Investigation on the Effect of Electron and Hole Doping on Electronic Structure and Superconductivity in MgB$_2$

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Abstract

In this paper the effect of electron doping (through partial replacement of B by C) and hole doping (through partial replacement of B by Be) on electronic structure of MgB$_2$ has been investigated by using WIEN2K code, based on Density Functional Theory. Perdew-Burke-Ernzerhof (96) pseudo-potential is used for solving the Schrödinger equation in self-consistent manner and the exchange and correlation effects are accounted for through the use of Generalized Gradient Approximation. The band structure and density of states obtained from the above mentioned pseudo-potential for the doped MgB$_2$ with doping levels of 25% and 50% of C and Be, are found to provide satisfactory explanation to the experimentally observed superconducting behaviour of this material both for electron and hole doping. The Dirac point like structure obtained in the band structure of MgB$_2$ at symmetry point K, when used with hole filling of p$_{\sigma}$ bands in $\Gamma$ - A direction and Density of States at Fermi level, is found to be quite useful in explaining the effect of electron/hole doping on superconductivity in MgB$_2$.

Keywords: DFT calculations, electron/hole doped MgB$_2$, electronic structure of doped MgB$_2$, Superconductivity

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Introduction

Since the discovery of superconductivity in MgB$_2$ with transition temperature (T$_c$) of the order of 40K in 2001 by Nagamatsu et al. (2001), much activity has taken place in scientific community. A large number of researches, both experimental and theoretical, were reported soon after its discovery on superconducting and other properties of MgB$_2$ and other related materials. MgB$_2$ has a planer structure in which boron atoms form a honeycomb lattice and hexagonal layers of Mg atoms act as fillers in between two boron layers, such that an Mg atom lies just above the centre of a hexagon in boron layer. The origin of T$_c$ of the order of 40 K in MgB$_2$, higher than other conventional superconductors, has been a matter of concern for theoretical researchers. Kortus et al. (2001) observed that MgB$_2$ is essentially the metallic boron, held together by means of strong covalent B-B in-plane bonding and weak ionic B-Mg out of the plane bonding. It is electronically a typical sp metal, with a typical Density of States (DOS) at Fermi level. Strong bonding and high frequency vibrations in boron plane result in strong electron-ion scattering and strong electron-phonon coupling. According to them, the fortunate combination of strong bonding, reasonable density of states at the Fermi level and higher values of phonon frequencies, give rise to strong electron-phonon coupling, which may be considered responsible for the higher values of T$_c$ in this compound. Kong et al. (2001) concluded that the unexpectedly high value of T$_c$ in MgB$_2$ may be considered to arise as a result of the large value of electron-phonon coupling strength (\lambda), which in turn may be attributed to the presence of holes in the B-B bonding \sigma-bands and bond stretching due to optical phonon vibrational modes. Ravindran et al. (2001) identified a doubly degenerate quasi-two dimensional energy band in the vicinity of the Fermi level, along the $\Gamma$-A direction of Brillouin zone, which along with non-zero Density of States at the Fermi level, 2D structure of honeycomb B-layers in MgB$_2$ and large anisotropy of phonon modes may be considered to be responsible for the observed superconductivity in MgB$_2$. They also investigated iso-electronic compounds, like BeB$_2$, CaB$_2$, SrB$_2$, LiBC and MgB$_2$C$_x$ and found that the hole doped LiBC and MgB$_2$C$_x$ may be considered as the potential superconducting materials. Okatov et al. (2001) observed that quasi-2D bands in MgB$_2$ are obtained from dispersion E(k) of B 2p$_{\sigma}$-like bands in the k$_z$ ($\Gamma$-K) direction. They form a flat zone in k$_z$ ($\Gamma$-A) direction and reflect the distribution of pp$_{\sigma}$ states in the boron layers. These states make considerable contribution to DOS at Fermi level, resulting in metallic properties of diborides. The 3D type of bands originating from weaker pp$_{\sigma}$ interactions due to B 2p$_{\sigma}$-like bands, show maximum dispersion in the k$_z$ ($\Gamma$-A) direction. According to them, the peculiar electronic properties of MgB$_2$ can be associated with the metal like 2p states of...
boron atom layers, which also determine the DOS distribution in the vicinity of Fermi level. Similar observations were also made by Maker (2008), Milman and Warren (2001) and Fan et al. (2002) regarding the electronic behaviour of MgB$_2$ and other related compounds.

Investigations made by Sharma et al. (2010) in BCS-Eliashberg framework by employing McMillan’s $T_c$ equation (Mc-Millan, 1968) reveal that the phonon mediated e-e interaction, coupled with higher values of phonon frequencies due to vibrational modes of light mass B-atoms, particularly in the plane of boron layers, give rise to higher values (of the order of 1) electron-phonon coupling strength ($\lambda$), which may be considered responsible for the superconducting phase transition of MgB$_2$, at comparatively higher values of $T_c$. The conditions are not that favourable in other metallic oxides, like AlB$_2$, BeB$_2$, CaB$_2$, NbB$_2$, etc., which either do not become superconductor or show superconductivity at much lower values of $T_c$, as compared to MgB$_2$ (Ravindran et al., 2001; Goyal et al., 2012; Medvedeva et al., 2001). Medvedeva et al. (2001) used full potential linear muffin-tin potential in Generalized Gradient Approximation (GGA) for electronic structure calculations of MgB$_2$ and other metallic diborides. They observed that superconductivity in these compounds is related to the existence of p$_x$-band holes at $\Gamma$ point. On that basis, they were able to explain the experimentally observed superconducting features of MgB$_2$ and other metallic diborides like BeB$_2$, AlB$_2$, ScB$_2$ and YB$_2$. They also predicted possibility of medium-$T_c$ superconductivity in CaB$_2$ with $T_c$ values higher than that of MgB$_2$ through a similar treatment, though it could not be experimentally verified so far.

According to Liu et al. (2001), the E$_{2g}$ phonons in MgB$_2$, which involve in-plane B displacements along $\Gamma$-A line, couple strongly with the p$_x$ electron bands. They noticed presence of multiple gaps in the band structure of MgB$_2$ and by using two-phonon scattering, observed that the E$_{2g}$ phonons are strongly anharmonic and the nonlinear contribution to the coupling between E$_{2g}$ modes and the p$_x$ bands is significant. They obtained effective value of electron-phonon coupling constant to be $\lambda \approx 1.01$. An and Pickett (2001) observed that MgB$_2$ can be characterized by its ionic form Mg$^{2+}$(B$_2$)$^{2-}$. The attractive potential of Mg$^{2+}$ between B$_2$ layers lowers the $\pi$ bands, resulting in $\sigma \rightarrow \pi$ charge transfer that derives the hole doping of the s bands. The $\sigma$ bands are strongly 2D, the dispersion along $\Gamma$-A direction being very little. The E$_{2g}$ phonon modes break the symmetry and split the $\sigma$ bands by about 1.5 eV along $\Gamma$-A line. They further observed that coupling of the $\sigma$ bands to the bond stretching phonon modes may provide most of the coupling to account for the observed values of $T_c$. Choi et al. (2002) proposed two band model to explain superconductivity in MgB$_2$. According to them the strong coupling results in strong electron pair formation of $\sigma$-bonding states of boron p$_{xy}$ orbitals, confined to the boron planes, which give rise to an average energy gap of $\Delta_s \approx 6.8$ meV and correspond to two cylindrical sheets of the Fermi surface around $\Gamma$-A line, bulging out at the centre. The $\pi$-bonding states of boron p$_x$ orbitals, which correspond to the remaining two sheets of Fermi surface, form much weaker pairs with average energy gap $\Delta_{\pi} \approx 1.8$ meV. These energy gaps are temperature dependent and become zero as $T \rightarrow T_c$. The size of the gap also changes on different sections of the Fermi surface. According to them, the $\sigma$-bonding states and inter band scattering contribute to higher $T_c$ superconductivity in MgB$_2$. It may, therefore, be concluded that the origin of higher value of $T_c$ in MgB$_2$ lies in its electronic structure. As such, the electronic structure studies of MgB$_2$ and related materials are important, as the same can be correlated with their $T_c$ values.

The present authors noticed that in addition to the above, the presence of a Dirac point like structure in the energy band diagram of MgB$_2$, at symmetry point K, similar to that obtained in the energy band diagram of graphene (Sharma et al., 2017), is also an important feature of the electronic band structure of MgB$_2$, which may be used to explain superconductivity in MgB$_2$ and related materials. But there is one important difference between them. In graphene it is obtained at the Fermi level, whereas in MgB$_2$ it appears about 2.0 eV above the Fermi level, as apparent from the band structure diagrams for this material reported by Medvedeva et al. (2001), Ruiz-Chavarria et al. (2006) and Pena et al. (2002). At the Dirac point the E-K diagram is linear and electrons behave as mass-less particles, which may facilitate their pairing and correlated motion. Thus, the presence of Dirac electrons at K point and filling of holes in the valence band in $\Gamma$-A direction, along with moderate values of density of states at the Fermi level and strong coupling of high frequency phonon modes of boron lattice with p$_{xy}$ ($\sigma$) bands may be considered to be responsible for creating favourable conditions in MgB$_2$ for its phase transition to superconducting state at higher temperatures of the order of 40K. It may be observed from Medvedeva et al. (2001) that although in AlB$_2$, a Dirac point like structure exists at Fermi level, but the valence band in $\Gamma$-A region is well below the Fermi level. As such, there is no possibility of hole filling in the valence band, with the result that the conditions in AlB$_2$ are not favourable for it to become superconducting. On the other hand, for BeB$_2$, valence band in $\Gamma$-A region lies just above the Fermi level so that hole filling in it becomes possible, but the Dirac point like structure at K point is absent. The result is that in BeB$_2$ also, the conditions are not as favourable as in
For electron doping of MgB$_2$, several works have been reported on superconducting and other properties of carbon substituted MgB$_2$. Some of these works, which need to be mentioned here are Medvedeva et al. (2001), Bateni et al. (2015), Sunseri et al. (2014), Gargee Sharma (2016), Kim and Choi (2015), Shaikh et al. (2013), Yeoh et al. (2011), Mudgel et al. (2009), Kazakov et al. (2005), Mickelson et al. (2002), Dai et al. (2011) and Prabhakar P. Singh (2003).

Through substitution of B by C from 3% to 20%, Kazakov et al. (2005) observed that $T_c$ of MgB$_2$ decreased from 38.5 to 10.2 K. Also the lattice parameter ‘a’ was found to decrease with increasing carbon percentage, whereas the lattice parameter ‘c’ was found to increase first and then decrease. Shaikh et al. (2013), on the other hand, observed by co-doping of MgB$_2$ with nano-Alumina and nanocarbon, that on doping with 2% Al, $T_c$ of MgB$_2$ decreases from about 36 K to 28 K, which starts increasing on its carbon doping and may attain a value of the order of 37 K for 3% carbon. Experimental investigations made by Dai et al. (2011) on carbon doped MgB$_2$ thin films, show that both the lattice parameters (a and c) increase with carbon content in the thin films. It was found that $T_c$ dropped slowly, and the residual resistivity increased considerably with increase in carbon doping. Medvedeva et al. (2001) also demonstrated that the electron doping of MgB$_2$, by substitution of B by C, N or O or creation of defects in B-sublattice are not favourable for superconductivity.

According to them, the hole doping or isoelectronic substitution of Mg by Ca, Na, Cu or Zn or substitution of B by Li or Be may give rise to a superconductor with similar or higher values of $T_c$, although the experimental verification of the same is not yet available. Prabhakar P. Singh (2003) has studied electronic structure and determined $T_c$ values of MgB$_{1-x}$C$_x$ for 0 ≤ $x$ ≤ 0.3. He observed that the changes in electronic structure of MgB$_2$ on its carbon doping, specially near the Fermi energy, come mainly from outward movement of $E_F$ with increasing x, accompanied by a sharp decline in both B and C$_{stoi}$ states for 0.2 ≤ $x$ ≤ 0.3. The calculations made by them show a decline in $T_c$ with increase in x.

Chavarria et al. (2006) investigated the band structure of carbon doped MgB$_2$. It was shown that on doping MgB$_2$ with carbon, valence band goes down, so much so that for $x$ = 0.68 the valence band for MgB$_{1-x}$C$_x$ in Γ-A direction is completely below the Fermi level and becomes full with electrons, so that there is no possibility of hole filling in the valence band. Also it may be observed from the band structure calculated by them that the Dirac point like structure at K point now goes below the Fermi level. These may be considered as the probable reasons for reduction in $T_c$ of MgB$_2$ on doping it with carbon, $T_c$ approaching 0 K for $x$ ≈ 0.36. On doping MgB$_2$ with Al, it was observed by them that in Mg$_{0.56}$Al$_{0.44}B_2$, $T_c$ almost approaches 0K for $x$ ≈ 0.56, although in that case the Dirac point like structure at K point is found to lie just above the Fermi level. This shows that for favourable conditions for superconductivity to occur, the position of both the Dirac point like structure at K point and valence band in Γ-A direction are very critical, which should lie just above the Fermi level for superconductivity to occur. Kortus et al. (2005) also observed that the decrease in $T_c$ on doping MgB$_2$ with Al or C can be explained in terms of band filling effect due to electron doping by Al or C. They observed that the dependence of $T_c$ on electron doping can be explained in terms of dependence of electron-phonon coupling strength (λ) and density of states at Fermi level N($E_F$) on electron doping. They further observed that the reason for obtaining almost constant band gap for various levels of electron doping in MgB$_2$ lies in mutual compensation of the effects of band filling and inter-band scattering. They also observed that scattering by non-magnetic impurities should have a pair breaking effect, which along with the inter band scattering leads to a decrease in $T_c$.

Important works on Al doping of MgB$_2$ are due to Slusky et al. (2001), Shah et al. (2009), Lorentz et al. (2001) and Pena (2002). Slusky et al. (2001) reported that in Mg$_{0.56}$Al$_{0.44}B_2$, $T_c$ drops smoothly up to $x$ = 0.1, beyond which 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, i.e., filling of \( \sigma \) bands destroys superconductivity. According to the rigid band model, the filling of \( \sigma \) bands decreases \( T_c \) moderately initially, but as the \( \sigma \) bands become nearly full, the coupling decreases abruptly and \( T_c \) vanishes. Neaton and Perali (2001) investigated the effect of substitution of Mg by Ca, Na and Al in MgB\(_2\). Whereas Ca is isoelectronic to Mg, Al substitution gives rise to electron doping and Na substitution produces hole doping in MgB\(_2\). They found \( T_c \) to decrease almost linearly with increase in percentage of Al, but on increasing the percentage of Ca or Na in MgB\(_2\), \( T_c \) was found to increase linearly. They attributed increase in \( T_c \) on substitution of Mg by Ca to increase in unit cell volume. For substitution of Mg by Na, the removal of an electron from the unit cell and increase in the unit cell volume were considered to be the possible reasons for increase in \( T_c \). For Al doping of MgB\(_2\), the addition of an electron in the unit cell and decrease in unit cell volume were considered to be responsible for decrease in \( T_c \). Structure and superconducting state properties of Ca-doped MgB\(_2\) superconductors were experimentally investigated by Sun et al. (2007), who observed that both the lattice parameters \( a' \) and \( c' \) of MgB\(_2\) are enlarged on its Ca-doping and the transition temperature \( T_c \) is suppressed, its value changing from 37.8 K for pure MgB\(_2\) to 36.5 K for Mg\(_{0.92}\)Ca\(_{0.08}\)B\(_2\). This indicates a research gap in the theory and mentioned above.

Cai et al. (2014) have compared the superconducting properties of carbon doped MgB\(_2\), bulk fabricated from presynthesized Mg/CNT and Mg/amorphous carbon composites. They found that the performance of critical current density \( J_c \) at high fields was improved for CNT-doped samples, whereas in amorphous C-doped samples, \( J_c \) performance was improved over the entire field range. The doping effect of carbon nano tubes (CNT) and nanocarbon (NC) in MgB\(_2\), bulk was also studied by Lim et al. (2009). They observed higher \( T_c \) values for CNT-doped MgB\(_2\) as compared to NC-doped samples. They also observed that \( J_c \) behaviour was improved both for CNT and NC doping.

Recent works on investigation of superconducting state properties of graphene doped MgB\(_2\), are Sudesh et al. (2013), De Silva et al. (2011; 2012), Li et al. (2017) and Wu et al. (2016). All these authors report improvement in \( J_c \) performance and increase in \( H_c \) on doping MgB\(_2\) with graphene. Whereas Sudesh et al. (2013) have reported no change in \( T_c \) on doping of MgB\(_2\) with graphene up to 10 wt\%, Li et al. (2017) observed that \( T_c \) of MgB\(_2\) monotonically decreases with increasing graphene content. This anomaly needs to be resolved by further experimental work in this regard.

Gonnelli et al. (2006) have used point contact spectroscopy to study the superconducting gaps in Al- and C-substituted MgB\(_2\) single crystals. They observed that while phase segregation is important in Mg\(_x\)Al\(_{2-x}\) system at \( x \geq 0.09 \), in Mg\(_{0.92}\)Al\(_{0.08}\) system a doping-induced transition takes place from two gaps to single gap superconductivity at \( y \approx 0.132 \).

To study effect of hole-doping on superconducting properties of MgB\(_2\), Ahn et al. (2002) investigated structural and superconducting state properties of MgB\(_{2-x}\)Be\(_x\) and observed that MgB\(_2\) structure is maintained up to \( x \approx 0.6 \). The in-plane lattice constants \( a \) and \( b \) were found to decrease with increase in \( x \), while the inter-plane lattice constant \( c \) was reported by them to increase with \( x \). They also observed that whereas the superconducting transition temperature \( T_c \) of Be doped MgB\(_2\) decreases monotonically with \( x \), \( T_c \) shows a maxima at \( x \approx 0.3 \). They further observed that the change in \( T_c \) can be correlated with the in-plane contraction of the lattice, which is consistent with 2D nature of \( \sigma \)-bands.

Xiu et al. (2009) have investigated theoretically the Be and C co-doped MgB\(_2\) system. They observed that on co-doping of MgB\(_2\) by electrons and holes, the compensation effect is clearly visible from the band structure and Density of States (DOS) diagrams of the system. For the co-doped system, the DOS and \( T_c \) values were found by them to lie in between the relevant values for Be-doped and C-doped systems, \( T_c \) value of co-doped system being almost equal to that of un-doped MgB\(_2\). They observed that for Be-doping, the total density of states at Fermi level is larger than that of MgB\(_2\) which should give rise to \( T_c \) values higher than that of MgB\(_2\). However, experimentally \( T_c \) values for this system are found to be lower than that of MgB\(_2\). This indicates a research gap in the theory and needs further clarification.

In the present work the effect of electron/hole doping on electronic structure of MgB\(_2\) has been re-investigated, particularly for changes in the valence band in \( T \)-A direction and the position of Dirac point like structure at K point with respect to the Fermi level on the band structure diagram, on increasing the level of electron/ hole doping in it. In the present theory both these parameters are considered to be very critical for transformation of the system into superconducting phase. The density of states at Fermi level is another important parameter for the observed superconductivity in MgB\(_2\) which is investigated in the present work for different levels of electron/hole doping in MgB\(_2\). The electron/hole doping of MgB\(_2\) is achieved by way of substitution of Boron by Carbon/Beryllium. In the above perspective, an attempt is made to investigate whether the changes in the band structure and density of states on increasing the
doping level, are indicative of changes in $T_c$, as revealed by experimental findings due to Takenobu et al. (2001) and Avdseev et al. (2003) for electron doping and Ahn et al. (2002) for hole doping. Electron density distribution also throws light on the electronic properties of different types of atoms in a system. As such, the effect of electron/hole doping on the electron density distribution of MgB$_2$ is also investigated in the present work, where for the sake of simplicity the investigations are restricted to (1,0,0) plane.

### Method and Computational Details

In the present study we take for lattice parameters of MgB$_2$, $a = b = 3.084\, \text{Å}$ and $c = 3.523\, \text{Å}$ along with $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, as the input parameters (Lorentz et al., 2001). These parameters were found to be justified as they satisfy the minimum energy requirement for MgB$_2$ primitive cell, as obtained from Energy-Volume diagram for a volume of 196.2952 $\text{au}^3$, which is in agreement with the cell volume of 195.8252 $\text{au}^3$, obtained from the above mentioned parameters. MgB$_2$ is a layered structure, for which the space group is 191(P6/mmm). The positions of Mg and two B atoms in the unit primitive cell were taken as (0, 0, 0), (1/3, 2/3, 1/2) and (2/3, 1/3, 1/2). WIEN2k software due to Blaha et al. (2001) is used for computation of electronic structure properties of MgB$_2$, which is based on the Density Functional Theory (DFT) (Hohenberg and Kohn, 1964). The functioning of this code is based on an iterative solution of Kohn Sham equations (Kohn and Sham, 1965), by using DFT in a plane wave set with projector-augmented wave pseudo potentials. The Perdew-Burke-Ernzerhof (PBE) potential functional (Perdew et al., 1996A), which has been widely used in DFT calculations and has been found to appropriately account for the electron-ion and exchange-correlation (XC) interactions in materials with metallic components and in particular the systems with AlB$_2$ structure (Goyal et al., 2012), is used in the present work. In PBE potential, the effects of exchange and correlation interaction are incorporated in the theory by using Generalized Gradient Approximation (GGA) due to Perdew et al. (1996B), which is theoretically more sound than other methods, viz. , the one based on Local Density Approximation (LDA) and provides better estimates of the material properties, like binding energy, lattice parameters etc., as observed by Fuchs et al. (1998).

A super cell of dimensions (2x2x1) was constructed for the electron / hole doping of MgB$_2$, which contains 4 Mg and 8 B atoms (in 4 pairs), out of which one of the pairs of the B atoms is replaced by carbon / beryllium atoms so that a doping level of 25% is achieved. Similarly, on replacing 2 pairs of B-atoms by C / Be atoms, the doping level of carbon / beryllium in MgB$_2$ becomes 50%. Each structure is investigated for its band structure, density of states and electron density distribution by using WIEN2K. In the present investigations, RMT×$K_{\text{max}}$ is taken = 7.0, and the number of K-points for lattice sums is taken as 1000. For checking convergence of sums, the minimum resolution for energy is taken = 0.0001eV, and for the charge convergence the minimum resolution is set = 0.001au.

Symmetry plays an important role in computational science, by virtue of which the requirement of summing on whole Brillouin Zone is reduced to summing over only on a wedge of it. It is found that the symmetry of space group 191(P6/mmm) for MgB$_2$ is reduced to that of 65(C/mmm) group in carbon / beryllium doped MgB$_2$ for doping level of 25%, so as to satisfy the minimum energy requirements. From similar considerations, the space symmetry group for doping level of 50% of C/Be in MgB$_2$ was found to be 51(P/mma).

### Results and Discussion

In the present study, the effect of electron/hole doping on band structure and density of states of MgB$_2$ has been investigated by substitution of carbon and beryllium atoms at B-sites. For electron / hole doping of MgB$_2$ at B-sites, C and Be are the natural choices, as they lie adjacent to B in the Periodic Table. The level of doping in the present investigations was kept 25% and 50% for both the impurities. The 2D projections of the primitive unit cell of MgB$_2$ and super cells of the structures MgB$_{2-x}$C$_{0.5}$, MgB$_{1.5}$Be$_{0.5}$, MgBC and MgBBe in (1,0,0) plane are shown in Figures 1(a) to 1(e) respectively, along with the electron density contours for these structures, as projected in the (1,0,0) plane for the sake of simplicity. It is apparent from these diagrams that although the cell structures of MgB$_{13}$C$_{30}$ and MgB$_{11}$Be$_{15}$ crystals shown in Figures 1(b) and 1(c) are identical, they differ in the sense that in the former C-atoms do not show bonding with B-atoms, whereas in the latter Be-atoms form bonds with B-atoms. The latter is in accordance with the fact that in Be-doped MgB$_2$, a fraction of electrons donated by Mg atoms fill up holes on Be atoms, undergoing sp3 bonding with B atoms. The core size of Be atoms is also very nearly equal to that of B-atoms, it being slightly larger than that of B-atoms, which creates favourable environment for formation of covalent bonds of B and Be atoms. On the other hand, the core size of C-atoms is somewhat less than that of B-atoms. This gives rise to lattice distortion near C-sites. As a result of it, C-atoms have lesser tendency to undergo covalent bonding with B-atoms. The unit cells for the case of 50% doping of C/Be atoms in MgB$_2$ at B-sites (shown in Figures 1(d) and 1(e)) are much simpler as compared to the relevant MgB$_2$ cells with 25% doping of C/Be. This is
because the symmetry involved in this case is comparatively higher than that of 25% doping. In this case, the two adjacent Mg atoms are so closely packed that they touch each other.

As apparent from Fig. 1(a), in pure MgB$_2$ the electron density contours are in the form of circular arcs centred at Mg atoms. The circular arcs are obtained without any deformation till they touch B-atoms. However, for 25% C-doping of MgB$_2$, i.e. for MgB$_{1.5}$C$_{0.5}$, the contours are obtained in the form of deformed circles or circular arcs around Mg atoms, bulging out towards C-atoms. For the centrally placed Mg atoms, the deformed circles point towards the centre of the line joining the centrally placed C-atoms and the outer circular arcs of the two Mg atoms join together through carbon atoms to form a closed loop, as shown in Fig. 1(b). On the other hand, for 25% doping of MgB$_2$ by Be, i.e. for MgB$_{1.5}$Be$_{0.5}$, the deformation of circular contours around Mg atoms is found to be comparatively less. For centrally placed Mg atoms, the deformed circles are compressed from the side of Be atoms, so that they are densely populated on that side. On the other side, the contours are rarely populated towards B-atoms. The electron density contours also connect the nearby Be atoms with each other, as shown in Fig. 1(c). The difference in the behaviour of C-doped and Be-doped MgB$_2$ may be understood as follows: when C-atoms are substituted in MgB$_2$ crystal, they undergo sp$^3$ bonding with B-atoms and reside in the B-layer. An extra electron on C-atom is contributed by it to the $\pi$ band, which makes the interlayer bonding stronger. After donating an electron, C-atom behaves as if carrying $+$ve charge and attracts electrons. On the other hand, Be atom is short of one electron to form sp$^3$ bonding, which it takes from the electrons residing on the boron sheet or $\pi$ band, on being donated by the Mg atoms. The Be atoms, therefore, behave as if carrying $-$ve charge and repeal electrons.
In case of 50% doping of MgB$_2$ by C/Be atoms, it is observed that the electron density contours are quite different from the case of 25% doping of MgB$_2$. Now for C-doping, the contours are in the form of curves going around C-B bond, on both the sides of the bond. These curves are more curved in the vicinity of the C and B atoms and become less curved and less dense as we approach Mg atoms, as shown in Fig. 1(d) for MgBC. Closed loops encircling C and B atoms are also obtained in this case. This shows that in the symmetry 51(P/mma), the extra electrons of C-atoms after they form sp3 bonds with B-atoms, are shared equally by C and B atomic sites, so that the electron density contours are symmetric around the two types of atoms. The outer curves converge on Mg atoms, showing that the electrons are attracted by Mg atoms. This is because in MgBC, Mg atoms acquire +ve charge after donating two electrons to the B-C layer and form ionic bonds. In case of Be-doping, the contours form closed loops in between Be and B atoms and also on the two sides of these atoms, showing that after undergoing sp3 hybridization, Be and B atoms acquire opposite polarity, which gives rise to closed contours. The opposite polarity on Be and B atoms may be on account of a hole present on Be-atom when it undergoes sp3 hybridization in the B-lattice and sharing of electrons donated by Mg atoms by different sites on B-layer, so that Be and B sites effectively acquire +ve and -ve charges respectively. Away from Be-B bond, the e-contours are almost straight lines as we approach Mg atoms, as shown in Fig. 1(e) for MgBBe. These lines also converse on Mg atoms, showing that they carry +ve charge and form ionic bonds.

The band structure diagrams for MgB$_2$, MgB$_{1.5}$C$_{0.5}$, MgB$_{1.5}$Be$_{0.5}$, MgBC and MgBBe are shown in Figures 2(a) to 2(e), whereas the relevant Density of States (DOS) diagrams of these materials are given in Figures 3(a) to 3(e). Fig. 2(a) shows band structure for MgB$_2$, from where it is seen that in this case a Dirac point like structure is obtained at symmetry point K at 1.81 eV above the Fermi level. Also a doubly degenerate valence band in the Γ-A direction is in the form of a straight line with positive slope lying above the Fermi level, above 0.43 eV at Γ point and above 0.86 eV at A point, so that hole filling in this band in the states lying above the Fermi level becomes possible (The point Γ in Fig. 2(a) and other diagrams of Fig. 2 is represented by G). Hole filling in the valence band can also take place at symmetry point K, where the band projects 1.81 eV above the Fermi level. The valence band also projects just above the Fermi level at symmetry point M. On the other hand, the conduction band projects below the Fermi level at symmetry point L, where it can be filled up with electrons, favouring pair formation. The above mentioned features obtained in the band structure of MgB$_2$ are inline with the observations made by An and Pickett (2001), Liu et al. (2001), Mater (2008) and Kortus et al. (2005), according to which the filling of holes in σ bands, coupling of σ-bands to the optical phonons of B-lattice and bond stretching due to E$_{2g}$ phonon modes may be considered responsible for lifting of degeneracy of P$_{33}$ bands along Γ-A direction, opening of band gaps, phase
transformation to the superconducting state and creating conditions for higher $T_c$ in this material. Further, It may be observed from Fig. 3(a), showing DOS of MgB$_2$, that the total DOS at Fermi level in this material is $\approx 0.71$ states/eV, which along with the band structure features mentioned as above, forms appropriate conditions for MgB$_2$ to become superconductor at temperatures of the order of $T_c \approx 40$ K. It is also apparent from Fig. 3(a) that the major contribution to DOS at Fermi level comes from B-atoms, which shows that the layered honeycomb type structure of B-atoms plays a major role in superconducting behaviour of MgB$_2$. The important peaks in the DOS curve for MgB$_2$ on the two sides of Fermi level lie at -8.46, -2.19, +6.30 and +8.22 eV with peak heights of 0.58, 1.33, 1.73 and 1.44 states/eV respectively, which may correspond to different energy bands of MgB$_2$ shown in Fig. 2(a).

For 25% doping of MgB$_2$ with C, the relevant band structure diagram is shown in Figure 2(b). It is clear from this figure that the Fermi level goes up as a result of C-doping, so that the degenerate valence band in $\Gamma$-$\Lambda$ direction falls below the Fermi level and becomes full with electrons. Consequently, there is no possibility of hole filling in this region of the valence band for MgB$_{1.5}$C$_{0.5}$. For 25% doping of MgB$_2$ with Be, the relevant band structure diagram is shown in Figure 2(d). It is clear from this figure that the Fermi level goes up as a result of Be-doping, so that the degenerate valence band in $\Gamma$-$\Lambda$ direction falls below the Fermi level and becomes full with electrons. Consequently, there is no possibility of hole filling in this region of the valence band for MgB$_{1.5}$Be$_{0.5}$.
are obtained at -14.26, -4.47, +4.26 and +6.81 eV, with peak heights of 3.17, 6.42, 6.00 and 5.92 states/eV respectively.

The energy band diagram for the case of 25% doping of MgB$_2$ with Be, is given in Fig. 2(c). The relevant DOS curves for this case are displayed in Fig. 3(c). It may be observed from Fig. 2(c) that as a result of Be-doping, the Fermi level goes down, so that the valence band in MgB$_2$, now goes up and the flat band in $\Gamma$-A direction lies above the Fermi level, the relevant energy values being +1.2 eV at $\Gamma$ point and +1.6 eV at A point. Now, other lower lying band of MgB$_2$ serves as the valence band for this material. The shape of this band in $\Gamma$-A direction is found to be quite different from that of MgB$_2$. It is in the form of a straight line with –ve slope, which crosses the Fermi level, the energy values being about +1.2 eV at $\Gamma$ point and -1.8 eV at A point. The lines forming Dirac point like structure at symmetry point K become curved and it is shifted to a position about 2.4 eV above the Fermi level. The value of DOS at Fermi level in this material is found to be 3.57 states/eV (Fig. 3(c)), but since the conditions of filling of valence band with holes in $\Gamma$-A direction and existence of a Dirac point like structure at symmetry point K are not satisfied, the conditions are not as favourable in this material as in MgB$_2$, for superconducting phase transition to occur. As such, $T_c$ value for this material cannot be as high as in MgB$_2$. This is in consonance with the experimental observations made by Ahn et al. (2002) and provides a theoretical basis for decrease in $T_c$ on hole-doping of MgB$_2$. This also provides a solution to the contradiction between the experimental findings of Ahn et al. (2002) and theoretical predictions made by Medvedeva et al. (2001) and Xiyu et al. (2009) for increase in $T_c$ on doping MgB$_2$ with Be. The prominent DOS peaks obtained in this case on two sides of Fermi level lie at -2.22, -0.80, +6.00, +6.84, +8.09 and +9.38 eV, with peak heights of 5.17, 5.89, 6.70, 6.25, 6.07 and 5.71 states/eV respectively.

For 50% doping of C in MgB$_2$ (Fig. 2(d)), it is observed that the Fermi level further goes up, so that the valence band of MgB$_2$ further goes down below the Fermi level and the degeneracy of the flat band in MgB$_2$ in $\Gamma$-A direction is now lifted up. The flat bands in $\Gamma$-A region are now obtained slightly shifted towards the symmetry point K and lie in the energy range -5.4 eV to -6.0 eV. Another band lying above the Fermi level in MgB$_2$, now passes through the Fermi level and behaves as the valence band. This band crosses the Fermi level in $\Gamma$-A region, with E < $E_c$ at $\Gamma$ point and E > $E_c$ at A point. This band is also like a pair of two parallel bands, the position of the lower band being below the Fermi level. This band supports hole filling along A-L, L-M and M-A directions, but hole filling in $\Gamma$-A direction can be possible to a very little
extent. However, the Dirac point like structure at K point is now completely absent, which suggests that conditions favourable to superconductivity are not present in this material (MgBC). Fig. 3(d) reveals that DOS at Fermi level for this material is 1.30 states/eV, which along with hole filling tendency of valence band, as discussed above, make conditions favourable for superconductivity, but absence of Dirac point like structure at symmetry point K and rare possibility of hole filling in Γ- A direction reveal that on the whole favourable conditions for superconductivity do not exist in this material. This is in agreement with the observations made by Slusky et al. (2001) that for electron doping of 25% or more a non-superconducting phase is restored. The important DOS peaks on the two sides of the Fermi level in this case lie at -15.86, -12.00, -6.00, +3.43, +3.86 and +7.93 eV, with peak heights of 1.30, 1.30, 2.77, 3.42, 3.26 and 2.61 states/eV, respectively. Thus, on the whole, the conditions favourable for superconducting state do not exist in MgBC.

On the other hand for 50% doping of Be in MgB₂, it is observed from Fig. 2(e) that the Fermi level now further goes down, so that the valence band of MgB₂ is further shifted above the Fermi level. The shape of the doubly degenerate flat band of MgB₂, along Γ- A direction also gets distorted. Now the twin bands in Γ- A region touch only at a point at about 2.6 eV above the Fermi level. Another lower lying band of MgB₂ which now passes through the Fermi level, behaves as the valence band. This band crosses the Fermi level in Γ- A region, with E > E₀, at Γ point and E < E₀, at A point. Another similarly placed band also crosses the Fermi level in Γ- A region, with E > E₀ at Γ point and E < E₀ at A point. The Dirac point like structure observed in MgB₂ at symmetry point K is now completely absent, showing that favourable conditions for this material (MgBBBe) to become superconductor do not exist. The hole filling in these bands becomes possible in Γ- A region as well as along L-M direction and at symmetry points Γ and M. The conduction band in this material also projects below the Fermi level near the K point. The electronic transition may, therefore, take place from the valence band to the conduction band. This may facilitate pairing of electrons. As such, limited chances exist for this material to become superconductor. MgBeB, therefore, becomes superconducting at Tc values lower than MgB₂. From Fig. 3(e), it can be observed that DOS at Fermi level is 1.89 states/eV, which also supports superconducting phase transition of this material. The important DOS peaks on this curve on the two sides of Fermi level lie at -10.07, -4.18, -2.80, -1.34, +3.73 and +7.84 eV, with respective DOS values of 0.95, 2.58, 2.47, 2.26, 1.89 and 3.37 states/eV. Higher values of DOS at Fermi level, chances of hole filling in Γ- A region and transition of electrons from valence band to conduction band make this material more suitable for becoming a superconductor, as compared to C-doped MgB₂. This suggests that Be-doped MgB₂ stands better chances than C-doped MgB₂ to become a superconductor.

Conclusion

From the above analysis, it may be inferred that DOS at Fermi level is not the only deciding factor for a material to become superconductor. The hole filling in valence band in Γ- A direction, the appearance of Dirac point like structure at symmetry point K in the vicinity of the Fermi level, and presence of large amplitude high frequency phonon modes causing bond stretching and anharmonicity and their coupling with the in-plane σ bands of boron lattice are those important parameters which decide the occurrence of superconductivity and transition temperature (Tc) in the MgB₂ based materials. However, for moderate values of Tc, DOS at Fermi level should have substantial value, say of the order of 0.7 states/eV or more.

As all these conditions are fulfilled in MgB₂, it shows superconductivity at about 40K. In the absence of any of these characteristic properties, the superconducting phase either does not exist or occurs at lower values of Tc. On doping MgB₂ with carbon or beryllium, the delicate equilibrium of above mentioned conditions is disturbed. Therefore, Tc decreases as we increase the electron/ hole doping level in them and beyond a certain level of doping the material may no more show superconducting transition. It is learnt that at a particular level of doping, Be-doped MgB₂ stands better chances to become superconductor as compared to the C-doped MgB₂. A careful analysis of electronic structure of MgB₂ and related materials can, therefore, be of great help in predicting their transition to superconducting phase.

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