Enhancement of superconductive critical temperatures in almost empty or full bands in two dimensions: possible relevance to $\beta$-HfNCl, $\text{C}_6\text{O}_2$ and MgB$_2$

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We examine possibility of enhancement of superconductive critical temperature in two-dimensions. The weak coupling BCS theory is applied, especially when the Fermi level is near the edges of the electronic bands. The attractive interaction depends on $\mathbf{k}$ due to screening. The density of states(DOS) does not have a peak near the bottom of the band, but $\mathbf{k}$-dependent contribution to DOS (electron density on the Fermi surface) has a diverging peak at the bottom or top. These features lead to significant enhancement of the critical temperatures. The results are qualitatively consistent with the superconductive behaviors of HfNCl ($T_c \leq 25K$) and ZrNCl($T_c \leq 15K$), $\text{C}_6\text{O}_2$ with a field-effect transistor configuration ($T_c = 52K$), and MgB$_2$ ($T_c \approx 40K$) which have the unexpectedly high critical temperatures.

I. INTRODUCTION

There are much interests in the anisotropic superconductors. It is definitely influenced by the discovery of the high $T_c$ cuprates superconductors in which CuO$_2$ planes are considered to play an essential role [1]. Many properties are not simply described by the standard classical BCS theory [3].

Recently a number of compounds having unexpectedly high superconductive critical temperatures ($T_c$) without CuO$_2$ planes were found. These include layered nitride (ZrNCl($T_c \leq 15K$) [8], HfNCl ($T_c \leq 25K$) [9], $\text{C}_6\text{O}_2$ with a field-effect transistor configuration ($T_c = 52K$) [10], and MgB$_2$ ($T_c \approx 40K$) [11]. The common feature of these superconductors is notable anisotropy. Therefore it is mandatory to scrutinize the effects of two-dimensionality on superconductivity.

In this paper we address a question of the role of quasi two-dimensionality in superconductivity. We choose a model of two-dimensional electronic band. Significant enhancement of $T_c$ was obtained when the band is almost empty or full. This result does not qualitatively depend on the details of the model.

II. DENSITY OF STATES AND ELECTRON DENSITY OF THE TWO DIMENSIONAL BAND

The band in two dimensions is often modeled by

$$\varepsilon(\mathbf{k}) \simeq -2t(\cos k_x + \cos k_y),$$

where $t$ is the transfer integral of the tight-binding model on the square lattice. This band has the van Hove singularity in the density of states(DOS) at half-filling. There are a number of works [8–14] that try to explain high $T_c$ cuprates by the van Hove singularity.

On the other hand, here we focus on the van Hove singularity at the edge of band, namely a nearly empty band (or an almost full band) is considered. The density of states(DOS) does not diverge, but the $k$-dependent density of states kDOS (electron density at the Fermi surface) diverges at $\mathbf{k}$ ($\mathbf{k} = 0$) (the bottom of the band) and ($\pm \pi, \pm \pi$) (the top of the band). See Fig. 1. This is the key difference from the case for a degenerate semiconductor [14] which is three dimensional and does not have a van Hove singularity at the band edges. The density of states is given by

$$N(E) = \int \frac{1}{| \nabla \varepsilon(\mathbf{k}) |} dl = \int \frac{1}{v} dl,$$  

where $l$ is the Fermi surface (line in two dimensions) and $v$ is the semiclassical velocity. Here

$$k\text{DOS} = 1/| \nabla \varepsilon(\mathbf{k}) |$$

and it is plotted in Fig. 1. Note that kDOS is diverging near the $\Gamma$ point $\mathbf{k} = (0,0)$ as well as at ($\pm \pi, \pm \pi$) and at ($\pm \pi, 0$), ($0, \pm \pi$).
FIG. 1. kDOS. All the peaks are actually diverging. The peak at $Γ(0,0)$ corresponds to the bottom of the band. The four peaks at $(±\pi,±\pi)$ are at the top of the band and the others give van Hove singularities at half-filling.

These singularities are not seen in DOS since it is integrated on a vanishingly short Fermi line. Instead DOS is almost constant near the band edges. See Fig. 2.

These behaviors near the band edges are rather universal since the band dispersion may be approximated by $E_{\text{edge}} \pm (k_x^2 + k_y^2)/2m^*$ in general including that of the honeycomb lattice which is relevant to HfNCl and MgB$_2$ where $m^*$ is the effective band mass, $E_{\text{edge}}$ is the band edge, and $+$ and $-$ apply to near the bottom and top of the band respectively. The important point is that if the interactions depend on $k$, kDOS has to be considered carefully.

III. BCS FORMULA AND SCREENING

With the properties of the band above in mind, we consider the gap equation,

$$\Delta_k = -\sum_{k'} V_{kk'} \Delta_{k'}(T) \frac{E_{k'}}{2k_B T},$$

(4)

where $E_k = \sqrt{[\varepsilon(k) - \mu]^2 + \Delta_k(T)^2}$, $\Delta_k(T)$ is the gap order parameter and $V_{kk'}$ is the interaction. The sum is restricted within the cutoff $\mu - E_c < \varepsilon(k') < \mu + E_c$ where $\mu$ is the chemical potential.

From the gap equation (4), one can obtain $T_c$ and $\Delta(T)$. Near $T_c$, $\Delta$ is very small; then (4) is linearized. $T_c$ is determined by the linearized equation. The gap $\Delta(T)$ is obtained by iteration of (4).

In the usual BCS interaction one takes $-V$ a constant if two particles are both within the cutoff and vanishes otherwise. This implicitly assumes point-like electron-electron interactions, namely the screening is perfect. In this case the classical BCS result is

$$T_c \sim 1.13 E_c \exp(-1/N V),$$

(5)

where $N$ is the DOS near the bottom of the band. When one takes physically reasonable value of $V$, enhancement of $T_c$ can not be expected even if kDOS is large. This is because the Fermi line is a small circle and the range of integration is very small. It offsets the large but uniform kDOS. This behavior is totally analogous to the fact that the behavior of DOS –integral of kDOS along the Fermi line– that is not enhanced near the bottom of the band. See Fig. 2.

On the other hand if the interaction depends on $q = k - k'$, i.e. is not a constant in the integral, the effect of the large kDOS is not necessarily canceled by the short length of the Fermi line. Specifically we choose an interaction which is screened and has a peak at $q = k - k' = 0$.

$$V_q = -\frac{g_q^2}{q^2 + g_0^2}.$$  

(6)

Here $g_q$ is the coupling constant and $g_0$ is the inverse of the screening length $L$: $g_0 \simeq 1/L$. The screening length actually depends on $\mu$, but we neglect this effect for the sake of simplicity. The attractive interaction (6) depends on $k$ and has a peak at $q = 0$. Thus the effect of the large kDOS can not be totally canceled by the small Fermi line, as discussed above.

IV. EFFECTIVE INTERACTION

Let us first give an estimate of the effective interaction. For the chemical potential $\mu = -4t + \eta$ where $-4t$ is the energy of the bottom of the band in the noninteracting case and $\eta$ is small but larger than the cutoff $E_c$, one has, from (4),

$$2 = \int_0^{2\pi} d\phi \int_{k_{\text{Inf}}^c}^{k_{\text{Sup}}^c} \frac{g_q^2 \tanh(k^2 - \eta)}{2k_B T_c} \frac{dk'}{2k_B T_c} \frac{k'^2 dk'}{k'^2 + k^2 - 2k'^2 \cos \theta + g_q^2 k'^4}$$

(7)

with $k^2 t = \eta$, $\eta \gg E_c$ and $|k^2 t - \eta| < E_c$. This leads to

$$2 = \pi g_q^2 t \int \frac{\tanh(\frac{\kappa}{2k_B T_c})}{\kappa} \frac{d\kappa}{A}$$

(8)

with $k^2 t - \eta = \kappa$ and $A = k^2 + 4\eta q_0^2 t + \cdots$. With the preceding conditions, and if $\eta$ is large enough versus $E_c$, $A$ reduces to $1/4\eta q_0^2 t$. One reverts to the BCS case of $V$ constant but with

$$V_{kk'} = \frac{g_q^2}{g_0^2},$$

(9)

thus higher $T_c$ is expected. This result is also apply when the Fermi energy is near the top of the band (hole doped) as seen by changing the signs of $t$ and $\eta$. 

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V. NUMERICAL RESULTS

The numerical solution is consistent with the above analysis and gives enhancement of critical temperatures near the bottom of the band. They are plotted in Fig. 3 for a number of screening lengths and cutoffs. They take the maximum values at $\mu_{\text{op}}$ near the bottom of the band. The decrease of $T_c$'s for $\mu$ smaller than $\mu_{\text{op}}$ is due to the semiconductor gap where DOS vanishes. But note that $T_c$'s remain finite at the bottom of the band in the noninteracting case. They extend to the band gap region due to the superconductive coherence effect. It is natural that $T_c$'s do not depend on the cutoff in this region. The transition temperature $T_c$ also decreases for $\mu$ larger than $\mu_{\text{op}}$. This is because the kDOS is getting smaller in this region. Note that if screening is poorer, $T_c$ is higher.

![Critical temperature as a function of $\mu/t$. The total band width is $8t$ and $4t$ is the bottom of band. The parameters are: transfer $t = 0.25\text{eV}$, screening lengths $L = 5, 10, 15, 20, 25$ lattice spacings respectively for the lower to higher curves. The cutoffs $E_c$ are $30\text{meV}$ (an occupied square mark) and $50\text{meV}$ (an empty square mark).](image)

![The upper set of curves are the ratios $\Delta(0)/T_c$ for the maximum of $\Delta(0)$'s. Within this set, the curves from lower to higher ones correspond to screening lengths $L = 10, 15, 20, 25$ lattice spacings for the cutoff energy $E_c = 30\text{meV}$ by an occupied square mark, $E_c = 50\text{meV}$ by an empty circle mark. The lower set of curves are the ratios $\Delta(0)/T_c$ for the minimum of $\Delta(0)$'s. Screening lengths are $L = 10, 15, 20, 25$ lattice spacings for the higher to lower curves respectively for the cutoff energy $E_c = 30\text{meV}$ by a star mark, $E_c = 50\text{meV}$ by an empty square mark.](image)

We have a typical s-wave pairings, but the gaps depend on the absolute value of $k, |k|$. The maximum and minimum of $\Delta(0)/T_c$'s are plotted in Fig. 4. Note that the maxima of the gaps are almost independent of the cutoff. They are about $1.8T_c$ which is close to the BCS value $1.76T_c$ at $\mu \approx -3.4$. They increase as $\mu$ is lowered. On the other hand the minima of the gap depend on the cutoff as expected, since the minima occur at the edge of the cutoff. They are less than the BCS value and decrease as $\mu$ is decreased. However, less anisotropic $s$ gap is possible in cases with shorter screening lengths [14].

Note that $\Delta(0)/T_c$'s approach zero in a similar manner to the $T_c$'s. This implies that $\Delta(0)$ decay faster than $T_c$.

VI. MEDIUM TO HIGH $T_c$ ANISOTROPIC SUPERCONDUCTORS

In this Section we briefly discuss the known superconductive properties of some of the anisotropic compounds which have unexpectedly high critical temperatures. Most of the properties are consistent with our results qualitatively.

A. ZrNCl and HfNCl

It is known that a series of transition-metal nitrides with the rock-salt structure become superconductors, such as TiN, ZrN, HfN and NbN with $T_c$s at 5.5, 10.7, 8.8 and 18.0K, respectively [17]. Among these $\beta$-ZrNCl is characterized as a semiconductor with a band gap of $\sim 3\text{eV}$. On lithium intercalation the electrons are transferred from the intercalated lithium atoms to the ZrN layers through chlorine layers, and the empty $t_{2g}$ band is partially filled with electrons, giving the metallic behavior. It becomes a superconductor with a $T_c$ of $\leq 15K$. It is suggested that the superconductivity occurs within the thin two-dimensional ZrN layers separated by the close-packed chlorine layers [18].

$\beta$-HfNCl is isostructural with $\beta$-ZrNCl. However, expanded spacings indicate the formation of co-intercalated phases of THF molecules with lithium between the layers [1]. The much higher $T_c = 25K$ of $\text{Li}_{0.38}(\text{THF})_y\text{HfNCl}$ than that of the zirconium analogue ($T_c = 15K$) may be attributed to more prominent two-dimensionality due to the co-intercalation. Note that $T_c = 8.8K$ of HfN the
rock-salt structure is lower than that of ZnN (=10.7K). Recently it has been shown that a larger interlayer spacing leads to weaker screening within a layer [19]. This result may explain the above phenomenon.

B. C$_{60}$

A crystal of C$_{60}$ molecules superconducts when doped with alkali metal atoms, which donate electrons to the C$_{60}$ lattice [20-22]. The critical temperature range from below 10K to 33K, depending on dopant. Recently, Schön et al. [2] succeeded in making a field-effect transistor (FET) device on a C$_{60}$ crystal. This enables to adding holes or electrons into the top layer of a C$_{60}$ crystal. Doping level is continuously varied by means of the applied gate voltage, without the crystallographic changes. The peaked behaviors of $T_c$ are observed in both electron and hole doped cases. The peak value in the hole-dope case is remarkably high 52K. That in the electron-dope case is 11K. The result was discussed in relation to the band structure calculation for the bulk three dimensional solid [23]. The Fermi energy is not near the 3D band edge. However, the energies of the surface states which are pertinent to the present case have tendency to be in the energy gaps of the bulk states. The present situation of the two-dimensional superconductivity requires appropriate new calculations.

C. MgB$_2$

The critical temperature of MgB$_2$ $T_c \sim 40$K is by far the highest in any binary compound [3]. Boron forms layers of honeycomb lattices with magnesium as a space filler. A number of band structure calculations are available [24-26]. There is no major disagreement in these calculations and indicate that Mg is substantially ionized. The bands at the Fermi energy derive mainly from B orbitals. These are the bonding ($p_{x,y}$) $\sigma$ bands (2D like), the bonding ($p_z$) $\pi$ bands (3D like) and the antibonding ($p_z$) $\pi$ bands (3D like).

There is a close analogy between MgB$_2$ and graphite. They have the same layer structure. Graphite is iso-electronic with MgB$_2$. The 2D-like $\sigma$ band of graphite is completely filled and it is not related to the superconductive instability. Graphite becomes superconducting up to 5K, but only when electron-doped (intercalated) [27]. On the other hand MgB$_2$ superconducts at stoichiometry at $T_c \sim 40$K. This comparison strongly suggests that 2D-like $\sigma$ band plays an important role in MgB$_2$. The Fermi energy is near the top of this band. This situation corresponds to the case we investigated above for enhancement of $T_c$. The other states on the 3D-like bands become superconductive due to interband setterings [28,29].

VII. CONCLUSIONS

We study the superconductive properties of the two-dimensional bands which is almost full (hole-doped) or empty (electron-doped). The crucial and specific point is the large electron density kDOS near the top or the bottom of the bands. It is shown that screened interaction leads to enhancement of superconductive critical temperature $T_c$ from the approximate analysis and the numerical computations. The poorer the screening, the stronger the enhancement of $T_c$ is.

Since the physical origin of the enhancement of $T_c$ is rather clear (large electron density), the strong coupling treatment which might be more appropriate for some compounds will not likely to change the results qualitatively.

The present results are not in conflict with most of the known superconductive properties of some of the anisotropic compounds which have unexpectedly high critical temperatures such as $\beta$-HfNCl, C$_{60}$ and MgB$_2$.

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