Superconductivity Induced by Site-Selective Arsenic Doping in Mo$_5$Si$_3$

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Arsenic doping in silicides has been much less studied compared with phosphorus. In this study, superconductivity is successfully induced by As doping in Mo$_5$Si$_3$. The superconducting transition temperature ($T_c$) reaches 7.7 K, which is higher than those in previously known W$_5$Si$_3$-type superconductors. Mo$_5$Si$_3$As is a type-II BCS superconductor with upper and lower critical fields of 6.65 T and 22.4 mT, respectively. In addition, As atoms are found to selectively take the 8$h$ sites in Mo$_5$Si$_2$As. The emergence of superconductivity is possibly due to the shift of Fermi level as a consequence of As doping, as revealed by the specific heat measurements and first-principles calculations.

Our work provides not only another example of As doping, but also a practical strategy to achieve superconductivity in silicides through Fermi level engineering.

Arsenic doping in elemental silicon has been known for more than half a century. [1] And the kinetics for As diffusion in silicon had been well established. [2, 3] However, reports on arsenic doping in silicides are unexpectedly scarce. To the best of our knowledge, there are only 5 examples in bulk materials, namely: Cr$_3$Si$_{1-x}$As$_x$, [4] Fe$_5$SiAs, [5] ZrSi$_{1-x}$As$_x$, Te, [6] and Zr(HF)$_2$As$_2$–Si$_x$. [7, 8]

On the other hand, phosphorus doping had been reported in more than 30 silicides: CoSi$_{0.61}$P$_{0.39}$, [9] USi$_{0.17}$P$_{0.83}$, [10] Fe$_5$SiP, [5] Nb$_5$Si$_{3-x}$P$_{0.5+x}$, [11] Gd$_5$Si$_{6-x}$P$_x$, [12] and MSi$_2$P$_y$ (M = Fe, Co, Ru, Rh, Pd, Os, Ir, Pt, $x+y \geq 4$), [13, 14] to name a few. Compared to the P dopant, the much less studied As doping offers an opportunity to chase for new compounds in this field.

Our group has been working on MoAs-based superconductors, and has discovered a series of quasi-one-dimensional superconductors $A_2$Mo$_n$As$_3$ ($A = K, Rb, Cs$). [15–17] Recently, superconductivity was reported in Re doped Mo$_5$Si$_3$ with a transition temperature ($T_c$) of 5.8 K, setting a new record in the isostructural compounds. [18] We, thus, naturally conducted a systematic As doping study on Mo$_5$Si$_3$, which led to the discovery of superconductivity in Mo$_5$Si$_{3-x}$As$_x$.

Mo$_5$Si$_3$ crystallizes in a tetragonal W$_5$Si$_3$-type structure (space group $I4/mcm$), as illustrated in Figure 1(a). Notice there are two kind of Si atoms taking different Wyckoff positions: Si1 at the 4$a$ sites, and Si2 at the 8$h$ sites. In addition, Si1 atoms are bonded with each other, forming one-dimensional Si–Si chains along the c-axis. The formation of Si–Si bonds is justified by the short distance between them (2.45 Å, which is comparable with those in α-ThSi$_2$ [19] or CaSi$_2$ [20]), as well as the calculated charge density (Figure S1).

In this study, we show that arsenic can be doped into Mo$_5$Si$_3$. Interestingly, As atoms selectively take the Si2 (8$h$) sites. Furthermore, bulk superconductivity with a $T_c$ of 7.7 K is induced in Mo$_5$Si$_2$As.

Polycrystalline samples of Mo$_5$Si$_{3-x}$As$_x$ ($0 \leq x \leq 1.25$) were obtained by solid state reactions. Details for the preparation, characterization, and first-principles calculation can be found in the Supporting Information. Upon As doping, the lattice parameters $a$ and $c$ increase monotonously. In our study, the doping limit for As was found to be $x \sim 1.0$. Superconductivity was observed in all the samples with $x \geq 0.5$, with $T_c$ increases from 4.4 K in Mo$_5$Si$_2.5$As$_{0.5}$ to 7.7 K in Mo$_5$Si$_2$As (the optimal-doped sample). The data for Mo$_5$Si$_2$As are shown in the main text, while additional information about Mo$_5$Si$_{3-x}$As$_x$ ($x \neq 1.0$) is shown in Figure S2–S4.

Figure 1(c) demonstrates the powder x-ray diffraction (XRD) pattern of Mo$_5$Si$_2$As. For Mo$_5$Si$_2$As, there are at least two configurations (configs.) in which As atoms take different sites. (Figure 1(b)) In config. 1, As atoms randomly take the Si2 (8$h$) sites, while in config. 2, As atoms take all the Si1 (4$a$) sites. However, the observed XRD pattern can only be refined with config. 1. In particular, any occupation of As at the Si1 (4$a$) sites will cause a significant enhancement of the (200) peak, which prevents the refinement from convergence. (See Figure S5) A brief list of the refined crystallographic parameters is shown in Table I. More details about the refinement results can be found in Table S1. According to the refinement, there is about 10.3 wt.% of Mo$_5$Si$_3$ impurity in the sample. The refined composition is Mo$_5$S$_{0.00(1)}$S$_{1.97(3)}$As$_{1.05(8)}$, which is close to that determined by energy-dispersive x-ray spectroscopy. (For the sample morphology and elemental mapping, see Figure S6)
FIG. 1: (a) Crystal structure of Mo$_5$Si$_3$. (b) Two possible configurations of Mo$_5$Si$_2$As and the corresponding enthalpies from DFT calculations. (c) Room-temperature XRD pattern of Mo$_5$Si$_2$As and its Rietveld refinement. The vertical bars indicate the Bragg positions for Mo$_5$Si$_2$As and the Mo$_3$Si impurity. The relevant (200) peak of Mo$_5$Si$_2$As is marked.

| Atom(site) | x   | y   | z   | U$_{eq}$(0.01Å$^2$) | Occupancy |
|------------|-----|-----|-----|---------------------|-----------|
| Mo1(4e)   | 0   | 0.5 | 0.25| 0.137(27)           | 0.987(2)  |
| Mo2(16k)  | 0.07652(4) | 0.221965(5) | 0   | 0.392(17)           | 1.0       |
| Si1(4a)   | 0   | 0   | 0.25| 0.84(15)            | 1.0       |
| Si2/As(8h) | 0.16592(8) | 0.66592(8) | 0   | 1.36(6)             | 0.474(4)/0.526 |

The site-selective doping of As is further backed by the first-principles calculations. As shown in Figure 1(b), the enthalpy ($H$) for config. 1 is lower compared with config. 2, which means As doping at the Si2 (8h) sites is more favorable in energy. The above conclusion is based on zero temperature calculations, but it is also true for finite temperatures. This is because the free energy $G = H - TS$, and the entropy $S$ for config. 1 is larger. (Notice the Boltzmann relation $S = k_B \ln \Omega$, where $k_B$ is the Boltzmann constant, and $\Omega$ is the number of microstates)

While both the XRD refinement and first-principles calculation suggest a site-selective As doping, we do not rule out the possibility that a tiny amount of As atoms, which is beyond the resolution limit of powder XRD, may also take the Si1 (4a) sites. Nevertheless, even if this is the case, the amount of As at 4a sites should be negligible.

Figure 2(a) shows the temperature dependence of resistivity ($\rho$) of Mo$_5$Si$_2$As. The monotonous decrease of $\rho$ upon cooling indicates a metallic nature. Superconducting transition is observed below 7.7 K ($T_{c\text{onset}}$), with zero resistivity achieved at 7.4 K ($T_{c\text{zero}}$). Figure 2(b) emphasizes the region of the superconducting transition. Upon the application of magnetic field, the transition is gradually suppressed. The temperature dependence of upper critical field ($\mu_0 H_{c2}(T)$) can thus be determined, which is shown in the inset of Figure 2(a). A Ginzburg–Landau (G–L) fit gives $\mu_0 H_{c2}(0) = 6.65(4)$ T.

DC magnetic susceptibility ($4\pi \chi$) of Mo$_5$Si$_2$As from 1.8 K to 10.0 K under 10 Oe is demonstrated in Figure 2(c). Bulk superconductivity is confirmed in $4\pi \chi(T)$ curves, with large diamagnetic signals observed below 7.4 K. The value of $T_c$ determined from $4\pi \chi(T)$ agrees very well with that from $\rho(T)$. We also measured the isothermal magnetization curves for Mo$_5$Si$_2$As. The results are shown in Figure 2(d). The lower critical fields ($\mu_0 H_{c1}(T)$) are determined from the deviation of the curves from initial Meissner states. As shown in the inset of Figure 2(c), $\mu_0 H_{c1}(T)$ can be fitted with the G–L relation: $\mu_0 H_{c1}(T) = \mu_0 H_{c1}(0)[1 - (T/T_c)^2]$, giving $\mu_0 H_{c1}(0) = 22.4(5)$ mT.

A series of superconducting parameters can be determined using $\mu_0 H_{c2}(0)$ and $\mu_0 H_{c1}(0)$. The values of these
By setting the Coulomb screening parameter \( \mu^* \approx 0.13 \), a typical value for intermetallics, we get \( \lambda_{ep} = 0.66(1) \). These results suggest a weak to moderate coupling in Mo\(_5\)Si\(_2\)As.

For comparison, we also measured the temperature dependence of \( C_p \) of Mo\(_5\)Si\(_3\), which is shown in Figure 3(a). \( \gamma \) and \( \Theta_D \) for Mo\(_5\)Si\(_3\) are estimated to be 19.80 mJ mol\(^{-1}\) K\(^{-2}\) and 659 K, respectively. These values are comparable with previous report on Mo\(_5\)Si\(_3\) single crystals. Notice that \( \gamma \) in Mo\(_5\)Si\(_2\)As is significantly larger than the undoped Mo\(_5\)Si\(_3\), and the large decrease of \( \Theta_D \) suggests substantial softening of the lattice. To take more insight into this, the density of states (DOS) was calculated for Mo\(_5\)Si\(_3\) and Mo\(_5\)Si\(_2\)As. The results are shown in Figure 3(c). One may notice the similar shapes of the DOS curves, which means that the bands can be considered rigid in our case. (For the band structures, see Figure S7) Arsenic doping shifts the Fermi level \( (E_F) \) to higher energy, causing a significant enhancement of DOS at \( E_F \) \( (N(E_F)) \). This is as expected, since As hosts one more valence electron compared with Si.
FIG. 3: (a) Temperature dependence of specific heat \((C_p)\) of Mo\(_5\)Si\(_2\)As under zero magnetic field, and under a field of 8 T. The \(C_p\) data for Mo\(_5\)Si\(_3\) are also plotted for comparison. Solid lines are fittings with Debye model. (b) Temperature dependence of the electronic contribution of \(C_p\) under zero magnetic field. (a) and (b) share the same \(y\)-axis range. (c) Calculated DOS for Mo\(_5\)Si\(_3\) and Mo\(_5\)Si\(_2\)As near the Fermi level.

TABLE II: Superconducting and Thermodynamic Parameters of Mo\(_5\)Si\(_2\)As.

| Parameter (unit)       | Value       |
|------------------------|-------------|
| \(T_{c,\text{max}}\) (K) | 7.7(1)      |
| \(T_{c,\text{zero}}\) (K) | 7.4(1)      |
| \(\mu_0 H_{c1}(0)\) (mT) | 22.4(5)    |
| \(\mu_0 H_{c2}(0)\) (T) | 6.65(4)    |
| \(\mu_0 H_c(0)\) (T) | 0.22(0)    |
| \(\xi_{\text{GL}}\) (nm) | 7.03(2)    |
| \(\lambda_{\text{GL}}\) (nm) | 159.5(4)  |
| \(\kappa_{\text{GL}}\) | 22.7(1)    |
| \(\gamma\) (mJ mol\(^{-1}\) K\(^{-2}\)) | 34.7(4)    |
| \(\beta\) (mJ mol\(^{-1}\) K\(^{-4}\)) | 0.273(1)   |
| \(\Theta_D\) (K) | 385(2)      |
| \(\lambda_{\text{ep}}\) | 0.66(1)     |
| \(\Delta C_e/\gamma T_c\) | 1.46(2)    |

\(N(E_F)\) for Mo\(_5\)Si\(_3\) is \(4.13 \text{ eV}^{-1} \text{f.u.}^{-1}\), while \(N(E_F)\) for Mo\(_5\)Si\(_2\)As is \(7.37 \text{ eV}^{-1} \text{f.u.}^{-1}\). The enhancement of \(N(E_F)\) lead to the change of \(\gamma\). We can theoretically estimate the value of \(\gamma\) for Mo\(_5\)Si\(_2\)As by:

\[
\gamma = \frac{1}{3} N(E_F)\pi^2 k_B^2 (1 + \lambda_{\text{ep}})
\]

(2)
to be \(\approx 29.02 \text{ mJ mol}^{-1} \text{K}^{-2}\), which agrees well with the experimental value. According to McMillan’s formalism, \(\lambda_{\text{ep}} = [N(E_F)\langle F^2 \rangle]/[M\langle \omega^2 \rangle]\), where \(M\) is the atomic mass, \(\langle F^2 \rangle\) and \(\langle \omega^2 \rangle\) stand for averages of the squared electronic matrix elements on the Fermi surface, and of the squared phonon frequencies, respectively. [23] The emergence of superconductivity in Mo\(_5\)Si\(_3-x\)As\(_x\) should be due to the enhancement of \(N(E_F)\), and possibly the softening of lattice (as evidenced by the large decrease of \(\Theta_D\)).

Last but not least, we would like to point out that a \(T_c\) of 7.7 K is fairly high in W\(_5\)Si\(_3\)-type superconductors. A comparison of \(T_c\) between Mo\(_5\)Si\(_2\)As and previously reported W\(_5\)Si\(_3\)-type superconductors is illustrated in Figure 4. [18, 25–32] One may notice that the average number of valence electrons per atom \((e/a)\) clearly affects the value of \(T_c\) in this structural family. Maximal \(T_c\) occurs when \(e/a \sim 4.6\) or 5.4. Notice the second peak (at \(e/a \approx 5.4\)) is just a
tentative guide, and is less reliable as there are only a few examples with $e/a > 5$. The phenomenon that $T_c$ peaks at certain $e/a$ values, known as the Matthias rule, has also been observed in other intermetallics. [33] Currently, the region of $e/a > 5.5$ remains unexplored, more superconductors may be discovered if more electrons can be introduced into this structural family.

In summary, we report the discovery of superconductivity in Mo$_5$Si$_3$$_x$As$_x$ $(0.5 \leq x \leq 1.25)$, in which a maximal $T_c$ of 7.7 K is observed in Mo$_5$Si$_2$As. Arsenic doping in Mo$_5$Si$_3$ is found to be site-selective. According to specific heat measurements and first-principles calculations, the emergence of superconductivity is related to the shift of Fermi level. Our method of As doping should be generally applicable to other silicides, in which more superconductors can be expected.

Note: This manuscript has been published in June, 2022. We also reported superconductivity in Mo$_5$Si$_3$$_x$P$_x$ (maximal $T_c = 10.8$ K), see arXiv: 2208.02392

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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