Superconductivity of MgB$_2$: Covalent Bonds Driven Metallic

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(October 22, 2018)

A series of calculations on MgB$_2$ and related iso-electronic systems indicates that the layer of Mg$^{2+}$ ions lowers the non-bonding $\pi$ ($p_z$) bands relative to the bonding $\sigma$ ($sp, p_y$) bands compared to graphite, causing $\sigma \rightarrow \pi$ charge transfer and $\sigma$ band doping of 0.13 holes/cell. Due to their two dimensionality the $\sigma$ bands contribute strongly to the Fermi level density of states. Calculated deformation potentials of $\Gamma$ point phonons identify the B bond stretching modes as dominating the electron-phonon coupling. Superconductivity driven by $\sigma$ band holes is consistent with the report of destruction of superconductivity by doping with Al.

The dependence of the superconducting critical temperature $T_c$ on structure is unclear after decades of study, and recent discoveries have further confused the issues. In conventional superconductors (the high $T_c$ cuprates comprise a special case) it has been generally thought that high symmetry, preferably cubic, is favorable for higher $T_c$. This trend has held up in elemental superconductors (Nb, La under pressure, at 9 K and 13 K, respectively), for binaries (Nb$_3$(Al,Ge), 23 K [8]), (pseudo)ternaries such as (Ba,K)BiO$_3$, [9] and even fullerene superconductors ($T_c$ to 40 K [10]).

Recently several intriguing counterexamples to this trend have come to light. Semiconducting HfNCl (and ZrNCl) is a van der Walls bonded set of covalent/ionic bonded layers, but superconducts up to 25 K when doped (intercalated) with alkali metals. [6] There is evidence that the surface layer of solid Ca$_{60}$ becomes superconducting up to 52 K when it is injected to high hole concentrations. [7] And most recently, it is reported that the layered metal/metalloid compound MgB$_2$ superconducts at $\sim$40 K, [11,12] which is by far the highest $T_c$ for a binary system. The B isotope shift of $T_c$ reported by Bud’ko et al. [10] and most other early experimental data suggests conventional BCS strong-coupling $s$-wave electron-phonon (EP) pairing. These examples suggest there are important aspects of two dimensionality (2D) for conventional superconductors that are yet to be understood.

A close analogy for MgB$_2$, structurally, electronically, and regarding superconductivity, is graphite. Graphite has the same C layer structure as B has in MgB$_2$. The layer stacking that occurs in graphite is central to its semimetallic character but is not important in our analogy. Graphite is iso-electronic with MgB$_2$; previous studies have established that the Mg atom is effectively ionized. Finally, graphite becomes superconducting up to 5 K, but only when doped (intercalated). [9] Both graphite and MgB$_2$ have planar $sp^2$ bonding, and in graphite it is well established that three of carbon’s four valence electrons are tied up in strong $\sigma$ bonds lying in the graphite plane, and the other electron lies in non-bonding ($p_z$) $\pi$ states. Electron doping of graphite, achieved by intercalating alkali atoms between the layers (Na is the most straightforward case) leads to occupation of otherwise unfilled $\pi$ states and leads to $T_c$ as high as 5 K. MgB$_2$, on the other hand, superconducts at $\sim$40 K at stoichiometry.

The light masses in MgB$_2$ enhance the phonon frequency ($\omega_{ph} \propto M^{-1/2}$) that sets the temperature scale of $T_c$ in BCS theory. Even considering this tendency, there must be some specific feature(s) that produces such a remarkable $T_c$, and moreover does so with no $d$ electrons, nor even the benefit of a density of states (DOS) peak. [10-11] In this paper we identify these features: (1) hole doping of the covalent $\sigma$ bands, achieved through the ionic, layer character of MgB$_2$, (2) 2D character of the $\sigma$ band density of states, making small doping concentrations $n_h$ give large effects $N(\varepsilon_F) \sim m^*/\pi h^2$ independent of $n_h$, and (3) an ultrastrong deformation potential of the $\sigma$ bands from the bond stretching modes.

In this paper we exploit the similarities between graphite and MgB$_2$ to build a basic understanding of its electronic structure, then focus on the differences that are connected to strong EP coupling, and finally provide an estimate of $T_c$ that indicates the picture we build can account for the observations. This picture further predicts that electron doping by $\sim$0.2 carriers per cell will strongly affect $T_c$, adversely, a result that has been reported by Slusky et al. [12] Although Hirsch has also focussed on the hole character of the $\sigma$ bands, [13] his emphasis is otherwise quite different from that described here.

Calculations of the electronic structure have been done using the linearized augmented plane wave (LAPW) method [14] that utilizes a fully general shape of density and potential, as implemented in the WIEN97 code. [15] Experimental lattice con-
stans of $a=3.083$ Å, $c=3.521$ Å were used. LAPW sphere radii (R) of 2.00 a.u. and 1.65 a.u. were chosen for the Mg and B atoms, respectively, with cut-off $R_{K_{max}}=8.0$, providing basis sets with more than 1350 functions per primitive cell. The generalized gradient approximation exchange-correlation functional of Perdew et al. [10] was used in the present work.

![Band structure](image)

**FIG. 1.** Band structure along main hexagonal symmetry lines, for (top) MgB$_2$, (middle) $\Gamma^{2+}$B$_2$, (bottom) primitive graphite C$_2$. The planar $\sigma$ states, highlighted with larger symbols, fall in energy in this progression, and only in MgB$_2$ are they partially unoccupied. The point $A = (0,0,\pi/c)$ is perpendicular to the $(k_x,k_y)$ plane.

The band structure of MgB$_2$ is shown in Fig. [1] (top panel) in comparison with that of primitive graphite (bottom panel) with a single layer per cell like the B$_2$ sublattice in MgB$_2$. For each two distinct sets of bands are identifiable: the highlighted $sp^2(\sigma)$ states, and the $p_z(\pi)$ states. The striking difference is in the position of the $\sigma$ bands, which is evident in Fig. [2]. Whereas the $\sigma$ bonding states are completely filled in graphite and provide the strong covalent bonding, in MgB$_2$ they are unoccupied and hence metallic, with a concentration of 0.067 holes/B atom in two fluted cylinders surrounding the $\Gamma$-A line of the Brillouin zone. [11] There are correspondingly more electron carriers in the $\pi$ bands. This decrease in occupation on the strongly bonding $\sigma$ bands partially accounts for the greatly increased planar lattice constant of MgB$_2$ (3.08 Å) compared to graphite (2.46 Å). Our results agree with previous conclusions that MgB$_2$ can be well characterized by the ionic form Mg$^{2+}$(B$_2$)$^{2-}$.

To identify the origin of the relative shift of the $\sigma$ and $\pi$ bands by $\sim$3.5 eV between graphite and MgB$_2$, we have considered a fictitious system $\Gamma^{2+}$B$_2$ in which the Mg ion is removed but the two electrons it contributes are left behind (and compensated by a uniform background charge). The band structure, shown in the middle panel of Fig. [1], is very similar, except the energy shift of $\sim$1.5 eV downward with respect to MgB$_2$ completely fills the $\sigma$ bands, as in graphite. This shift is the result of the lack of the attractive Mg$^{2+}$ potential in MgB$_2$, which is felt more strongly by the $\pi$ electrons than by the in-plane $\sigma$ electrons: the attractive potential of Mg$^{2+}$ between B$_2$ layers lowers the $\pi$ bands, resulting in $\sigma \rightarrow \pi$ charge transfer that drives the hole doping of the $\sigma$ bands. Belashchenko et al. [17] have also considered a sequence of materials to come to related conclusions about the band structure, but they did not use isoelectronic systems as has been done here.

The $\sigma$ bands are strongly 2D (there is very little dispersion along $\Gamma$-A), but it will be important to establish the magnitude and effects of interplanar coupling. The light hole and heavy hole $\sigma$ bands in MgB$_2$ can be modeled realistically in the region of interest (near and above $\varepsilon_F$) with dispersion of the form

$$\varepsilon_k = \varepsilon_0 - \frac{k_x^2 + k_y^2}{2m^*} - 2t\cos(k_zc),$$

where the planar effective mass $m^*$ is taken to be positive and $t \sim 92$ meV is the small dispersion perpendicular to the layers. The light and heavy hole masses are $m^*_h/m = 0.20$, $m^*_l/m = 0.53$, and the mean band edge is $\varepsilon_0 = 0.6$ eV. In general, the in-plane ($v_{xy}$) and perpendicular ($v_z$) Fermi velocities are expected to be anisotropic: $v_{xy} \sim k_F/m^*$, $v_z \sim 2ct\perp$ where $t\perp$ is small. Near the band edge ($k_F \leq 2m^*ct\perp$) this anisotropy becomes small, and this is roughly the case in MgB$_2$. The $\pi$ bands are also effectively isotropic. [11] [11]

Now we discuss why the quasi-2D character of the $\sigma$ bands is an important feature of MgB$_2$ and its superconductivity. Neglecting the $k_z$ dispersion, the 2D hole density of states is constant: $N_h^\sigma(\varepsilon) = \frac{m^*_l + 2m^*_l}{\pi A} = 0.25$ states/eV-cell, independently of
the fact that the hole doping level is small. The $k_2$ dispersion has only the small effect displayed in Fig. 2, where the discontinuity in the quasi-2D DOS is seen to be broadened by $\sim 2t_1$. For MgB$_2$, the $\sigma$ band contribution to $N(\varepsilon_F)$ is reduced by about 10% by $k_2$ dispersion.

If superconductivity is primarily due to the existence of holes in the $\sigma$ band, and we provide evidence for such a picture below, then the DOS in Fig. 2 suggests that electron doping will decrease $N(\varepsilon_F)$. The decrease will be smooth to a doping level corresponding to an increase by 0.4 eV of the Fermi level. Then $N(\varepsilon_F)$ should drop precipitously with further doping. A rigid band estimate gives a value of $n_{h,cr}$ = 0.08 electrons necessary to fill the $\sigma$ bands to the crossover region. Electrons must also be added to the $\pi$ bands that lie in the same temperature range, making the total doping level $n_{cr} \approx 0.25$ per cell.

Fig. 2 therefore suggests a critical region of electron doping around 0.25 carriers per cell. Slusky et al. have reported [12] a study of such electron doping in the Mg$_{1-x}$Al$_x$B$_2$ system. $T_c$ drops smoothly up to $x=0.1$, beyond which point a two phase mixture of B-rich and Al-rich phases occurs. At $x=0.25$ and beyond, a single phase, non-superconducting system is restored, strongly supporting our picture that filling the $\sigma$ bands will destroy superconductivity. Using the rigid band picture, filling them decreases $T_c$ moderately initially, but as the $\sigma$ bands become nearly filled, the coupling decreases abruptly and $T_c$ vanishes, as observed. Although our results do not bear directly on the two-phase question, we note that this occurs just as the $\sigma$ bands are filling. At this point $N(\varepsilon_F)$ is dropping, which normally favors stability. The observed instability suggests that a very small density of $\sigma$ holes that are very strongly coupled to the lattice is what underlies the lattice instability.

Now we address the question of EP coupling strength $\lambda$. The calculated value of $N(\varepsilon_F)$ = 0.71 states/eV-cell corresponds to a bare specific heat coefficient $\gamma_0 = 1.7$ mJ/mole-K$^2$. The available experimental estimate is $\gamma_{exp} = (1 + \lambda)\gamma_0 = 3 \pm 1$ mJ/mole-K$^2$, giving $\lambda_{exp} \sim 0.75$. Kurtus et al. have used the rigid muffin tin approximation [13] to obtain an idea of the coupling strength. However, this approximation is not well justified in $sp$ metals and neglects distinctions between bands of different character that we expect to be crucial for high $T_c$. If one assumes the wavevector dependence of coupling is not strong, there is another simple way to identify strong coupling using deformation potentials $D = \Delta\varepsilon_k/\Delta Q$ due to frozen-in phonon modes with mode amplitude $Q$. [19] The underlying concept is that a phonon that is strongly coupled to Fermi surface states will produce a large shift in $\varepsilon_k$ for states near the Fermi level. [19]

We have studied these deformation potentials for the $k=0$ phonons $B_{1g}$, $E_{2g}$, $A_{2u}$, $E_{1u}$ whose energies, 86, 58, 48, 40 meV respectively, have been calculated by Kurtus et al. [11] This mode (and others) destroy the symmetry of the crystal. The Brillouin zone remains unchanged, however, and we plot the bands along the same directions as in Fig. 1. This mode, as well as the $B_{1g}$ mode, involves only out-of-phase motion of the two B atoms in the primitive cell, $E_{2g}$ involving in-plane vibrations (bond stretching), $B_{1g}$ having displacements perpendicular to the plane. In Fig. 3 the actual rms B displacement of $\Delta u_B = 0.057$ Å was used, to provide a clear picture of the very large effect of EP coupling strength.

![Figure 2](image2.png)

**FIG. 2.** Density of states (solid lines) of the light hole band, the heavy hole band, and the total, for the model of Eq. (1). Note that $N(\varepsilon)$ drops rapidly only 0.4 eV above $\varepsilon_F$. The dashed lines give the 2D ($t_1=0$) analogs.

![Figure 3](image3.png)

**FIG. 3.** Band structure with frozen-in $E_{2g}$ mode, plotted along the same lines as in Fig. 1 to facilitate comparison. (Note that the point labelled K is no longer a symmetry point.) The $E_{2g}$ phonon breaks the symmetry and splits the $\sigma$ bands by 1.5 eV along Γ-A.

The $E_{2g}$ phonon strongly splits the $\sigma$ band nearly uniformly all along the Γ-A line and near $\varepsilon_F$, with the “gap” opening $\Delta\varepsilon_{gap}/\Delta u_B = 26$ eV/Å = 2$D_{E_{2g}}$; note that it will be the square of $D$ that enters the
expression (below) for $\lambda$. In stark contrast, the $B_{1g}$, $A_{2u}$, and $E_{1u}$ modes produce no visible effect in the bands; we estimate that their deformation potentials are at least a factor of 25 smaller. Thus the only significant deformation potential is for the $\sigma$ bands ($\pi$ band shifts are always small), and only due to the $E_{2g}$ mode. This one is extremely large, suggesting that non-linear coupling may even be occurring. This strong coupling should be observable as a large $E_{2g}$ linewidth, and the superconducting gap can be expected to be larger on the $\sigma$ Fermi surface sheets than on the $\pi$ sheets.

To estimate the coupling from this mode alone, we use Eq. (2.34) of Kahn and Allen [19] for the EP matrix element $M$ in terms of $D_{E_{2g}} = 13$ eV/Å, including only the two $\sigma$ bands $N_N = 0.11$ eV$^{-1}$ per spin (from Fig. 2) and the two $E_{2g}$ modes:

$$\lambda_{E_{2g}} = N_h(\varepsilon_F) \sum_{\nu = 1, 2} \frac{|M_{k,k}^{\sigma}|^2}{\omega_{\nu}} \varepsilon_F$$

$$= 2N_h(\varepsilon_F) \left[ \frac{\hbar}{2MB_\omega^2} \right] \sum_{j=1,2} \hat{e}_j \cdot \hat{D}_j \approx 1.0.$$  

The sum on $j$ runs over the two moving B atoms of the $E_{2g}$ mode. Using this value of $\lambda$, the $E_{2g}$ mode frequency, and the Allen-Dynes [20] or McMillan equation with Coulomb pseudopotential $\mu^* = 0.10 - 0.15$, the resulting range is $T_c = 32-46$ K. There is considerable uncertainty in this estimate, but it seems quite plausible that coupling of the $\sigma$ band to the bond stretching mode may provide most of the coupling to account for the observed value of $T_c$.

Now we summarize, beginning with the effects of low dimensionality mentioned in the introduction: (1) the $B_2$ layers provide a strong differentiation between $B$ states ($\sigma$ vs. $\pi$) that results in the Mg$^{2+}$ layer giving a 3.5 eV $\sigma - \pi$ energy shift, driving self-doping of the $\sigma$ bands, (2) due to their 2D dispersion, the contributions of the $\sigma$ bands to $N(\varepsilon_F)$ is almost independent of the doping level; specifically, for low doping level $N(\varepsilon_F)$ is not small. Then, the strong covalent nature of the $\sigma$ bands leads to an extremely large deformation potential for the bond stretching modes. Judging from the very small deformation potentials of the other three $\Gamma$ point modes, the bond-stretching modes dominate the coupling.

W.E.P. is grateful to P. C. Canfield for conversations and for early communication of manuscripts. This work was supported by Office of Naval Research Grant N00017-97-1-0956.

Note added: Since this paper was submitted, two reports of EP coupling in MgB$_2$ that support our results 21,22 have come to our attention.