Critical Temperature $T_c$ versus Charging Energy $E_c$ in MgB$_2$ and C$_{60}$/CHBr$_3$

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Abstract

The boride compounds MB$_x$ related to the magnesium-boron stacking layered material MgB$_2$ are discussed in terms of the B-B layers in the borides analogous to the Cu-O ones in the cuprates. We propose a possibility of superconducting materials which exhibit higher critical temperature $T_c$ than 39 K of MgB$_2$. We point out a role of interstitial ionic atoms M (e.g., Mg in MgB$_2$) as capacitors, which reduce the condensation-energy loss due to the charging energy $E_c$ between the B-B layers. In the viewpoint of the present model, the recently discovered 117-Kelvin superconductor C$_{60}$/CHBr$_3$ is also discussed in terms of the intercalation molecules CHBr$_3$ as possible capacitors among the superconducting grains of C$_{60}$ molecules.

Key words:
MgB$_2$, C$_{60}$/CHBr$_3$, Josephson Junction Array model, Electric polarizability, Charging energy
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1 Introduction

Since Akimitsu and co-workers presented a remarkably high temperature ($\sim 39$ K) superconducting magnesium diboride MgB$_2$ in the beginning of 2001 [1,2],

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much attention has been focused on this diboride material and some related boride compounds [2–5]. The material MgB$_2$ takes the layered structure of B-Mg-B stacking and has a coupling between 2-dimensional (2D) B-B layers [1,2,6]. According to several band calculations [7–10], in the MgB$_2$-type crystal structure there exist a strong covalent B-B bonding and an ionic B-Mg bonding. The strong covalent B-B bonding and the presence of the ionic Mg atoms lead to hole-like cylindrical Fermi surfaces in MgB$_2$ [7,8], and the holes are conducted in each 2D B-B layer. It is observed that the 2D B-B layers, like the Cu-O layers in high-$T_c$ cuprates, play an important role in the electrical transport properties [11]. The superconductor MgB$_2$ can then be beautiful realization of the essential physics of superconductivity in cuprates, without the complications of Cu $d_{x^2-y^2}$ orbitals [12].

In a previous paper [13], on the basis of a theoretical model of the B-B layers analogous to the Cu-O layers [15–19], we investigated the ionic diboride compounds (M$^{2+}$)(B$^-$)$_2$, (e.g., (Mg$^{2+}$)(B$^-$)$_2$ in the case of MgB$_2$), and discussed their superconducting critical temperature $T_c$. We made investigation into $T_c$ assuming a simple linear relation between $T_c$ and the inter-layer charging energy $E_c$ [13]. In the present paper, instead of assuming the linear relation, we will analyze $T_c$ and $E_c$ in more detail on the basis of an original formula for $T_c$ presented in Refs. [15–17], and also mention general boride compounds MB$_x$ in which the interstitial ionic atoms M between B-B layers are not restricted to M$^{2+}$. The purpose of this paper is to grope for various possible boride compounds with $T_c$ over 39 K and to give a hint as to new material synthesis. In the viewpoint of our theoretical model, the recently discovered 117-Kelvin superconductor C$_{60}$/CHBr$_3$ [14] is also discussed.

2 Physical Model

We model the boride compounds MB$_x$ (M= Mg, Be, etc.) as quantum-capacitive Josephson junction arrays (JJA) with weakly coupled superconducting grains on a 3D lattice, following Kawabata-Shenoy-Bishop (KSB) theory [15–19], originally proposed to the high-$T_c$ cuprates with 2D Cu-O layers and a coupling between the Cu-O layers. In the present JJA model, the Josephson coupling energy $E_J$ via the Cooper pair tunneling within and between the B-B layers enhances the critical temperature $T_c$, while the charging energy $E_c$ between the B-B layers depresses $T_c$. The origin of $E_c$ is that, when the Cooper pairs tunnel between the layers, local inter-layer charge unbalance is induced between the superconducting grains in JJA. This charge unbalance gives rise to the electric fields between the grains and it costs the electromagnetic energies and destroys the phase coherence of superconductivity [15–17,20]. Here, an important point for our analysis is that the interstitial ionic atoms, M, located between the B-B layers play a role of capacitors, reducing the charging
energy $E_c$ by the electric polarization of the ionic atom.

We estimate $T_c$ which is a function of $E_c$. According to the KSB theory [15–17], in the present JJA model $T_c$ is expressed, with an unknown function $f$, as

$$\frac{E_J}{k_B T_c} = 0.454 f(\gamma_0^2, E_c/E_J),$$  \hfill (1)

and for zero charging energy $E_c = 0$ it must reduce to a known equation

$$\frac{E_J}{k_B T_c} = 0.454 f(\gamma_0^2, 0),$$  \hfill (2)

which is the dimensionless critical coupling [21,22] in terms of the coupling anisotropy $\gamma_0^2$ in the classical anisotropic 3D XY/JJA system ($\gamma_0^2 = E_{J \perp}/E_{J \|}$, where $E_{J \perp}$ is the inter-layer Josephson coupling energy, $E_{J \|}$ the intra-layer one, and $E_J = \sqrt{E_{J \perp} E_{J \|}}$). In the 3D limit $\gamma_0^2 \rightarrow 1$, the present JJA model may be applied to the superconductor C$_{60}$/CHBr$_3$, where the coupled superconducting grains on a 3D lattice in the 3D JJA are composed of C$_{60}$ molecules. We discuss this superconductor in Sec. 4.

Expanding $f$ with respect to $E_c/E_J$, we obtain from Eq. (1) the expression for $T_c$ as [15–17]

$$k_B T_c \sim \frac{E_J}{f_0 + f_0 E_c/E_J},$$  \hfill (3)

where $f_0 = f(\gamma_0^2, 0)$. In this paper, we rewrite Eq. (3) as

$$T_c = \frac{T_c^{\text{max}}}{1 + A E_c}$$

$$\equiv F(E_c),$$  \hfill (4)

with the phenomenological parameters $T_c^{\text{max}}$ and $A$, which should be determined empirically. We use Eq. (4) to fit data and estimate $T_c$ for some borides in the next section.

3 Estimation of $E_c$ and $T_c$ in the boride compounds

Referring to Kittel's textbook and Shockley’s tables [23–26] for the ionic radius $d$ and electronic polarizability $\varepsilon$ of the ionic atoms M, we have obtained the
charging energy $E_c \sim d/\varepsilon$ between the B-B layers as in Table 1, following the KSB theory [15–19].

We discuss first the ionic compounds $M^{2+}(B^-)_2$ expected to have nearly the same electronic structure [9] as MgB$_2$ ($Mg^{2+}(B^-)_2$) and to have almost the same Josephson coupling energy $E_J$ [i.e., the same “bare $T_c$” ($T_c^{\text{max}}$) without any influence of the M-atom-dependent charging energy $E_c$, and the same value of $A$ in Eq. (4)]. By hypothesizing the same $E_J$ for any $M^{2+}(B^-)_2$ compounds, we estimate critical temperatures $T_c (= F(E_c))$. In Fig. 1 we show two points, as experimentally known data, for BeB$_2$ ($T_c \simeq 0$ K ($< 5$ K) [3], $E_c = 43.75$) and MgB$_2$ ($T_c = 39$ K [1], $E_c = 6.91$), where $E_c (\sim d/\varepsilon)$ are of Table 1 and in arbitrary units. From Eq. (4) and the values of $T_c$ and $E_c$ for MgB$_2$, we obtain an equation $T_c^{\text{max}} = 39 \times (1 + 6.91 A)$. From this equation and Eq. (4) with $T_c < 5$ K and $E_c = 43.75$ for BeB$_2$, we obtain $A < 0$, which is contrary to the condition that the charging energy $E_c$ decreases $T_c$ in Eq. (4). It should be remedied by taking higher order terms of $E_c/E_J$ when obtaining Eq. (3). Instead, we plot the $T_c$ vs. $E_c$ curve in Fig. 1 on the basis of Eq. (4), assuming $T_c^{\text{max}} = 120$ K as representative. In this case $T_c(\text{BeB}_2) = 8.6$ K at $E_c = 43.75$. Even if $T_c^{\text{max}}$ is increased further, $T_c$ at $E_c = 43.75$ only decreases a little. On the other hand, when $T_c^{\text{max}}$ is decreased, $T_c$ at $E_c = 43.75$ is increased and deviates more from the experimental result [3] $T_c(\text{BeB}_2) < 5$ K. We then believe that the $T_c$ vs. $E_c$ curve drawn in Fig. 1 is not so unreasonable. It is expected that the diborides, which contain the ionic atoms M with the electric polarizability $\varepsilon$ and have the corresponding $E_c$ in Table 1, are distributed on the $T_c$ vs. $E_c$ graph along the curve drawn in Fig. 1.

In Ref. [4], $T_c = 0.72$ K is observed in BeB$_{2.75}$, which has the crystal structure different from MgB$_2$. It has also been suggested that nonstoichiometry may be an important point in the superconductivity of some boride compounds [2]. It is then interesting to synthesize various borides MB$_x$ and try to measure their $T_c$. We give in Table 1 various atoms M for which the polarizability has been obtained [24,25]. The present theory can be applied to the borides MB$_x$ which have the B-M-B stacking structure. In this case the values of the Josephson coupling energy $E_J$ and the coupling anisotropy $\gamma_0^{-2}$ (and thus, the corresponding $T_c^{\text{max}}$ and $A$ in Eq. (4)) would be different in general for each compound. It is, however, expected that the compounds with smaller $E_c$ is adventageous to the superconductivity, which can be a guide in the synthesis of new materials. The thin films of MB$_x$ with the B-M-B stacking structure could be synthesized by, for example, the epitaxial methods.
Quite recently, Schön et al. [14] found a new superconducting system $C_{60}/CHBr_3$ which exhibits very high critical temperature $T_c = 117$ K. It is a $C_{60}$ superconductor intercalated with CHBr$_3$ molecules. This $T_c$ is about two times larger than 52 K [27] of $C_{60}$ without intercalations. The critical temperatures of $C_{60}$ superconductors increase with the lattice constants $a$; $C_{60}$ ($T_c = 52$ K, $a = 14.15$ Å), $C_{60}/CHCl_3$ ($T_c \sim 70$ K, $a = 14.29$ Å), and $C_{60}/CHBr_3$ ($T_c = 117$ K, $a = 14.45$ Å) [14]. One of the promising courses of attaining higher $T_c$ is certainly to search for new spacer molecules which expand the separation between $C_{60}$ molecules [14]. However, it seems to be open to further discussion whether the only 2 % expansion of the lattice constant is sufficient for the increase of the electronic density of states which corresponds to rather drastic rise of $T_c$ from 52 to 117 K.

In the viewpoint of our theory, we would like to point out another possibility that the intercalation molecules would play a role of the capacitors in the $C_{60}$ superconductors as discussed for the atoms M in the boride compounds MB$_x$. By the electric polarization of the neutral molecules, the intercalation molecules such as CHBr$_3$ may reduce the charging energy $E_c$ between the $C_{60}$ molecules which constitute a 3D JJA as superconducting grains on a 3D lattice. The smaller the charging energy $E_c$ is, the higher the critical temperature $T_c$ is, as discussed in the preceding sections. According to experimental data listed in Table 11 of Ref. [28], the molecular polarizability of CHBr$_3$ is indeed larger than that of CHCl$_3$, which is in accord with the present scenario that the intercalation molecules act as capacitors which reduce $E_c$.

We can estimate $T_c$ of other intercalated $C_{60}$ superconductors as follows. The experimental values of the molecular polarizability are $\varepsilon(CHCl_3) = 57.56$ au and $\varepsilon(CHBr_3) = 79.9$ au [28]. Assuming an approximately constant value of the lattice constant $a$, the charging energies $E_c \sim a/\varepsilon \sim \varepsilon^{-1}$ in arbitrary units are obtained as $E_c(C_{60}/CHCl_3) = 0.0174$ and $E_c(C_{60}/CHBr_3) = 0.0125$. On the $T_c$ vs. $E_c$ graph, extrapolating the straight line which goes through two points $(T_c, E_c) = (70, 0.0174)$ for $C_{60}/CHCl_3$ and $(117, 0.0125)$ for $C_{60}/CHBr_3$, namely, $T_c = -9592E_c + 237$, we predict $T_c \approx 158$ K ($C_{60}/CHI_3$), 127 K ($C_{60}/CH_2I_2$), 137 K ($C_{60}/C_6H_4Cl_2$), 127 K ($C_{60}/C_6H_5NO_2$), 121 K ($C_{60}/C_6H_5Cl$), and 175 K ($C_{60}/C_{12}H_{26}$). Here, we use $\varepsilon = 121.74$ au (CHI$_3$), 87.05 au (CH$_2$I$_2$), 95.83 au (C$_6$H$_4$Cl$_2$), 87.19 au (C$_6$H$_5$NO$_2$), 82.67 au (C$_6$H$_5$Cl), and 153.86 au (C$_{12}$H$_{26}$) [28]. Depending on actual lattice constants, other molecules with relatively large polarizability listed in Ref. [28] may also be interesting as candidates of the intercalation molecules.
5 Conclusions

We indicated that, if the boride compounds are synthesized by using ionic atoms with larger polarizability $\varepsilon$ or smaller diameter instead of the Mg atoms, the critical temperatures $T_c$ will become higher than 39 K of MgB$_2$. We also pointed out that the recently discovered superconductor C$_{60}$/CHBr$_3$ will owe its very high critical temperature to the intercalation molecules CHBr$_3$ as *electronic capacitors* which reduce the charging energy $E_c (\sim a/\varepsilon)$ among the superconducting grains of C$_{60}$ molecules, rather than as simple spacer molecules which expand the separation $a$ between C$_{60}$ molecules. We hope that the present proposals are a hint or an encouragement to future synthesis of new materials.

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Fig. 1. The plot of the critical temperature $T_c$ versus charging energy $E_c$ (see text). Points are for MgB$_2$ ($T_c = 39$ K [1]) and BeB$_2$ ($T_c \simeq 0$ K ($< 5$ K) [3]). The values of $E_c$ are of Table 1 for Mg$^{2+}$ and Be$^{2+}$. 
Table 1

Ionic radius $d$ [23] ionic electric polarizability $\varepsilon$ [24] and charging energy $E_c \sim d/\varepsilon$. The data of $\varepsilon$ in brackets are of Ref. [25] originally and the values of $d$ for Cu are of Ref. [26].

| Ionic atom | Ionic radius $d$ [23,26] | Ionic electric polarizability $\varepsilon$ [24,25] | Charging coupling energy $d/\varepsilon (E_c)$ | Critical temperature $T_c$ [K] |
|------------|--------------------------|--------------------------------------------------|-----------------------------------------------|-------------------------------|
| Be$^{2+}$  | 0.35 (0.008)             | (43.75)                                          | $\simeq 0$ (< 5) [3]                          | 0.72                          |
| Mg$^{2+}$  | 0.65 (0.094)             | (6.91)                                           | 39 [1]                                        |
| Ca$^{2+}$  | 0.99 (1.1) (0.47)        | 0.9 (2.11)                                       |
| Sr$^{2+}$  | 1.13 (1.6) (0.86)        | 0.71 (1.31)                                      |
| Ba$^{2+}$  | 1.35 (2.5) (1.55)        | 0.54 (0.87)                                      |
| Zn$^{2+}$  | 0.74 (0.8)               | 0.93                                             |
| Cd$^{2+}$  | 0.97 (1.8)               | 0.54                                             |
| Cu$^{2+}$  | 0.73 (0.2)               | 3.65                                             |
| Pb$^{2+}$  | 0.84 (4.9)               | 0.17                                             |
| Li$^+$     | 0.68 (0.03) (0.029)      | 22.67 (23.45)                                    |
| Na$^+$     | 0.97 (0.41) (0.179)      | 2.37 (5.42)                                      |
| K$^+$      | 1.33 (1.33) (0.83)       | 1 (1.6)                                          |
| Rb$^+$     | 1.48 (1.98) (1.4)        | 0.75 (1.06)                                      |
| Cs$^+$     | 1.67 (3.34) (2.42)       | 0.5 (0.69)                                       |
| Cu$^+$     | 0.77 (1.6)               | 0.48                                             |
| Ag$^+$     | 1.26 (2.4)               | 0.53                                             |
| Tl$^+$     | 0.95 (5.2)               | 0.18                                             |
| Al$^{3+}$  | 0.5 (0.052)              | (9.62)                                           |
| Sc$^{3+}$  | 0.81 (0.286)             | (2.83)                                           |
| Y$^{3+}$   | 0.93 (0.55)              | (1.69)                                           |
| La$^{3+}$  | 1.15 (1.04)              | (1.11)                                           |
| C$^{4+}$   | 0.15 (0.013)             | (115.38)                                         |
| Si$^{4+}$  | 0.41 (0.0165)            | (24.85)                                          |
| Ti$^{4+}$  | 0.68 (0.185)             | (3.68)                                           |
| Ge$^{4+}$  | 0.53 (1)                 | 0.53                                             |
| Zr$^{4+}$  | 0.8 (0.31)               | (2.58)                                           |
| Sn$^{4+}$  | 0.71 (3.4)               | 0.21                                             |
| Ce$^{4+}$  | 1.01 (0.73)              | (1.38)                                           |