

Finding high-temperature superconductors by metalizing the σ -bonding electrons*

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Abstract Raising superconducting transition temperature (T_c) is an important task of fundamental research on superconductivity. It is also a prerequisite for the large-scale application of superconductors. Since the microscopic mechanism of high- T_c superconductivity is unknown, the conventional approach for increasing T_c is either to apply high pressure to a material that has the potential to become superconducting or to push it close to an antiferromagnetic or some other quantum instability point by chemical doping. In this article, the authors point out that another general approach for raising T_c is to lift the σ -bonding bands to the Fermi level or to metalize the σ -bonding electrons. This approach can increase the probability of finding a novel high- T_c superconductor because the coupling of σ -bonding electrons with phonons is generally strong and the superconducting transition induced by this interaction can occur at relatively high temperatures. After elucidating the underlying mechanism, the authors discuss a number of schemes to metalize σ -bonding electrons and present their recent prediction for the crystalline and electronic structures of two potential high- T_c superconductors, $\text{Li}_2\text{B}_3\text{C}$ and $\text{Li}_3\text{B}_4\text{C}_2$, with T_c higher than 50 K.

Keywords superconductivity, electron-phonon coupling, first-principles calculations

1 Introduction

Exploring and discovering new superconductors, especially high-temperature superconductors, is a goal continuously pursued in superconductivity research. This endeavor serves as a driving force behind the advancement of superconducting physics. In 1986, Swiss physicists Bednorz and Müller made a groundbreaking discovery of high-temperature superconductors based on copper oxides^[1]. Their finding ignited a research boom in high-temperature superconductivity and deepened the study of strongly correlated quantum physics. In 2008, Japanese physicist Hosono and his colleagues discovered iron-based superconductors^[2], further expanding the scope of research in high-temperature superconductivity. High-temperature superconductivity has garnered

widespread attention for two primary reasons. Firstly, the discovery and development of economically viable high-temperature superconductors are crucial prerequisites for expanding the range of applications for superconductors, thus bearing significant practical implications. Secondly, uncovering novel high-temperature superconductors is typically accompanied by the revelation of new phenomena and effects. Studying these phenomena and effects facilitates a deeper understanding of the microscopic mechanisms underlying high-temperature superconductivity and guides the exploration and discovery of new microscopic quantum effects and methodologies.

Superconductivity is a macroscopic quantum phenomenon characterized by zero direct current resistance and perfect diamagnetism, known as the Meissner effect. The study of superconductivity traces back to 1911 when the Dutch physicist Onnes

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observed the phenomenon in mercury at temperatures near 4.2 K, marking the inception of superconductivity research. High-temperature superconductors, which have relatively high critical temperatures (T_c), lack a strict temperature range definition, but generally refer to materials with a T_c close to or above 40 K. The cuprate superconductor $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ holds the record for the highest T_c , reaching 133 K under ambient pressure^[3]. Its critical temperature rises to 164 K under pressure^[4]. Iron-based superconductors represent another class of high-temperature superconductors, exhibiting a maximum T_c of 55 K^[5], approximately one-third of the highest transition temperature observed in copper oxide superconductors.

Revealing and elucidating the microscopic mechanism underlying superconductivity is a fundamental topic in condensed matter physics. In 1957, Bardeen, Cooper, and Schrieffer (BCS) proposed that the origin of superconductivity is the formation of bound electron pairs (Cooper pairs) due to an attractive interaction between two electrons with opposite spins and momenta near the Fermi level generated through the exchange of virtual phonons^[6]. Their theory explains the experimental phenomena observed in element and alloy superconductors. However, electron-phonon coupling is not the only interaction capable of inducing electron pairing. For example, electron pairing in copper oxide and iron-based superconductors may result predominantly from antiferromagnetic fluctuations, although a microscopic picture still needs to be established.

The superconducting phase transition temperature is primarily determined by two key parameters: the effective coupling constant responsible for superconducting pairing and the characteristic energy scale near the Fermi surface that facilitates the formation of Cooper pairs. In the context of electron-phonon interaction systems, these parameters correspond to the electron-phonon coupling constant and the characteristic coupling frequency of phonons. The strong-coupling theory of superconductivity allows for an approximate calculation of these parameters through first-principles density functional theory calculations. However, determining these parameters in copper oxides, iron-based materials, and other superconductors, where electron-phonon coupling may not be the dominant mechanism, poses a challenge that requires further research and

exploration.

2 How to increase the superconducting transition temperature

There are at least two approaches that can be used to enhance the critical temperature of superconductivity:

The first approach is to apply high pressure to materials that have the potential to form superconducting pairs, especially in pure elements or compound materials composed of light elements, to increase the superconducting phase transition temperature. High pressure is an effective means of manipulating material properties. It can simultaneously enhance the interaction between superconducting electron pairs and the characteristic energy scale. It can also stabilize crystal structures that are unstable or metastable under normal pressure, revealing novel physical phenomena. For example, semiconductor materials like germanium and silicon can become superconductors under high pressure, with superconducting transition temperatures of 6.7 K and 5.3 K, respectively. In 1968, Ashcroft predicted solid hydrogen could become metallic under high pressure and exhibit room-temperature superconductivity^[7]. However, achieving the necessary pressure for the metallic solid hydrogen is extraordinarily challenging and has yet to be achieved experimentally. One approach to overcome this difficulty is to select hydrogen-rich materials that utilize attractive interactions generated by chemical bonding between hydrogen and other elements to lower the pressure required for metalizing hydrogen. A German research group recently discovered superconductivity in hydrogen sulfide at a high pressure of 200 GPa, with a transition temperature of 190 K^[8]. If their experimental results are confirmed, it would be the highest superconducting phase transition temperature discovered.

The second approach involves elevating T_c by introducing doping or other means to bring the material close to antiferromagnetic or other quantum critical points. This proximity amplifies the pairing energy of superconducting electrons through antiferromagnetic or other quantum fluctuations. Antiferromagnetic interaction serves as a potent force between two electrons. In the case of copper oxide

superconductors, the characteristic energy scale of antiferromagnetic interaction is approximately $130 \text{ meV}^{[9]}$, which is roughly an order of magnitude higher than the electron-phonon interaction observed in metals. Consequently, compared to systems reliant on electron-phonon interactions, the pairing energy of superconducting electrons resulting from antiferromagnetic interaction is substantially greater. However, a strong antiferromagnetic interaction may lead to the formation of antiferromagnetic spin ordering, which proves detrimental to the emergence of superconductivity. Thus, to effectively harness the influence of antiferromagnetic interaction on superconducting electron pairing while avoiding the formation of long-range antiferromagnetic order, it is critical to approach, but not surpass, the critical point of the antiferromagnetic phase transition.

However, both of these approaches encounter certain limitations. First, achieving and controlling pressures above 100 GPa is extremely challenging experimentally. The critical pressure for hydrogen transition into solid metal has yet to be determined. Theoretical calculations predict that the critical pressure is above $500 \text{ GPa}^{[10]}$, but the actual value may be higher than the theoretical estimate. Such high pressures pose significant challenges for high-pressure experiments. Currently, the highest reliably attainable pressure using diamond anvil cell techniques is approximately $350 \text{ GPa}^{[11]}$. In 2012, Dubrovinsky and colleagues improved the hardness anisotropy of single crystal diamonds by using nanocrystalline diamond particles as anvils. They designed a two-stage high-pressure device to generate static pressures up to $640 \text{ GPa}^{[11]}$. Despite this, there have been no experimental reports on solid metallic hydrogen. Second, controlling the growth of materials to approach antiferromagnetic or other quantum critical points remains challenging. As reliable rules or guidelines for achieving this outcome are still unavailable, discovering new high-temperature superconductors through this approach is serendipitous. The findings of copper oxide and iron-based superconductors exemplify this fortuitous nature of discovery.

Is there a more feasible experimental approach that offers a higher probability of successfully synthesizing or discovering new high-temperature superconductors? The answer is yes: to metalize the σ -bonding electrons in a material, driving them into

conducting electrons and ultimately leading to superconductivity.

The σ -bond is a spin singlet formed by two electrons with opposite spins, bound together by the head-to-head overlapping of two orbitals along the axis linking the two orbitals, which may have the same or different orbital symmetries. It has a considerable overlap and corresponds to a strong covalent bond. For example, the bond energy of σ -bonds formed by the sp^3 hybridized orbitals in the diamond is approximately 3.9 eV . In a crystal, the σ -bonding electrons further hybridize and form energy bands called the σ -bonding bands or simply the σ -bands. The σ -bonding electrons are sensitive to lattice vibrations of the ions, hence coupling strongly with phonons. This coupling is generally the primary interaction that stabilizes the crystal structure. However, σ -bonding electrons are typically below the Fermi level and do not contribute to conductivity. Therefore, to achieve superconductivity through metalized σ -bonding electrons, we must use various methods, such as chemical doping, to move the σ -bonding bands to the Fermi level. While the metalization of σ -electrons will inevitably reduce the electron-phonon interactions and weakens the pairing energy of electrons, assuming the band structure of the σ -electrons does not change significantly, the remaining electron-phonon interactions can still be strong. Once forming superconducting pairs, the corresponding superconducting energy gap can be potentially high.

MgB_2 is a superconductor that arises from the metallization of the σ -electrons within the boron layers. It exhibits a remarkably high superconducting transition temperature of 39 K , which stands as the highest among all phonon-mediated superconductors discovered under ambient pressure^[12]. In cuprate superconductors, the $3d_{x^2-y^2}$ -orbitals of copper atoms hybridize with the $2p$ oxygen orbitals to form a σ -bonding band. Upon hole doping, this σ -bonding band is elevated to the Fermi level and becomes conducting. In particular, a doped hole on the in-plane oxygen $2p$ -orbital couples with a copper $3d_{x^2-y^2}$ electron to form a Zhang-Rice singlet^[13], whose propagating and pairing leads to high- T_c superconductivity. Therefore, there are at least two examples that support the notion of achieving high-temperature superconductivity through the metallization of σ -electrons. However, it has not been widely recognized that this scenario applies *universally* and

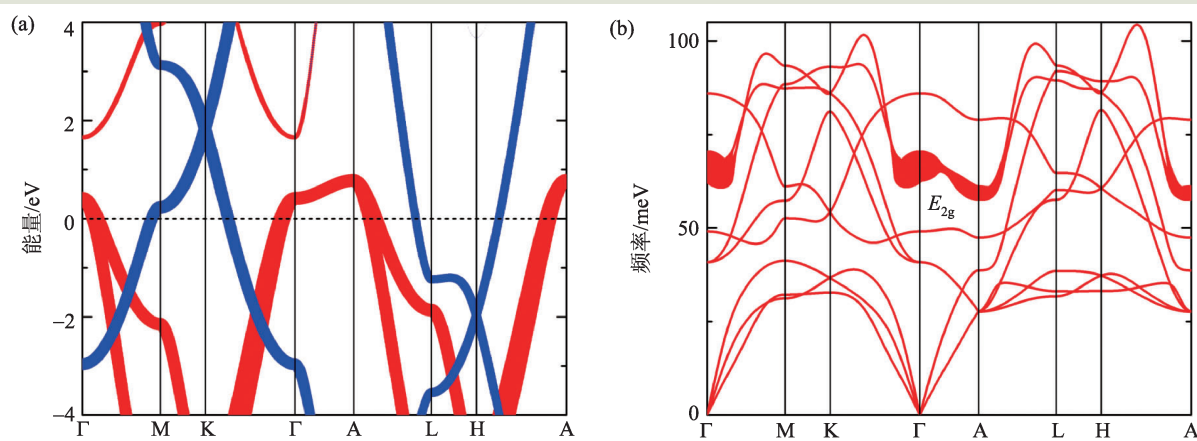


Figure 1 (a) Band structure of MgB_2 . Red and blue lines represent the bands mainly contributed by the σ and π electrons of boron. The linewidth is proportional to the weight of σ or π electrons. The Fermi level is set to zero. (b) Phonon spectrum of MgB_2 . The red linewidth represents the coupling strength between E_{2g} phonon modes and electrons.

can be effectively utilized in the quest for new high-temperature superconductors.

3 Possible methods of metalizing σ -electrons

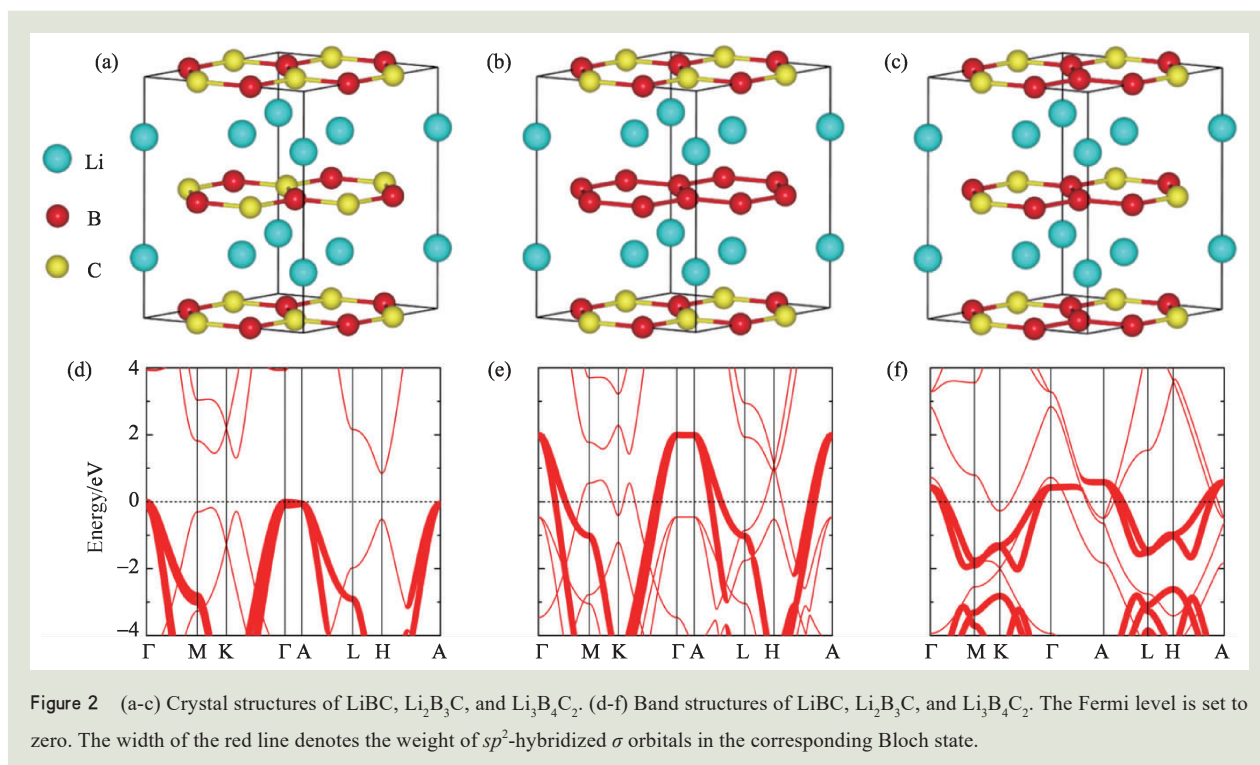
Metallization by lifting the σ -electron band to the Fermi level depends on the chemical compositions and crystal structures of the materials studied and does not follow a fixed model. The following discussion will explore several specific examples to illustrate potential methods toward metallization.

(1) Crystal field effect: The interaction between electrons and the crystal field can vary across different bands. Manipulating this interaction can lower the energy of valence bands or raise the energy of conduction bands, leading to the metallization of σ -bonding electrons. A prominent example demonstrating high- T_c superconductivity through this effect is MgB_2 . In MgB_2 , boron atoms form a two-dimensional honeycomb structure, while magnesium atoms are positioned above the hexagonal centers of the boron atoms between adjacent boron layers. The Mg^{2+} ions strongly attract the π -electrons but exert a weaker attraction on the σ -electrons within the boron layers. Consequently, this interaction significantly lowers the Fermi energy, resulting in an energy overlap between the σ and π bands and leading to the metallization of the σ -bands [see Fig. 1(a)]^[14]. These metallized σ -electrons couple with the E_{2g} phonon mode on

the boron layers [see Fig. 1(b)], ultimately enabling MgB_2 to exhibit superconductivity at 39 K^[15].

(2) High pressure: High pressure can induce structural changes in crystals, stabilize metastable structures, and modify the band structure by increasing the electron bandwidth. Metallization of the σ band occurs when the increase in bandwidth is significant enough for the conduction and valence bands (often containing the σ bands) to start overlapping. An illustrative example is the hydrogen sulfide under high pressures, which exhibits superconductivity with a remarkable transition temperature of 190 K. Both experimental and theoretical investigations indicate that H_2S decomposes under high pressure and the primary superconducting compound is H_3S ^[8, 16–18]. Notably, the σ band, formed by hybridizing hydrogen s electrons with sulfur p electrons, was found to undergo metallization under high pressure^[18]. If the superconducting properties of H_3S at 190 K and 200 GPa are experimentally confirmed, it will be an example of σ -electron metallization through high pressure.

(3) Charge doping: Charge doping plays a crucial role in the investigation of cuprate and iron-based superconductors. It is an effective method for adjusting the position of the Fermi level and metalizing the σ band. In 2004, Ekimov and his colleagues discovered superconductivity in boron-doped diamonds (with a boron doping level of 2.8%) with a transition temperature of 4 K^[19]. This superconductivity results from the raising of the valence band, specifically



the σ band formed by the hybridized sp^3 orbitals, above the Fermi level due to the boron doping, rather than the contribution of impurity bands^[20–22]. Theoretical calculations suggest that increasing the concentration of boron doping in diamonds to 20%–30% can result in a higher transition temperature^[23]. However, achieving such high boron doping concentrations in diamonds poses significant challenges. In the case of cuprate superconductors, hole doping lift the σ band formed by the hybridization of copper's $3d_{x^2-y^2}$ electrons and oxygen's $2p$ electrons to the Fermi level. Nevertheless, the mechanism of electron pairing for superconductivity based on this foundation remains unclear.

The preceding discussion underscores the universal nature of metalizing σ -electrons in the search for new high-temperature superconductors. In line with this, Pickett and his colleagues predicted that Li_{0.5}BC, achieved by introducing 50% lithium vacancies to LiBC, represents a strongly coupled electron-phonon superconductor with a superconducting temperature potentially reaching 100 K^[24]. In its undoped state, LiBC is a semiconductor with a crystal structure resembling that of MgB₂, featuring intercalated lithium layers positioned above the boron-carbon honeycomb layers [see Fig. 2(a)]. The top valence band is formed by the hybridized sp^2 σ -

bonding electrons [see Fig. 2(d)]. The introduction of lithium vacancies causes the σ -bonding states to intersect the Fermi level. However, the experimental observation of superconductivity in Li_{0.5}BC has not yet been accomplished due to the significant structural alterations in the boron-carbon layers caused by the partial absence of lithium atoms, resulting in a complete modification of the band structure and the prevention of σ band metallization^[25]. This example underscores the significance of maintaining structural stability while achieving σ band metallization through hole doping.

An approach proposed to hole dope LiBC without introducing crystal instability is substituting part of carbon atoms with boron atoms instead of creating lithium vacancies^[26]. Theoretical calculations have identified two structure-stable materials, Li₂B₃C and Li₃B₄C₂, as depicted in Figure 2(b) and 2(c), respectively, which show promising potential for achieving high superconducting transition temperatures. In Li₂B₃C, one boron-carbon layer is replaced by a boron layer for every two boron-carbon layers in LiBC. In Li₃B₄C₂, the boron-carbon layers maintain a 2:1 ratio of boron to carbon. The band structures of these materials are illustrated in Figure 2(e) and 2(f), respectively. Encouragingly, first-principles calculations of the electron-phonon interaction reveal a

strong coupling between the σ -bonding electrons and phonons in both materials. Further calculations, employing the Eliashberg theory for strong coupling superconductivity, suggest that both materials exhibit superconducting transition temperatures above 50 K^[26]. Notably, the phonon spectra of these materials display no imaginary frequencies, indicating their dynamical stability. Should experimental investigations confirm the theoretical predictions, these materials would represent a significant breakthrough in the discovery of phonon-mediated high- T_c superconductors under ambient pressure.

Ensuring the stability of the crystal structure is critical during the metalization of the σ bands and demands careful attention. Several crucial considerations arise in this context: Firstly, the strong coupling between σ electrons and phonons can induce structural transitions, potentially compromising the stability of the crystal. It is preferred to mitigate this instability by prioritizing optical phonon modes that exhibit a strong coupling with electrons while minimizing the influence of acoustic phonon modes. Acoustic phonons have lower frequencies and are more prone to further softening under electron-phonon coupling, potentially triggering structural transitions. Secondly, the σ bands play a vital role in maintaining the stability of the crystal structure. Attempting to metalize all σ bands is neither practical nor desirable. Instead, a selective approach is necessary, focusing on metalizing one or a few σ bands closest to the Fermi level. This selective strategy preserves the structural integrity of the crystal while facilitating the desired metalization process. Thirdly, a σ band exhibits minimal dispersion in two-dimensional systems along the direction perpendicular to the two-dimensional plane. Consequently, upon metalization, the σ electrons in two-dimensional systems tend to possess a higher density of states at the Fermi level than in three-dimensional systems. Therefore, reducing the dimensionality can effectively increase the density of states on the Fermi surface and enhance the superconducting transition temperature.

4 Concluding remarks

In conclusion, pursuing new high-temperature superconductors through the metalization of σ bands represents a promising research avenue. Beyond

$\text{Li}_2\text{B}_3\text{C}$ and $\text{Li}_3\text{B}_4\text{C}_2$ mentioned above, this approach holds immense potential for a wide range of materials, including semimetals or semiconductors, to emerge as strongly coupled high-temperature superconductors. By focusing on the metalization of σ bands, this method can circumvent the blind and arbitrary nature associated with the discovery of high-temperature superconductors. Moreover, it can facilitate better integration with theoretical calculations, particularly with density functional theory, providing valuable guidance and enhancing the probability of successfully uncovering new high-temperature superconductors.

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通过金属化 σ 电子寻找高温超导体*

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摘要 提高超导相变温度是超导基础研究的一个重要目标,也是超导广泛应用的一个前提。在高温超导微观机理尚不清楚的情况下,寻找高温超导体一般是通过对材料施加高压或通过掺杂使材料尽可能地接近反铁磁或其他量子不稳定点来实现。这篇文章介绍的是一种通过金属化 σ 电子能带来提高超导相变温度的方法。这种方法之所以有效,能够提高发现新的高温超导体的概率,是因为 σ 电子与声子之间通常存在很强的相互作用,可以显著增强电子的超导配对能,从而提升超导相变温度。作者以具体材料为例介绍了金属化 σ 能带的几种可行途径,并介绍了他们最近预言的两个相变温度可能超过50 K的超导体 $\text{Li}_3\text{B}_4\text{C}_2$ 与 $\text{Li}_2\text{B}_3\text{C}$ 的晶体及电子结构。

关键词 超导电性, 电声耦合, 第一性原理计算

Abstract Raising superconducting transition temperature (T_c) is an important task of fundamental research on superconductivity. It is also a prerequisite for the large scale application of superconductors. Since the microscopic mechanism of high- T_c superconductivity is unknown, the conventional approach for increasing T_c is either to apply high pressure to a material which has the potential to become superconducting, or to push it close to an antiferromagnetic or some other quantum instability point by chemical doping. In this article, the authors point out that another general approach for raising T_c is to lift the σ -bonding bands to the Fermi level, or to metalize the σ -bonding electrons. This approach can increase the probability of finding a novel high- T_c superconductor because the coupling of σ -bonding electrons with phonons is generally strong and the superconducting transition induced by this interaction can occur at relatively high temperatures. After elucidating the underlying mechanism, the authors discuss a number of schemes to metalize σ -bonding electrons, and present their recent prediction for the crystalline and electronic structures of two potential high- T_c superconductors, $\text{Li}_2\text{B}_3\text{C}$ and $\text{Li}_3\text{B}_4\text{C}_2$, with T_c higher than 50 K.

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1 引言

探索和发现新的超导体，特别是高温超导体，是超导研究不断追求的一个目标，也是推动超导物理研究和发展的一个重要动力。1986年，瑞士物理学家 Bednorz 和 Müller 发现了铜氧化物高温超导体^[1]，掀起了高温超导的研究热潮，同时也深化和带动了强关联量子物理的研究。2008年，Hosono 等日本物理学家发现了铁基超导体^[2]，又进一步扩展了高温超导的研究领域。高温超导的研究，之所以受到广泛的重视，有两方面的原因：一是发现和开发经济实用的高温超导体，是扩大超导体应用范围的前提，有很强的应用背景；二是伴随新的高温超导体的发现，通常都有新现象和新效应的发现。对这些新现象和新效应的研究，不仅对探索高温超导的微观机理有直接的帮助，而且对探索和发现新的微观量子规律和方法有指导意义。

超导是一种宏观量子现象。超导体在超导态的直流电阻完全消失，同时还表现出完全抗磁性，即迈斯纳效应。1911年，荷兰物理学家 Onnes 首次在 4.2 K 的低温附近观测到了汞的超导现象，自此拉开了超导研究的序幕。所谓高温超导体，是指超导相变临界温度 T_c 比较高的超导体。至于临界温度达到何种范围才属于高温超导体并没有严格的定义，但一般是指超导相变温度接近或高于 40 K 的超导体。在铜氧化物高温超导体中，超导相变温度最高的是 $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ ， T_c 在常压下为 133 K^[3]，加压后可以进一步升至 164 K^[4]。铁基超导体是另一类高温超导体，最高的超导相变温度为 55 K^[5]，大约是铜氧化物超导体最高相变温度的三分之一。

探索并阐明发生超导电性的微观量子机理是超导研究领域的一个重要课题。1957年，Bardeen, Cooper 与 Schridffer(BCS)提出超导电性的起因，是由于费米能级附近自旋和动量均相反的两个电子通过交换虚声子产生有效吸引相互作用，形成束缚电子对(即库珀对)所致^[6]。他们的理论可以很好地解释元素和合金超导体的实验现象。但是，电声相互

作用并不是唯一可以产生电子配对的相互作用。铜氧化物和铁基超导体中产生电子配对的微观量子机理目前还是一个谜，但一般认为主要是系统中的反铁磁涨落，而不是电声相互作用造成的。

超导相变温度主要由两个特征参数决定：一是导致电子配对的有效耦合常数；二是费米面附近能够形成电子配对的特征能量尺度。在纯电声相互作用系统中，这两个参数分别是电声耦合常数和特征耦合频率。在强耦合的超导理论框架下，这两个参数可以通过密度泛函理论第一性原理计算近似得到。但对铜氧化物、铁基或其他非电声耦合所导致的超导体，如何确定这两个参数还不清楚。

2 如何提高超导相变温度

提高超导临界温度，一般采用的是以下两种方法：

一是通过对可能形成超导配对的材料，特别是轻元素组成的单质或化合物材料，施加高压来提高超导相变温度。高压是调控材料性质的有效手段，可同时提高超导电子配对的相互作用和特征能量尺度，也可以使在常压下不稳定或者亚稳的相变稳定，展现出新奇的物理现象。例如，半导体锗和硅在高压下可以被金属化，进入超导状态，超导相变温度分别为 6.7 K 和 5.3 K。1968年，Ashcroft 就曾预言固态氢在高压下能被金属化，成为室温超导体^[7]。但固态氢的金属化所需的压强很高，目前实验上还达不到。克服这个困难的一种方式选择富氢材料，利用氢与其他元素之间的化学键所产生的有效吸引相互作用，来降低金属化氢所需的压强。最近德国的一个实验组发现硫化氢在 200 GPa 的高压下出现了 190 K 的超导电性^[8]，就是一个典型的例子，如果他们的实验结果得到证实，将是迄今为止发现的超导相变温度最高的超导体。

二是通过掺杂或其他手段使材料尽可能地接近反铁磁或其他量子不稳定点，借助反铁磁或其他量子涨落来提高超导电子的配对能。反铁磁相互作用是两个电子之间的一种有效相互作用，在

铜氧化物高温超导体中，其特征能量尺度大约在130 meV左右^[9]，比金属中的电声相互作用高约一个量级。很显然，相比于电声相互作用系统，由反铁磁相互作用导致的超导电子的配对能也会高很多。但是，如果系统中的反铁磁相互作用太强，也可能导致自旋的反铁磁有序，不利于或压制超导的出现。因此，要充分利用反铁磁相互作用对超导电子配对的作用，同时不让系统出现反铁磁长程序，就要尽可能地接近但不要超越反铁磁相变临界点。

但是，以上两种方法均存在各自的局限性。第一，实验上100 GPa以上高压的实现和控制非常困难。氢在高压下变为固态金属氢的临界压强至今没有确切值，理论计算预言临界压强在500 GPa以上^[10]，但是实际情况可能高于这一理论值。如此高的压强对高压实验提出了很大的挑战。目前金刚石单晶压砧技术可以达到的最高压强约为350 GPa^[11]。2012年，Dubrovinsky及其合作者利用金刚石纳米晶体颗粒作为砧，改善了金刚石单晶硬度的各向异性，设计了双级高压装置，可以产生高达640 GPa的静态压强^[11]。但遗憾的是，目前仍未有固态金属氢的实验报道。第二，使材料趋近反铁磁或其他量子不稳定点在材料生长上很难控制，没有可靠的规律可循，依靠这种手段发现新的高温超导体具有很强的偶然性。铜氧化物超导体和铁基超导体的发现就是这样的例子。

那么，是否存在实验上更易控制并且有比较高的可能性合成或发现新的高温超导体的方法呢？答案是肯定的，那就是金属化材料中的 σ 键电子，使其成为导电电子并超导。

σ 键是自旋相反的两个电子形成的束缚在一起的自旋单态，这种化学键由两个相同或不同的原子轨道沿轨道对称轴方向相互重叠而成，具有较大的重叠程度，对应的键能很大，是最强的共价键。例如金刚石中由 sp^3 杂化形成的 σ 键的键能约为3.9 eV。在固体材料中， σ 键电子之间会进一步杂化，形成能带，称之为 σ 能带。 σ 键电子对离子实的晶格振动非常敏感，与声子的相互作用很强，是稳定晶体结构的一个重要因素。但杂化所

形成的 σ 能带通常会被填满，处于费米能级之下，不导电。因此，通过金属化 σ 能带电子来实现超导，就是要通过掺杂等各种手段把 σ 能带提到费米面之上，变成导电电子，并通过与声子耦合形成超导电子配对。金属化 σ 电子，会部分减少电子与离子实的相互作用，减弱电子的配对能，但只要 σ 电子的能带结构没有发生大的变化，剩余的电声相互作用依然会很强，一旦形成超导配对，对应的超导相变温度就可能很高。

事实上， MgB_2 就是硼的 σ 电子被金属化后形成的超导体，其超导相变温度高达39 K，是迄今为止常压下发现的临界温度最高的电声耦合超导体^[12]。在铜氧化物高温超导体中，铜的 $3d(x^2-y^2)$ 轨道会与氧的 $2p$ 轨道杂化形成 σ 键，空穴掺杂后，氧上的 σ 电子会被提升到费米面，成为导电电子，并与二价铜离子的自旋形成Zhang—Rice自旋单态^[13]，进而产生超导。因此，通过金属化 σ 电子来诱导高温超导体并不是一个新的物理现象。只是过去大家没有意识到，这实际上是一个普遍成立并可用于发现新的高温超导体的一般性规律。

3 金属化 σ 电子的可能途径

如何将 σ 电子能带提升到费米能级，使其金属化，依赖于材料的化学成分和结构，没有固定的模式。下面我们以一些具体的例子来介绍几种可能的途径。

(1) 晶体场效应：晶体场与电子的相互作用对不同的能带可以是不一样的，利用这个性质，通过调节晶体场与电子的相互作用，可以提升价带电子的能量或降低导带电子的能量，使得 σ 电子金属化。通过这种方式实现超导的一个典型例子就是 MgB_2 。在这个材料中，硼原子排成二维蜂巢结构，镁原子位于硼六边形中心的正上方，坐落在相邻两层硼原子层之间， Mg^{2+} 离子实对硼的 π 电子有很强的吸引相互作用，但与硼的 σ 电子相互作用很小。镁离子与硼的 π 电子的相互作用大幅降低了 π 电子能带的能量，使得 σ 能带和 π 能带在能量上发生重叠，从而导致了 σ 能带的金属化(见

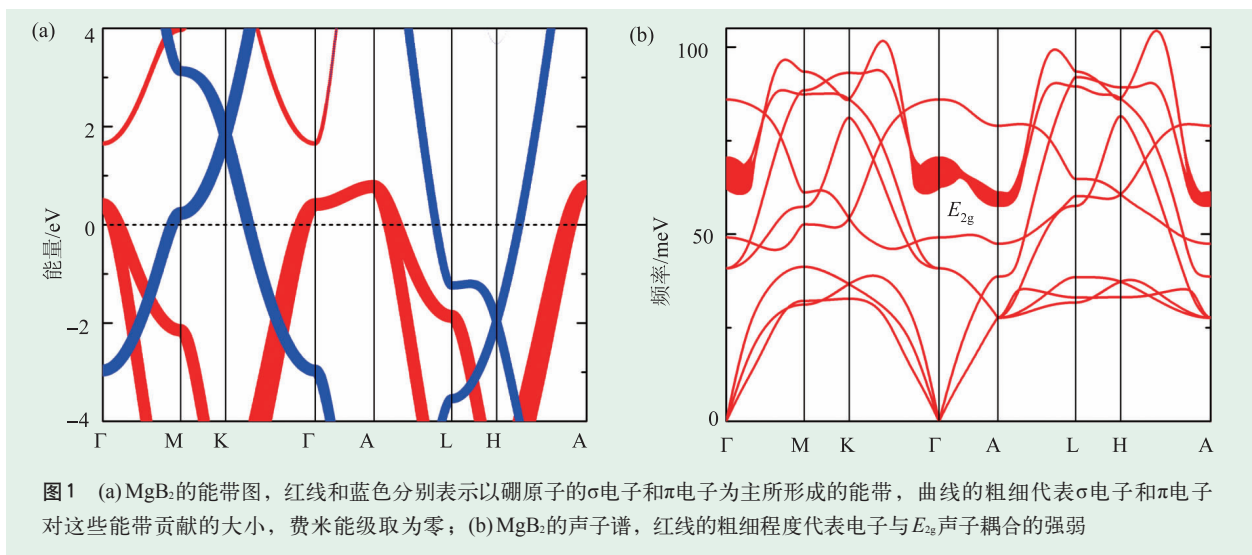


图1 (a) MgB_2 的能带图, 红线和蓝色分别表示以硼原子的 σ 电子和 π 电子为主所形成的能带, 曲线的粗细代表 σ 电子和 π 电子对这些能带贡献的大小, 费米能级取为零; (b) MgB_2 的声子谱, 红线的粗细程度代表电子与 E_{2g} 声子耦合的强弱

图1(a)^[14]。这些金属化的 σ 电子又进一步与二维平面内硼原子的 E_{2g} 声子模式耦合, 使得 MgB_2 成为一个39 K的超导体(见图1(b))^[15]。

(2) 高压: 高压可以改变晶体的结构, 稳定一些亚稳态结构, 也可以通过调节电子能带的宽度改变能带的结构。在高压下, 由于原子轨道之间的重叠积分增加, 能带宽度增加。如果能带宽度的增加使得导带和价带(很多情况下是 σ 能带)发生了显著的重叠, 就可以使得 σ 能带金属化。在超导相变温度可能达190 K的硫化氢材料中, 实验和理论计算均认为 H_2S 在高压下将分解, 超导主要是 H_3S ^[8,16-18]。 H_3S 中氢的 s 电子与硫的 p 电子杂化形成的 σ 能带就是通过高压得以金属化的^[18]。如果 H_3S 在200 GPa下的190 K超导电性得到实验进一步的证实, 那么这种材料就是通过高压金属化 σ 电子实现超导的一个例子。

(3) 电荷掺杂: 电荷掺杂在铜氧化物和铁基超导体的研究中发挥了重要的作用, 也是有效调节费米能级的位置、金属化 σ 能带的一种手段。2004年Ekimov和合作者发现2.8%硼掺杂的金刚石出现了超导^[19], 相变温度为4 K, 这种超导电性就是由于硼掺杂把金刚石的价带, 也就是 sp^3 杂化形成的 σ 能带, 提升到费米能之上造成的, 而不是杂质能带的贡献^[20-22]。理论计算发现, 如果把金刚石中硼的掺杂浓度提高到20%—30%, 超导相变温度还可以得到进一步的提高^[23], 但对金刚石高浓度的硼掺杂现在还难以实现。铜氧化物高

温超导体中空穴掺杂也是把铜的 $3d(x^2-y^2)$ 电子与氧的 $2p$ 电子杂化形成的 σ 键提升到了费米能级, 但在此基础上电子如何实现超导配对, 其机理目前还不清楚。

以上讨论说明, 通过金属化 σ 电子是一种普适并有效发现新的高温超导体的方法。基于这种图像, Pickett和合作者曾预言, 有50%锂空位(锂空位等价于空穴掺杂)的 LiBC 是一个强耦合的电声超导体^[24], 超导温度可达100 K。没有掺杂情况下, LiBC 是一个半导体, 其晶体结构与 MgB_2 相似, 由交错排列的蜂巢状硼碳层和在硼碳正六边形中心上方插层的锂原子层所组成(见图2(a)), 价带顶是硼碳原子形成的 sp^2 杂化的 σ 能带(见图2(d))。通过锂空位掺杂空穴后, 部分 σ 能带电子穿过了费米能级。但实验尚未观测到 $\text{Li}_{0.5}\text{BC}$ 的超导电性, 原因是锂原子部分缺失后, 硼碳原子层会发生结构改变, 完全改变了能带结构, 未能实现 σ 能带的金属化^[25]。这个例子说明, 在通过空穴掺杂提升 σ 能带的过程中, 应尽可能保持原晶体结构的稳定性, 使得 σ 能带在空穴掺杂后不会发生大的畸变。

为了避免通过锂空位掺杂导致的晶体不稳定性, 最近我们建议对 LiBC 进行空穴掺杂, 最好是利用硼原子部分替换碳原子, 而不是产生锂空位^[26]。通过理论计算, 我们发现有两种相对比较稳定的材料, $\text{Li}_2\text{B}_3\text{C}$ 和 $\text{Li}_3\text{B}_4\text{C}_2$, 其结构如图2(b)和2(c)所示, 都可能是相变温度比较高的超导

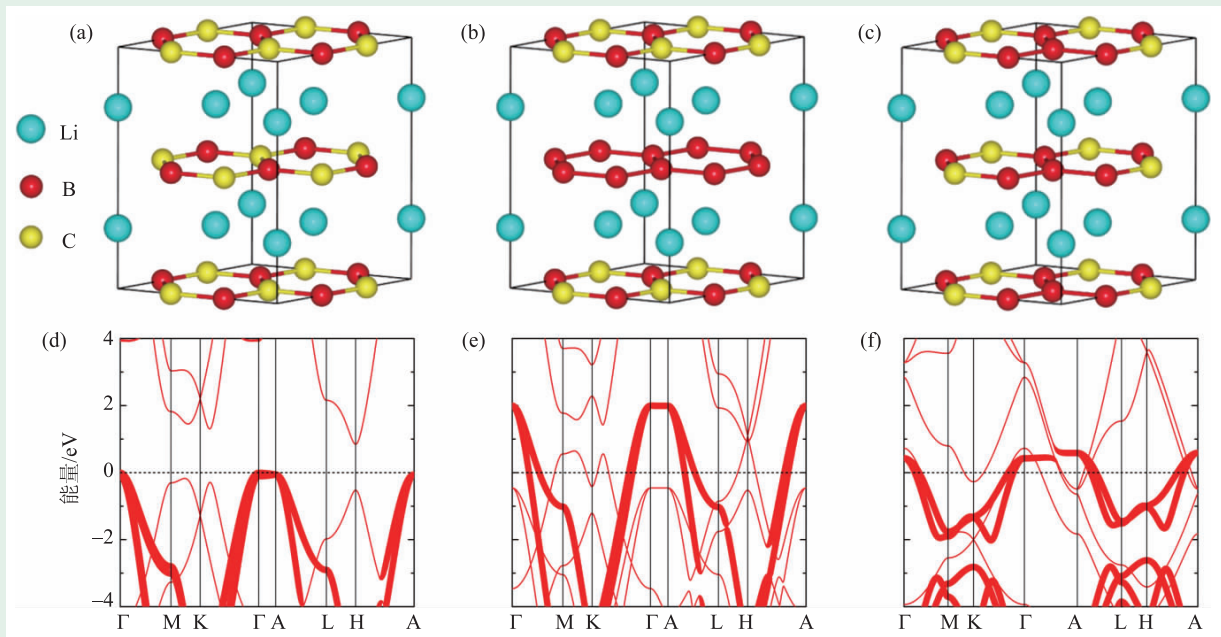


图2 (a—c) LiBC, $\text{Li}_2\text{B}_3\text{C}$ 和 $\text{Li}_3\text{B}_4\text{C}_2$ 的晶体结构图; (d—f) LiBC, $\text{Li}_2\text{B}_3\text{C}$ 和 $\text{Li}_3\text{B}_4\text{C}_2$ 的能带图, 费米能级取为零。红线的粗细程度代表 sp^2 杂化的 σ 轨道在相应的布洛赫态中的权重

体。 $\text{Li}_2\text{B}_3\text{C}$ 是在 LiBC 晶体结构的基础上, 将中间的硼碳层完全替换成硼原子层而形成。在 $\text{Li}_3\text{B}_4\text{C}_2$ 中每层硼碳原子层均保持硼碳 2:1 的比例, 层内两个碳原子排成正六边形结构。图 2(e) 和 2(f) 分别是这两种材料的能带结构, $\text{Li}_2\text{B}_3\text{C}$ 和 $\text{Li}_3\text{B}_4\text{C}_2$ 均有 sp^2 杂化的 σ 能带穿越费米能级。通过对电声相互作用的第一性原理计算, 我们发现在这两种材料中, 正如所预期的, σ 能带电子与声子有很强的相互作用。进一步根据强耦合超导的 Eliashberg 理论计算, 我们发现它们的超导相变温度都在 50 K 以上^[26]。通过计算, 我们还发现, 这两种材料的声子谱中都不存在虚频, 动力学上是稳定的, 有很大的可能性在实验室中合成出来。如果我们的理论预言得到实验的证实, 这将在常压下得到的超导相变温度最高的电声超导体。

在金属化 σ 能带过程中, 保持晶体结构的稳定性是一个需要认真对待的问题。其一, σ 电子与声子之间的强耦合可能诱导材料发生结构相变, 使晶体存有潜在的不稳定性。要克服这一缺点, 应尽量使与电子有强耦合的声子模式是光学支声子, 而不是声学支声子。声学支声子频率低, 强电声耦合可能会使其进一步软化, 从而触

发结构相变。其二, σ 键对晶体结构的稳定有重要的作用, 我们不可能也不应该尝试把所有的 σ 能带都金属化, 而是要有选择地把最接近费米能级的某一支或很少几支 σ 能带, 在布里渊区的某些部分金属化即可。其三, 由于二维系统的 σ 能带沿垂直于二维平面方向几乎无色散, 金属化后二维系统的 σ 电子在费米能级的态密度通常比在三维系统中大, 有利于超导。因此降低体系的维度, 可以有效地增加费米面上的态密度, 提高超导相变温度。

4 结束语

总之, 通过金属化 σ 能带来发现新的高温超导体是一个值得探索和研究的方向, 有广泛的施展空间, 除了前面提到的 $\text{Li}_2\text{B}_3\text{C}$ 和 $\text{Li}_3\text{B}_4\text{C}_2$, 大量的半金属或半导体材料通过 σ 能带的金属化都有可能成为强耦合的高温超导体。这种探索目标明确, 可以避免高温超导研究中的盲目性和偶然性, 也可以更好地与理论(特别是密度泛函理论)计算结合, 发挥理论的指导作用, 增加成功发现新的高温超导体的概率。

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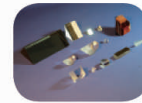
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