Magnetic surface on nonmagnetic bulk of electride Hf$_2$S

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Recent experiment reported the self-passivated electride Hf$_2$S with excellent stability and continuous electrocatalytic ability [S. H. Kang et al., Sci. Adv. 6, eaba7416 (2020)]. Starting from its 2H-type layered structure, we have studied the electronic, magnetic, and transport properties of the electride Hf$_2$S in the monolayer and multilayer forms by combining first-principles electronic structure calculations and Kubo formula approach. Our calculations indicate that these thin films of Hf$_2$S electride are both dynamically and thermodynamically stable. Astonishingly, the calculations further show that the outmost Hf atoms and the surface electron gas of the Hf$_2$S multilayers are spin polarized, while the inner Hf atoms and the electron gas in the interlayer regions remain nonmagnetic. Due to the magnetic surface, the multilayer Hf$_2$S exhibits many unusual transport properties such as the surface anomalous Hall effect and the electric-field-induced layer Hall effect. Our theoretical predictions on Hf$_2$S call for future experimental verification.

Electrides, identified by the anionic electrons locating at the vacant crystallographic sites and being unbounded to any nuclei in the lattice, have attracted widespread attention recently [1, 2]. The diverse distributions of interstitial electrons in the electrides endow them with particular properties, including high electronic concentration and conductivity, high density active sites, low work function, etc [1–4]. These outstanding properties make electrides serve as excellent candidates for the applications in catalysts, rechargeable batteries, electron emitters, light-emitting diodes, and so on [1, 2, 5–7]. Besides the practical applications, many interesting quantum phenomena, such as superconductivity [8], magnetism [9], and non-trivial topological property [10], have also been discovered in the electrides. And the role of the interstitial electrons playing in the those properties of electrides has been revealed. Nevertheless, the research on the electrides is still in its infancy and there are still plenty of properties remaining unexplored.

According to the space distribution property of its interstitial electron gas, electride can also perform dimensionality characters (0–3D) [11]. Specially, the 2D electrides with layered structures have attracted intensive attention due to their unique physical properties, feasible exfoliation down to atomically thin films, as well as potential integrations with other 2D materials. For instance, versatile topological band features were found in the 2D electrides such as Y$_2$C, Sc$_2$C, etc [12, 13]. The nonmagnetic 2D electride Ca$_2$N [14] may become magnetic via the hydrogenation [15]. The ferromagnetic 2D electride Gd$_2$C [16] owns high Curie temperature [9] and multiple pairs of Weyl points [16]. Recently, it was reported that a self-passivated 2D electride namely dihafnium sulfide, written as [Hf$_2$S]$^{2+}$.2e$^-$, exhibits a strong oxidation resistance in water and acid solutions and can persist the electrocatalytic hydrogen evolution reaction [17]. Since Hf$_2$S owns a 2H-type layered structure, whether its thin-film forms are stable and whether it hosts interesting quantum phenomena as the reduction of dimensionality wait for further in-depth studies.

In this work, based on first-principles electronic structure calculations and Kubo formula approach, we have studied the electronic, magnetic, and transport properties of the multilayers of Hf$_2$S electride. Our calculations indicate that distinct from the nonmagnetic bulk phase, multilayer Hf$_2$S can hold a magnetic electron gas at the surface along with the nonmagnetic electron gas in the inner interlayer regions. We then analyzed the origin of the surface magnetism, and further studied the electric-field-induced layer Hall effect and the abnormal Hall effect of multilayer Hf$_2$S.

The structural, electronic, and magnetic properties of n-layer (n = integer) Hf$_n$S were investigated with the spin-polarized density functional theory (DFT) [18, 19] calculations as implemented in the Quantum ESPRESSO (QE) [20] and VASP [21, 22] packages. The generalized gradient approximation of Perdew-Burke-Ernzerhof [23] (PBE) type was adopted for the exchange-correlation functional. The 2D anomalous Hall conductivity ($\sigma_{xy}$) was calculated with the Kubo-formula approach in the linear response scheme [24] via the Berry curvature by using the WannierTools package [25], which is interfaced to the Wannier90 software [26]. More computational details are described in the Supplemental Information (SI) [27].

We firstly studied Hf$_2$S in the monolayer limit. From the side view of monolayer Hf$_2$S [Fig. 1(a)], we can see that the S atomic plane is sandwiched by two Hf atomic planes with the mirror symmetry. In each atomic plane, S or Hf atoms form a triangular lattice. Considering the partially filled 5d orbitals of Hf atoms, we performed the spin-polarized DFT calculations to check the possible magnetism on the Hf lattice. Several typical spin configurations have been considered (see Fig. S1 in the

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FIG. 1: (Color online) (a) Side view of monolayer Hf₂S. The orange (purple) balls represent the Hf (S) atoms. The red (green) arrows label the up (down) spins. Spatial distributions of (b) the electron localization function (ELF) and (c) the spin density \( n_{\text{spin}}(r) = n_{\uparrow}(r) - n_{\downarrow}(r) \). The red and blue regions in panel (c) indicate the signs of \( n_{\text{spin}}(r) \). The orbital distributions derived from the maximally localized Wannier functions (MLWF) for the top-surface electron gas \( e^- \) in the (d) spin-up and (e) spin-down channels. (f) Phonon dispersion. (g) Time evolution of free energy at 300 K from a molecular dynamic simulation. (h) Electronic band structure. The sizes of red and blue dots on the bands represent the weights of the \( e^- \) and Hf-d MLWF orbitals. (i) Partial density of states (PDOS) for the \( e^- \) (red lines) and Hf d (blue lines) MLWF orbitals in the top surface. The upper and lower parts correspond to the spin-up and spin-down channels, respectively.

We then explore the electronic and magnetic properties of monolayer Hf₂S in the AFM ground state. As shown by the electron localization function (ELF) [28] in Fig. 1(b), there are electron gases floating on both surfaces of monolayer Hf₂S. These electron gases exhibit the AFM spin polarization as indicated by the real-space spin densities \( [n_{\text{spin}}(r) = n_{\uparrow}(r) - n_{\downarrow}(r)] \) in Fig. 1(c), which are different from the nonmagnetic electron gas in the interlayer regions of bulk phase [17, 30]. With the maximally localized Wannier function (MLWF) method [26], we can describe the electron gas on the surface of monolayer Hf₂S by a Wannier orbital \( (e^-) \), whose spatial distributions in the spin-up and spin-down channels are demonstrated in Figs. 1(d) and 1(e), respectively. The electronic band structure calculated with the MLWF is displayed in Fig. 1(h), which matches well with the DFT result in SI [27]. There are several bands crossing the Fermi level, indicating a metallic behavior. The electronic states around the Fermi level mainly originate from the electron gas \( (e^-) \) and the Hf d orbitals, whose weights scale with the dot sizes on the bands. The corresponding partial density of states (PDOS) are shown in Fig. 1(i), which indicates that the spin polarization of the electron gas \( (e^-) \) is parallel to that of its neighbor Hf atoms.

To explore the origin of the interesting surface magnetism of monolayer Hf₂S, we simulated the exfoliating process from the bulk material to the monolayer limit step by step. Figure 2 exhibits the evolution of electronic DOS with the interlayer distance \( d \). In the nonmagnetic bulk phase [Fig. 2(a)], there is no obvious peak around the Fermi level. Once the interlayer distance is enlarged by 1 Å \( (d = 1 \text{ Å}) \), the DOS shows dramatic changes with two large peaks below and above the Fermi level [Fig. 2(b)]. When the interlayer distance increases to \( d = 2 \text{ Å} \) [Fig. 2(c)], the nonmagnetic DOS (black line) produces a peak at the Fermi level, and the AFM state becomes the ground state and reduces the intensity of DOS at \( E_F \) (red line). With further increasing \( d \) (3 or 4 Å) [Figs. 2(d) and 2(e)], the peak of nonmagnetic DOS (black line) around the Fermi level is more prominent, which then splits into the upper and lower peaks.
in the AFM state (red line), forming a V-shaped DOS around the Fermi level. A natural explanation is that the cleavage of the layered structure weakens the original interlayer orbital hybridization, makes the surface electron gas of monolayer Hf$_2$S more localized, and then results in the peak of DOS around the Fermi level. According to the Stoner criterion, a large DOS around the $E_F$ can drive the system into magnetic phase, forming FM exchange interaction in same-layered (upper or lower) Hf atoms by itinerant surface electron gas and AFM super-exchange interaction among different Hf atomic layers by middle S atoms. When the interlayer distance $d$ becomes large enough, the DOS converges to the monolayer limit as shown in Fig. 2(f).

Considering that Hf$_2$S is nonmagnetic in the bulk form but AFM in the monolayer phase [Fig. 1(a)], we are curious about the evolution of magnetic properties with the layer thickness. According to the 2H-type stacking of bulk Hf$_2$S, we obtained the atomic structures of 2-layer, 3-layer, and 4-layer Hf$_2$S. The distributions of electron localization functions (ELF) and spin densities $n_{\text{spin}}(r)$ in the monolayer and multilayer forms are demonstrated in Fig. 3. From the ELF plots along the $z$ direction, we can see that there are electrons localized on the S planes. Meanwhile, the positions of localized electrons around the Hf atoms slightly deviate from the Hf planes, which results from the accumulation of electron gases in the interstitial regions. Astonishingly, we find that the electron gases locating in the interlayer regions of the Hf$_2$S multilayers are not spin-polarized, while the electron gases at the upper and bottom surfaces still hold their original spin polarizations as in the monolayer form [Figs. 3(d), 3(f), and 3(h)]. The interlayer electron gases in multilayer Hf$_2$S can be viewed as the one obtained by superposing the surface electron gases of two neighboring Hf$_2$S monolayers with the opposite spin polarizations. When the interlayer distance $d$ is small enough, the electron gases with opposite spins from different Hf$_2$S layers coalesce and form a nonmagnetic interstitial one, which is in accordance with its nonmagnetic bulk counterpart. The magnetic electron gas on the surface of the nonmagnetic bulk is an unexpected finding for the electride Hf$_2$S. In real materials, the cleaved Hf$_2$S surface often exhibits the amorphous structure [17]. To observe such magnetic surface electron gas, one should obtain a flat and clean surface of Hf$_2$S by using the molecular beam epitaxy (MBE) growth technique [29].

As the spin-polarized charge only exists on the surfaces (Fig. 3), Hf$_2$S may show novel transport behaviors that resemble but differ from previous Hall effects. In the conventional anomalous Hall effect, an intrinsic ferromagnetic bulk state generates a non-zero anomalous Hall conductivity (AHC) in a zero magnetic field. Here for the Hf$_2$S, the AHC could only exist on the surface since its inner part is nonmagnetic. However, the upper and bottom surfaces of multilayer Hf$_2$S own opposite spin polarizations and there is no net magnetic moment. Hence, a non-zero AHC can just exist on a single surface of multilayer Hf$_2$S. This situation is very similar to...
that the spin-polarized electronic states only exist on the surface. The calculated 2D AHC on the single surface is shown in Fig. 5(b). The $\sigma_{xy}^{2D}$ at the Fermi level is about 0.6 $e^2/h$, close to that of the previously reported 2D ferromagnets, such as Fe$_3$GeTe$_2$ (0.4 $\sim$ 1.5 $e^2/h$) [32, 33].

In summary, we have studied the electride Hf$_2$S in the monolayer and multilayer forms by using first-principles electronic structure calculations and Kubo formula approach. Our calculations indicate that in monolayer Hf$_2$S both the Hf atoms and the surface electron gases are spin polarized, which are ferromagnetic in the same Hf layer but antiferromagnetic between the upper and bottom Hf layers. After stacking to the multilayer, the interstitial electron gases between the neighboring Hf$_2$S layers become nonmagnetic, while the surface electron gases retain the original spin polarizations as in the monolayer case. The coexistence of nonmagnetic bulk states and ferromagnetic surface states may produce some interesting physics properties, such as the surface-related LHE and the non-zero surface AHC. The electride Hf$_2$S, as well as its isostructural compounds Hf$_2$Se$_3$ [30] and Hf$_2$Te$_3$, can thus hold exotic quantum phenomena that are worth of further theoretical and experimental investigations.

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Note added: In preparing our manuscript, we learned that a related work posted on the arXiv [34], which also found the magnetic surface electron gas on Hf$_2$S but paid more attention to the topological properties.
[1] H. Hosono and M. Kitano, Chem, Rev. 121, 3121 (2021).
[2] X.-H. Yang and G.-C. Zhang, J. Phys. Chem. Lett. 11, 3841 (2020).
[3] S. W. Kim, S. Matsuishi, T. Nomura, Y. Kubota, M. Takata, K. Hayashi, T. Kamiya, M. Hirano, H. Hosono, Nano Lett. 7, 1138 (2007).
[4] Y. Toda, H. Yanagi, E. Ikenaga, J. J. Kim, M. Kobata, S. Ueda, T. Kamiya, M. Hirano, K. Kobayashi, H. Hosono, Adv. Mater. 19, 3564 (2007).
[5] R. H. Huang, J. L. Dye, Chem. Phys. Lett. 166, 133 (1990).
[6] J. Wu, J. Li, Y. Gong, M. Kitano, T. Inoshita, H. Hosono, Angew. Chem., Int. Ed. 58, 825 (2019).
[7] E. Feizi, A. K. Ray, J. Disp. Technol. 12, 451 (2016).
[8] M. Miyakawa, S. W. Kim, M. Hirano, Y. Kohama, H. Kawai, T. Atake, H. Ikegami, K. Kono, and H. Hosono. J. Am. Chem. Soc. 129, 7270 (2007).
[9] S. Y. Lee, J.-Y. Hwang, J. Park, C. N. Nandadasa, Y. Kim, J. Bang, K. Lee, K. H. Lee, Y.-W. Zhang, Y.-M. Ma, H. Hosono, Y. H. Lee, S.-G. Kim, and S. W. Kim, Nat. Commun. 11, 1526 (2020).
[10] J.-C. Gao, Y.-T. Qian, H.-X. Jia, Z.-P. Guo, Z. Fang, M. Liu, H.-M. Weng, Z.-J. Wang, Sci. Bull. 67, 598 (2022).
[11] Y.-W. Zhang, H. Wang, Y.-C. Wang, L.-J. Zhang, and Y.-M. Ma, Phys. Rev. X 7, 011017 (2017).
[12] H. Tamatsukuri, Y. Murakami, Y. Kuramoto, H. Sagayama, and H. Hosono, Phys. Rev. B. 102, 224406 (2020).
[13] M. Hirayama, S. Matsuishi, H. Hosono, and S. Murakami, Phys. Rev. X 8, 031067 (2018).
[14] D. L. Druffel, K. L. Kuntz, A. H. Woomer, F. M. Alcorn, J. Hu, C. L. Donley, and S. C. Warren, J. Am. Chem. Soc. 138, 16089 (2016).
[15] X.-L. Qiu, J.-F. Zhang, Z.-Y. Lu, and K. Liu, J. Phys. Chem. C 123, 24698 (2019).
[16] S. Liu, C. Wang, L. Liu, J.-H. Choi, H.-J. Kim, Y. Jia, C. H. Park, and J.-H. Cho, Phys. Rev. Lett. 125, 187203 (2020).
[17] S. H. Kang, J. Bang, K. Chung, C. N. Nandadasa, G. Han, S. Lee, K. H. Lee, K. Lee, Y. Ma, S. H. Oh, S.-G. Kim, Y.-M. Kim, S. W. Kim, Sci. Adv. 6, eaba7416 (2020).
[18] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
[19] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[20] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., J. Phys.: Condens. Matter 21, 395502 (2009).
[21] G. Kresse and J. Furthmüller, Comput. Mater. Sci 6, 15 (1996).
[22] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[24] D. Xiao, M.-C. Chang, and Q. Niu, Rev. Mod. Phys. 82, 1959 (2010).
[25] Q. Wu, S. Zhang, H.-F. Song, M. Troery, and A. A. Soluyanov, Comput. Phys. Commun. 224, 405 (2018).
[26] A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun. 185, 2309 (2014).
[27] See Supplemental Material for more calculation details.
[28] B. Silvi and A. Savin, Nature 371, 683-686 (1994).
[29] Z. Sun, X. Han, Z. Cai, S. Yue, D. Geng, D. Rong, L. Zhao, Y.-Q. Zhang, P. Cheng, L. Chen, X. Zhou, Y. Huang, K. Wu, B. Feng, Sci. Bull. in proof.
[30] X. Wang, X. Qiu, C. Sun, X. Cao, Y. Yuan, K. Liu, and X. Zhang, Chin. Phys. Lett. 38, 017302 (2021).
[31] A. Gao, Y.-F. Liu, C. Hu, J.-X. Qiu, C. Tzchaschel, B. Ghosh, S.-C. Ho, D. BšŠrubsšš, R. Chen, H. Sun, Z. Zhang, X.-Y. Zhang, Y.-X. Wang, N. Wang, Z. Huang, C. Felser, A. Agarwal, T. Ding, H.-J. Tien, A. Akay, J. Gardener, B. Singh, K. Watanabe, T. Taniguchi, K. S. Burch, D. C. Bell, D. B. Zhou, W. Gao, H.-Z. Lu, A. Bansil, H. Lin, T.-R. Chang, L. Fu, Q. Ma, N. Ni, and S.-Y. Xu, Nature 595, 521 (2021).
[32] Y. Deng, Y. Yu, Y. Song, J. Zhang, N. Z. Wang, Z. Sun, Y. Yi, Yi Z. Wu, S. Wu, J. Zhu, J. Wang, X. H. Chen, and Y. Zhang, Nature 563, 94 (2018).
[33] X. Lin and J. Ni, Phys. Rev. B 100, 085403 (2019).
[34] S. Liu, C. Wang, H. Jeon, Y. Jia, and J.-H. Cho, arXiv:2206.03689 (2022).