Helium-bearing superconductor at high pressure

Jingyu Hou,1,2 Xiao Dong,1 Artem R. Oganov,3 Xiao-Ji Weng,1,2 Chun-Mei Hao,2 Guochun Yang,2 Hui-Tian Wang,4 Xiang-Feng Zhou,4,5,* and Yongjun Tian2

1Key Laboratory of Weak-Light Nonlinear Photonics and School of Physics, Nankai University, Tianjin 300071, China
2State Key Laboratory of Metastable Materials Science and Technology, Key Laboratory for Microstructural Material Physics of Hebei Province, School of Science, and Center for High Pressure Science, Yanshan University, Qinhuangdao 066004, China
3Skolkovo Institute of Science and Technology, Bolshoy Boulevard 30, bld. 1, Moscow 121205, Russia
4National Laboratory of Solid State Microstructures, School of Physics, and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

(Received 11 July 2022; revised 29 November 2022; accepted 1 December 2022; published 12 December 2022)

DOI: 10.1103/PhysRevB.106.L220501

Helium (He) is the most inert noble gas at ambient conditions. It was predicted to adopt a hexagonal close packed structure ($P6_3/mmc$) and remains in the insulating phase up to 32 TPa. In contrast, lithium (Li) is one of the most reactive metals at zero pressure, while its cubic high-pressure phase ($Fd\bar{3}m$) is a weak metallic electride above 475 GPa. Strikingly, computations predict a stable compound of Li$_3$He$_2$ ($R\bar{3}m$) by mixing $Fd\bar{3}m$ Li with $P6_3/mmc$ He above 700 GPa from ab initio evolutionary searches. The presence of helium promotes the lattice transformation from $Fd\bar{3}m$ Li to $Pm\bar{3}m$ Li, and turns the three-dimensional distributed interstitial electrons into the mixture of zero- and two-dimensional anionic electrons. This significantly increases the degree of metallization at the Fermi level; consequently, the coupling of conductive anionic electrons with the Li-dominated vibrations is the key factor to the formation of superconducting electride Li$_3$He$_2$ with a transition temperature up to 26 K, dynamically stable to pressures down to 210 GPa.

The element lithium had attracted much attention because of its complex phase diagram and fascinating properties. Li has a body-centered-cubic (bcc) structure at ambient conditions and is viewed as a simple metal due to the formation of half-filled nearly free-electron band and a nearly spherical Fermi surface [1-4]. Below the pressure of 120 GPa, lithium undergoes a series of symmetry-breaking phase transitions with the sequence bcc $\rightarrow$ fcc $\rightarrow$ $hR1$ $\rightarrow$ $c16$ $\rightarrow$ $oC88$ $\rightarrow$ $oC40$ $\rightarrow$ $oC24$ [2,5,6]. Within this pressure range, the calculated band structures show an unusual electronic transition of metal $\rightarrow$ insulator $\rightarrow$ Dirac semimetal [7,8]. As pressure increases, the interatomic distances of materials generally decrease. The valence and conduction bands are thus expected to broaden, leading to pressure-induced metallization [9]. The abnormal phase transitions for various Li allotropes are mainly due to the distribution of interstitial electrons. Up to $\sim$80 GPa, superconductivity in Li had also been observed while the calculations suggested the semimetallic or even insulating behavior [1,2,10-12] and therefore the mechanism for the emergence of superconductivity in Li is not yet fully resolved.

As lithium’s neighbor in the Periodic Table, owing to the closed-shell electronic structure, helium is the most inert noble gas that generally does not interact with other materials at ambient conditions. Moreover, helium was predicted to remain in the insulating phase up to 32 TPa because of the highest ionization potential ($\sim$25 eV) and zero electron affinity [13]. However, the crystal structures and electronic properties of materials can be significantly tuned by pressure, leading to the formation of various new materials and complex physical behaviors. For instance, small helium atoms occupy voids in structures and thus increase their packing density, which is helpful to the formation of compounds under pressure, e.g., solid van der Waals materials [14-20] or novel ionic compounds [21-24]. Recently, a compound of helium and sodium, Na$_2$He with a fluorite-type structure, was successfully synthesized at pressure above 113 GPa and discovered to be an insulator with electron pairs localized in interstices [9]. Since Li is a member of alkali metals, an interesting question arises, that is, whether there are stable Li-He compounds under pressure and what are their distinguishing properties.

The variable-composition evolutionary algorithm USPEX [25,26] was utilized to predict thermodynamically stable compounds in the Li-He system. At each pressure, we performed structure searches with an unbiased sampling of the entire range of compositions, varying the stoichiometries and their structures simultaneously. To make the prediction more reliable, two independent searches at every single pressure were performed with the number of atoms per primitive cell ranging from 8 to 24 and from 18 to 40, respectively. For each structure search, the first generation was produced randomly and the fittest 60% of the population were given

*xfzhou@ysu.edu.cn; zx888@163.com
all other generations combined add up to \( \sim 3000 \) structures. The total number for variable-composition structure search is \( \sim 24,000 \) at pressures of 250, 500, 800, and 1000 GPa, respectively. Only one stable compound, \( \text{Li}_3\text{He}_2 \), was found in these searches [9,27]. Structure relaxation and electronic property calculations were carried out within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional [28] implemented in the VASP code [29]. We used the projector-augmented wave method [30], with \( 1s^22s^1 \) and \( 1s^2 \) electrons of Li and He, respectively, treated as valence. A plane-wave cutoff energy of 600 eV and uniform \( \Gamma \)-centered \( k \) meshes with a resolution of \( 2\pi \times 0.06 \text{ Å}^{-1} \) were used for structure searching, which were further increased to 900 eV and \( 2\pi \times 0.025 \text{ Å}^{-1} \) to guarantee the total energy converges to better than 1 meV/atom. Phonons and electron-phonon coupling (EPC) coefficients were computed on the \( 7 \times 7 \times 7 \) \( q \)-point meshes via the QUANTUM ESPRESSO package [31]. The Kresse-Joubert projector-augmented wave pseudopotentials [32] were adopted with the cutoff energy of 110 Ry. The 21 \( \times 21 \times 21 \) \( k \)-point meshes in combination with a Methfessel-Paxton smearing [33] of 0.01 Ry are used to calculate the self-consistent electron densities.

In principle, a stable material under pressure has a negative enthalpy of formation with respect to either elemental solids or any other possible compounds. For the structure searches in the Li-He system above 500 GPa, the most stable reactants of \( Fd\overline{3}m \) Li and \( P6_3/mmc \) He are used as pure elements, and thus the enthalpy of formation is defined as

\[
\Delta H = H(\text{Li}_3\text{He}_2) - x H(\text{Li}) - (1 - x)H(\text{He}).
\]

The enthalpy \( H \) is calculated according to \( H = U + PV \), where \( U, P, \) and \( V \) represent the internal energy, pressure, and volume, respectively. The results show \( \text{Li}_3\text{He}_2 \) is stable above \( \sim 778 \) GPa [Fig. S1 and Fig. 1(a)]. If the calculations include the contribution of zero-point energy, the stabilization pressure decreases to \( \sim 700 \) GPa [Fig. 1(a)]. Note that static high pressures above 600 GPa were realized in a laser-heated double-stage diamond anvil cell [34]. Hence \( \text{Li}_3\text{He}_2 \) may be synthesized in future experiments by using similar techniques. The crystal structure of \( \text{Li}_3\text{He}_2 \) belongs to the trigonal crystal system with the space group \( R\overline{3}m \). Its hexagonal form is shown in Fig. 1(e) with the lattice parameters of \( a = \beta = 2.01 \text{ Å} \) and \( c = 12.48 \text{ Å} \) at 800 GPa. The He atoms occupy the crystallographic 6c sites at \((0.000, 0.000, 0.097)\), and the Li atoms occupy 6c sites with coordinates \((0.000, 0.000, 0.607)\), \((0.000, 0.000, 0.800)\) and \(3a\) sites at \((0.000, 0.000, 0.000)\). The sublattice of Li has a simple cubic structure (\( Pm\overline{3}m \)) with the transformation matrix \( \begin{bmatrix} 1 & T & 0 \\ 5 & 5 & 5 \end{bmatrix} \), which matches well with the rhombohedral-centered substructure of He [Fig. 1(c)]. To reveal the origin of thermodynamical stability in \( \text{Li}_3\text{He}_2 \), the evolution of \( \Delta U \) and \( \Delta(PV) \) terms as a function of pressure was plotted in Fig. 1(b). It shows that the value of \( \Delta U \) increases slightly (approximately remaining constant), while \( \Delta(PV) \) dramatically decreases as the pressure increases. The presence of helium increases the packing density, reducing the enthalpy of formation, and results in the formation of \( \text{Li}_3\text{He}_2 \) above \( \sim 700 \) GPa. The next step is to understand which role helium plays in the electronic structure.

Electrides represent a class of exotic compounds where valence electrons reside at interstices of a host structure and behave as anionic quasiatoms, which significantly determines their properties [35,36]. According to the distribution and dimensionality of anionic electrons, electrides can be classified into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) ones [37]. At high pressure, \( Fd\overline{3}m \) Li consists of Li ions arranged in the diamond structure. In this structure, the interstitial electrons and the Li ions form interpenetrating diamond lattices; taking the Li and electron sites together, they form a 3D electrode state with \( \text{Zintl} \) structure (NaTi-type) above 475 GPa [1]. As mentioned above, \( R\overline{3}m \) \( \text{Li}_3\text{He}_2 \) can be formed by mixing \( Fd\overline{3}m \) Li with \( P6_3/mmc \) He above 700 GPa and therefore it is intriguing to study its electronic properties. Interestingly, the sublattice of Li in \( \text{Li}_3\text{He}_2 \) (\( Pm\overline{3}m \)) is also a 3D electrode, in which the interstitial electrons occupy the body center of the lattice and interconnect with each other [Fig. 1(d) and Fig. S2(a)]. However, the sublattice of He in \( \text{Li}_3\text{He}_2 \) alters the number and distribution of interstitial electrons in \( Pm\overline{3}m \) Li, leading to the formation of two inequivalent interstitial quasiatoms (ISQs) which occupy the \( 3b \) sites (termed ISQ1) at \((0.000, 0.000, 0.500)\) and \( 6c \) sites (termed ISQ2) at \((0.000, 0.000, 0.300)\). Here, the centers (positions) of ISQs were determined by the electron localization function (ELF) combined with Bader maxima [38]. The nearest distance of Li-ISQ1-Li and Li-ISQ2-Li are 2.67 Å and 2.41 Å at 800 GPa, whereas the average bond length of Li-Li is 1.43 Å. Based on...
density of Li$_5$He$_2$ with the energy range from $-8.5$ to $-7.0$ eV shows that ISQ1 is mainly responsible for the less dispersive band c. In addition, there are sharp PDOS peaks and strong hybrids within the energy range from $-6.5$ to $-3.0$ eV, implying the major electrostatic interaction between Li 2p states and ISQ1 cage states. All these are related to the cage states of ISQ1, indicating that the localized states of ISQ1 make no contribution to the conductivity of Li$_5$He$_2$. The corresponding Fermi surface is plotted in Fig. 2(e). The band a makes the toroidal and multiterminal tubelike hole pockets (i.e., around the high-symmetry point of F), while band b makes the irregular cage-like electron pockets (e.g., around the high-symmetry point of Z). A good Fermi surface nesting appears in Li$_5$He$_2$ along the Γ → F line with highly dispersive bands along this direction. Therefore, the band structure reveals a good metallicity with large dispersion bands crossing $E_F$ and a relatively flat band in the vicinity of $E_F$ close to the Z point. The coexistence of steep and flat bands near $E_F$ implies a favorable condition for enhancing the formation of Cooper pairs by providing a vanishing Fermi velocity to part of the conduction electrons [39], which is essential to the superconductivity of Li$_5$He$_2$ under pressures [40,41].

The phonon dispersion curves in conjunction with EPC at different pressures were calculated to investigate the dynamical stability and superconductivity of Li$_5$He$_2$. The superconducting transition temperature ($T_c$) was estimated by the Allen-Dynes-modified McMillan equation [42,43]

$$T_c = \frac{\omega_{ph}}{2 \lambda} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right].$$

where $\lambda$ is the EPC strength, $\omega_{ph}$ is the logarithmic average phonon frequency, and $\mu^*$ is the Coulomb pseudopotential parameter. The parameters $\lambda$ and $\omega_{ph}$ are defined as

$$\lambda = 2 \int_0^{\infty} \frac{\omega^2 F(\omega)}{\omega} d\omega$$

and

$$\omega_{ph} = \exp \left[ 2 \int_0^{\infty} \frac{d\omega}{\omega} - \frac{1}{\lambda} \int_0^{\infty} \frac{\omega^2 F(\omega) d\omega}{\omega} \right].$$

respectively. Here a typical value of $\mu^* = 0.1$ was used for the calculation of $T_c$. The absence of imaginary phonon frequencies in the whole Brillouin zone indicates that it is dynamically stable in the pressure range from 210 to at least 1000 GPa (Fig. 3 and Fig. S3). For instance, the calculated $\lambda$ and $\omega_{ph}$ at 800 GPa are 0.48 and 1438 K; thus the predicted $T_c$ contribution to the conductivity of Li$_5$He$_2$. In contrast, the band-decomposed charge density with energy range from $-8.5$ to $-7.0$ eV shows that ISQ1 is mainly responsible for the less dispersive band c. In addition, there are sharp PDOS peaks and strong hybrids within the energy range from $-6.5$ to $-3.0$ eV, implying the major electrostatic interaction between Li 2p states and ISQ1 cage states. All these are related to the cage states of ISQ1, indicating that the localized states of ISQ1 make no contribution to the conductivity of Li$_5$He$_2$. The corresponding Fermi surface is plotted in Fig. 2(e). The band a makes the toroidal and multiterminal tubelike hole pockets (i.e., around the high-symmetry point of F), while band b makes the irregular cage-like electron pockets (e.g., around the high-symmetry point of Z). A good Fermi surface nesting appears in Li$_5$He$_2$ along the Γ → F line with highly dispersive bands along this direction. Therefore, the band structure reveals a good metallicity with large dispersion bands crossing $E_F$ and a relatively flat band in the vicinity of $E_F$ close to the Z point. The coexistence of steep and flat bands near $E_F$ implies a favorable condition for enhancing the formation of Cooper pairs by providing a vanishing Fermi velocity to part of the conduction electrons [39], which is essential to the superconductivity of Li$_5$He$_2$ under pressures [40,41].

The phonon dispersion curves in conjunction with EPC at different pressures were calculated to investigate the dynamical stability and superconductivity of Li$_5$He$_2$. The superconducting transition temperature ($T_c$) was estimated by the Allen-Dynes-modified McMillan equation [42,43]

$$T_c = \frac{\omega_{ph}}{2 \lambda} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right].$$

where $\lambda$ is the EPC strength, $\omega_{ph}$ is the logarithmic average phonon frequency, and $\mu^*$ is the Coulomb pseudopotential parameter. The parameters $\lambda$ and $\omega_{ph}$ are defined as

$$\lambda = 2 \int_0^{\infty} \frac{\omega^2 F(\omega)}{\omega} d\omega$$

and

$$\omega_{ph} = \exp \left[ 2 \int_0^{\infty} \frac{d\omega}{\omega} - \frac{1}{\lambda} \int_0^{\infty} \frac{\omega^2 F(\omega) d\omega}{\omega} \right].$$

respectively. Here a typical value of $\mu^* = 0.1$ was used for the calculation of $T_c$. The absence of imaginary phonon frequencies in the whole Brillouin zone indicates that it is dynamically stable in the pressure range from 210 to at least 1000 GPa (Fig. 3 and Fig. S3). For instance, the calculated $\lambda$ and $\omega_{ph}$ at 800 GPa are 0.48 and 1438 K; thus the predicted $T_c$ contribution to the conductivity of Li$_5$He$_2$. In contrast, the band-decomposed charge density with energy range from $-8.5$ to $-7.0$ eV shows that ISQ1 is mainly responsible for the less dispersive band c. In addition, there are sharp PDOS peaks and strong hybrids within the energy range from $-6.5$ to $-3.0$ eV, implying the major electrostatic interaction between Li 2p states and ISQ1 cage states. All these are related to the cage states of ISQ1, indicating that the localized states of ISQ1 make no contribution to the conductivity of Li$_5$He$_2$. The corresponding Fermi surface is plotted in Fig. 2(e). The band a makes the toroidal and multiterminal tubelike hole pockets (i.e., around the high-symmetry point of F), while band b makes the irregular cage-like electron pockets (e.g., around the high-symmetry point of Z). A good Fermi surface nesting appears in Li$_5$He$_2$ along the Γ → F line with highly dispersive bands along this direction. Therefore, the band structure reveals a good metallicity with large dispersion bands crossing $E_F$ and a relatively flat band in the vicinity of $E_F$ close to the Z point. The coexistence of steep and flat bands near $E_F$ implies a favorable condition for enhancing the formation of Cooper pairs by providing a vanishing Fermi velocity to part of the conduction electrons [39], which is essential to the superconductivity of Li$_5$He$_2$ under pressures [40,41].

The phonon dispersion curves in conjunction with EPC at different pressures were calculated to investigate the dynamical stability and superconductivity of Li$_5$He$_2$. The superconducting transition temperature ($T_c$) was estimated by the Allen-Dynes-modified McMillan equation [42,43]

$$T_c = \frac{\omega_{ph}}{2 \lambda} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right].$$

where $\lambda$ is the EPC strength, $\omega_{ph}$ is the logarithmic average phonon frequency, and $\mu^*$ is the Coulomb pseudopotential parameter. The parameters $\lambda$ and $\omega_{ph}$ are defined as

$$\lambda = 2 \int_0^{\infty} \frac{\omega^2 F(\omega)}{\omega} d\omega$$

and

$$\omega_{ph} = \exp \left[ 2 \int_0^{\infty} \frac{d\omega}{\omega} - \frac{1}{\lambda} \int_0^{\infty} \frac{\omega^2 F(\omega) d\omega}{\omega} \right].$$

respectively. Here a typical value of $\mu^* = 0.1$ was used for the calculation of $T_c$. The absence of imaginary phonon frequencies in the whole Brillouin zone indicates that it is dynamically stable in the pressure range from 210 to at least 1000 GPa (Fig. 3 and Fig. S3). For instance, the calculated $\lambda$ and $\omega_{ph}$ at 800 GPa are 0.48 and 1438 K; thus the predicted $T_c$
The superconducting properties of $R\bar{3}m$ Li$_5$He$_2$ at high pressures. (a)–(c) Phonon dispersion curve, projected phonon DOS, Eliashberg spectral function $\alpha^2 F(\omega)$, and EPC parameter $\lambda$ of Li$_5$He$_2$ at 800 GPa. The area of blue solid circles is proportional to the partial EPC $\lambda_{q,v}$, the logarithmic average phonon frequency $\omega_{\log}$, and the critical temperature $T_c$ were plotted as a function of pressure.

is equal to $\sim$15 K. Note that the values of $T_c$ are decreased as $\mu^*$ is increased (Fig. S4), whereas the $U$-shaped behavior of $T_c$ is reserved [44]. These calculations prove that $R\bar{3}m$ Li$_5$He$_2$ is the phonon-mediated superconducting electrode. By contrast, the superconducting properties of reference phase $Fd\bar{3}m$ Li were also calculated by using the same method at pressures of 600, 800, and 1000 GPa. As shown in Table SII, both the parameters of $\lambda$ and $\omega_{\log}$ of $Fd\bar{3}m$ Li are lower than those of Li$_5$He$_2$ at the corresponding pressures [27]. The predicted $T_c$ of $Fd\bar{3}m$ Li is less than 1 K from 600 to 1000 GPa, indicating it is a very weak superconductor at high pressures. Since helium is the most inert noble gas at ambient conditions, it is very interesting to explore helium’s contribution to the superconductivity of Li$_5$He$_2$ under pressure. As shown in Figs. 3(a)–3(c), the phonon dispersion curves associated with the partial EPC $\lambda_{q,v}$ suggest that almost all the phonon modes contribute to the EPC strength $\lambda$. However, there is also a distinct character in the projected phonon DOS (PHDOS); that is, the Li atoms dominate the vibrations below 1550 cm$^{-1}$, while Li and He contribute to the coupling vibration modes above 1550 cm$^{-1}$. In general, the PHDOS can be divided into two parts: one is the Li-dominated vibrations and the other is the coupled vibrations. According to this definition, these two parts contribute 77% and 23% to the EPC strength $\lambda$, respectively. As pressure is varied, the values of $T_c$ show a nonmonotonic dependence with $T_c$ decreasing from $\sim$26 K at 210 GPa to $\sim$6 K (600 GPa), and then increasing to $\sim$25 K at 1000 GPa. To clarify such unusual superconducting behavior, the pressure-dependent superconducting properties of Li$_5$He$_2$ were plotted in Fig. 3(d). One can see that $\omega_{\log}$ increases rapidly up to 600 GPa and then remains almost a constant, while $\lambda$ shows a similar trend to $T_c$. Based on the PHDOS and Eliashberg phonon spectral function $\alpha^2 F(\omega)$ at different pressures (Fig. S3 and Table I), the contributions to EPC $\lambda$ from the Li-dominated vibrations are $\sim$67% both at 210 GPa and 400 GPa, 68% at 600 GPa, 77% at 800 GPa, and 85% at 1000 GPa, respectively [27]. Obviously, the Li-dominated vibrations play a decisive role in the superconductivity of Li$_5$He$_2$ at high pressures.

In conclusion, the high-pressure phases of the Li-He system were systematically investigated by the ab initio evolutionary searches. We predicted that there is only one stable compound, Li$_5$He$_2$, which is thermodynamically stable above 700 GPa. The first-principle calculations reveal that Li$_5$He$_2$ is an exotic electrode with the coexistence of 0D and 2D anionic electrons. Further EPC calculations identified Li$_5$He$_2$ as a phonon-mediated superconducting electrode with $T_c$ up to 26 K. This prediction establishes a helium-bearing superconductor at high pressure, which greatly enriches the systems and types of superconducting materials.

This work was supported by the National Natural Science Foundation of China (Grants No. 52025026, No. 11874224, and No. 52090020), National Key R&D Program of China (Grant No. 2022YFA1402300), and the Young Elite Scientists Sponsorship Program by Tianjin (Grant No. TJSQNTJ-2018-18). A.R.O. acknowledges funding from the Russian Science Foundation (Grant No. 19-72-30043).

[1] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. 102, 146401 (2009).
[2] J. Lv, Y. Wang, L. Zhu, and Y. Ma, Phys. Rev. Lett. 106, 015503 (2011).
[3] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. 107, 087201 (2011).
[4] A. M. J. Schaeffer, W. B. Talmadge, S. R. Temple, and S. Deemyad, Phys. Rev. Lett. 109, 185702 (2012).
[5] C. L. Guillaume, E. Gregoryanz, O. Dегtyaрева, M. I. McMahon, M. Hanfland, S. Evans, M. Guthrie, S. V. Sinogeikin, and H.-K. Mao, Nat. Phys. 7, 211 (2011).
[6] T. Matsuoka, M. Sakata, Y. Nakamoto, K. Takahama, K. Ichimaru, K. Mukai, K. Ohta, N. Hirao, Y. Ohishi, and K. Shimizu, Phys. Rev. B 89, 144103 (2014).
[7] S. A. Mack, S. M. Griffin, and J. B. Neaton, Proc. Natl. Acad. Sci. U.S.A. 116, 9197 (2019).
[8] S. F. Elatresh, Z. Zhou, N. W. Ashcroft, S. A. Bonev, J. Feng, and R. Hoffmann, Phys. Rev. Mater. 3, 044203 (2019).
[9] X. Dong, A. R. Oganov, A. F. Goncharov, E. Stavrou, S. Lobanov, G. Saleh, G. R. Qian, Q. Zhu, C. Gatti, V. L. Deringer, R. Dronskowski, X. F. Zhou, V. B. Prakapenka, Z. Konnopkova, I. A. Popov, A. I. Boldyrev, and H. T. Wang, Nat. Chem. 9, 440 (2017).
[10] V. V. Struzhkin, M. I. Eremets, W. Gan, H. k. Mao, and R. J. Hemley, Science 298, 1213 (2002).
[11] K. Shimizu, H. Ishikawa, D. Takao, T. Yagi, and K. Amaya, Nature (London) 419, 597 (2002).
[12] J. B. Neaton and N. W. Ashcroft, Nature (London) 400, 141 (1999).
[13] B. Monserrat, N. D. Drummond, C. J. Pickard, and R. J. Needs, Phys. Rev. Lett. 112, 055504 (2014).
[14] W. L. Vas, L. W. Finger, R. J. Hemley, J. Z. Hu, H. K. Mao, and J. A. Schouten, Nature (London) 358, 46 (1992).
[15] Y. Li, X. Feng, H. Liu, J. Hao, S. A. T. Redfern, W. Lei, D. Liu, and Y. Ma, Nat. Commun. 9, 722 (2018).
[16] D. Li, Y. Liu, F. Tian, S. Wei, Z. Liu, D. Duan, B. Liu, and T. Cui, Solid State Commun. 283, 9 (2018).
[17] C. Liu, H. Gao, Y. Wang, R. J. Needs, C. J. Pickard, J. Sun, H. T. Wang, and D. Xing, Phys. Rev. X 10, 021007 (2020).
[18] J. Shi, W. Cui, J. Hao, M. Xu, X. Wang, and Y. Li, Nat. Commun. 11, 3164 (2020).
[19] J. Hou, X. J. Weng, A. R. Oganov, X. Shao, G. Gao, X. Dong, H. T. Wang, Y. Tian, and X. F. Zhou, Phys. Rev. B 103, L060102 (2021).
[20] B. Monserrat, M. Martinez-Canales, R. J. Needs, and C. J. Pickard, Phys. Rev. Lett. 121, 015301 (2018).
[21] Z. Liu, J. Botana, A. Hermann, S. Valdez, E. Zurek, D. Yan, H. Q. Lin, and M.-S. Miao, Nat. Commun. 9, 951 (2018).
[22] 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).
[23] H. Gao, J. Sun, C. J. Pickard, and R. J. Needs, Phys. Rev. Mater. 3, 015002 (2019).
[24] A. R. Oganov and C. W. Glass, J. Chem. Phys. 124, 244704 (2006).
[25] A. O. Lyakhov and A. R. Oganov, H. T. Stokes, and Q. Zhu, Comput. Phys. Commun. 184, 1172 (2013).
[26] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.106.L220501 for additional calculations and electronic properties.
[27] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[28] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[29] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[30] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceriotti, M. Cococcioni, and I. Dabo, J. Phys.: Condens. Matter 21, 395502 (2009).
[31] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[32] M. Methfessel and A. T. Paxton, Phys. Rev. B 40, 3616 (1989).
[33] L. Dubrovinsky, S. Khandarkhaeva, T. Fedotenko, D. Laniel, M. Bykov, C. Giacobbe, E. L. Bright, P. Sedmak, S. Chariton, V. Prakapenka, A. V. Ponomareva, E. A. Smirnova, M. P. Belov, F. Tasnádi, N. Shulumba, F. Trybel, I. A. Abrikosov, and N. Dubrovinskaia, Nature (London) 605, 274 (2022).
[34] Z. Zhao, S. Zhang, T. Yu, H. Xu, A. Bergara, and G. Yang, Phys. Rev. Lett. 122, 097002 (2019).
[35] Z. Liu, Q. Zhuang, F. Tian, D. Duan, H. Song, Z. Zhang, F. Li, H. Li, D. Li, and T. Cui, Phys. Rev. Lett. 127, 157002 (2021).
[36] Y. Tsuji, P. L. V. K. Dasari, S. F. Elatresh, R. Hoffmann, and N. W. Ashcroft, J. Am. Chem. Soc. 138, 14108 (2016).
[37] W. Tang, E. Sanville, and G. Henkelman, J. Phys.: Condens. Matter 21, 084204 (2009).
[38] A. Simon, Angew. Chem. Int. Ed. Engl. 36, 1788 (1997).
[39] J. S. Tse, Y. Yao, and K. Tanaka, Phys. Rev. Lett. 98, 117004 (2007).
[40] X. F. Zhou, A. R. Oganov, X. Dong, L. Zhang, Y. Tian, and H. T. Wang, Phys. Rev. B 84, 054543 (2011).
[41] P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).
[42] P. B. Allen, Phys. Rev. Lett. 59, 1460 (1987).
[43] G. Profeta, C. Franchini, N. N. Lathiotakis, A. Floris, A. Sanna, M. A. L. Marques, M. Lüders, S. Massidda, E. K. U. Gross, and A. Continenza, Phys. Rev. Lett. 96, 047003 (2006).