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Two dimensional superconductors in electrides

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Abstract

Two-dimensional (2D) superconductors are always a research hotspot in superconductivity, due to the huge importance of 2D superconductors in quantum phenomena transitions. And the natural metallic 2D electride with exceptional physical properties is one member of candidate materials for 2D superconductors in the Bardeen–Cooper–Schrieffer theory. The properties of electron–phonon induced superconductivity in 2D electrides, Y\textsubscript{2}C and MgONa, are investigated by using first-principles calculations. Because of the weak electron–phonon coupling between surface electronic states and phonons, critical temperature of the prototypical Y\textsubscript{2}C and MgONa are estimated to be 0.9 K and 3.4 K, respectively. It is also found that the electronic doping can improve superconductivity to \( T\textsubscript{c} = 2.4 \) K and 4.5 K, resulting from the increase of density of states and the coupling between inner-layer electrons and phonons. In addition, a small tensile strain can enhance the critical temperature of MgONa to 6.15 K at \( n = 5.5 \times 10^{14} \text{ cm}^{-2} \), due to the increase of density of states and phonon softening.

1. Introduction

Since the discovery of superconductivity in metallic films\cite{1}, two-dimensional (2D) superconductivity has attracted a lot of interest for many novel properties, such as Berezinskii–Kosterlitz–Thouless transitions\cite{2–4}, and also provides a platform to explore the quantum phenomena transitions\cite{5}. Recently, the polarized interface shows a high electronic mobility\cite{6} and forms the interfacial superconductivity, which is also found in the the Mott-insulator-based interface\cite{7–9}. But the possible factors of interfacial superconductivity are still in dispute\cite{10}. Subsequently, the technological developments of preparation for 2D materials\cite{11–13} and carrier doping\cite{14–16} pave the way for the useful study of highly crystalline 2D superconductors. For example, the dome-shaped superconducting diagram with carrier density is established in transition metal dichalcogenides (TMDs)\cite{17}, and the spin-valley locking of TMDs can also enhance the upper critical field\cite{18–20}.

Electrides refer to a unique kind of ionic compound, in which the free electrons, serving as the anions, spatially confined and separated from the cations in the crystal. Recently, 2D electrides\cite{21–25} are successfully synthesized in the experiments and have unique 2D metallic state. Because of the special inter-layered anionic confinement region and the loosely bound anionic electrons in 2D electrides, these materials present exciting properties such as the electron concentration comparable to typical metals and high electronic mobility, which make 2D electrides an attractive material for the 2D Bardeen–Cooper–Schrieffer (BCS) superconductor. Besides, the inherent magnetic anisotropy is also observed in 2D electride Y\textsubscript{2}C\cite{24}. The special physical properties all bring a great application prospect and have attracted extensive attention. The high specific capacity and suitable migration energy barrier suggest that 2D electride is a promising anode material for sodium ion batteries\cite{26–28}. In addition, utilizing the powerful predictive ability of the first-principles calculations, many works\cite{29–32} suggest abundant compounds to be 2D electride. Since the loosely bounded anionic electrons distributed in the free space, one may naturally ask the question: does the superconductivity exist in 2D electride? If possible, the versatility and the large number of compounds make 2D electride an ideal platform for the realization of quantum phenomena transitions, topological state\cite{33} and a broad application prospect.
Here, the focus is mainly on the monolayer structure of 2D electrides. In consideration of the advantage of light atoms in BCS theory, we systematically study the electron–phonon coupling and particularly superconductivity in electrides carbide Y2C and ternary oxide MgONa, based on first-principles calculations. The prototypical monolayer Y2C and MgONa, because of the weak electron–phonon coupling between surface electronic states and phonons, the low critical temperatures are obtained as 0.9 K and 3.4 K, respectively. It is also found that the electronic doping can improve superconductivity to \(T_c = 2.4\) K and 4.5 K, as a result of the increase of density of states (DOS) and the coupling between inner-layer electrons and phonons. In addition, under small tensile strain, the critical temperature of MgONa can be enhanced to be 6.15 K@\(n_{2D}^2 = 5.5 \times 10^{14}\) cm\(^{-2}\) because of the increase of DOS and phonon softening.

Our paper is organized as follows. In section 2, we first introduce our computational methods. Then discuss the results of electronic structures in section 3, followed by the electron–phonon coupling in section 4 and the effect of strain in section 5. Finally, section 6 summarizes the results of this study.

2. Methods

The microscopic electron–phonon matrix elements \(M_{k,k+q}^{n\nu}\) describe the electronic scattering from the state with momentum \(k\) to another state \(k + q\) by a phonon mode \((\nu, \nu)\) and can be expressed as [34–36]

\[
M_{k,k+q}^{n\nu} = \left( \frac{\hbar}{m^*\omega_{n\nu}} \right)^{1/2} \langle i, k | \delta^{n\nu}V | j, k + q \rangle,
\]

(1)

where \(m^*\) is the atomic mass, and \(\delta^{n\nu}V\) is the derivative of the self-consistent effective potential with respect to atomic displacement associated with the phonon mode \((\nu, \nu)\) of frequency \(\omega_{n\nu}\). It follows that the Eliashberg function reads

\[
\alpha^2F(\omega) = \frac{1}{\hbar N(E_F)} \sum_{\nu, \nu'} \delta(\omega - \omega_{n\nu}) \sum_{i,j,k} |M_{k,i,k+q}^{n\nu}|^2 \delta(\epsilon_{ik} - \epsilon_F) \delta(\epsilon_{jk+q} - \epsilon_F)
\]

\[
= \frac{\gamma_{n\nu}}{4\pi\omega_{n\nu}N(E_F)} \delta(\omega - \omega_{n\nu}),
\]

(2)

where \(\gamma_{n\nu}\) is the atomic displacement associated with the phonon mode. \(\omega_{n\nu}\) is the band energy of the Bloch state \(|i, k\rangle\), \(N(E_F)\) is DOS at the Fermi energy, and \(\gamma_{n\nu}\) indicates the phonon linewidth. Moreover, \(T_c\) is thus estimated by the Allen–Dynes-modified McMillan formula [37]

\[
T_c = f_1 f_2 \frac{\langle \omega \rangle_{\log}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],
\]

(3)

where \(f_1\) and \(f_2\) are defined as

\[
f_1 = \left\{ 1 + \frac{\lambda}{2.46(1 + 3.8)\mu^*} \right\}^{3/2},
\]

\[
f_2 = 1 + \frac{(\omega_{\nu}/\langle \omega \rangle_{\log}) - 1}{\lambda^2 + [1.82(1 + 6.3\mu^*)(\omega_{\nu}/\langle \omega \rangle_{\log})]^2}.
\]

(4)

These two functions are required to be in unity for the weak electron–phonon coupling [37]. \(\langle \omega \rangle_{\log}\) and \(\omega_2\) are defined as

\[
\langle \omega \rangle_{\log} = \exp \left[ \frac{2}{\lambda} \int_0^{\infty} \alpha^2F(\omega) \log \omega d\omega \right] \omega,
\]

\[
\omega_2 = \frac{2}{\lambda} \int_0^{\infty} \omega \alpha^2F(\omega) d\omega, \quad \text{with}
\]

(5)

which represent the logarithmically averaged phonon frequency and the second moment of the normalized weight function, respectively.

The present studies, including the electronic structures, the phonon spectra, and the electron–phonon couplings, were carried out using the ABINIT package [38–42] with the local-density approximation [43]. By requiring convergence of results, the kinetic energy cutoff of 650 eV and the Monkhorst–Pack \(k\)-mesh of \(48 \times 48 \times 1\) with a smearing width of 0.05 eV were used in all calculations of electronic properties. In our slab model, a vacuum layer with \(\sim 1.7\) nm was set to avoid the interactions between the adjacent atomic layers. The phonon spectra and the electron–phonon couplings were calculated on a \(16 \times 16 \times 1\) \(q\)-grid. Within the rigid-band approximation, we tuned the electronic doping concentration by shifting the Fermi level as well as the band structure and phonon spectra remained unchanged. The strain was introduced by adjusting the lattice constant \(a\) with the strain capacity \(\varepsilon = (a - a_0)/a_0 \times 100\%.\)
3. Electronic structures

The bulk structure of Y$_2$C has the symmetry of R-3 m space group (No.166). There is a large separation about 3.6 Å and weak van der Waals interaction between unit layers. And the monolayer structure has been predicted to be stable, along with the disappearance of magnetism [27, 29]. The structure MgONa is similar to Y$_2$C but the inner O atom is not halfway between two metal atoms, due to the different electronegativity of Mg and Na (figures 1(b) and (d)). The optimized lattice parameters of monolayer Y$_2$C and MgONa are 3.36 Å and 3.15 Å, respectively, and the atomic positions in the strained-free condition are summarized in table 1. As shown in figures 1(a) and (c), the band structures indicate the metallic properties, with the DOS at Fermi level of 1.36 and 0.48 states/eV/ unitcell for Y$_2$C and MgONa. The partial electron density isosurfaces illustrate the conduction electrons confined on the surface (figures 1(b) and (d)), which play the role of anions in the electride [21]. Figures 1(b) and (d) show a bit more electron density distributed between atoms in Y$_2$C, which demonstrates that the electronic states around the Fermi level of MgONa are much more focused on surface than that of Y$_2$C.

4. Electron–phonon coupling

In order to ensure the stability of Y$_2$C and MgONa, we have calculated the phonon spectra using the density functional perturbation theory [39] and observed the absence of imaginary frequency in the entire Brillouin
zone (figures 2(a) and 3(a)). For the low frequency region (<300 cm$^{-1}$) in phonon spectrum of Y$_2$C, in addition to the acoustic branches, there are three modes of relative vibration between two Y atoms along the three directions (inset in figure 2(b)) and the two vibration modes in the xy plane are degenerate at $\Gamma$ point. Three modes in the high frequency region belong to the relative vibration between Y and C atoms, as shown in the inset in figure 2(a). For the case of MgONa, due to the off-center position of O atom, the atomic motions of optical vibrational modes in the low frequency region are slightly more complex and asymmetry (inset in figures 3(a) and (b)), as all optical modes involve the vibrations of three atoms.

Combining the results of phonon linewidths and the Eliashberg function of Y$_2$C, it is found that the optical vibration modes along all directions contribute to the main electron–phonon coupling, especially the relative vibration of two Y atoms along the $z$ direction; the relative vibration between Y and C atoms along the xy plane; the relative vibration between Y and C atoms. The electronic states around the Fermi level are much more focused on surface (figure 1), the contributions from optical modes along $z$ direction are larger than that in the xy plane (figure 3). And it is important that the acoustic modes along the $z$ direction (ZA) around the M point have large phonon linewidths, consistent with the peak around 80 cm$^{-1}$ in the Eliashberg function, which distinguishes with Y$_2$C markedly.

For 2D materials, electronic doping has been introduced by using electric–double-layer transistor [17, 44] and can modulate the physical properties, thus doping is considered in the present work. After electronic doping in Y$_2$C, the entire Eliashberg function increases, as shown in figure 2(c). And the increase of electron–phonon coupling from optical modes in the xy plane is particularly obvious (100 cm$^{-1}$ ~ 150 cm$^{-1}$ and 540 cm$^{-1}$ ~ 570 cm$^{-1}$). The reason is that the electronic doping make the states around the Fermi level penetrate internal layer (the region of atomic bonding) and interact with optical modes in the xy plane, which also occurs in MgONa (figures 3(b) and (c)).

The electron–phonon coupling strength $\lambda$ and critical temperature $T_c$ with $\mu^* = 0.1$ are shown in figure 4. In the condition without electronic doping, $\lambda$ and $T_c$ of Y$_2$C are 0.53 and 0.9 K, as well as the higher superconductivity of MgONa with $\lambda = 0.82$ and $T_c = 3.4$ K. It is obvious that the results of electrides are much lower than that of MoS$_2$ [17]. The cause of this phenomenon is that the separate of electronic states and atomic layer leads to the weak interaction between electrons and phonons. To solve this problem, we have introduced the electronic doping to couple the inner-layer electron and phonon, as stated previously. The increase and decrease of electron in Y$_2$C both enhance the electron–phonon coupling and critical temperature, as the proximate V type curve versus doping concentration (figure 4), because of the increase of DOS (figure 1(a)).

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**Figure 2.** Phonon spectra and Eliashberg function of Y$_2$C. (a) Phonon spectra and phonon linewidths of Y$_2$C without, and (b) with electronic doping of $n_D = 3.5 \times 10^{14}$ cm$^{-2}$. The magnitude of the phonon linewidth is indicated by the size of red error bar. The insets illustrate the most significant motions of vibrational modes. The length of the arrows represents the amplitude of motions. The optical vibration modes contribute the main electron–phonon coupling, such as the relative vibration of two Y atoms (along xy plane ~150 cm$^{-1}$ at $\Gamma$; along z direction ~225 cm$^{-1}$ at $\Gamma$); and the relative vibration between Y and C atoms (along xy plane ~470 cm$^{-1}$ at $\Gamma$; along z direction ~525 cm$^{-1}$ at $\Gamma$). (c) Eliashberg function $\alpha^2 F(\omega)$ of Y$_2$C without and with electronic doping of $n_D = 3.5 \times 10^{14}$ cm$^{-2}$. The electronic doping enhances the electron–phonon coupling from the relative vibration of two Y atoms along xy plane and the relative vibration between Y and C atoms.
contrast, DOS of MgONa only increase with the increase of electron (figure 1(c)), thus superconductivity has an approximate monotonic trend with electronic doping. The maximum critical temperatures of Y$_2$C and MgONa are 2.4 K and 4.5 K, respectively.
5. Strain effect

Strain has long been successfully used to tune electronic properties of 2D materials [45], so we study the strain effect on the superconductivity of electride. And because of the presence of imaginary frequency in Y2C under strain, there are only the results of MgONa under small strain (tension and compression) shown in order to secure the stability. Figure 5 plots the electronic structures and phonon spectra of MgONa under the strain ($\varepsilon = \pm 2.5\%$). The band structures do not change markedly, except to the slight increase of DOS with tensile strain, which also increases phonon linewidths. And the phonon frequency of entire spectrum drops under tensile strain for the weak bond energy. The opposite happens in the case of compressive strain precisely. Due to the double effects of electronic doping and tensile strain, the electron–phonon coupling can be improved to

\[ \text{Figure 5. Electronic structures and phonon spectra of MgONa under the strain. (a) (c) Electronic structures, (b) (d) phonon spectra and phonon linewidths of MgONa under tensile strain ($\varepsilon = 2.5\%$) and compressive strain ($\varepsilon = -2.5\%$). The tensile strain enhances the DOS around the Fermi level thus increases the phonon linewidths, contrary to the effect of compressive strain.} \]

\[ \text{Figure 6. Superconductivity of MgONa under the strain. For the case of undoping, $\lambda$ and $T_c$ of MgONa under tensile strain of $\varepsilon = 2.5\%$ are 0.86 and 4.40 K. When $n_{2D} = 5.5 \times 10^{14} \text{ cm}^{-2}$, tensile strain can enhance $T_c$ to 6.15 K due to the increase of DOS. On the contrary, the compressive strain reduces the superconductivity of MgONa.} \]

\[ \text{5. Strain effect} \]
$\lambda = 0.92$, with $T_c = 6.15$ K (figure 6). In addition, it found that $\lambda$ increases with the electronic doping under compressive strain ($\varepsilon = -2.5\%$) but $T_c$ is trending downward. The main reason is the change of $\langle \omega \rangle_{\text{gap}}$, 81.8K@n_{2D}^* = 0.0 \times 10^{14}$ cm$^{-2}$ dropping to 22.1 K@n_{2D}^* = 5.5 \times 10^{14}$ cm$^{-2}$.

6. Discussion

We have investigated the properties of electron–phonon induced superconductivity in 2D electrodes, Y$_2$C and MgONa, using first-principles calculations. For the prototypical Y$_2$C and MgONa, critical temperatures are obtained as 0.9 K and 3.4 K, respectively, originating from the weak electron–phonon coupling between surface electronic states and phonon. It is also found that the electronic doping can improve superconductivity to $T_c = 2.4$ K and 4.5 K, because of the increase of DOS and the coupling between inner-layer electron and phonon. In addition, under small tensile strain, critical temperature of MgONa can be enhanced to be 6.15 K@n_{2D}^* = 5.5 \times 10^{14}$ cm$^{-2}$ on the premise of dynamic stabilization since the increase of DOS and phonon softening.

Acknowledgments

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