Face-centered cubic MoS$_2$: a novel superconducting three-dimensional crystal more stable than layered T-MoS$_2$†

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Beyond graphene, MoS$_2$ has been intensively studied because of its unique properties. To date, several distinct isomers of MoS$_2$ have been experimentally synthesized. These include semiconducting H-MoS$_2$ and metal T-MoS$_2$ as well as topological insulating T'-MoS$_2$ but only in van der Waals layered materials. Here we authenticate a previously unknown phase of three-dimensional Kagome MoS$_2$ in the face-centered cubic (FCC) space group $Fdar{3}m$ using first-principles calculations. We show that the FCC-MoS$_2$ is a Bardeen–Cooper–Schrieffer superconductor with a relatively high transition temperature ($\sim 16.16$ K) higher than that ($\sim 12$ K) of pristine 2H$_c$-MoS$_2$ recently synthesized in experiments. The mechanism for superconducting in this crystal originates from the high s–p–d band hybridizations compatible with the cubic lattice symmetry in the vicinity of the Fermi level. Remarkably, FCC-MoS$_2$ is $\sim 33.51$ meV per atom lower and thermally more stable than the layered T-MoS$_2$. Pure FCC-MoS$_2$ may be prepared by the removal of Ga atoms from the single crystal GaMo$_4$S$_8$, thus holding great promise for superconducting device applications and stimulating further efforts on transition metal-based superconducting materials.

Introduction

Transition-metal dichalcogenides (TMDs) are well-known inorganic layered two-dimensional (2D) materials with general formula MX$_2$ where M is a transition-metal atom from group IV, group V or group VI, and X is a chalcogen atom. These materials usually exhibit diverse properties that mostly depend on their composition and can be metals (e.g., NbS$_2$, VSe$_2$), superconductors (e.g. NbSe$_2$, TaS$_2$), semiconductors (e.g., MoS$_2$, WS$_2$) and dirac materials (e.g., WTe$_2$, TiSe$_2$). These features endow TMDs with enormous potential in ultrathin field-effect transistors, photo detectors, light-emitting diodes, solar cells, electrocatalysis and superconductors. Among the various TMDs, molybdenum disulfide (MoS$_2$) is undoubtedly the most representative member of this class. In general, MoS$_2$ admits two typical polymorphs differing in the coordination of the Mo atom, i.e., the thermodynamically stable H-phase (space group, $P6_3/mmc$), and the meta-stable T-phase (space group, $P3m1$), which exhibit entirely different electronic properties. H-MoS$_2$ with edge-sharing [MoS$_6$] trigonal prisms is an intrinsic semiconductor which shows extraordinary layer-dependent photoelectric properties and has been successfully used in logic circuits, and low-power field effect transistors. In contrast, the meta-stable T-MoS$_2$ with an edge-sharing [MoS$_6$] octahedron is a true metal and displays an inverted hexagonal symmetry. Specifically, the Mo atoms in the T-phase could undergo a variety of metal-atom clustering processes due to metal–metal bond formation and then dimerize into alternating zigzag chains to further form the topological insulating T'-MoS$_2$. Besides, theoretical studies have revealed that some meta-stable 2D MoS$_2$ polymorphs were composed of four- and eight-membered rings, as well as six-membered rings, which exhibit fascinating topological states with tunable nontrivial band gaps. Meanwhile, other crystal structures and possible stoichiometries for new materials have been predicted by applying modern widely-available enthalpy-based tools, such as Calypso, USPEX and XtalOpt. These research studies have greatly promoted the development of materials science.

More recently, the crystal structure of layered T-MoS$_2$ has been successfully re-determined from single-crystal X-ray studies and experimentally verified to possess an intrinsic superconducting transition temperature of $T_c = 4$ K. First-principles calculations have demonstrated enhanced superconductivity in monolayer H-MoS$_2$ by chemical intercalation, electrostatic gating, and increased pressure. Additionally, Raman spectra and X-ray diffraction patterns, which are obtained at pressures up to $\sim 81$ GPa in diamond anvil cells, provide evidence for pressure-induced metallization of H-MoS$_2$ from 2H$_c$ to 2H$_p$. When extending...
pressure beyond the megabar range, an intrinsic superconductivity emerges in the 2H-MoS2 with an onset critical temperature \( T_c \) being stabilized at \( \sim 12 \) K over a wide pressure range up to \( \sim 220 \) GPa.\(^{33}\) These findings will greatly stimulate further studies on superconductivity of MoS2 in experiment and theory.

Although multiple polymorphs of MoS2 have been reported via experiments or first-principles methods, all of them are van der Waals layered materials\(^{34}\) and none in three-dimensional (3D) covalently linked structures have been reported. A natural question then arises: does there exist a 3D covalently linked phase for MoS2 as a superconductor? Motivated by the coexistence of van der Waals layered graphite and 3D covalently linked diamond in C-based materials, herein we identify for the first time a previously unknown phase of 3D covalently linked MoS2, which possesses the face-centered cubic (FCC) space group \( Fd\bar{3}m \) and holds the edge-sharing \([\text{MoS}_6]\) octahedron the same as the layered T-MoS2. We find that this 3D phase (denoted as FCC-MoS2) is thermally more stable than the experimentally synthesized T-MoS2.

Using first-principles calculations, we show that FCC-MoS2 is a typical Bardeen–Cooper–Schrieffer (BCS) superconductor with a high transition temperature of \( 16.16 \) K. The high \( T_c \) in FCC-MoS2 is caused by the outermost orbitals of Mo and S atoms fully participating in hybridization around the Fermi level, which is clearly different from H-MoS2 and T-MoS2. The stability, electronic properties, and mechanical properties are also discussed.

**Methods**

First-principles calculations were performed within the framework of the density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP).\(^{35}\) The core electrons were represented by the projector-augmented wave potentials\(^{16}\) and the exchange–correlation functional was treated within the generalized gradient approximation of Perdew–Burke–Ernzerhof type, which were widely used in the development of new materials.\(^{17}\) The van der Waals interaction (vdW-DF) of Dion et al.\(^{18–40}\) was considered in the MoS2. Geometries were fully relaxed until the residual forces on each atom became less than 0.01 eV Å\(^{-1}\). The 0.03 Å\(^{-1}\) spacing Monkhorst–Pack mesh with a cutoff of 500 eV was used in the optimization. The cohesive energies, electronic structures, and orbital contributions were analyzed by VASP with the plane-wave basis sets being 500 eV on the 0.01 Å\(^{-1}\) spacing Monkhorst–Pack mesh. In addition, our results on electronic structures were also tested with spin–orbit interactions. Even though electrons in transition-metal materials were highly correlated and predictions obtained using DFT on the band gaps of transition-metal materials were often wrong, we neglected this effect since it was less important in describing the electronic structures around the Fermi level for metals.\(^{2}\)

The superconducting properties were calculated by the QUANTUM ESPRESSO (QE) code\(^{41,42}\) using the norm-conserving pseudopotentials with a cutoff energy of 80 Ry (1088 eV) for the wave functions. The Brillouin zone (BZ) sampling of \( 16 \times 16 \times 16 \) for FCC-MoS2 was used on Monkhorst–Pack \( k \)-point grids with a Gaussian smearing width of 0.02 Ry (0.27 eV). Using the above \( k \)-point samplings for the self-consistent cycle, the dynamic matrices were calculated on a \( 4 \times 4 \times 4 \) \( q \)-point mesh.\(^{45}\) Then a dense \( 36 \times 36 \times 36 \) grid was used in the BZ integrations to produce accurate electron–phonon interaction matrices. To estimate \( T_c \), the McMillan–Allen–Dynes formula was used with a regular Coulomb pseudopotential \( \mu^*\).\(^{44–46}\) The vibrational properties of this system were further checked by the phonon calculations via density functional perturbation theory\(^{43}\) as implemented in the PHONOPY code\(^{47}\) bundled with VASP.\(^{35}\) All the calculations in VASP and QE were based on the primitive unit cell MoS2.

**Results and discussion**

Fig. 1 shows the atomic structure of the FCC-MoS2 in the space group of \( Fd\bar{3}m \) (no. 227). The structure features a novel 3D framework comprising the \([\text{MoS}_6]\) octahedron, which is totally different from those of the layered H-, T- and T’-MoS2 being associated through van der Waals forces to form their own 3D frames (Fig. S1, ESI†). The optimized lattice of FCC-MoS2 is 9.59 Å and can be defined in terms of the primitive lattice with a value of 6.78 Å (Fig. S2, ESI†). In the conventional cell, there are forty-eight atoms with two crystallographically independent sites, which are 16c (0.00, 0.00, 0.00) and 32e (0.25, 0.25, 0.25) for Mo and S atoms, respectively. Fig. 2 shows the schematic of the 3D network for FCC-MoS2. From the side view of the crystal structure, we can see that the compound adopts a 3D framework structure that consists of alternate stacking of two distinct octahedral layers (Fig. 2a). The crossways stacking 2D layers (layer1 and layer2) are constituted by the slightly distorted \([\text{MoS}_6]\) octahedron. Overall speaking, as listed in Table 1, the Mo atoms in FCC-MoS2 are octahedrally bonded with the six nearest neighboring S atoms in two type of distances (2.38 and 2.54 Å), which are different from the feature in (2.44 Å) H-MoS2 and (2.39 Å) T-MoS2 with six identical Mo–S bonding. Compared to T-MoS2, layer1 and layer2 of FCC-MoS2 have the same S–Mo–S sandwiched structures but with interlayer charge disproportionation of Mo1 trimers. To gain a clearer insight into the structure, only Mo atoms are shown in Fig. 2b. Without showing S atoms, the Mo–Mo bonding forms the Kagome lattice\(^{50}\) which has served as the most intriguing playground for many exotic

**Fig. 1** The crystal structure of FCC-MoS2. The octahedrons of \([\text{MoS}_6]\) are emphasized by red and blue colors for the adjacent layers.
single crystals of T-MoS$_2$ have been synthetized in a recent experiment. We note that the 2D crystals of H-MoS$_2$ are the most stable phase, which is consistent with the reported results. However, we note that the 2D crystals of FCC-MoS$_2$ is lower by 33.51 meV per atom, demonstrating that the relative total energy of H-MoS$_2$. Our results show that the relative total energy of FCC-MoS$_2$ is calculated to be 0.39, which is larger than that of bulk H-MoS$_2$. According to Pugh's criterion, if $G/K > 0.57$, the material behaves in a brittle manner, while if $G/K < 0.57$, the material behaves in a ductile manner. The $G/K$ values of FCC-MoS$_2$ and H-MoS$_2$ are 0.87 and 0.39. The orientation-dependent elastic properties for the crystal are also calculated and presented in Fig. S3 and Table S1 (ESI†), which reveal strong anisotropy of the Young's modulus, the shear modulus, and Poisson's ratio, as well as the isotropic linear compressibility.

The calculated orbital-resolved band structure of FCC-MoS$_2$ is shown in Fig. 3a. The corresponding high-symmetry points are indicated in the first Brillouin zone (Fig. S4, ESI†). The crystal exhibits an intrinsic metallic nature with the valence band (VB) and conduction band (CB) crossing the Fermi level. The orbitals from Mo atoms dominate around the Fermi level with only some contributions from S-p orbitals, which is to some extent analogous to the layered TMDs. More specifically, in the case of FCC-MoS$_2$ (Fig. 3b and c), the frontier orbitals involve all of the outermost-shell orbitals for Mo and S atoms. The Mo-d orbitals and S-p orbitals hybridize with a small quantity of S-s orbitals, which leads to a high density of states of the s-p-d electron gas at the Fermi level. The highly symmetric cubic lattice in FCC-MoS$_2$ causes the fully hybridized orbitals to be in the small energy range of $-0.3$ to 0.3 eV, which gives rise to distinct electronic properties from those of other MoS$_2$ polymorphs (H-, T-, and T'-phases). Accordingly, such a high electronic density of states of 9.61 states per eV per unit cell apparently favors superconducting in our newly predicted crystal.

The Fermi surface contour of FCC-MoS$_2$, shown in Fig. 3a and Fig. S5 (ESI†), clearly indicates that the electron ellipsoid (blue) and the hole pocket (red) coexist at the Fermi surface. Deduced from the previous orbital-contribution analysis, both the electron ellipsoid and the hole pocket have the characteristics of hybridized bands stemming from Mo-S bonding. This feature of electron and/or hole pockets formed by the d-orbitals of transition metals and p-orbitals of group-VI elements also appears to play a key role in the triggering of the superconductivity in single layer FeSe and 2D organic superconducting Cu-BHT. Fig. 4 shows the
whole phonon dispersion $\omega_{qn}$, which clearly confirms the dynamic stability of FCC-MoS$_2$ in the absence of negative phonon vibrational modes. The acoustic modes exhibit normal linear dispersions in the low-energy region, which is totally different from the parabolic acoustic dispersions in layered MoS$_2$.\(^{62}\)

According to the microscopic theory of Bardeen, Cooper, and Schrieffer,\(^{65}\) the electron–phonon coupling (EPC) strength $\lambda_{qp}$ is resolved by

$$\lambda_{qp} = \frac{4}{\omega_{qp}N(0)N_k} \sum_{k,m,n} |g_{kn,k+qm}^r|^2 \delta(\epsilon_{kn}) \delta(\epsilon_{k+qm})$$

(3)

where $N(0)$ and $N_k$ are respectively the electron DOS and the number of $k$ points at the Fermi level, $\omega_{qp}$ is the amplitude of displacement of the phonon, $V$ is the Kohn–Sham potential, $g_{kn,k+qm}^r$ is the scattering amplitude of an electronic state $|kn\rangle$ into another state $|k+qm\rangle$ resulting from the change in the self-consistent field potential $\delta V/\delta \phi_{kn}$ arising from a phonon $\omega_{qp}$. The size and color of the circles in Fig. 4 are drawn proportional to the EPC $\lambda_{qp}$ for the corresponding phonon vibrational mode. Clearly, the three acoustic branches and low-energy optical branches with frequencies below 150 cm$^{-1}$ possess strong electron–phonon coupling, while the contributions from other optical branches can be negligible. Specifically, $\Gamma$- (at $\sim$ 74.6 cm$^{-1}$) and $W$-phonon (at $\sim$ 78.1 cm$^{-1}$) modes along the optical branches show ultra-strong EPC $\lambda_{qp}$. When the phonon wave vector $q$ moves away from $\Gamma$ or $W$ points, the coupling strength decreases slowly. This is different from the doped monolayer MoS$_2$\(^{33}\) and intercalated bilayer MoS$_2$\(^{28–30}\) in which the softened acoustic branch has the strong EPC $\lambda_{qp}$.

Next, we calculate the partial phonon density of states (PhDOS), the Eliashberg function

$$\chi^2 F(\omega) = \frac{1}{2N_q} \sum_q \lambda_{q} \omega_{q} \delta(\omega - \omega_{q})$$

(5)

and the cumulative frequency-dependent EPC function

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

(6)

to analyze the contributions of atomic vibration to the EPC constant. On the basis of the above values, the superconducting transition temperature $T_c$ is estimated according to the modified McMillan equation:\(^{65}\)

$$T_c = \frac{\omega_{log}}{1.2} \exp \left[ -\frac{1.04(1+\mu^*)}{\lambda - 1.62(1+0.62\mu^*)} \right]$$

(7)

where $\mu^*$ is the effective Coulomb repulsion parameter and $\omega_{log}$ is the logarithmically averaged frequency given by

$$\omega_{log} = \exp \left[ 2 \int_0^\infty \frac{d\omega}{\lambda} \chi^2 F(\omega) \log \omega \right]$$

(8)

Here we take a typical value $\mu^* = 0.1$ (Fig. S6, ESI\(^+\)). To explicitly illustrate the superconducting properties, the frequency-dependent PhDOS, $\chi^2 F(\omega)$, $\lambda(\omega)$, and $T_c$ are schematically represented in four stages (I, II, III, and IV) in Fig. 5. From the PhDOS, one can see that the phonon vibrations below 150 cm$^{-1}$ (I and II stages) mainly stem from Mo atoms hybridized with 32.7% contributions from S atoms. Stage I, from 0 cm$^{-1}$ to 85 cm$^{-1}$, contributes largely to total EPC with large $\lambda_{qp}$ from the three acoustic branches and...
the two lowest energy optical branches. As a consequence, the cumulative frequency-dependent function EPC possesses its maximum slope for this range and the value of frequency-dependent $T_c$ increases rapidly up to $\sim 10.57$ K. For stage II, the low-energy optical branches with strong EPC result in the increase of $T_c$ from $\sim 10.57$ K to $\sim 13.09$ K. In stages III and IV, the S atomic contributions become predominant with 80.8% and 85.5% weights, whereas the phonon modes contribute little to the optical branches with strong EPC result in the increase of $T_c$ from $\sim 13.09$ to $\sim 15.93$ and then to $\sim 16.16$ K. These results indicate that FCC-MoS$_2$ is an intrinsic BCS-type superconductor with a strong EPC ($\lambda > 1$).65,67,68

We emphasize that this novel finding of FCC-MoS$_2$ being superconducting is a significant issue, as it reveals a new family of 3D covalently linked structures in TMDs beyond van der Waals layered materials. It can be viewed as the diamond-like polymorph in TMDs, in analogy to carbon materials inclusive of graphite and diamond. Meanwhile, our finding represents an alternative strategy for achieving superconductivity in MoS$_2$ in addition to chemical intercalation, electrostatic gating, and increased pressure.33 In fact, the single crystal GaMo$_4$S$_8$ possessing the basic framework of FCC-MoS$_2$ has already been observed in the experiment.69 We expect that experimental realization of our theoretical prediction will come with bulk synthesizing subsequently via the chemical equation: GaMo$_4$S$_8$ $\rightarrow$ 4MoS$_2$ + Ga$^{3+}$ + 3e$^-$. The efforts here should be removing the Ga atoms from the bulk samples while keeping the framework of [MoS$_2$] unchanged.

**Conclusions**

In summary, we predict a new kind of 3D covalently linked structures in MoS$_2$, which features one family of Kagome TMDs beyond van der Waals layered materials. Here the outermost-shell orbitals of Mo and S atoms fully participate in hybridizations, leading to a high electronic density of states, and accordingly a relatively high superconducting transition temperature of about 16 K for FCC-MoS$_2$. The discovery of superconductivity in the three-dimensional Kagome lattice potentially opens up a new avenue to explore superconductors in MoS$_2$ and its congeners.

**Conflicts of interest**

There are no conflicts to declare.

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**References**