Effects of C, Cu and Be Substitutions in Superconducting MgB$_2$

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Density functional calculations are used to investigate the effects of partial substitutional alloying of the B site in MgB$_2$ with C and Be alone and combined with alloying of the Mg site with Cu. The effect of such substitutions on the electronic structure, electron phonon coupling and superconductivity are discussed. We find that Be substitution for B is unfavorable for superconductivity as it leads to a softer lattice and weaker electron-phonon couplings. Replacement of Mg by Cu leads to an increase in the stiffness and doping level at the same time, while the carrier concentration can be controlled by partial replacement of B by C. We estimate that with full replacement of Mg by Cu and fractional substitution of B by C, $T_c$ values of 50K may be attainable.

The discovery of superconductivity with critical temperature $T_c = 39$ K in hexagonal MgB$_2$ has led to considerable interest in this material, both for practical applications and from a more fundamental point of view. In particular, although it is not the highest $T_c$ conventional (in the sense of $s$-wave with likely substantial electron-phonon coupling) superconductor, its substantial $T_c$ combined with its chemistry and other properties may make it particularly useful. A variety of experimental measurements, including B isotope effect, neutron scattering, phonon densities of states, tunnelling transport, and specific heat, have been done. Taken together, they yield a consistent clear picture of MgB$_2$ as a conventional electron-phonon $s$-wave superconductor. This is also consistent with most of the reported theoretical work.

The underlying electronic structure and bonding were discussed by Ripplinger before the discovery of superconductivity. This was based on density functional calculations using the linearized augmented planewave (LAPW) method and provided results consistent with an early calculation by Armstrong and Perkins. Subsequently, several authors have extended this work presenting the electronic structure in detail and discussing the origin of superconductivity. The electronic structure is dominated by the chemical bonding of the hexagonal B sheets in MgB$_2$. Although the nominal electron count is the same as in graphite (Mg has its nominal 2+ charge), unlike graphite, the top of the B derived bonding band structure contains holes related to fractional occupation of bands derived from B $p$ states directed perpendicular to the layers. As pointed out by An and Pickett, the negative charge of the B layers and the corresponding positive charge of the Mg layers leads to a lowering of the $p_z$ bands relative to their position in graphite. Detailed calculations of the phonon spectra and electron phonon coupling have been reported. These show strong coupling between the hole "doped" bonding bands and high frequency optical phonons associated with motions of the B atoms affecting the covalent bonds. Kong et al. reported detailed calculations of electron-phonon couplings over the whole Brillouin zone obtaining couplings consistent with the measured $T_c$ as well as the boron isotope effect, the specific heat enhancement, the reported gap values and transport data.

The picture that emerges is one where the high $T_c$ is due to strong electron phonon coupling associated with the hole doped metallic $\sigma$ bonding bands in the B sheets. This is due to the strong bonding of these sheets, which along with the light B mass is responsible for the high average frequency of the strongly coupled phonons, setting the temperature scale. However, there are also significant interactions with lower frequency modes and this may be needed to explain the upper critical field.

The present work is to explore some possible substitutions and provide suggestions for experimental work aimed at finding related high temperature superconducting phases. Along these lines, Medvedeva et al. have investigated a number of possible substitutions of Mg by monovalent, divalent and trivalent ions. They focussed on the band structure, and particularly the density of states (DOS) and presence or absence of the $\sigma$ band at $E_F$. They concluded that trivalent substitutions like Y, Al etc. are not favorable as they fill the hole doped (in MgB$_2$) $\sigma$ bands, while certain monovalent substitutions for Mg may be favorable. This is consistent with the experimental observation that Al substitution destroys superconductivity. They also mentioned the possibility of vacancies or substitutions on the B sheets, but concluded that these are all unfavorable.

Here we briefly reexamine the effect of Be substitution on the B planes, including band structure, lattice stiffness and electron-phonon calculations. Although Be substitution lowers the electron count, we find that it is
so detrimental to the bonding that superconductivity is suppressed both due to a strong decrease in the lattice stiffness and a drop in the electron-phonon coupling. We then report calculations investigating the effect of a combined partial substitution of C for B and Cu for Mg. The rationale for this combination is that C-B bonds are expected to be very strong in this structure, and so this substitution may lead to a stiffening of the sheets relative to MgB2, while the replacement of Mg by Cu may be expected to first of all compensate for the extra charge provided by the substitution in the plane, and secondly, perhaps maintain the hole doping of the σ bonding band, present in MgB2 but absent in graphite. The basis of this latter conjecture is that the crystal field in materials can arise both from ionic (Coulomb) effects, as seem to dominate in MgB2, and hybridization, which is important e.g. in transition metal oxides. The hope then was that such effects with monovalent Cu might be sufficient to keep the σ band at the Fermi energy. As discussed below we find that both these effects do occur and that for modest C incorporation and Cu replacement of Mg superconductivity should be enhanced. Based on rigid muffin tin approximation (RMTA) calculations, we estimate that \( T_c \) may be near 50K.

Our results were obtained in the local density approximation (LDA) using the general potential LAPW method, including local orbitals \( \Gamma \) and well converged basis sets and zone samplings. Band structures, lattice stiffnesses and electron phonon couplings were all determined at the calculated lattice parameters as determined by energy minimization. Commonly in LDA calculations, lattice constants are slightly underestimated. For MgB2 we get \( a = 5.736 \ a_0 \) and \( c = 6.522 \ a_0 \), as compared to the experimental values \( a = 5.826 \ a_0 \) and \( c = 6.653 \ a_0 \). This is a 5\% volume compression. As shown in Fig. 1 this has a very small effect on the band structure near the Fermi energy, \( E_F \) with a small effect on \( N(E_F) \). To proceed to the alloys and discuss superconductivity, we make three more significant approximations. First of all, we employ the virtual crystal approximation (VCA) to account for partial substitutions on the B sheets. A partial justification for this is provided by the strong covalency and corresponding large bandwidths, which may limit the amount of scattering due to potential disorder in the alloy (this is the same effect that allows alloys, like Al\(_2\)Ga\(_{1-x}\)As, to have high enough mobilities to be useful in semiconductor technology). We tested the VCA by comparing with ordered cells at the compositions MgBeB and CuBC and found some quantitative differences (discussed below), but the key features of the band shapes, velocities and the position of the σ bonding band relative to \( E_F \) were little changed. The second approximation we made was to characterize the lattice stiffness that combined with the mass gives average phonon frequencies by the calculated tensile stiffness of the B sheets, \( i.e. \ \frac{\partial^2 E}{\partial a^2} \). This number and the average mass of the atoms in the B sheets was used to scale the average frequencies as calculated by Kong et al. Considering that the dominant phonons determining \( T_c \) are the B modes, we think that this is a reasonable approximation. Finally, we use the RMTA to characterize the electron-phonon coupling \( \eta \).

We used well converged DOS calculations based on first principles eigenvalues at over 2000 k points in the irreducible zone to get \( N(E_F) \) and the corresponding angular momentum components. We used the self-consistent LAPW potentials at different concentrations to calculate the corresponding phase shifts and free scatterer DOS at \( E_F \). Sphere radii of 1.5 \( a_0 \) were used for B, Be and C for the RMTA calculations. The above quantities were used in the Gaspari-Gyorffy formula to compute the Hopfield parameters, \( \eta \), for each site. Negligible coupling is found on the Mg site, as expected, but not Cu, e.g. 0.78 eV/Å\(^2\) on Cu for CuB2. However, in Table 1 we give the values of \( \eta \) for B only, since that is the dominant contribution controlling superconductivity and we do not include any Cu contribution in the calculation of \( \lambda \) or \( T_c \). (Cu will have little involvement in the high frequency phonons associated with the B sheets). For the electron-phonon coupling we used the usual expression \( \lambda = \eta \langle M \omega^2 \rangle \).

For the denominator we used the average frequency calculated by Kong et al for MgB2 and scaled it using the tensile stiffness of the B sheets for various concentrations, \( i.e. \ \frac{\partial^2 E}{\partial a^2} \). The RMTA is not generally as well justified in \( sp \) metals as in transition metals and can considerably underestimate the deformation potentials when strong \( sp \) covalent bonding is present as it is here. Further, the RMTA neglects some differences between different bands, which may be significant here. In any case, Kortus et al. did use it for MgB2 to characterize electron phonon couplings. Comparing with the direct calculations of Kong et al. for MgB2 we find, not unexpectedly, that the values of \( \eta \) we obtain with our non-overlapping B spheres are too small, roughly by a factor of three. Here we use the RMTA to elucidate trends, while acknowledging its limitations. So we adopt the heuristic of scaling the calculated values of \( \eta \) by three in calculating \( \lambda \) and \( T_c \). Using the average phonon frequencies quoted by Kong et al. this heuristic closely reproduces their values of \( \lambda \) and \( T_c \) for MgB2. We used the McMillan equation to roughly estimate \( T_c \), setting the Coulomb pseudopotential \( \mu^* = 0.1 \). We emphasize here that we are not aiming at an accurate determination of the value of \( T_c \) but exploring the trends upon substituting Mg by Cu and B by Be or C. Because of our use of the RMTA our values should be taken as indicating trends not as quantitative predictions of \( T_c \).

The band structure for the starting compound, MgB2, (Fig. 1b) is practically identical to those obtained previously showing σ bonding states at \( E_F \). Results for the structural and electronic properties relevant to superconductivity are given in Table I while band structures are shown in Fig. 2a and Fig. 3a for MgBeB\(_{2-x}\) and CuB\(_{2-x}\)C\(_x\), respectively. In the table the values of \( \eta \) are the bare values as given by the RMTA, while the heuristically scaled values have been used for the values of \( \lambda \) and \( T_c \). An ordered band structure for CuBC is
shown in Fig. 4. This shows some differences from the corresponding VCA calculation, most notably, near $E_F$, a splitting at the H point involving $p_z$ bands. However, the general structure of bands near $E_F$ and the position of the $\sigma$ band is quite similar.

Substitution of Be into the B sheets lowers the electron count, though as seen in the band structure, not in a rigid band way. The hole concentration in the $\sigma$ bonding band does increase, but the bonds are strongly weakened. This is reflected in the band widths and lattice stiffness. The result (Table 3) is a rapid increase in the $\alpha$ lattice parameter, softening of the lattice and a decrease in the electron phonon coupling. Thus Be substitution is detrimental to superconductivity and is not further discussed.

The Cu substituted material is more interesting. In an ionic model, replacement of Mg by monovalent Cu should lower the electron count in the B sheets by one per formula unit. So perhaps a situation similar to that found with 50% Be substitution may be expected. This is not the case. The Cu is monovalent as in the ionic model. The five narrow Cu $d$ bands are in the valence region between -4 and -3 eV relative to $E_F$. Comparing the top panel of Figs. 1 and 3 and the structural information in Table 1 one sees that the bonding in the sheets is strengthened by the addition of Cu, even though the hole count in the $\sigma$ band is increased (note the relative positions of the band maxima on the $\Gamma - A$ line). Hybridization with Cu leads to quantitative changes in the band structure, affecting mostly the $p_z$ states, but there are also weak effects on the $\sigma$ bands near $E_F$, e.g. the reversed dispersion on the $\Gamma - A$ line presumably due to $d-p\pi$ interactions. The net effects of Cu substitution – stiffened lattice, increased $N(E_F)$ and higher hole concentration – are favorable for superconductivity. Related to this, there is a recent unconfirmed report of an enhancement of $T_c$ with partial replacement of Mg by Cu.

Partial substitution of C for B in CuB$_2$ has two effects – a stiffening of the lattice reflecting the strong bonding of C and B (favorable for $T_c$ and a reduction in the hole doping of the $\sigma$ band and in $N(E_F)$ (unfavorable for $T_c$). For low C concentrations, the first effect dominates, leading to an increase in the estimated $T_c$, but beyond 25% C substitution (here the van Hove from the $\sigma$ band at $A$ crosses $E_F$) the second dominates and $T_c$ falls.

In summary, band structure and RMTA calculations indicate that the $T_c$ of MgB$_2$ can be increased, perhaps to 50K by substitution of Cu for Mg and low C substitutions, around 25%, in the B sheets. We emphasize that to our knowledge these are not known equilibrium phases. However, the strong binding of the sheets suggests synthesis may be possible, e.g. starting with MgB$_2$ (n.b. Mg leaves the compound at high temperature).

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Note that $N(E_F)$ in Table I is at the LDA lattice parameters for consistency and so is $\sim 4\%$ smaller than obtained previously with experimental lattice parameters.

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TABLE I. Calculated properties of MgBe$_x$B$_{2-x}$ and CuB$_{2-x}$C$_x$ as obtained in the VCA. $S$ is the relative stiffness of the B sheets characterized by $\partial^2 E / \partial a^2 \ (S(MgB_2)=1)$, and the other symbols have their usual meanings. Lattice parameters are in $a_0$, $N(E_F)$ in eV$^{-1}$ and $T_c$ in K. The unscaled $\eta$ (in eV/Å$^2$) is for the alloyed B site only. Blank entries for $a$, $c$ and $S$ indicate that these were obtained by interpolation rather than direct computation for those concentrations.

|        | $a$  | $c$  | $S$  | $N(E_F)$ | $\eta$ | $\lambda$ | $T_c$ |
|--------|------|------|------|----------|--------|-----------|-------|
| MgB$_2$ | 5.74 | 6.52 | 1.00 | 0.68     | 3.60   | 0.78      | 38    |
| MgBe$_{0.5}$B$_{1.5}$ | 5.99 | 6.54 | 0.78 | 0.84     | 2.36   | 0.66      | 22    |
| MgBeB | 6.43 | 6.03 | 0.56 | 0.90     | 1.45   | 0.56      | 12    |
| MgBe$_{1.5}$B$_{0.5}$ | 6.90 | 5.53 | 0.48 | 0.98     | 1.04   | 0.47      | 6     |
| MgBe$_2$ | 7.32 | 5.34 | 0.47 | 0.95     | 0.93   | 0.43      | 4     |
| CuB$_2$ | 5.58 | 6.28 | 1.11 | 1.09     | 4.38   | 0.86      | 48    |
| CuB$_{1.75}$C$_{0.25}$ | 1.37 | 0.83 | 5.16 | 0.90     | 55     |
| CuB$_{1.5}$C$_{0.5}$ | 5.37 | 6.56 | 1.37 | 0.65     | 5.45   | 0.86      | 53    |
| CuB$_{1.4}$C$_{0.6}$ | 1.37 | 0.50 | 3.74 | 0.57     | 20     |
| CuB$_{1.25}$C$_{0.75}$ | 1.37 | 0.25 | 0.80 | 0.12     | 0      |
| CuBC | 5.11 | 7.28 | 1.63 | 0.40     | 1.02   | 0.14      | 0     |
FIG. 1. LDA band structure of MgB\textsubscript{2} with the experimental structure (solid) and calculated LDA lattice parameters (dashed). The zero is at \(E_F\).

FIG. 2. LDA virtual crystal band structure of MgBe\(_{x}\)B\(_{2-x}\) for \(x = 1\). The lattice parameters is the calculated relaxed value. The horizontal reference at 0 denotes \(E_F\).

FIG. 3. LDA virtual crystal band structures of CuB\(_{2-x}\)C\(_x\) for \(x = 0\) (top), \(x = 0.5\) (middle) and \(x = 1\) (bottom). The lattice parameters are the calculated relaxed values. Note the vertical scale of the lower panel. The horizontal reference at 0 denotes \(E_F\).

FIG. 4. LDA ordered band structure for CuBC note the splittings relative to the virtual crystal band structure in the bottom panel of Fig. 3.