Strong-coupling superconductivity with $T_c \sim 10.8$ K induced by P doping in the topological semimetal Mo$_5$Si$_3$

Bin-Bin Ruan$^{1*}$, Jun-Nan Sun$^{1,2,3\dagger}$, Yin Chen$^{1,4}$, Qing-Song Yang$^{1,5}$, Kang Zhao$^{1,6}$, Meng-Hu Zhou$^{1}$, Ya-Dong Gu$^{1,5}$, Ming-Wei Ma$^{1,7}$, Gen-Fu Chen$^{1,5,7}$, Lei Shan$^{2,3}$, and Zhi-An Ren$^{1,5\star}$

ABSTRACT By performing P doping on the Si sites in the topological semimetal Mo$_5$Si$_3$, we discover strong-coupling superconductivity in Mo$_{5-x}$Si$_{3+x}$P$_x$ ($0.5 \leq x \leq 2.0$). Mo$_5$Si$_3$ crystallizes in the W$_5$Si$_3$-type structure with space group of I4/mcm (No. 140), and is not a superconductor itself. Upon P doping, the lattice parameter $a$ decreases while $c$ increases monotonously. Bulk superconductivity is revealed in Mo$_{5-x}$Si$_{3+x}$P$_x$ ($0.5 \leq x \leq 2.0$) from resistivity, magnetization, and heat capacity measurements. $T_c$ in Mo$_{5-x}$Si$_{3+x}$P$_x$ reaches as high as 10.8 K, setting a new record among the W$_5$Si$_3$-type superconductors. The upper and lower critical fields for Mo$_{5-x}$Si$_{3+x}$P$_x$ are 14.56 T and 105 mT, respectively. Moreover, Mo$_{5-x}$Si$_{3+x}$P$_x$ is found to be a fully gapped superconductor with strong electron-phonon coupling. First-principles calculations suggest that the enhancement of electron-phonon coupling is possibly due to the shift of the Fermi level, which is induced by electron doping. The calculations also reveal the nontrivial band topology in Mo$_5$Si$_3$. The $T_c$ and upper critical field in Mo$_{5-x}$Si$_{3+x}$P$_x$ are fairly high among pseudobinary compounds. Both of them are higher than those in NbTi, making future applications promising. Our results suggest that the W$_5$Si$_3$-type compounds are ideal platforms to search for new superconductors. By examinations of their band topologies, more candidates for topological superconductors can be expected in this structural family.

Keywords: Mo$_5$Si$_3$, superconductivity, doping, topological insulator, electron-phonon coupling

INTRODUCTION

Topological superconductors, hosting both gapped bulk superconducting states and gapless surface states, have attracted much attention in recent years. The most fascinating feature in a topological superconductor is that its quasiparticle excitations form Majorana zero modes (MZMs) at boundaries and vortices [1–3]. The MZMs obey the non-Abelian statistics, and are thus suitable for the realization of fault-tolerant quantum computations [4,5].

In view of the above intriguing merits, much effort has been devoted to seeking for topological superconductivity in real materials. One approach is to search for superconductors with odd parity, as demonstrated in Sr$_2$RuO$_4$, Sn$_x$In$_{1-x}$Te, or T$_c$-MoTe$_2$ [6–9]. However, odd-parity superconductors are very rare, and their superconductivity is generally fragile to impurities or disorders. Moreover, all these superconductors have very low (<2 K) superconducting transition temperatures ($T_c$), limiting possible applications. Another approach, as proposed by Fu and Kane [10], is to fabricate heterostructures made of superconductors and topological insulators, where the topological surface states (TSSs) become superconducting from the proximity effect. The realizations [11–13], however, require delicate device fabrications and face the challenges of lattice mismatch and interface complexity.

Consequently, researchers in this field have been moving much of their attention to find bulk superconductors that also possess nontrivial band topologies. Such conception is simple but effective. In this spirit, superconducting topological materials such as β-PdBi$_{2}$, doped Bi$_2$Se$_3$, PdBi, and 2M-WS$_2$ were proposed to be candidates for topological superconductors [14–21]. In many of them, spectroscopy methods such as scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) successfully confirmed the existence of TSSs [20–23], which in turn verified the effectiveness of the conception.

Recently, superconductivity was observed in Re-doped Mo$_5$Si$_3$, with a maximal $T_c$ of 5.8 K in Mo$_5$Re$_2$Si$_3$ [24]. Not only did Ref. [24] set a record-high $T_c$ in W$_5$Si$_3$-type superconductors, it also emphasized the nontrivial band topology, making Mo$_{5-x}$Re$_x$Si$_3$ a candidate for topological superconductors. We noticed that, just like the cases of Cu/Sr/Nb-doped Bi$_2$Se$_3$ [14–17,19], superconductivity was successfully induced by carrier doping in topological material Mo$_5$Si$_3$. We thus systematically examined the doping effects not only on the Mo sites, but also on the Si.
sites in Mo\textsubscript{5}Si\textsubscript{3}.

In this paper, we report detailed characterizations of Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x} (0 ≤ x ≤ 2.0), in which bulk superconductivity with \( T_c \) as high as 10.8 K is observed. In addition, Mo\textsubscript{5}Si\textsubscript{x}P and Mo\textsubscript{5}Si\textsubscript{3}P\textsubscript{1.5} are found to host strong electron-phonon coupling. The enhancement of the coupling strength is due to the shift of the Fermi level, and possibly the phonon softening, as revealed by the heat capacity measurements and first-principles calculations. A series of superconducting parameters for Mo\textsubscript{5}Si\textsubscript{3}P\textsubscript{x} are determined, and the electronic band topologies are briefly discussed.

EXPERIMENTAL SECTION

Polycrystalline samples of Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x} (x = 0, 0.5, 1.0, 1.2, 1.3, 1.5, 1.6, and 2.0) were prepared by solid state reaction. Elements of Mo (99.9%, powder), Si (99.999%, powder), and P (99.99%, powder) were mixed thoroughly before being pressed into pellets. The pellets were placed into alumina crucibles before being sealed into silica tubes under argon. The tubes were slowly heated to 1073 K and held for 24 h. Then the products were thoroughly ground, pressed into pellets, put into alumina crucibles, and sealed into tantalum tubes under argon. The tubes were heated under high-purity argon at 1923 K for 20 h. All the manipulations except sealing and heating were carried out in a glove box filled with high-purity argon. The final products showed silver metallic lustres and were stable in air.

The room-temperature powder X-ray diffraction (XRD) data were collected on a PAN-analytical X-ray diffractometer with Cu-K\textalpha radiation. Rietveld refinements were carried out using the GSAS package [25]. The resistivity and heat capacity data were collected on a physical property measurement system (PPMS, Quantum Design). The magnetization measurements were performed on a magnetic property measurement system (MPMS, Quantum Design). The chemical compositions were determined by an energy-dispersive X-ray (EDX) spectrometer equipped on a Phenom ProX scanning electron microscope. More details about the measurements can be found in our previous study [26].

First-principles calculations were performed based on the density functional theory (DFT), as implemented in the Quantum ESPRESSO package [27]. The exchange-correlation functionals of Perdew-Burke-Ernzerhof (PBE) based on the generalized gradient approximation (GGA) were chosen. The optimized norm-conserving pseudopotentials [28] were used. Before the calculations for charge densities, the lattice parameters, as well as the atomic positions, were fully relaxed until the force on each atom was less than 0.0001 Ry Bohr\textsuperscript{-1}. A Monkhorst-Pack grid of 15 × 15 × 11 was applied in the self-consistent calculations. P doping on the Si sites was treated by the heat capacity measurements and first-principles calculations. A series of superconducting parameters for Mo\textsubscript{5}Si\textsubscript{3}P\textsubscript{x} are determined, and the electronic band topologies are briefly discussed.

RESULTS

Structural characterizations

Fig. 1a demonstrates the crystal structure of Mo\textsubscript{5}Si\textsubscript{3}P\textsubscript{x}, where one may notice that the structure features Si–Si chains along the c axis. XRD patterns of polycrystalline Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x} (0 ≤ x ≤ 2.0) are shown in Fig. 1e. Without P doping, a phase pure Mo\textsubscript{5}Si\textsubscript{3} sample, which is of the tetragonal W\textsubscript{5}Si\textsubscript{3} type (space group I4/mcm), is successfully obtained. Upon doping, an impurity phase of Mo\textsubscript{5}P emerges. Using MoP precursor instead of P in the preparation procedure was found to be beneficial to reducing the amount of Mo\textsubscript{5}P in the final products. However, we were not able to completely remove the Mo\textsubscript{5}P impurity. This is possibly due to the inevitable evaporation of P at high temperatures. As a result, the actual contents of P in the products should be less than the nominal ones, which was confirmed by our EDX measurements (Fig. S2). The measured values of x are listed in Table 1, and are plotted in Fig. 1d. Note that the measured P contents are not far from the nominal ones. For simplification, x in Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x} mentioned hereafter represents the nominal value.

The diffraction peaks of Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x} evidently shift with increasing x, as shown in Fig. 1f. To gain insights into the crystallographic parameters, we performed Rietveld refinements to each XRD pattern. Details of the refinement results are listed in Table 1. Two of them (x = 0.5 and x = 1.5) are shown as examples in Fig. 1b. The small values of \( R_p \), \( R_w \), and \( \chi^2 \) suggest the refinements are satisfactory. As shown in Fig. 1c, the a-axis shrinks while the c-axis expands monotonously, indicating a successful P doping into Mo\textsubscript{5}Si\textsubscript{3}. This doping behavior is different from that in Mo\textsubscript{x}Re\textsubscript{5}Si\textsubscript{3}, where only the a-axis was changed [24]. We note that the shrinkage of a-axis of Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x} compared with Mo\textsubscript{5}Si\textsubscript{3} is around 1.6%, while the changes of the lattice parameters of Mo\textsubscript{5}P impurity are less than 0.1%. This means that the Si doping content in Mo\textsubscript{5}P is insignificant (if not zero) in our samples. There are two different Wyckoff positions (Si1 at 4a and Si2 at 8b) of Si in Mo\textsubscript{5}Si\textsubscript{3}. Therefore, there could be a site-selection in P doping. We carefully examined the evolution of all the bond lengths in Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x}. However, no evidence backing this assumption was found. No reflections from the supercell were observed in the XRD patterns either. P is thus believed to randomly take all the Si sites (we should note that it is generally very difficult to distinguish P from Si by XRD measurements, so chances are that there still exists nonequivalent doping between the Si1 and Si2 sites). The shrinkage of \( a \) and expansion of \( c \) are consistent with our DFT relaxation results (see Fig. S3).

Superconducting properties

The temperature dependence of electrical resistivity (\( \rho \)) for Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x} (0 ≤ x ≤ 2.0) is shown in Fig. 2a. All of the samples show metallic behaviors. For the undoped sample Mo\textsubscript{5}Si\textsubscript{3} \( \rho \) reads ~0.22 m\Omega cm at 300 K and decreases monotonously with the decrease of temperature. \( \rho (T) \) for Mo\textsubscript{5}Si\textsubscript{3} shows no superconducting transitions down to 1.8 K. These results are in good agreement with those in the literature [24,29], where no superconductivity was observed above 0.15 K. P doping into Mo\textsubscript{5}Si\textsubscript{3} introduces superconductivity, as revealed by abrupt drops of \( \rho (T) \) curves for the doped samples. The region of the superconducting transitions is emphasized in Fig. 2b. For the samples with x ≥ 1.0, the normal state \( \rho (T) \) curves obviously show upwards concave features, similar to those observed in the A15 compounds, which can be interpreted by a parallel-resistor model [30].

To investigate the magnetic properties of the superconducting samples, the direct-current (DC) magnetic susceptibility (4\( \pi \)\( \chi \)) of Mo\textsubscript{5}Si\textsubscript{3−x}P\textsubscript{x} (0.5 ≤ x ≤ 2.0) was measured and is shown in Fig. 2c. Note that the data have been corrected with the corresponding demagnetization factors. In the zero-field-cooling (ZFC) run, 4\( \pi \)\( \chi \) of each sample quickly approaches a constant at low-
temperatures, indicating the occurrence of superconductivity. The shielding fractions are close to or larger than 100%, validating bulk superconductivity in Mo$_5$Si$_3$-P$_x$.

$T_c$ can be determined from the onset temperature to deviate from the normal states, which are in good agreement with those obtained from the $\rho(T)$ data. It should be mentioned that the diamagnetic signals of Mo$_3$P ($T_c = 5.6$ K \cite{31}) in the $4\pi\chi(T)$ curves are negligible (it is obvious only in the heavily doped sample Mo$_5$Si$_3$P$_2$). This is presumably due to the shielding effects of Mo$_5$Si$_3$-P$_x$, which have higher $T_c$ than Mo$_3$P. The absolute values of $4\pi\chi$ in the FC runs are significantly lower than those in the ZFC runs, indicating large pinning effects in the superconducting samples.

Gathering the data from $\rho(T)$ and $4\pi\chi(T)$, we are able to conclude the evolution of $T_c$ in Mo$_5$Si$_3$-P$_x$ ($0 \leq x \leq 2.0$), as listed in Table 1, and shown in Fig. 2d. Non-superconducting Mo$_5$Si$_3$ becomes superconducting with P doping. $T_c$ quickly increases,

Table 1  Crystallographic parameters, measured P contents (EDX), and superconducting $T_c$ of Mo$_5$Si$_3$-P$_x$ ($0 \leq x \leq 2.0$)

| parameter                  | $x = 0$ | $x = 0.5$ | $x = 1.0$ | $x = 1.2$ | $x = 1.3$ | $x = 1.5$ | $x = 1.6$ | $x = 2.0$ |
|----------------------------|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Measured P content \(x\)  | 0       | 0.46(5)   | 0.96(9)   | 1.14(12)  | 1.20(13)  | 1.43(14)  | 1.49(16)  | 1.75(18)  |
| \(a\) (Å)                 | 9.6444(1) | 9.6128(1) | 9.587(1)  | 9.5627(1) | 9.5555(1) | 9.5407(1) | 9.5332(1) | 9.4956(2) |
| \(c\) (Å)                 | 4.9063(1) | 4.9200(1) | 4.9345(1) | 4.9447(1) | 4.9492(1) | 4.9582(1) | 4.9674(1) | 4.9856(2) |
| \(x_{Si1}\)               | 0.1680(2) | 0.1657(3) | 0.1656(3) | 0.1663(3) | 0.1662(3) | 0.1661(3) | 0.1655(4) | 0.1650(4) |
| \(x_{Si2}\)               | 0.07694(6) | 0.07684(8) | 0.0767(1) | 0.0771(1) | 0.0770(1) | 0.07630(4) | 0.0767(1) | 0.0770(1) |
| \(y_{Mo1}\)               | 0.22356(7) | 0.2232(1) | 0.2226(1) | 0.2221(1) | 0.2219(1) | 0.2214(5) | 0.2218(2) | 0.2214(2) |
| \(R_p\)                   | 1.38%    | 2.10%     | 2.11%     | 2.15%     | 1.96%     | 1.94%     | 1.94%     | 2.07%     |
| \(R_{wp}\)                | 2.32%    | 2.89%     | 2.86%     | 2.92%     | 2.62%     | 1.34%     | 2.52%     | 2.75%     |
| \(\chi^2\)                | 4.84     | 2.51      | 2.08      | 2.24      | 1.74      | 1.56      | 1.76      | 1.74      |
| Mo$_x$P weight fractionb  | 0       | 3.4%      | 9.9%      | 9.4%      | 6.0%      | 12.3%     | 20.6%     | 30.2%     |
| $T_c$ from $\rho(T)$ (K)c  | –       | 6.77      | 8.70      | 10.09     | 10.42     | 10.74     | 10.74     | 10.70     |
| $T_c$ from $\chi(T)$ (K)  | –       | 7.01      | 9.26      | 10.18     | 10.40     | 10.71     | 10.54     | 10.71     |

a) Wyckoff positions: Si1 (4a), Si2 (8b), Mo1 (4b), Mo2 (16k). P randomly takes the Si1 and Si2 sites. \(x_{Si1} = y_{Si1} = z_{Si1} = z_{Si2} = x_{Mo1} = z_{Mo2} = 0\), \(y_{Si2} = x_{Si2} + 0.5\), \(y_{Mo1} = 2z_{Mo1} = 0.5\). b) Determined from XRD refinements. c) Determined from the midpoint of superconducting transition in $\rho(T)$.
shown in Fig. 3b, from which the lower critical field (typical behavior of a type-II superconductor is observed. The superconducting transition width of only 0.1 K. Upon the superconducting parameters can be obtained. The G-L coher-

Figure 2 (a) Temperature dependence of resistivity of Mo5Si1.5P1.5 under zero magnetic field. (b) Zoom-in of the datasets in (a) below 15 K. (c) DC magnetic susceptibility of Mo5Si1.5P1.5 under zero magnetic field. (d) Evolution of $T_c$, as well as RRR, with regard to the P doping content $x$.

exceeding 10 K in Mo5Si1.5P1.5, while further P doping brings up little change in $T_c$. Simultaneously, the residual resistivity ratio (RRR) decreases regularly upon P doping, which is reasonable since P doping introduces more defects in the sample.

Now we move on to the discussion of the superconducting nature by conducting a detailed investigation on the Mo5Si1.5P1.5 sample. We choose to characterize this sample in detail because it hosts the highest $T_c$, and has less MoP impurities compared with heavier-doped samples. $\rho(T)$ of Mo5Si1.5P1.5 under various magnetic fields ($\mu_0 H = 0 - 15.5$ T) is shown in Fig. 3a. Under zero magnetic field, $\rho(T)$ drops to start abruptly at a $T_{c_{\text{onset}}}$ of 10.80 K, and reaches zero at a $T_{c_{\text{zero}}}$ of 10.70 K, resulting in a superconducting transition width of only 0.1 K. Upon the application of magnetic field, the superconductivity in Mo5Si1.5P1.5 is gradually suppressed. $T_c$ under different magnetic fields is determined by the 50% criterion, i.e., the temperature where $\rho(T)$ reaches 50% of that of the normal state. The phase diagram of upper critical field ($\mu_0 H_{c2}$) versus $T$ is therefore plotted in Fig. 3d. It can be seen that the Ginzburg-Landau (G-L) model: $\mu_0 H_{c2}(T) = \mu_0 H_{c2}(0)[1 - (T/T_c)^2]/[1 + (T/T_c)^2]$ gives a satisfying fit of the experimental results in the whole temperature range. $\mu_0 H_{c2}(0)$ is fitted to be 14.56 T, which is lower than the Pauli paramagnetic limit (20.0 T).

We also performed isothermal magnetization measurements on Mo5Si1.5P1.5. The hysteresis loop at 2 K is shown in Fig. 3c. A typical behavior of a type-II superconductor is observed. The isothermal magnetization curves under various temperatures are shown in Fig. 3b, from which the lower critical field ($\mu_0 H_{c1}$) can be determined from the deviation of the curves from the initial Meissner states. $\mu_0 H_{c1}$ under different temperatures is plotted in Fig. 3d. One can easily fit $\mu_0 H_{c1}(T)$ with the well-known G-L expression: $\mu_0 H_{c1}(T) = \mu_0 H_{c1}(0)(1 - t)$, where $t$ is the normalized temperature $T/T_c$. The fit gives a $\mu_0 H_{c1}(0)$ of 105 mT.

Based on the results of $\mu_0 H_{c1}(0)$ and $\mu_0 H_{c2}(0)$, a series of superconducting parameters can be obtained. The G-L coherence length ($\xi_{\text{GL}}$) of Mo5Si1.5P1.5 is calculated to be 4.75 nm by the relation: $\mu_0 H_{c2}(0) = \Phi_0/(2\pi \xi_{\text{GL}}^2)$, in which $\Phi_0$ stands for the magnetic flux quantum. The superconducting penetration depth ($\lambda_{\text{GL}}$) is calculated by $\mu_0 H_{c1}(0) = \Phi_0/(4\pi \lambda_{\text{GL}}^2)\ln\kappa + 0.5$, where $\kappa \equiv \lambda_{\text{GL}}/\xi_{\text{GL}}$ is the G-L parameter. Consequently, we obtain $\lambda_{\text{GL}} = 70.5$ nm and $\kappa = 14.8$. The value of $\kappa$ is far larger than 1/√2, again suggesting Mo5Si1.5P1.5 to be a type-II superconductor. The thermodynamic critical field can therefore be determined by $\mu_0 H_{c2}(0) = \mu_0 \sqrt{\lambda_{\text{GL}}/(\xi_{\text{GL}}^2)}/\ln\kappa$ to be 0.75 T. All these superconducting parameters are summarized in Table 2.

In order to take more insight into the superconductivity, as well as the thermodynamic properties of Mo5Si1.5P1.5, we measured the specific heat ($C_p$) of Mo5Si1.5P1.5 ($x = 1.0, 1.5$). As the doped samples contained superconducting MoP samples, whose $C_p(T)$ was measured before subtraction from the raw data of Mo5Si1.5P1.5 (see Fig. S4). This approach is similar to that in Mo5P2 [32]. The corrected data are shown in Fig. 4. No superconducting transitions are observed in Mo5Si, while clear anomalies are found at 8.46 and 10.62 K for $x = 1.0$ and $x = 1.5$, respectively, evidencing the bulk superconductivity. The values of $T_c$ from $C_p$ measurements correspond well with those from the resistivity and the magnetization measurements. For each sample, the behavior of $C_p$ at the normal state up to 18 K can be well described with the Debye model: $C_p(T) = \gamma T + \beta T^3 + \delta T^5$, in which the three terms stand for the Sommerfeld term, the contributions from harmonic phonons and anharmonic phonons, respectively. The fitted curves are shown in Fig. 4a as the dash lines. $\gamma$ and $\beta$ for each sample are listed in Table 2. Note that from $x = 0$ to $x = 1.5$, $\gamma$ almost doubles, while $\beta$ becomes an order of magnitude larger. We calculate the Debye temperature ($\Theta_D$) by $\Theta_D = (12\pi^2 N R / 5\beta)^{1/3}$, in which $N$ is the number of atoms per formula unit (f.u.), and $R$ is the ideal gas constant. The results are also listed in Table 2. One may see that P doping greatly reduces the value of $\Theta_D$ (from 659 to 314 K), implying substantial softening of the lattice. This is quite surprising since the atomic mass of P is close to that of Si. The softening of phonons in P-doped samples may be related to the emergence of phonon soft modes. Detailed theoretical calculations will help to eluci-
The electronic contribution to $C_p$ can thus be obtained by subtracting the phonon terms. Temperature dependence of electronic specific heat ($C_e$) is shown in Fig. 4b. Note that the normalized $C_e$ jumps at $T_c$ ($\Delta C_e/\gamma T_c$) are 2.03 and 2.06 for Mo$_5$Si$_2$P and Mo$_5$Si$_{1.5}$P$_{1.5}$, respectively. These values are much larger than the Bardeen-Cooper-Schrieffer (BCS) weak coupling ratio (1.43), suggesting strong coupling in these samples.

For a strong-coupling superconductor, the electron-phonon coupling parameter ($\lambda_{ep}$) can be estimated by the McMillan formula modified by Allen and Dynes [33,34]:

$$
\frac{\Delta C_e}{T_c^2} = 1.43 \left[ 1 + 53 \left( \frac{T_c}{\omega_{2\lambda}} \right)^2 \ln \left( \frac{\omega_{2\lambda}}{\gamma T_c} \right) \right].
$$

By setting the Coulomb screening parameter $\mu^* = 0.13$, we get $\lambda_{ep} = 1.12$ and 1.15 for $x = 1.0$ and $x = 1.5$, respectively. We further calculate the density of states (DOSs) at the Fermi level using $N(E_F) = \frac{3\gamma}{\pi^2 k_B^2 (1 + \lambda_{ep})}$, where $k_B$ is the Boltzmann constant. The calculations give $N(E_F) = 4.99$ and 7.30 eV$^{-1}$f.u.$^{-1}$ for $x = 1.0$ and $x = 1.5$, respectively.

$C_e$ in the superconducting state is treated by calculating the entropy with [36]:

$$
S(T) = -\frac{3\gamma}{\pi^2 k_B} \int_0^{\pi^2} \int_0^{\pi^2} \left[ f \ln f + (1-f) \ln(1-f) \right] \text{d}\epsilon \text{d}\varphi,
$$

where $f = 1 / \left[ 1 + \exp \left( \frac{\sqrt{\epsilon^2 + \Delta^2(\varphi, T)} - \mu_T}{k_B T} \right) \right]$ stands for the
Fermi distribution of the quasiparticles. Here, we find that a conventional \( s \)-wave gap function reproduces the data well, and the so-called \( \alpha \) model is applied. In this model, the angular independent gap function \( \Delta(T) \) is expressed as

\[
\Delta(T) = \Delta_{\text{BCS}} \left( \frac{T}{T_c} \right)^{\frac{\alpha_{\text{BCS}}}{2}}
\]

where \( \alpha_{\text{BCS}} \) is the weak-coupling gap ratio (1.76) \cite{37}. \( C_e \) is calculated from \( C_e = T \frac{\partial^2 S}{\partial T^2} \). Fittings to the \( C_e \) data are illustrated in Fig. 4b, from which we obtain the superconducting gap values at zero temperature \( \Delta_0 = 1.48 \) and 1.96 meV for \( x = 1.0 \) and \( x = 1.5 \), respectively. The coupling strengths \( \Delta_0/k_B T_c \) are thus estimated to be 2.03 and 2.14. Again, these values apparently exceed \( \alpha_{\text{BCS}} \), evidencing strong-coupled superconductivity.

| Table 2 | Superconducting parameters of \( \text{Mo}_5\text{Si}_{1-x}\text{P}_x \). The thermodynamic parameters of \( \text{Mo}_5\text{Si}_5 \) and \( \text{Mo}_5\text{Si}_2\text{P} \) are also listed for comparison. |
|---------|----------------------------------|-----------------|-----------------|-----------------|
| Parameter | Unit | \( \text{Mo}_5\text{Si}_5 \) | \( \text{Mo}_5\text{Si}_2\text{P} \) | \( \text{Mo}_5\text{Si}_{1.5}\text{P}_{1.5} \) |
| \( T^\text{onset} \) | K | 10.80 | 10.70 | |
| \( T^\text{zero} \) | K | 10.70 | 10.70 | |
| \( \mu\mu H_c(0) \) | mT | 105 | 14.56 | 70.5 |
| \( \mu\mu H_c(0) \) | T | 70.5 | 14.56 | 70.5 |
| \( \xi_{\text{GL}} \) | nm | 4.75 | 4.75 | |
| \( \lambda_{\text{GL}} \) | nm | 70.5 | 70.5 | |
| \( \kappa \) | – | 14.8 | 14.8 | |
| \( \beta \) | mJ mol\(^{-1}\) K\(^{-1}\) | 0.054 | 0.24 | 0.50 |
| \( \gamma \) | mJ mol\(^{-1}\) K\(^{-2}\) | 19.80 | 25.10 | 37.23 |
| \( \Theta \) | – | 659 | 404 | 314 |
| \( \lambda_{\text{GL}} \) | – | 0.69 \({}^4\) | 1.15 \({}^4\) | |
| \( \Delta C_e/T_s \) | – | 2.03 | 2.06 | |
| \( \Delta_0/k_B T_c \) | – | 2.03 | 2.14 | |
| \( N(E_F) \) | eV\(^{-1}\) f.u.\(^{-1}\) | 6.30 | 7.30 | |
| \( N'(E_F) \) | eV\(^{-1}\) f.u.\(^{-1}\) | 4.13 | 7.24 | 8.04 |

\( a) \) Experimental value calculated from \( \gamma \). \( b) \) Theoretical value from DFT calculations. \( c) \) Estimated from Equation (4). \( d) \) Estimated from Equations (1) and (2).

First-principles calculations
The results of first-principles calculations for \( \text{Mo}_5\text{Si}_{1-x}\text{P}_x \) (\( x = 0, 1.0, 1.5 \)) are summarized in Fig. 5, with the electronic band structures of \( x = 0 \) (with and without spin-orbit coupling (SOC)), \( x = 1.0 \), and \( x = 1.5 \) shown in Fig. 5a–d, respectively. For all these samples, there are multiple bands crossing the Fermi level \( (E_F) \), consistent with the metallic nature of \( \text{Mo}_5\text{Si}_{1-x}\text{P}_x \). By comparing Fig. 5a, b, we conclude that the SOC has negligible effects on the band structures, although it opens finite gaps on several \( k \) points. The shapes of the electronic bands for \( \text{Mo}_5\text{Si}_2\text{P} \) and \( \text{Mo}_5\text{Si}_{1.5}\text{P}_{1.5} \) are basically the same with that of \( \text{Mo}_5\text{Si}_5 \), which means that the bands can be considered rigid in our case. One major feature of the band structure in Fig. 5a is the flat band.
dispersions at around 0.25 eV above $E_F$ (as indicated by the shadowy box), which gradually shift to $E_F$ when $x$ increases. This process is clearly observed when we examine the evolution of the DOS upon P doping (shown in Fig. 5g). $E_F$ of Mo$_5$Si$_3$ locates in a dip of DOS, and it shifts to a major peak for Mo$_5$Si$_1.5$P$_1.5$. Theoretical values of DOS at $E_F$ ($N(E_F)$) are 4.13, 7.24, and 8.04 eV$^{-1}$ f.u.$^{-1}$ for $x$ = 0, 1.0, and 1.5, respectively. The trend of $N(E_F)$ is consistent with the change of the Sommerfeld parameter $\gamma$. We notice that $N(E_F)$ of Mo$_5$Si$_1.5$P$_1.5$ corresponds fairly well with the experimental one, while $N(E_F)$ of Mo$_5$Si$_2$P is much larger compared with $N(E_F)$. This means that $\lambda_{ep}$ of Mo$_5$Si$_2$P is probably overestimated, and Equation (3) is not applicable. In fact, if we use the inverted McMillan formula [34]:

$$\lambda_{ep} = \frac{1.04 + \mu^* \ln(\Theta_D/1.45T_{c})}{(1-0.62\mu^*)\ln(\Theta_D/1.45T_{c}) - 1.04}.$$  

Equation (4) suggests that bulk Mo$_5$Si$_3$ (with SOC) falls into the weak topological insulator state. Unfortunately, this means that the TSSs in Mo$_5$Si$_3$ are fragile, and are unlikely to survive with P doping, which inevitably introduces defects. What makes it worse is that $E_F$ shifts to higher energies in the doped samples, which could push the system into a topologically trivial state. In a word, P doping into Mo$_5$Si$_3$ may destroy its TSSs, making it less possible to realize topological superconductivity in Mo$_5$Si$_3$$_x$P$_{1-x}$.

**DISCUSSION**

In McMillan’s formalism [34], the electron-phonon coupling strength is given by $\lambda_{ep} = \left[ N(E_F) \left< I^2 \right> / \left< M \left< \omega^2 \right> \right]$, where $M$ stands for the atomic mass, $\left< I^2 \right>$ and $\left< \omega^2 \right>$ are averages of the squared electronic matrix elements on the Fermi surface, and of the squared phonon frequencies, respectively. There are thus at least two approaches to enhance $\lambda_{ep}$: one is to increase $N(E_F)$, and the other is to lower $\left< \omega^2 \right>$ (or, in other words, to soften the lattice). In Mo$_5$Si$_3$$_x$P$_{1-x}$, $N(E_F)$ is enhanced by electron doping, which shifts $E_F$ to a peak in DOS. The lattice has been effectively softened too, as evidenced by the large decrease of $\Theta_D$. These two factors together give rise to the strong electron-phonon coupling, and should be responsible for the emergence of superconductivity in Mo$_5$Si$_3$$_x$P$_{1-x}$. The reason why P doping softens the lattice so much (unlike Re doping in Mo$_5$Re$_x$Si$_3$, which did not change $\Theta_D$ much [24]) is definitely worth further studies. Theoretical calculations of the phonon dispersions of Mo$_5$Si$_3$$_x$P$_{1-x}$ will

![Figure 5](image-url)
be illuminating. In particular, large phonon linewidths or soft modes can be expected.

As for the topological properties, although our results suggest that P doping may not be beneficial to the TSSs, there are other ways to chase for topological superconductivity in this system. We notice that the band gap between bands 156 and 158 is topologically nontrivial with strong topological indexes of (1;000) (see Fig. 5f). Therefore, TSSs are likely to survive and make future applications promising.

Lastly, we should mention that the $T_c$ of 10.8 K and $\mu_B H_{c2}(0)$ of 14.56 T are fairly high for a pseudobinary compound. For example, both of them are slightly higher than those in the commercial superconductor NbTi ($T_c = 9.6$ K, $\mu_B H_{c2}(0) = 14$ T) [40]. Most-absorbingly, Mo$_{5}Si_{3}$P$_{x}$ serves as a suitable platform to observe the possibly existing MZMs, which will be an intriguing topic in future ARPES or STM studies.

Recent theoretical studies suggested nontrivial band topologies in some of the A15 superconductors too [42]. Compared with the well-known A15 superconductor family, the W$_5$Si$_3$-type superconductor family, which Mo$_{5}Si_{3}$P$_{x}$ belongs to, has not been studied in depth. Currently, the family contains about ten members. Most of them superconduct below 4 K, with the maximal $T_c$ of 5.8 K observed in Mo$_{5}Re$_2Si$_3$ [24,43–48]. Our study almost doubles this maximum, making it comparable to those in the A15 family. W$_5$Si$_3$-type compounds are hence a fertile ground to be explored for new superconductors.

CONCLUSIONS

To summarize, we discover that P doping introduces superconductivity in non-superconducting Mo$_{5}Si$_3, which hosts a nontrivial band topology. $T_c$ increases with the doping level, reaching 10.8 K in Mo$_{5}Si$_3P$_{1.5}$. Mo$_{5}Si$_3P$_{1.5}$ is a type-II, fully gapped superconductor with strong electron-phonon coupling, as evidenced by the large values of $\Delta_{J}/\gamma T_c$, $\Delta_{J}/k_B T_c$, and $\lambda_{p}$, $\mu_B H_{c2}(0)$ and $\mu_B H_{c2}(0)$ for Mo$_{5}Si$_3P$_{1.5}$ are 105 mT and 14.56 T, respectively. According to first-principles calculations, the large electron-phonon coupling is related to the increase of $\langle N(E_F) \rangle$. Mo$_{5}Si$_3P$_{1.5}$ sets a new record of $T_c$ in W$_5$Si$_3$-type superconductors. Compared with the previously reported Mo$_{5}Re$_2Si$_3$ superconductor [24], or the widely used commercial superconducting material NbTi [40], the higher $T_c$ and inexpensive raw materials of Mo$_{5}Si$_3P$_x$ make future applications promising. We point out that the superconducting properties of Mo$_{5}Si$_3P$_x$ are very similar with those in the A15 superconductors. Our findings suggest that the $T_c$ levels in W$_5$Si$_3$-type superconductors can be comparable to the A15 superconductors. Novel superconductors with higher $T_c$ values can be anticipated in W$_5$Si$_3$-type structural family. In particular, superconductivity, or even topological superconductivity, could be achieved through carrier doping, whose effectiveness has been testified in our study.
Supplementary information Comparison of VCA and supercell results, SEM image and elemental mapping of Mo$_{5}$Si$_{3-x}$Ru, the relaxed lattice parameters from DFT compared with the experimental ones, and the subtraction of Mo$_{2}$P contribution from the raw data. Supporting data are available in the online version of the paper.

Bin-Bin Ruan received his PhD degree in 2018, and is currently a post-doctoral researcher at the Institute of Physics, Chinese Academy of Sciences (IOPCAS). He received his bachelor degree from the University of Science and Technology of China in 2011. His research interests include the exploration, characterization, and calculation of novel superconductors based on the IVB–VIB elements.

Jun-Nan Sun is a master student of physics at Anhui University under the supervision of Prof. Zhi-An Ren and Prof. Lei Shan. His research work focuses on the exploration and research of superconducting materials containing light elements.

Lei Shan is a professor at the Institutes of Physical Science and Information Technology, Anhui University. He received his BS/PhD degrees from the Department of Physics, Nanjing University in 1996/2001. He was a researcher at the IOPCAS from 2013 to 2018. His research focuses on the mechanisms of novel superconductors and related quantum materials, scanning tunneling microscopy, and point contact Andreev spectroscopy.

Zhi-An Ren obtained his PhD degree in physics from the IOPCAS in 2004. He was an associate professor from 2007 and has been a professor at the IOPCAS since 2011. He is a group leader of IOPCAS on studies and explorations of novel high-$T_c$ superconducting materials, physics, and applications.