

This is the accepted manuscript made available via CHORUS. The article has been published as:

# Superconductivity in the van der Waals layered compound $\text{PS}_{\{2\}}$

Yan-Ling Li, Elissaios Stavrou, Qiang Zhu, Samantha M. Clarke, Yunguo Li, and Hong-Mei Huang

Phys. Rev. B **99**, 220503 — Published 10 June 2019

DOI: [10.1103/PhysRevB.99.220503](https://doi.org/10.1103/PhysRevB.99.220503)

# Superconductivity in the van der Waals layered compound PS<sub>2</sub>

Yan-Ling Li,<sup>1,\*</sup> Elissaios Stavrou,<sup>2</sup> Qiang Zhu,<sup>3</sup> Samantha M. Clarke,<sup>2</sup> Yunguo Li,<sup>1,4</sup> and Hong-Mei Huang<sup>1</sup>

<sup>1</sup>Laboratory for Quantum Design of Functional Materials, School of Physics and Electronic Engineering, Jiangsu Normal University, 221116, Xuzhou, People's Republic of China

<sup>2</sup>Lawrence Livermore National Laboratory, Physical and Life Sciences Directorate, Livermore, California 94550, USA

<sup>3</sup>Department of Physics and Astronomy, High Pressure Science and Engineering Center, University of Nevada, Las Vegas, NV 89154, USA

<sup>4</sup>Department of Earth Sciences, UCL, Gower Street, London, WC1E 6BT, UK

(Dated: May 30, 2019)

van der Waals (vdW) layered compounds provided a fruitful research stage for realization of superconductivity. However, an vdW layered superconductor with a high transition temperature ( $T_c$ ) at ambient conditions is still rare. Here, using variable-composition evolutionary structure predictions, we systematically explored the stable compounds in the P-S system up to 20 GPa. Opposed to the complex stoichiometries at ambient condition, only one compound, PS<sub>2</sub>, is predicted to be thermodynamically stable above 8 GPa. Strikingly, PS<sub>2</sub> is a vdW layered material isostructural to 3R-MoS<sub>2</sub> exhibiting a predicted  $T_c$  of around 11 K at ambient pressure, both in the bulk and the monolayer form. PS<sub>2</sub> has been successfully synthesized via high-pressure experiments in excellent agreement with the theoretical predictions. This enables replacing transition metals with group V elements in transition metal dichalcogenides and paves the way in the search for new vdW layered materials with superior properties.

vdW layered materials such as graphite, black phosphorus, and transition metal dichalcogenides (TMDs) have attracted extensive interest due to the weak interlayer interactions that make them easily exfoliable [1–5]. The electronic properties, such as superconductivity, can change dramatically upon reduction from bulk to 2D and can effectively be tailored by an external field or charge-carrier doping [3–8]. Recently, superconductivity for the vdW layered compounds has been extensively investigated [4–8]. At ambient pressure conditions, the majority of vdW layered materials are semiconductors while few of them show metallic or semimetallic behaviors. For semiconducting vdW layered materials, superconductivity can be induced by chemical intercalation, external pressure, and electrostatic gating [9–17]. In the TMD family, there is a strong competition between charge density wave (CDW) and superconductivity. The transition from CDW state to superconducting state can be triggered by the external stimulus, as observed in TiSe<sub>2</sub> [12], MoS<sub>2</sub> [15], and MoTe<sub>2</sub> [14]. Bulk MoS<sub>2</sub> exhibits superconductivity with a  $T_c$  of  $\sim 12$  K at ultrahigh pressure of 120 GPa [13]. Thin film MoS<sub>2</sub> becomes superconducting when it is heavily gated to the conducting regime, in which  $T_c$  reaches 10 K at optimal gating [15]. Electrostatically induced superconductivity has also been realized in thin films of 2H-WS<sub>2</sub> [16] and 2H-MoSe<sub>2</sub> [17]. For semimetallic vdW materials, superconductivity has been observed in Weyl semimetal MoTe<sub>2</sub> but with low  $T_c$  values ( $\sim 0.1$  K) under ambient conditions [14]. Upon compression, the  $T_c$  of MoTe<sub>2</sub> dramatically increases to a maximum value of 8.2 K at 11.7 GPa accompanied by a 1T'-to-2H polytype transformation [14]. Metallic 2H-NbSe<sub>2</sub>, a record holder in intrinsic superconducting TMDs, exhibits a transition temperature of 7.2 K at ambient conditions [18].

Economically, it is also valuable to replace transition metals in TMD materials with more abundant and inexpensive main group elements. Group IVA chalcogenides have attracted great attention because of their emergent physics phe-

nomena such as surface state, quantum spin Hall effects, and superconductivity [19]. SnSe<sub>2</sub> has been reported to become superconducting by organometallic intercalation [20], physical gating [19], and external pressure [21]. Recently, Zeng *et al* induced a superconductivity state ( $T_c \approx 3.9$  K) in 1T-SnSe<sub>2</sub> by using the ionic liquid gating technique [19]. It was also reported that 1T-SnSe<sub>2</sub> exhibits robust superconductivity with a nearly constant  $T_c \approx 6.1$  K between 30.1 and 50.3 GPa [21].

In recent years, the search for layered vdW materials that exhibit superconductivity has intensified [6–8]. In this letter, we report that phosphorus and sulfur, two neighboring elements in the periodic table, can form an unexpectedly stable layered compound PS<sub>2</sub> under relatively low-pressure conditions. Following this prediction, PS<sub>2</sub> was confirmed by performing high-pressure experiments in a laser-heated diamond anvil cell (LHDAC), starting from an elemental P-S mixture. The synthesized compound was characterized via *in situ* synchrotron X-ray diffraction (XRD) and Raman spectroscopy measurements. PS<sub>2</sub> is predicted to be superconducting with a transition temperature ( $\sim 11.3$  K) comparable to that (11.5 K) of CaC<sub>6</sub> at ambient pressure [10].

The *ab initio* evolutionary algorithm USPEX [22, 23] was used to explore thermodynamically stable P-S compounds and their structures. In these calculations, all stoichiometries were allowed (with the constraint that the total number of atoms in the unit cell is no more than 32 atoms), and calculations were performed at 1, 5, 10, and 20 GPa, respectively. The pressure-composition phase diagram of the P-S system is shown in Fig. 1 and Supplemental Fig. S1 [24], in which the convex hull was constructed from the normalized formation enthalpies of all the stable structures for each pressure. Thermodynamically, the convex hull at a given pressure connects all stable phases against decomposition into other binaries or elements. We first considered the phase transitions on two ending members (elemental P and S). Phosphorus transforms from the orthorhombic A17 structure (*Cmca*) to

the rhombohedral  $A7$  phase ( $R\bar{3}m$ ) to the simple cubic phase in the pressure range considered [25, 26], whereas sulfur in this pressure range undergoes a series of phase transitions from  $Fddd$  to  $P3_221$  to  $R\bar{3}$  and to  $I4_1/acd$  [27–29]. Using variable-composition evolutionary searches, we found that the P-S system holds a richer phase diagram at pressures lower than 3 GPa. Four previously reported compounds with discrete cage-like molecules,  $P_4S_3$  [30],  $P_4S_7$  [31],  $P_4S_9$  [32], and  $P_2S_5$  [31] (Supplemental Fig. S2) [24], are thermodynamically stable at zero pressure within a narrow pressure range:  $P_4S_3$  ( $< 2$  GPa);  $P_4S_7$  ( $< 6$  GPa);  $P_4S_9$  ( $< 1$  GPa), and  $P_2S_5$  ( $< 2$  GPa). The reported phosphorous polysulfide,  $P_2S_7$  [33] with neutral polymeric strands, is thermodynamically stable one from 1 GPa to 8 GPa. Surprisingly, an unreported compound  $PS_2$  is found to be the only compound thermodynamically stable above 8 GPa as shown in Fig. 1 and Fig. S3 [24]. Below 8 GPa,  $PS_2$  is metastable compound. We also performed the phonon dispersion curves for  $PS_2$  at a series of pressures (Fig. S4) [24]. The absence of imaginary phonon frequencies confirmed its dynamical stability within the entire range of pressure.

As shown in Fig. 2(a),  $PS_2$  is a layered vdW solid isostructural to  $3R$ - $MoS_2$ , belonging to  $D_{3d}$  ( $R\bar{3}m$ ) space group [34, 35]. Its unit cell is composed of three phosphorous atoms occupying 3a Wyckoff sites (0, 0, 0) and six sulfur atoms at 6c (0, 0,  $z$ ). We mention that  $MoS_2$  has two different forms of  $3R$  polytypes: one is the  $CdCl_2$ -type structure (space group  $R\bar{3}m$ ) with inversion symmetry [34, 35] which occurs in  $\gamma$ - $TaS_2$  [35] and  $\beta$ - $TaSe_2$  [35] as well as our  $PS_2$ , another is the  $R\bar{3}m$  structure with broken inversion symmetry which is well-known in the TMDs family [4, 35, 36]. Considering that layered TMDs exhibit a variety of polytypes [2–4, 14] such as  $2H$ ,  $1T$ ,  $1T'$ , and  $T_d$ , we also examined the possibility of these structures occurred in  $PS_2$ . Our DFT calculations suggested  $3R$ - $MoS_2$  with  $R\bar{3}m$  symmetry is indeed the ground state among these polytypes [24]. In addition, in order to evaluate the influences of interlayer vdW interaction on structural parameters of  $PS_2$  [24], we considered the SCAN+rVV10 method [37], which can produce excellent interlayer spacing and intralayer lattice constants. The calculated lattice parameters are 3.258 Å for  $a$  and 17.344 Å for  $c$  at ambient conditions, which yields the density of 2.971 g/cm<sup>3</sup> and the interlayer spacing of 5.782 Å. The optimized internal free parameter  $z$  is 0.256.  $PS_2$  holds a slightly lower interlayer spacing than that (6.15 Å) of  $3R$ - $MoS_2$  [34].

In order to verify the theoretical predictions and explore the pressure range of the stability of  $PS_2$ , we performed LHDAC experiments (Fig. S5 [24]) on the phosphorous-sulfur mixture at various pressures, from 10 to 20 GPa and temperatures, from 800 K to 2000 K. All synthesis experiments concluded the formation of the layered  $PS_2$  compound independently of the starting pressure, the maximum achieved temperature and the presence or not of thermal insulation (LiF). This observation agrees with the theoretical prediction that the layered  $PS_2$  is the only thermodynamically stable composition above 8 GPa. In Fig. 2(b) we show the XRD patterns ( $\lambda = 0.4959$

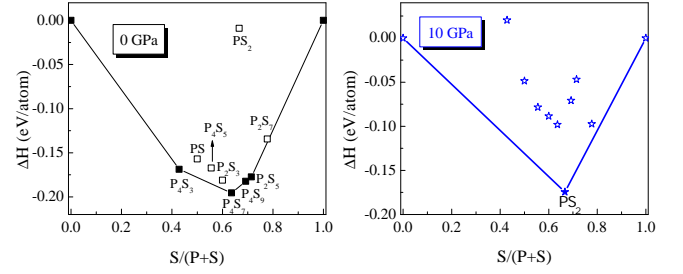


FIG. 1. The predicted convex hull diagrams in P-S system at the pressure of 0 GPa and 10 GPa.

Å) acquired during a synthesis attempt at 14 GPa. The XRD pattern before LH at room temperature (RT) is representative of a heterogeneous mixture of orthorhombic sulfur (S-I) and simple cubic phosphorous (SC-P). As expected, amorphous red phosphorous converts to the corresponding crystal structures of black phosphorous above 7 GPa [38, 39]. The corresponding cell volumes are in excellent agreement with previous high-pressure equation of state (EOS) studies of sulfur and phosphorous [26, 28]. New narrow Bragg peaks appear after LH (see Fig. 2(b)), while the Bragg peaks of S-I disappear and the ones of SC-P become narrower due to temperature annealing. The new Bragg peaks can be indexed with a mixture of the predicted  $PS_2$  structure and tetragonal S-III. According to previous studies, at elevated pressure S-I transform to tetragonal S-III at temperatures below the temperatures achieved by LH in this study and S-III is quenchable at ambient temperature [29]. Bragg peaks of S-III were indexed with  $a = 8.423$  Å and  $c = 3.521$  Å at 14 GPa in excellent agreement with Ref. [29]. The remaining Bragg peaks can be indexed with the  $R\bar{3}m$ - $PS_2$  with  $a = 3.149$  Å and  $c = 15.501$  Å in good agreement with the theoretically predicted values ( $a = 3.120$  Å and  $c = 15.231$  Å at 14 GPa). A representative Le Bail refinement ( $\lambda = 0.3344$  Å) is shown in the Supplemental Fig. S6 [24].

With decreasing pressure, the newly synthesized phase remains stable down to 4 GPa, as evidenced from XRD measurements and optical observations. Below this pressure the XRD patterns is representative of a mixture of crystalline P and a disordered-like (broad Bragg peaks) phase. It is plausible to assume that this disordered phase is the disordered metastable phase of sulfur previously observed on pressure release of S-III by Degtyareva *et al.* [29]. Thus, we conclude that  $PS_2$  decomposes to P+S below 3 GPa. However, our phonon calculations suggested that  $PS_2$  should be quenchable to the ambient condition. The observed decomposition may be a result of small grain size and large ratio of interfaces, which to some extent reduce the decomposition barrier[40]. Pressure dependence of the lattice parameters and EOS of  $PS_2$  together with the theoretically predicted ones are shown in Fig. 2(c). Experiment and theory agree closely for the lattice parameters and the cell volume. In particular, the experimental and theoretical unit cell volumes differ by less than

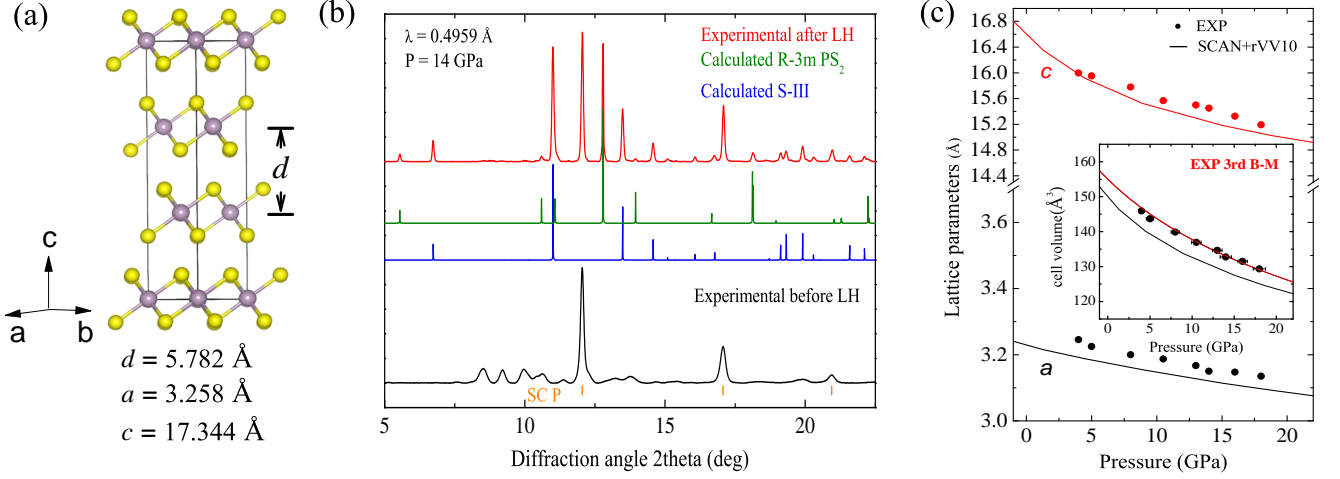


FIG. 2. (a) The crystal structure of vdW layered compound PS<sub>2</sub>. The lattice parameters  $a$  and  $c$  and interlayer spacing  $d$  at zero pressure given. (b) Integrated XRD patterns before laser heating (LH) and after LH to 800 K, respectively. Vertical ticks correspond to expected (assuming continuous Debye rings, see supplementary materials [24]) positions and intensities of XRD peaks of SC-P, S-III and PS<sub>2</sub>. (c) Pressure dependence of lattice parameters of PS<sub>2</sub>. The inset shows the pressure dependence of the cell volume. Experimental data are shown with solid symbols and theoretical predictions with solid lines. The solid red curve in inset is the third-order Birch-Murnaghan (3rd B-M) equation of states fit to the experimental data.

4 %, which is within the expected accuracy of DFT calculations [41]. We conducted EOS fits to the experimental and calculated  $PV$  data using a third-order Birch-Murnaghan EOS and determined the bulk modulus  $B_0$  and the first derivative  $B_0'$  [42]. The results of the fits are  $V_0 = 152.5 (7) \text{ \AA}^3$ ,  $B_0 = 78.7(15) \text{ GPa}$ ,  $B_0' = 4.0 (5)$ , for the experimental EOS and  $V_0 = 149.5 \text{ \AA}^3$ ,  $B_0 = 56.5 \text{ GPa}$ ,  $B_0' = 5.9$  for the calculated one.

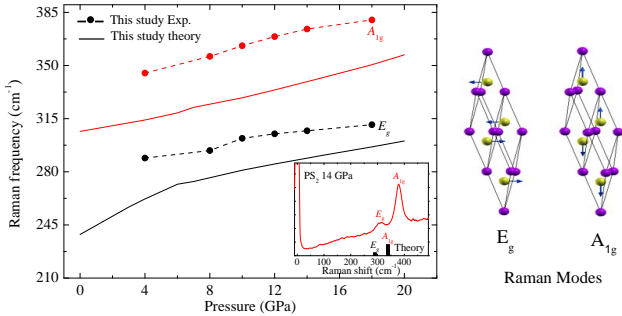


FIG. 3. Frequencies of Raman modes of PS<sub>2</sub> against pressure upon decompression. Experimental results with solid symbols and theoretically predicted with solid lines. The inset shows the experimental Raman spectrum at 14 GPa in comparison with the theoretically predicted Raman modes. Eigenvectors of Raman modes  $E_g$  and  $A_{1g}$  also given.

For PS<sub>2</sub>, there are four distinct optical phonon modes at the zone center: two Raman active modes  $E_g$  (two-fold degeneracy, S in-plane, basal plane vibrations) and  $A_{1g}$  (S out-of-plane, along  $c$ -axis vibrations) along with two infrared active modes  $E_u$  (two-fold degeneracy, in-plane S and P displacements) and  $A_{2u}$  (out-of-plane S and P displacements) (see the Fig. 3 and Fig. S7 [24]). The Raman spectrum, using the

514.5 nm line of an Ar ion laser for excitation, of the new phase depicted in Fig. 3 shows the presence of two distinct Raman active modes. Relative intensity and frequency separation of the modes allowed us to confidently assign the two modes to the  $A_{1g}$  (higher intensity/frequency) and  $E_g$  (lower intensity/frequency) of the layered PS<sub>2</sub> compound. Upon pressure release both modes show normal mode behavior (red shift) and can be traced down to 3~4 GPa in agreement with XRD measurements. Experimental Raman modes frequencies and frequency-pressure slopes are in good agreement with the theoretically calculated ones, given the fact that GGA underestimates the phonon frequencies [43].

The distinctive layered features in PS<sub>2</sub> aroused our intense interests in exploring its electronic properties. Remarkably, PS<sub>2</sub> is predicted to be a phonon-mediated superconductor even at zero pressure. The energy bands of PS<sub>2</sub> at 3 GPa are shown in Fig. 4(a). There is only one energy band crossing the Fermi level along several high symmetry directions in the Brillouin zone (BZ, see Fig. 4(b)). The most interesting feature is the presence of nearly flat bands lying right at the Fermi level along B<sub>1</sub>-B and XQ directions in the BZ. The occurrence of flat and steep slopes near the Fermi level resembles a favorable condition for enhancing Cooper pair formation, which is essential to phonon-mediated superconductivity [44]. The calculated density of states (DOS) shows that there is a strong hybridization between the S- $p$  and P- $s$  electrons in the whole BZ, indicating that these electrons dominate the electronic properties of PS<sub>2</sub>. As shown in Fig. 4(c), the Fermi surface (FS) of the PS<sub>2</sub> consists of a small electron-like pocket around  $\Gamma$  point and six linked electron-hole tubes (nearly elliptical sections) with a large surface area running through the BZ borders along the  $\Gamma$ -Z direction, exhibiting an evident 2D

behavior. The existence of nearly parallel pieces of the FS is beneficial to the electron-phonon coupling.[45] Both the Fermi pockets and the obvious Fermi nesting lead to strong electron-phonon interactions in PS<sub>2</sub>.

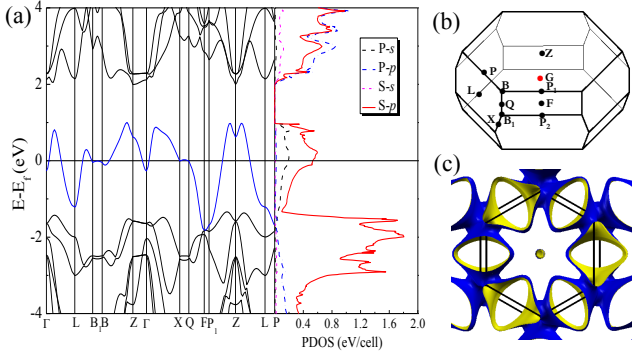


FIG. 4. Energy band, projected electronic density of states (PDOS) (a), Brillouin zone (b), and Fermi surface (c) of PS<sub>2</sub> at 3 GPa. The Fermi level was taken as the energetic reference point.

The phonon dispersion curve, partial atomic phonon DOS, Eliashberg spectral function  $\alpha^2F(\omega)$ , and integrated  $\lambda(\omega)$  of PS<sub>2</sub> at 3 GPa are shown in Fig. 5. To gain further insights into the nature of electron-phonon coupling, the linewidths for phonon mode  $\mathbf{q}\nu$  (i.e.,  $\gamma_{\mathbf{q}\nu}$ ) were attached to phonon dispersion curves. One can identify the contribution to the electron-phonon coupling strength from each phonon mode based on the calculated phonon linewidths. The softening of the  $E_g$  branch is observed along the X- $\Gamma$ -L, B-Z, and P<sub>1</sub>-Z-L directions, signaling again strong electron-phonon coupling in PS<sub>2</sub>. Such a softening of the mode was previously observed in the superconducting MgB<sub>2</sub> [46]. Combining the calculated phonon linewidths with electronic structure, we conclude that the  $E_g$  modes are strongly coupled to electronic bands from S- $p_x$  and S- $p_y$  as well as P- $s$  states since  $E_g$  modes involve atomic displacements in the  $x$ - $y$  plane. Delta-like peak around 251 cm<sup>-1</sup> in both spectral function  $\alpha^2F(\omega)$  and phonon DOS originates mostly from the  $E_g$  modes with calculated energies in the ranges of 207 to 257 cm<sup>-1</sup>, which contributes to 33.3 % of the total  $\lambda$  value. The  $A_{1g}$  branch possess energies in the ranges of 292 to 371 cm<sup>-1</sup> and holds the highest phonon linewidth around  $\Gamma$  point. However, it contributes to only 3.1 % of the total  $\lambda$  value because of strong anisotropy of the line width of  $A_{1g}$  branch in the BZ. These results indicate that the sulfur atoms dominate superconductivity in PS<sub>2</sub>, due to the prominent contributions to the electron-phonon interaction. Phonons from the sulfur atoms together with the electrons from the S- $p$  and P- $s$  states provide the strong electron-phonon coupling indispensable for superconductivity in PS<sub>2</sub>.

From the value of  $\lambda$ , one can estimate the  $T_c$  using the Allen and Dynes formula [47]. Taking a typical value of 0.11 for  $\mu^*$  along with the calculated  $\omega_{\log}$  of 235 cm<sup>-1</sup>, we obtained a  $T_c$  of 11.3 K for PS<sub>2</sub> at zero pressure. The changes of  $\lambda$ ,  $\omega_{\log}$ , and  $T_c$  with increasing pressure in PS<sub>2</sub> are depicted in Fig. 6. Applying pressure on PS<sub>2</sub> clearly leads to a significant

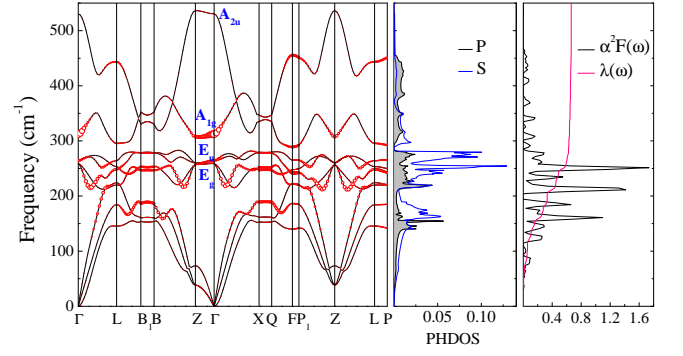


FIG. 5. Phonon spectrum, in which the linewidths for phonon mode  $\mathbf{q}\nu$  (i.e.,  $\gamma_{\mathbf{q}\nu}$ ) are represented by the area of the red circle, partial atomic phonon DOS, Eliashberg spectral function  $\alpha^2F(\omega)$  and integrated  $\lambda(\omega)$  for PS<sub>2</sub> at the pressure of 3 GPa.

decrease of  $\lambda$  and  $T_c$ . At 20 GPa,  $T_c$  is only 2.4 K. The sharp drop of  $\lambda$  is closely associated with the decrease of DOS at the Fermi level because the Fermi level moves up as the pressure increases.

The single or few-layered thick, two-dimensional (2D) crystals are particularly interesting due to their potential use in low dimensional electronics [2, 5, 8]. Therefore, it is interesting to discuss the superconductivity of the monolayer PS<sub>2</sub>. Compared with bulk superconductors, 2D superconductors are more convenient for fabrication in modern electronic applications. So far, the well-defined 2D intrinsic superconductors were rarely reported. For TMDs, only monolayer 2H-NbSe<sub>2</sub> [48] were found to exhibit intrinsic superconductivity with a relatively lower transition temperature (below 3 K) than that of its bulk counterpart (7.2 K) [18, 49, 50]. The weakened superconductivity due to the reduction of the dimensionality is a universal behavior in the TMD family except TaS<sub>2</sub> [51]. For our PS<sub>2</sub>, the superconductivity also persisted from bulk to monolayer. Different from the NbSe<sub>2</sub>, we surprisingly found that at ambient pressure the monolayer PS<sub>2</sub> has a slightly lower  $T_c$  (about 10.8 K) than bulk because of a slightly lower coupling constant (about 0.8) than bulk, indicating that bulk PS<sub>2</sub> could be an ideal 2D superconductor.

In conclusion, we report a novel layered PS<sub>2</sub> compound from a joint effort between theory and experiment. Our complete survey on the pressure-composition phase diagram for the P-S system at pressures up to 20 GPa yielded a novel compound PS<sub>2</sub> to become thermodynamically stable above 8 GPa. PS<sub>2</sub> is predicted to be an unusual example of superconducting vdW layered material, exhibiting superconductivity with an unexpected high transition temperature ( $\sim 11.3$  K) at ambient conditions. Monolayer PS<sub>2</sub> retains the superconducting property of bulk PS<sub>2</sub>, suggesting that PS<sub>2</sub> is an ideal candidate material for exploring 2D superconductivity. Experimental results, from diffraction and spectroscopic techniques, unambiguously identified the synthesized compounds as the predicted layered  $R\bar{3}m$ -PS<sub>2</sub>. We believe the discovery of non-intuitive vdW layered compound between group V and



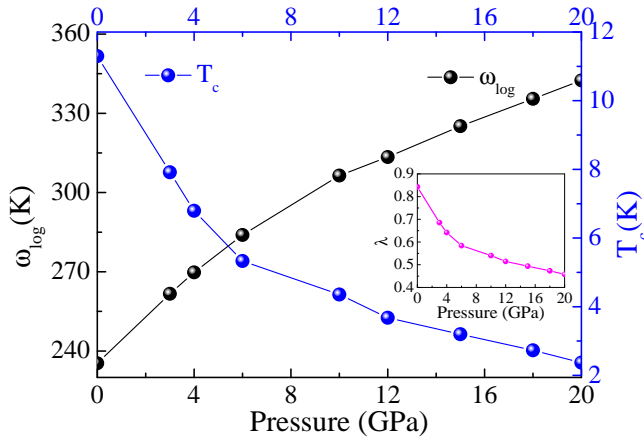


FIG. 6. Calculated  $T_c$  values and logarithmic phonon momentum  $\omega_{\log}$  versus pressure. Inset shows the integrated electron-phonon coupling  $\lambda$  as a function of pressure.

VI elements will opens a new avenue in vdW layered materials design.

We acknowledge supports from the National Natural Science Foundation of China (Grant No. 11674131) and the 333 project of Jiangsu province. Part of this work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Security, LLC under Contract DE-AC52-07NA27344. We gratefully acknowledge the LLNL LDRD program for funding support of this project under 18-LW-036. Part of this work was performed at GeoSoilEnviroCARS (The University of Chicago, Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation-Earth Sciences (EAR-1634415) and Department of Energy-GeoSciences (DE-FG02-94ER14466). This research used resources of the Advanced Photon Source, a U. S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The ALS is supported by the Director, Office of Science, BES of DOE under Contract No. DE-AC02-05CH11231, DE-AC02-06CH11357.

Y. L. L and E. S. contributed equally to this work.

\* ylli@jsnu.edu.cn

- [1] X. Qiu and W. Ji, Illuminating interlayer interactions, *Nat. Mater.* **17**, 211 (2018).
- [2] A. V. Kolobov and J. Tominaga, *Two-Dimensional Transition-Metal Dichalcogenides* (Springer, 2016).
- [3] H. Yang, S. Kim, M. Chhowalla, and Y. Lee, Structural and quantum-state phase transition in van der Waals layered materials, *Nat. Phys.* **13**, 931 (2017).
- [4] G. H. Han, D. L. Duong, D. H. Keum, S. J. Yun, and Y. H. Lee, van der Waals metallic transition metal dichalcogenides, *Chem. Rev.* **118**, 6297 (2018).

- [5] S. Manzeli, D. Ovchinnikov, D. Pasquier, O. V. Yazyev, and A. Kis, 2D transition metal dichalcogenides, *Nat. Rev. Mater.* **2**, 15. 17033 (2017).
- [6] R. P. Smith, T. E. Weller, C. A. Howard, M. P. Dean, K. C. Rahnejat, S. S. Saxena, and M. Ellerby, Superconductivity in graphite intercalation compounds, *Physica C* **514**, 50 (2015).
- [7] R. A. Klemm, Pristine and intercalated transition metal dichalcogenide superconductors, *Physica C* **514**, 86 (2015).
- [8] Y. Saito, T. Nojima, and Y. Iwasa, Highly crystalline 2D superconductors, *Nat. Rev. Mater.* **2**, 16094 (2016).
- [9] G. Csányi, P. B. Littlewood, A. H. Nevidomskyy, C. J. Pickard, and B. D. Simons, The role of the interlayer state in the electronic structure of superconducting graphite intercalated compounds, *Nat. Phys.* **1**, 42 (2005).
- [10] N. Emery, C. Hérod, M. d'Astuto, V. Garcia, C. Bellin, J. F. Marêché, P. Lagrange, and G. Loupías, Superconductivity of bulk  $\text{CaC}_6$ , *Phys. Rev. Lett.* **95**, 087003 (2005).
- [11] A. Gauzzi, S. Takashima, N. Takeshita, C. Terakura, H. Takagi, N. Emery, C. Hérod, P. Lagrange, and G. Loupías, Enhancement of superconductivity and evidence of structural instability in intercalated graphite  $\text{CaC}_6$  under high pressure, *Phys. Rev. Lett.* **98**, 067002 (2007).
- [12] E. Morosan, H. W. Zandbergen, B. S. Dennis, J. W. G. Bos, Y. Onose, T. Klimczuk, A. P. Ramirez, N. P. Ong, and R. J. Cava, Superconductivity in  $\text{Cu}_x\text{TiSe}_2$ , *Nat. Phys.* **2**, 544 (2006).
- [13] Z. Chi, X. Chen, F. Yen, F. Peng, Y. Zhou, J. Zhu, Y. Zhang, X. Liu, C. Lin, S. Chu, Y. Li, J. Zhao, T. Kagayama, Y. Ma, and Z. Yang, Superconductivity in pristine  $2\text{H}_a\text{-MoS}_2$  at ultrahigh pressure, *Phys. Rev. Lett.* **120**, 037002 (2018).
- [14] Y. Qi *et al.*, Superconductivity in Weyl semimetal candidate  $\text{MoTe}_2$ , *Nat. Commun.* **7**, 11038 (2016).
- [15] J. T. Ye, Y. J. Zhang, R. Akashi, M. S. Bahramy, R. Arita, and Y. Iwasa, Superconducting dome in a gate-tuned band insulator, *Science* **338**, 1193 (2012).
- [16] S. Jo, D. Costanzo, H. Berger, and A. F. Morpurgo, Electrostatically induced superconductivity at the surface of  $\text{WS}_2$ , *Nano Lett.* **15**, 1197 (2015).
- [17] W. Shi, J. Ye, Y. Zhang, R. Suzuki, M. Yoshida, J. Miyazaki, N. Inoue, Y. Saito, and Y. Iwasa, Superconductivity series in transition metal dichalcogenides by ionic gating, *Sci. Rep.* **5**, 12534 (2015).
- [18] T. Yokoya, T. Kiss, A. Chainani, S. Shin, M. Nohara, and H. Takagi, Fermi surface sheet-dependent superconductivity in  $2\text{H-NbSe}_2$ , *Science* **294**, 2518 (2001).
- [19] J. Zeng *et al.*, Gate-induced interfacial superconductivity in  $1\text{T-SnSe}_2$ , *Nano Lett.* **18**, 1410 (2018).
- [20] D. O'Hare, H.-V. Wong, S. Hazell, and J. W. Hodby, Relatively isotropic superconductivity at 8.3 K in the lamellar organometallic intercalate  $\text{SnSe}_2\{\text{Co}(\eta\text{-C}_5\text{H}_5)_2\}_{0.3}$ , *Adv. Mater.* **4**, 658 (1992).
- [21] Y. Zhou *et al.*, Pressure-induced metallization and robust superconductivity in pristine  $1\text{T-SnSe}_2$ , *Adv. Electron. Mater.* **4**, 1800155 (2018).
- [22] A. R. Oganov and C. W. Glass, Crystal structure prediction using ab initio evolutionary techniques: Principles and applications, *J. Chem. Phys.* **124**, 244704 (2006).
- [23] A. O. Lyakhov, A. R. Oganov, H. T. Stokes, and Q. Zhu, New developments in evolutionary structure prediction algorithm USPEX, *Comput. Phys. Commun.* **184**, 1172 (2013).
- [24] See Supplemental Material at [http://link.aps.org/\\*\\*\\*\\*](http://link.aps.org/****), which includes Refs. [52-65], for a detailed description of theoretical calculations and experimental methods, convex hull, crystal structures, phonon spectrum, Le Bail refinement, XRD patterns, structural parameters of  $\text{PS}_2$  using different vdW corrections,

and supplemental Figs. S1-S7.

- [25] J. C. Jamieson, Crystal structures adopted by black phosphorus at high pressures, *Science* **139**, 1291 (1963).
- [26] T. Kikegawa and H. Iwasaki, An X-ray diffraction study of lattice compression and phase transition of crystalline phosphorus, *Acta Cryst.* **B39**, 158 (1983).
- [27] J. Donohue, A. Caron, and E. Goldish, The crystal and molecular structure of S<sub>6</sub> (Sulfur-6), *J. Am. Chem. Soc.* **83**, 3748 (1961).
- [28] Y. Akahama, M. Kobayashi, and H. Kawamura, Pressure-induced structural phase transition in sulfur at 83 GPa, *Phys. Rev. B* **48**, 6862 (1993).
- [29] O. Degtyareva, E. Gregoryanz, M. Somayazulu, P. Dera, H.-k. Mao, and R. J. Hemley, Novel chain structures in group VI elements, *Nat. Mater.* **4**, 152 (2005).
- [30] G. R. Burns, J. R. Rollo, and R. W. Syme, Raman spectra of single crystals of  $\alpha$ -P<sub>4</sub>S<sub>3</sub>, *J. Raman Spectrosc.* **19**, 345 (1988).
- [31] A. Vos, R. Olthof, F. Van Bolhuis, and R. Botterweg, Refinement of the crystal structures of some phosphorus sulphides, *Acta Cryst.* **19**, 864 (1965).
- [32] W. Hilmer, Die struktur eines phosphor (III, V)-sulfids der ungefähren zusammensetzung P<sub>4</sub>S<sub>9</sub>, *Acta Cryst.* **B25**, 1229 (1969).
- [33] T. Rödl, R. Wehrich, J. Wack, J. Senker, and A. Pfitzner, Rational syntheses and structural characterization of sulfur-rich phosphorus polysulfides:  $\alpha$ -P<sub>2</sub>S<sub>7</sub> and  $\beta$ -P<sub>2</sub>S<sub>7</sub>, *Angew. Chem. Int. Ed.* **50**, 10996 (2011).
- [34] R. E. Bell and R. E. Herfert, Preparation and characterization of a new crystalline form of molybdenum disulfide, *J. Am. Chem. Soc.* **79**, 3351 (1957).
- [35] F. Lévy (Ed.), *Crystallography and Crystal Chemistry of Materials with Layered Structures* (Reidel, 1976).
- [36] R. Suzuki *et al.*, Valley-dependent spin polarization in bulk MoS<sub>2</sub> with broken inversion symmetry, *Nat. Nanotech.* **9**, 611 (2014).
- [37] H. Peng, Z.-H. Yang, J. P. Perdew, and J. Sun, Versatile van der Waals density functional based on a meta-generalized gradient approximation, *Phys. Rev. X* **6**, 041005 (2016).
- [38] J. M. Zaug, A. K. Soper, and S. M. Clark, Pressure-dependent structures of amorphous red phosphorus and the origin of the first sharp diffraction peaks, *Nat. Mater.* **7**, 890899 (2008).
- [39] E. Rissi, E. Soignard, K. McKiernan, C. Benmore, and J. Yarger, Pressure-induced crystallization of amorphous red phosphorus, *Solid State Commun.* **152**, 390 (2012).
- [40] R. Liu, T. Zhang, L. Yang, and Z. Zhou, Effect of particle size on thermal decomposition of alkali metal picrates, *Thermochim. Acta* **583**, 78 (2014).
- [41] Y. L. Li, S. N. Wang, A. R. Oganov, H. Gou, J. S. Smith, and T. A. Strobel, Investigation of exotic stable calcium carbides using theory and experiment, *Nat. Commun.* **6**, 6974 (2015).
- [42] F. Birch, Finite strain isotherm and velocities for single-crystal and polycrystalline NaCl at high pressures and 300 K, *J. Geophys. Res.* **83**, 1257 (1978).
- [43] F. Favot and A. Dal Corso, Phonon dispersions: Performance of the generalized gradient approximation, *Phys. Rev. B* **60**, 11427 (1999).
- [44] Y. L. Li, W. Luo, Z. Zeng, H. Q. Lin, H. k. Mao, and R. Ahuja, Pressure-induced superconductivity in CaC<sub>2</sub>, *Proc. Natl. Acad. Sci.* **110**, 9289 (2013).
- [45] Y. L. Li, W. Luo, X. J. Chen, Z. Zeng, H. Q. Lin, and R. Ahuja, Formation of nanofoam carbon and re-emergence of superconductivity in compressed CaC<sub>6</sub>, *Sci. Rep.* **3**, 3331 (2013).
- [46] A. Q. R. Baron, H. Uchiyama, Y. Tanaka, S. Tsutsui, D. Ishikawa, S. Lee, R. Heid, K.-P. Bohnen, S. Tajima, and T. Ishikawa, Kohn anomaly in MgB<sub>2</sub> by inelastic X-ray scattering, *Phys. Rev. Lett.* **92**, 197004 (2004).
- [47] P. B. Allen and R. Dynes, Transition temperature of strongly-coupled superconductors reanalyzed, *Phys. Rev. B* **12**, 905 (1975).
- [48] M. Ugeda *et al.*, Characterization of collective ground states in single-layer NbSe<sub>2</sub>, *Nat. Phys.* **12**, 92 (2016).
- [49] X. Xi, Z. Wang, W. Zhao, J. Park, K. Law, H. Berger, L. Forró, J. Shan, and K. Mak, Ising pairing in superconducting NbSe<sub>2</sub> atomic layers, *Nat. Phys.* **12**, 139 (2016).
- [50] H. Wang *et al.*, High-quality monolayer superconductor NbSe<sub>2</sub> grown by chemical vapour deposition, *Nat. Commun.* **8**, 394 (2017).
- [51] E. Navarro-Moratalla *et al.*, Enhanced superconductivity in atomically thin TaS<sub>2</sub>, *Nat. Commun.* **7**, 11043 (2016).
- [52] J. Hafner, Materials simulations using VASP-a quantum perspective to materials science, *Comput. Phys. Commun.* **177**, 6 (2007).
- [53] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [54] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* **59**, 1758 (1999).
- [55] P. Giannozzi *et al.*, Advanced capabilities for materials modelling with Quantum ESPRESSO, *J. Phys.: Condens. Mat.* **29**, 465901 (2017).
- [56] K. Syassen, Ruby under pressure, *High Press. Res.* **28**, 75 (2008).
- [57] M. Matsui, *International Conference On High Pressure Science and Technology, Joint AIRAPT-22 and HPCJ-50* 215, 012197 (2010).
- [58] V. B. Prakapenka, A. Kubo, A. Kuznetsov, A. Laskin, O. Shkurikhin, P. Dera, M. L. Rivers, and S. R. Sutton, Advanced flat top laser heating system for high pressure research at GSECARS: application to the melting behavior of germanium, *High Press. Res.* **28**, 225 (2008).
- [59] M. Kunz *et al.*, A beamline for high-pressure studies at the advanced light source with a superconducting bending magnet as the source, *J. Synchrotron Radiat.* **12**, 650 (2005).
- [60] C. Prescher and V. B. Prakapenka, DIOPTAS: a program for reduction of two-dimensional x-ray diffraction data and data exploration, *High Press. Res.* **35**, 223 (2015).
- [61] W. Kraus and G. Nolze, POWDER CELL-a program for the representation and manipulation of crystal structures and calculation of the resulting x-ray powder patterns, *J. Appl. Crystallogr.* **29**, 301 (1996).
- [62] B. H. Toby and R. B. Von Dreele, GSAS-II: the genesis of a modern open-source all purpose crystallography software package, *J. Appl. Crystallogr.* **46**, 544 (2013).
- [63] V. V. Struzhkin, D. Y. Kim, E. Stavrou, T. Muramatsu, H.-k. Mao, C. J. Pickard, R. J. Needs, V. B. Prakapenka, and A. F. Goncharov, Synthesis of sodium polyhydrides at high pressures, *Nat. Commun.* **7**, 12267 (2016).
- [64] A. Boultif and D. Lour, Powder pattern indexing with the dichotomy method, *J. Appl. Crystallogr.* **37**, 724 (2004).
- [65] E. Stavrou, A. Muhtar, F. M. Mohammad, and A. F. Goncharov, Probing the different spatial scales of Kel F-800 polymeric glass under pressure, *Sci. Rep.* **3**, 1290 (2013).