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A Structure and the Superconductivity of LiBC

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Abstract: MgB2 has been found to be superconductor with a critical temperature of 39K by Akimitsu and coworkers in 2000. Then, extensive search has been made for searching similar superconductor among related intermetallic compounds. Lithium borocarbide (LiBC) is an analogue with similar structure to MgB2. In the structure of LiBC (P63/mmc), hexagonal sheets of B-C is in the place of B-B and Li is in the place of Mg contrast to MgB2. These result in the material being an insulator. LiBC is expected to be a new phonon-mediated Bardeen-Cooper-Schrieffer (BCS) superconductor. But to be this kind of superconductor, the material should be a conductor, so hole-doped method is used to make it a conductor. In the paper, a new stable structure of LiBC is discovered. Using structure prediction software CALYPSO and first principles calculation software, a new type structure of LiBC under ordinary pressure is discovered, and it has a crystal structure of $P\bar{6}m2$. Quantum Espresso software is used to study the superconductivity of the structure, when the μ^*=0.10, election-phonon coupling parameter λ=0.4112, the critical temperature of superconductivity is 2.77 K, and the bands structure and the density of states of LiBC are obtained by the software. The structure and the superconductivity are also studied under some high pressure.

Keywords: Superconductivity, Election-Phonon Coupling, Crystal Structure, Critical Temperature

1. Introduction

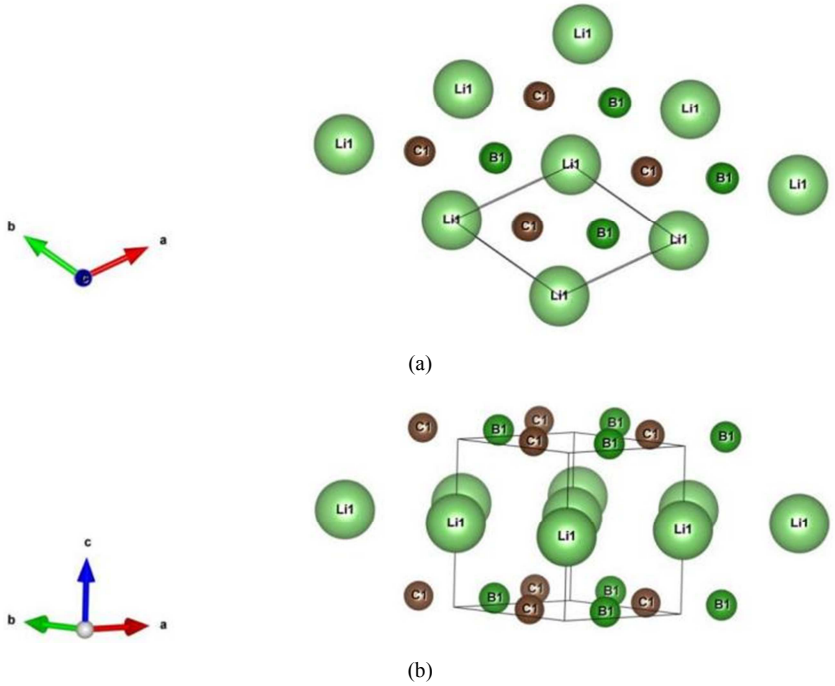
Onnes discovered in 1911 that the resistance of Hg suddenly dropped to zero near the temperature of 4.2K [1], and the current can transmit unhindered. This discovery opened up a new field of condensed matter physics, namely superconducting physics. In 1957 Bardeen J, Cooper, L. N and Schrieffer, J. R developed the BCS theory to explain the phenomenon of low-temperature superconductivity [2]. It is an important goal in condensed matter physics to explore new superconductors with high temperature at ordinary pressure. According the McMillian-Allen-Dynes formula [3], there are two ways to increase the superconducting transition temperature of electroacoustic coupled superconductors, one is to increase the phonon vibration frequency $\omega_{\log}$, the other is to increase the electroacoustic coupling constant λ. The magnitude of the phonon vibration frequency is inversely proportional to the square root of the atomic mass, so the lighter the element, the bigger the $\omega_{\log}$.

Michael Wŏrle and Reinhard Nesper' first reported the substance LiBC in 1995 [4], it's made up entirely of light elements and has a ZrBSi structure, P63/mmc space group, a=2.752 Å, c=7.058 Å, c/a=2.564, B and C form a graphite-like layered structure, the spaces between the layers are filled with Li atoms, and aπbond forms between B and C. Besides, Li3B4C2 and Li2B3C are predicted to be two superconductors with transition temperatures above 50 K [5], the single-layer LiC6 predicts a superconducting temperature of 8.1K [6], the superconducting temperatures of Li2C2 with Cmcm structure at atmospheric pressure and 5GPa are 13.2K and 9.8K, respectively [7], and at the same time, LiC2 has been observed having a 1.9K transition temperature under 30 kbar pressure [8]. So it is of certain significance to further study the superconductivity of Li-B-C series compounds.

In recent years, breakthroughs have been made in the field of ultra-high voltage superconductivity [9-12], but it is almost impossible to realize such a high pressure in practical application, so the application of ultra-high voltage superconducting materials is very limited. In this paper, we explore a new ternary atmospheric superconductor LiBC, and it has superconducting properties under ordinary pressure.

2. Methods and Results

Under ordinary pressure, using structural search software CALYPSO [13-16], extensive calculations have been made for searching ternary compounds containing Li, B and C elements, and a stable structure of LiBC has been successfully obtained. The structure was further optimized, confirmed that the structure is $P\bar{6}m2$, space group 187, with symmetry, a=2.74090, b=2.74090, c=3.54860, unit-cell volume is 23.087349Å3, α=β=90 degree, γ=120 degree, Li takes up site (0.00000 0.00000 0.5), B (0.66667 0.33333 0.00000), and C (0.33333 0.66667 0.00000). The structure of LiBC is shown in figure 1.



(a)

(b)

Figure 1. *The sketch map of crystal structure of LiBC material, (a) is from the top view, (b) from the side view.*

Using BURAI software based on Quantum Espresso, we calculated the electronic structure of the material, as shown in Figures 2 and 3. The electron states are concentrated in the energy range from -15 eV to 23 eV, because the atomic numbers of the three elements are close and they are all light elements, the energy distribution of the densities of state of the three elements is basically the same, the shape of the densities of state of the three elements is similar, and the interaction of each other is obvious. At the Fermi level, the densities of state is not 0, indicating that LiBC is a kind of conductor material.

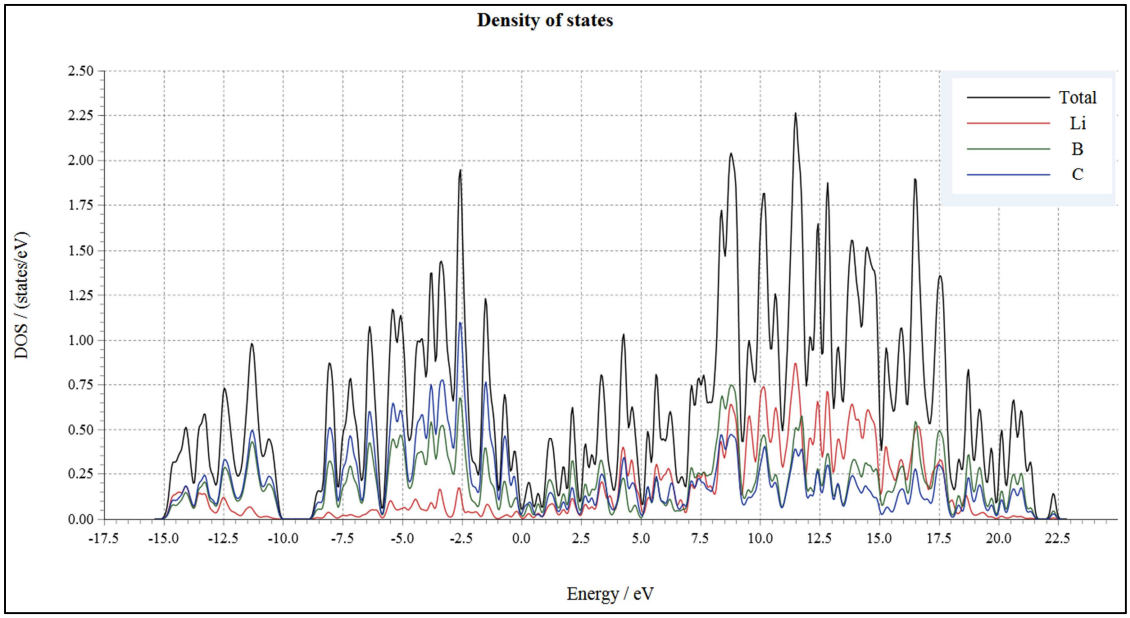


Figure 2. *The density of state of LiBC.*

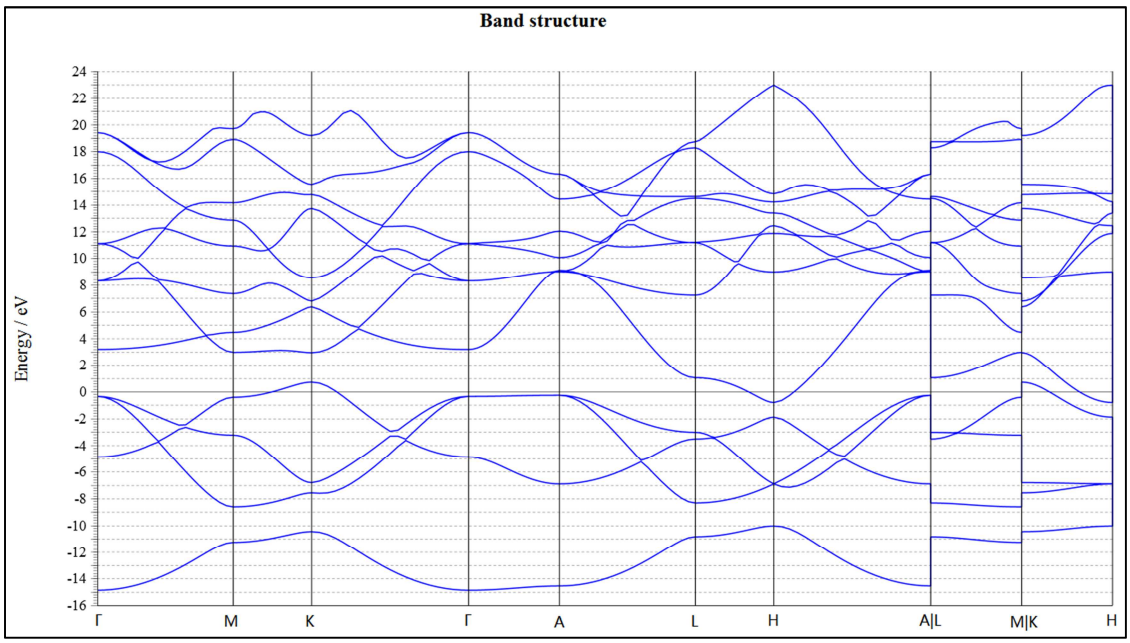


Figure 3. *The band structure of LiBC.*

The energy interval for band calculation is also chosen between -15 eV and 23 eV. In the interval of energy distribution, because the number of valence electrons of the material is relatively small, so the number of bands is small, the Fermi energy level passes through the top of valence band and bottom of the conduction band, which also reflects that the material has the property of conduction.

Using Density Function Perturbation (DFPT) method, the phonon spectrum of LiBC is obtained by QE software package to analyze its stability, as plotted in figure 4. In the spectrum, there is no negative frequency along all the directions between high symmetry points, so the studied structure is reasonable under ordinary pressure. The highest frequency is 1350cm^{-1}, which means the weak electron-phonon coupling.

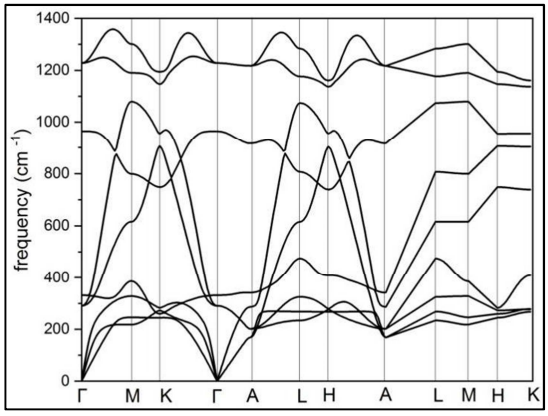


Figure 4. *Phonon dispersion curves of LiBC.*

The McMillian-Allen-Dynes formula [3] which can calculate the superconducting critical temperature is as below

$$T_C = f_1 f_2 \frac{\omega_{\log}}{1.2} exp[\frac{1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}] \quad (1)$$

in which

$$f_1 = \sqrt[3]{1+[\frac{\lambda}{2.46(1+3.8\mu^*)}]^{3/2}} \quad (2)$$

$$f_2 = 1 + \frac{(\omega_2 / \omega_{\log} - 1)^2}{\lambda^2 + [1.82(1+6.3\mu^*)(\omega_2 / \omega_{\log})]^2} \quad (3)$$

$$\lambda = 2\int_{\omega_{\min}}^{\omega_{\max}} \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln \omega \quad (4)$$

$$\omega_{\log} = \exp[\frac{2}{\lambda}\int_{\omega_{\min}}^{\omega_{\max}} \frac{d\omega}{\omega} \alpha^2 F(\omega) \ln \omega] \quad (5)$$

f_1 is the strong coupling correction, f_2 is the spectral function correction, λ is the election-phonon coupling parameter, $\omega_{\log}$ is the logarithmic average frequency and μ^* is the Colomb potential. When λ is relative small, the value of f_1 and f_2 can be regard as 1, then the (1) becomes

$$T_C = \frac{\omega_{\log}}{1.2} exp(\frac{1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}) \quad (6)$$

The Eliashberg spectral function $\alpha^2 F(\omega)$ is plotted in figure 4. The effective integral mainly concentrates upon the range of 200 to 400cm^{-1} and 1000 to 1200 cm^{-1}. When degauss= 0.035, the electron density on the Fermi surface N(E_f) is 1.2143, the value of Ep-ph constant λ is 0.4111, μ^* takes value 0.10, one can obtain T_c is 2.77 K, this is a relatively low superconducting temperature, but LiBC is a superconducting material at atmospheric pressure, the research has certain significance.

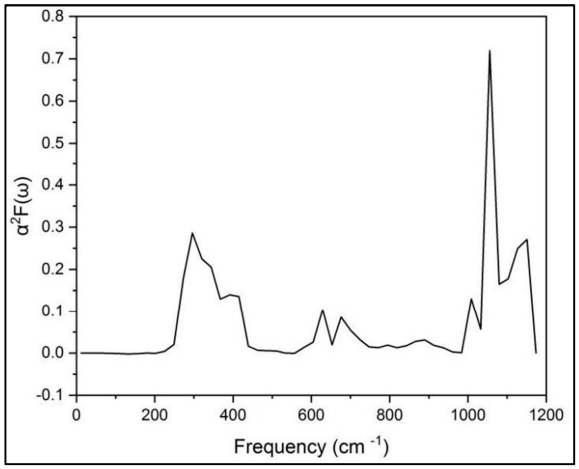


Figure 5. *The Eliashberg spectral function* $\alpha^2 F(\omega)$.

The influence of pressure on LiBC structure and superconducting properties is further investigated. The pressure of 80, 100 and 120GPa is added to the material respectively. The calculated results shows that the original structure $P\bar{6}m2$ is maintained under three different pressures, but the lattice parameters change. Firstly, the stability of the structure under different pressures is studied. Using DFPT method, phonon spectra of material under three pressures are obtained as shown in the figure 6. As can be seen from the figure, since the symmetry of the structures is the same under the three pressures and the high symmetric points are consistent, the images of the three phonon spectra are similar. All phonon spectra have no negative value along the paths of all the high symmetric points, indicating that the structure is stable under the three different pressures. With the increase of pressure, the maximum frequency of phonon vibration becomes higher, which is higher than the maximum frequency of phonon spectrum under normal pressure. Using the electron-phonon coupling module of QE, the superconductivity of the material under three kinds of pressure is calculated. At 100GPa, the material has superconductivity and the superconducting temperature is 2.44K when $\lambda = 0.3411$, $\mu^* = 0.1$, at 120GPa the superconducting temperature of the material is 0.65K when $\lambda = 0.2775$, $\mu^* = 0.1$, but at 80GPa the material is not superconductive. According to the double-band superconductivity theory [17], under high pressure, energy levels split to form energy bands, the spacing between energy levels narrows, and the Fermi surface is close to the upper energy band. As the pressure continues to increase, the energy band splitting is intensified, resulting in the energy band overlapping and the upper energy band merging into the Fermi surface. When the electrons on the Fermi surface transition to the upper empty zone, since exchange energy among the electrons near the top of the corner is higher than that among they and electrons in other corner regions, according to the principle of minimum energy, electrons preferentially fill one corner until they fill the next, and this creates an asymmetry in the distribution of electrons, resulting in a superconducting permanent current. When all the corner regions are filled, the asymmetric distribution of electrons in the corner regions disappears, and the superconductivity is eliminated. When the band gaps are not too large, the increasing pressure can lead to the formation of multiple superconducting phases. Under atmospheric pressure, the LiBC has superconductivity, under pressure, the gap between the Fermi surface and the band of the upper band decreases, it quickly merges into a new Fermi surface, and the superconductivity disappears. When pressed to 80 GPa, the electrons on the Fermi surface are not strong enough to jump into the upper corner zone, no superconductivity occurs, When the pressure is increased to 100GPa, the electrons on Fermi jump into the upper hollow band corner region, causing a new symmetry breaking, resulting in a new superconducting phase.

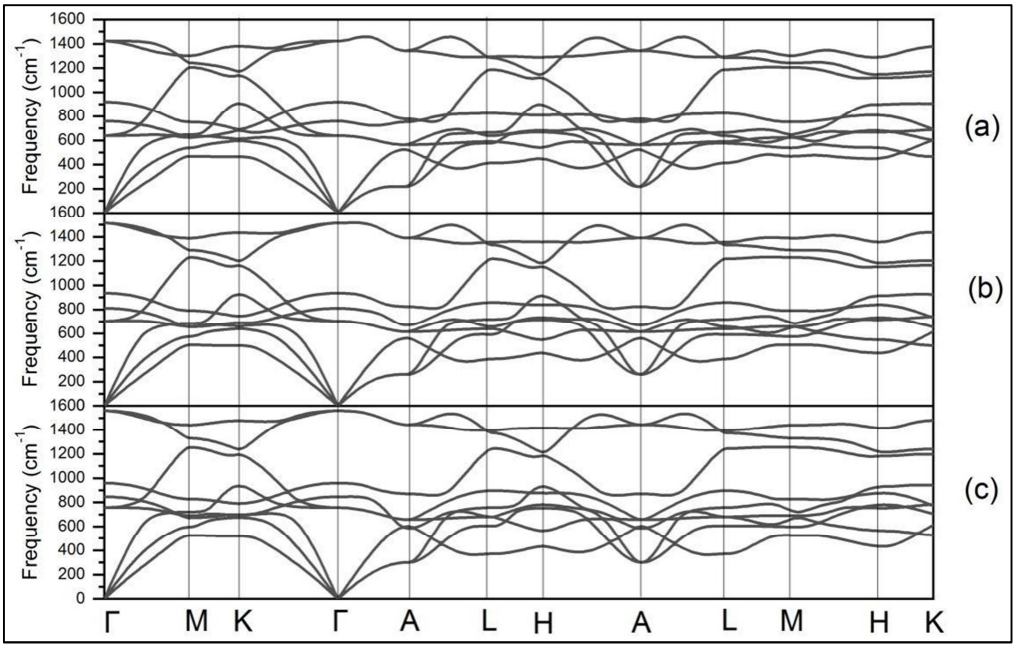


Figure 6. *The Eliashberg spectral function of LiBC under (a) 80GPa, (b) 100GPa, and (c) 120GPa.*

Table 1. *The structure parameters and the Tc of LiBC under different pressure.*

Press (GPa)	Space Group	Structure Parameters	Tc (K)
0	$P\bar{6}m2$	a=2.74090, b=2.74090, c=3.54860, α=β=90 degree, γ=120 degree	2.77
80	$P\bar{6}m2$	a=2.57140, b=2.57140, c=2.83850, α=β=90 degree, γ=120 degree	-
100	$P\bar{6}m2$	a=2.55000, b=2.55000, c=2.73760, α=β=90 degree,γ=120 degree	2.44
120	$P\bar{6}m2$	a=2.53090, b=2.53090, c=2.65540, α=β=90 degree, γ=120 degree	0.65

3. Discussion

LiBC is made up entirely of lightweight elements, and it is expected to have high superconducting temperatures similar to MgB2. With P63/mmc structure it is an insulator, but MgB2 is a conductor. The material is driven metallic, such as by hole doping, and it is supposed to have even higher critical temperature than MgB2, however, no experiment has reported superconductivity above 2 K in this compound up to date [18]. In the paper, without doping, a new structure $P\bar{6}m2$ of LiBC is found in theory under ordinary pressure, and with the structure, the compound is a superconductor with the critical temperature 2.77K. It is interesting to get the compound with the new structure in experiment, and measure the superconductivity. The preparation of the sample may require the use of non-equilibrium preparation methods because the material may be in a non-equilibrium state.

4. Conclusion

A new structure $P\bar{6}m2$ of LiBC is obtained using structure prediction software CALYPSO. By first principles calculation, LiBC is a superconductor with the structure, and the superconducting temperature is 2.77K when $\mu^* = 0.10$. So, LiBC is a new atmospheric superconductor with light elements, enriched the number of superconductor materials. The structure and the superconductivity are also studied under the high pressure of 80, 100, and 120GPa. At 100GPa, the material has a new superconducting phase with a superconducting temperature of 2.44K, we believe that as the pressure increases further, new superconducting phases will emerge.

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