, each \( N \) forms two \( \sigma \) bonds with two neighboring \( N \) atoms and one Fe-\( N \) bond. Due to the \( N\infty \) units, the electronic structures of these two phases both exhibit the metal properties (Figs S17,18). Such \( \infty \) units and electronic properties can be also found in works for LiN\(_3\), NaN\(_3\), and CsN\(_3\) under high pressure\(^{39-41}\). For the two phases, their different is that the \( Cmmm \) phase are composed of a Fe 8-coordination decahedrons, in stark contrast with 6-coordination in the octahedrons of \( P-1 \) structure (Fig. 2b,c). Analyses of the coordination number of Fe, we note that conventional coordination chemistry of Fe consists of four-, five-, and six-coordinate metal ions, while coordination numbers higher than six are seldom observed in only discotic molecules\(^{22-24}\). Despite much effort, the Fe atoms are found to be very resistive to become 8-fold coordinate in solids, and the search for solids containing 8-coordinate has so far been scarcely successful. To our knowledge, this is first time to identify the 8-fold coordination of Fe atoms in the Fe-N compounds.

To probe the electronic structures of the \( P6/\overline{m}cm \) structure, we calculated the band structure and density of states (DOS), finding that it exhibit metallic features. A comparison of the band structures of Fe\(_N\), Fe\(_N\) (all Fe atoms removed out of the lattice and a uniform compensated background charge (8e/Fe) is applied to preserve the total valence electrons of the system) is performed (Fig. 4a). The difference between the resultant band structure of a hypothetical Fe\(_N\) system (red dash lines) with the realistic one of Fe\(_N\), indicates that the Fe atoms not only act as electron donors but also bond with N. As shown in Fig. 4b, the DOS reveal that the Fe-\( d \) and \( N \) states are energetically degenerate in the valence bands region, which facilitates the \( Fe-N \) hybridization and the formation of covalent bond. These results offer further support for the ionic and covalent bonding nature of Fe-N bonds as described above. We noted that the large bands crosses the \( E_F \) and the bands appears “flat band-steep band” characteristic\(^{50}\) around the \( E_F \). These are typical features favorable for strong EPC and superconductors. Using the linear response theory, we calculated the phonom DOS (PHDOS), Eliashberg function \( \tau \) (\( \omega \)) and the strength of the \( \omega \)-ph coupling \( \lambda (\omega) \) of the \( P6/\overline{m}cm \) structure (Fig. 4c). The Eliashberg function integrates to \( \lambda = 0.62 \) and gives the logarithmic average ~400 cm\(^{-1}\) , being much closer to the \( \rho_{10} \) Fe-N value of ~430 cm\(^{-1}\). The main contributor to the EPC originates from the mixed Fe-N modes below 1000 cm\(^{-1}\) (85% of \( \lambda \) ) and the high-frequency vibrations from \( N \) units (15% of \( \lambda \) ) (Fig. 4d). Using the Allen-Dynes equation\(^{48}\), with the calculated \( \omega_{\lambda} \) of 643 K and typical \( \mu^* = 0.1-0.15 \), it reveals that the \( P6/\overline{m}cm \) structure is a weak-coupling BCS-type superconductor with a superconducting \( T_c \) of 4-8 K. Moreover, the most commonly known transition-metal pernitrides crystalize can act as hard materials, such as Mn\(_N\) (\( H_N = 19.9 \) GPa), CoN\(_2\) (16.5 GPa), and NiN\(_2\) (15.7 GPa)\(^{52}\). Fe in
Figure 3. (a) The structural feature of N$_4$ unit with Fe in the P6$_3$/mcm-FeN$_2$. (b) The ELF plots (001) of P6$_3$/mcm structure at 250 GPa with an isosurface value of 0.75. (c) The ELF plots of N$_4$ unit in the P6$_3$/mcm structure at 250 GPa. (d) The atomic model for hypothetic N$_4$ cluster with typical symmetry operations marked out. (e) The orbital interaction diagram of a N$_4$ unit with Fe atom.

Figure 4. (a) Electronic band structure and (b) the projected density of states for P6$_3$/mcm-FeN$_2$ structure at 250 GPa, the red dash lines represent the band structure of the N sublattice with a uniform compensated background. (c) The calculated Eliashberg EPC spectral function $\alpha^2 F(\omega)$ and its integral $\lambda(\omega)$ and (d) the projected phonon density of states for P6$_3$/mcm-FeN$_2$ structure at 250 GPa.
the same period as Mn, Co and Ni and the P6/mcm-FeN₄ phase is as a typical transition-metal pernitride, so the P6/mcm-FeN₂ is also regarded as hard material here. We calculated and obtained its mechanical properties including bulk modulus B (341 GPa), shear modulus G (247 GPa), young's modulus Yₑ (597 GPa), and Vicker's hardness (HV = 267 GPa) at ordinary pressure. As expected, the result shows that the P6/mcm-FeN₂ phase exhibits highly incompressible. Bases on a correlation the covalent bond with hardness, we attribute the excellent mechanical properties of this structure to the N₄ units with strong covalent bonds dominantly by providing coulomb repulsion between the nitrogen atoms as a result of charge transfer from Fe.

Conclusion
Using a structure search method based on CALYPSO methodology and density functional total energy calculations, we systematically studied the phase stabilities and the structures of Fe-N systems in the N-rich regime. We identify two stoichiometric FeN and FeN₂ compounds with unexpected structures that might be experimentally synthetizable under pressure. At 1:4 composition, the energetically favored structure stabilizes in a low P-1 symmetry at low pressure and adopts a high symmetric orthorhombic Cmcm structure at high pressure, both having an infinite 1D linear nitrogen chains. Differently, the Cmcm phase has Fe 8-coordination decahedrons, in contrast with Fe 6-coordination in the octahedrons of P-1 structure. At 1:2 composition, an unknown energetically favored hexagonal P6/mcm structure was firstly discovered at above 228 GPa. Structurally, it is intriguing with the appearance of exotic triadis-like N₄ unit. In the N₄ unit, the N₄ atom possesses one lone pair of electrons at its pz orbital and forms three N= N covalent bonds with peripheral N₄ atoms, owing to its sp² hybridization. To probe the electronic structures of the P6/mcm structure, it reveals that its intriguing feature gives rise to a set of remarkable properties with an unexpectedly Tc of 4–8 K and a good mechanical property.

References
1. Zhou, R. & Zeng, X. C. Polymorphic Phases of sp3-Hybridized Carbon under Cold Compression. J. Am. Chem. Soc. 134, 7530–7538 (2012).
2. Tornieporth-Oetting, I. C. & Klapotke, T. M. Covalent Inorganic Azides. Angew. Chem. Int. Ed. 43, 511 (1995).
3. Hansen, N. & Wodtke, A. M. Velocity Map Ion Imaging of Chlorine Azide Photolysis: Evidence for Photolytic Production of C3mimN₂⁺: Angew. Chem., Int. Ed. 41, 3051–3054 (2002).
4. Vij, A., Pavlovich, J. G., Wilson, W. W., Vij, V. & Christe, K. O. Experimental Detection of the Pentaazacyclopentadienide (Pentazolate) Anion, cyclo-N₅⁻: Angew. Chem., Int. Ed. 41, 3051–3054 (2002).
5. Vij, A. et al. Polynitrogen Chemistry. Synthesis, Characterization, and Crystal Structure of Surprisingly Stable Fluoroantimonate Salts of N₅⁻: J. Am. Chem. Soc. 123, 6308–6313 (2001).
6. Vij, A. & Deepak, S. The structure and reactivity of iron nitride complexes. Dalton Trans. 41, 1423–1429 (2012).
7. Suzuki, K., Morita, H., Kaneko, T., Yoshida, H. & Fujimori, H. Crystal structure and magnetic properties of the compound Fe₃N. J. Alloys. Compd. 201, 91–93 (1993).
8. Wessel, M. & Dronskowski, R. A New Phase in the Binary Iron Nitrogen System?—The Prediction of Iron Pernitride, FeN₂. Chem. Eur. J. 17, 2598 (2011).
9. Wang, Z. et al. Polynitrogen Chemistry. Synthesis, Characterization, and Crystal Structure of Surprisingly Stable Fluoroantimonate Salts of N₅⁻: J. Am. Chem. Soc. 123, 6308–6313 (2001).
35. Giannozzi, P. et al. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *J Phys: Condens Mater* **21**, 395052 (2009).
36. Parlinski, K., Li, Z. Q. & Kawazoe, Y. First-Principles Determination of the Soft Mode in Cubic ZrO2, *Phys. Rev. Lett.* **78**, 4063 (1997).
37. Samir, F. M. Chemical bonding and magnetic trends within the iron–nitrogen system. *J. Alloys. Compd.* **345**, 72–76 (2002).
38. Laniel, D. & Dewaele, A. Garbarino, G. High Pressure and High Temperature Synthesis of the Iron Pernitride FeN5, *Inorganic chemistry* **57**, 6245 (2018).
39. Prasad, D. L. V. K., Ashcroft, N. W. & Hoffmann, R. Evolving Structural Diversity and Metallicity in Compressed Lithium Azide. *J. Phys. Chem. C.* **117**, 20838–20846 (2013).
40. Zhu, H. et al. Pressure-induced series of phase transitions in sodium azide. *J. Appl. Phys.* **113**, 033511 (2013).
41. Wang, X., Li, J., Zhu, H., Chen, L. & Lin, H. Polymerization of nitrogen in cesium azide under modest pressure. *J. Chem. Phys.* **141**, 044717 (2014).
42. Patra, A. K. et al. Stable Eight-Coordinate Iron(III) Complexes. *Inorg. Chem.* **49**, 2032–2034 (2010).
43. Seredynuk, M. et al. Homoleptic Iron(II) Complexes with the Ionogenic Ligand 6,6′-Bis(1H-tetrazol-5-yl)-2,2′-bipyridine: Spin Crossover Behavior in a Singular 2D Spin Crossover Coordination Polymer. *Inorg. Chem.* **54**, 7424–7432 (2015).
44. Diebold, A. & Hagen, K. S. Iron(II) Polyamine Chemistry: Variation of Spin State and Coordination Number in Solid State and Solution with Iron(II) Tri(2-pyridylmethyl)amine Complexes. *Inorg. Chem.* **37**, 215–223 (1998).
45. Bu, X.-H. et al. Synthesis, characterization and crystal structures of the cobalt(II) and iron(II) complexes with an octadentate ligand, 1,4,7,10-tetrakis(2-pyridylmethyl)-1,4,7,10-tetraazacyclododecane (L), [ML]2+. *Polyhedron*, **19**, 431–435 (2000).
46. Armentano, D. et al. A novel supramolecular assembly in an iron(III) compound exhibiting magnetic ordering at 70 K. *Chem. Commun.* **211**, 1160–1161 (2004).
47. Boudalai, A. K. et al. A Family of Enneanuclear Iron(II) Single-Molecule Magnets. *Chem. – Eur. J.* **14**, 2514–2526 (2008).
48. Barsukova-Stuckart, M. et al. Polyoxopolypalladates Encapsulating 8-Coordintaed Metal Ions. *Inorg. Chem. – Eur. J.* **13**, 13214–13228 (2012).
49. Tsai, F.-T., Lee, Y.-C., Chiang, M.-H. & Liaw, W.-F. Nitrate-to-Nitrite-to-Nitric Oxide Conversion Modulated by Nitrate-Containing [Fe(NO)3]2 Dinitrosyl Iron Complex (DNIC). *Inorg. Chem.* **52**, 464–473 (2013).
50. Simon, A. Superconductivity and Chemistry. *Angew. Chem. Int. Ed.* **36**, 1788 (1997).
51. Liu, D., Gall, Z. T. Y. & Khare, S. V. Electronic and bonding analysis of hardness in pyrite-type transition-metal pernitrides. *Phys. Rev. B* **90**, 134102 (2014).

**Acknowledgements**

This work is supported by the China National Science Foundation (Grant No. 11604270); the Introduce Talents Start Scientific Research Funds of Southwest Jiaotong University (2017 × 05020); the Sichuan Province, Applied Science and Technology Project (Grant No. 2017Y0056); the Fundamental Research Funds for the Central Universities (2017 × 02012, 2018GF08); the Open Research Fund of Computational Physics Key Laboratory of Sichuan Province, Yibin University (No. 2016H01038, 2016Q3001); the Open Research Fund of Province Science and Technology Project (Grant No. 2017JY0056); the Fundamental Research Funds for the Central Universities (2017 × 02012, 2018GF08); the Open Research Fund of Computational Physics Key Laboratory of Sichuan Province, Yibin University (No. 2016H01038, 2016Q3001); the Open Research Fund of Province state key laboratory cultivation base construction, Inner Mongolia University of Science & Technology (No. 2015H01424).

**Author Contributions**

Yuanzheng Chen wrote the manuscript, Xinyong Cai prepared Figures 1–4. Hongyan Wang, Hongbo Wang, and Hui Wang reviewed the manuscript.

**Additional Information**

**Supplementary information** accompanies this paper at https://doi.org/10.1038/s41598-018-29038-w.

**Competing Interests:** The authors declare no competing interests.

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