Mn and Fe impurities in MgB$_2$

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Abstract

Based on first principles calculations, we show that Mn impurities are magnetic in MgB$_2$ due to exchange-splitting of d$_{3z^2-1}$ band. Thus, Mn impurities could act as strong magnetic scattering centres leading to pair-breaking effects in MgB$_2$. In contrast, we find Fe impurities in MgB$_2$ to be nearly non-magnetic.

PACS: 71.20.-b; 71.20.Be; 74.25.Jb; 71.15.Nc

Keywords: A. Impurity; D. Magnetic moment; D. Local-density approximation

Magnetic impurities in a conventional phonon-mediated single band superconductor [1] induce pair-breaking effects via spin-flip scattering [2]. However, for an unconventional multi-band superconductor, pair-breaking seems to be most probable from inter-band scattering [3–5], and thus it is not expected to depend solely on the exact atomic nature of the impurity. Since the discovery of superconductivity in MgB$_2$ [6], now confirmed to be a two-band superconductor [7–15], previous studies of chemical substitutions have been largely confined to examining the effects of inter-band and intra-band scattering of the electrons. However, due to the orthogonality of B p$_\sigma$ and p$_\pi$ orbitals, the inter-band scattering effects which could lead to gap merging have not been observed in MgB$_2$ so far, although the superconducting transition temperature $T_C$ showed a steady decrease as a function of increasing impurity concentration [5,16]. Of particular interests were Al [17–21] and 3d transition-metal substitutions [22–29] in the Mg sub-lattice and C substitutions [30–34] in the B sub-lattice of MgB$_2$.

Of all impurity substitutions studied so far, Mn shows the most rapid decrease in $T_C$ as a function of its increasing concentration in MgB$_2$ [22,23,25]. However, no evidence of inter-band scattering was observed, instead the role of magnetic exchange splitting of the bands in Mn-substituted MgB$_2$ was emphasized [23]. Earlier, it was shown that the inter-band scattering would be important if the lattice was distorted locally around the impurities [35]. In this regard, substituting C impurities for B atoms would have only a weak effect on inter-band scattering because it does not change the local symmetry. In contrast, substitutions in the Mg plane could create out-of-plane distortions and change the local point symmetry of nearby B atoms, resulting in a mixing of the in-plane p$_x$($p_y$) orbitals and the out-of-plane p$_z$ orbital. Under these circumstances significant $\sigma-\pi$ scattering would occur.

In this letter, we show that Mn impurities are magnetic in MgB$_2$ due to exchange-splitting of d$_{3z^2-1}$ band. In contrast, we find Fe impurities in MgB$_2$ to be nearly non-magnetic. Thus, the Mn impurities could act as strong magnetic scattering centres leading to pair-breaking effects in MgB$_2$. This may explain the rapid decrease of $T_c$ in Mg$_{1-x}$Mn$_x$B$_2$ with increasing $x$, while in Mg$_{1-x}$Fe$_x$B$_2$ a relatively slow decrease in $T_c$ with $x$ may only be due to disorder-induced scattering of the electrons. Before we discuss our results in detail, we briefly describe the computational details.

The normal metal electronic structure of the disordered alloys Mg$_{1-x}$Mn$_x$B$_2$ and Mg$_{1-x}$Fe$_x$B$_2$ is calculated using the Korringa–Kohn–Rostoker (KKR) Green’s function method formulated in the atomic sphere approximation (ASA) [36], which has been corrected by the use of both the muffin-tin correction for the Madelung energy, needed for obtaining an accurate description of ground state properties in the ASA [37], and the multipole moment correction to the
and Bloch spectral density terms of total, sub-lattice resolved partial densities of states, Mg
The effects of local lattice relaxation as well as any possible 2
of exchange splitting of the states, in particular for Mn
to the spin unpolarized calculations, suggesting the role
energy,
the irreducible BZ.
setup using the experimental lattice constant
symmetry points of the hexagonal BZ. The electronic structure
x
with
speeded up using the prescription of Abrikosov et al. [ 45].
Broyden’s mixing scheme [ 44], the CPA self consistency was
charge self-consistency iterations were accelerated using the
radii of the 3d substituents were kept the same as that of
Mg
and Mg
2
for
x
and Mg
1
for
x
were carried out at the experimental lattice parameters of MgB2 [6], assuming a rigid underlying lattice.
The effects of local lattice relaxation as well as any possible short-range ordering effects are not considered. Our results for
Mg1−xMnxB2 and Mg1−xFexB2 alloys with x = 0.05 are analyzed in terms of total, sub-lattice resolved partial densities of states, and Bloch spectral density \( A_B(E,k) \) [46] evaluated at high symmetry points of the hexagonal BZ. The electronic structure of body-centered cubic (bcc) Fe is calculated with a similar setup using the experimental lattice constant \( a = 5.425 \text{ au} \). The density of states of bcc Fe is calculated with 2470 k-points in the irreducible BZ.

The calculated density of states (DOS) at the Fermi energy, \( E_F \), of MgB2 was determined to be 3.493 states/Ry atom, which is consistent with previous reports [47,48]. For Mg
Mn
0.05B2 and Mg
Fe
0.05B2 alloys, the spin polarized calculations showed a lower total energy when compared to the spin unpolarized calculations, suggesting the role of exchange splitting of the states, in particular for Mn substituted MgB2. The magnetic energies for Mg
Mn
0.05B2 and Mg
Fe
0.05B2 alloys are calculated to be 5.319 mRy and 0.001 mRy, respectively.

The corresponding local magnetic moment for Mn is equal to 1.84 \( \mu_B \)/atom, while Fe tends to be feebly magnetic with a local magnetic moment of 0.04 \( \mu_B \)/atom. In Fig. 1 we show the spin polarized, total and sub-lattice resolved partial densities of states of Mg
Mn
0.05B2 and Mg
Fe
0.05B2 alloys. In the same figure we also show the transition-metal d and \( \text{B} \) and \( \text{p}_z \) DOS in these alloys. It is clear from Fig. 1 that the exchange-split

\[ \text{Mn} \text{ d} \text{ orbitals in Mg}_{0.95}\text{Mn}_{0.05}\text{B}_2 \text{ alloys make Mn impurities magnetic in MgB}_2. \text{ We also find some modifications in the majority and minority B } \text{p}_{\text{xy}} \text{ and } \text{p}_z \text{ bands due to their hybridization with the Mn } \text{d} \text{ orbitals.} \]

To gain further insight into such a contrasting behaviour of Mn and Fe impurities in MgB2, we show in Fig. 2 the transition-metal d-projected DOS in Mg
Mn
0.05B2 and Mg
Fe
0.05B2 alloys, resolved into three non-degenerate \( x^2-y^2 \), \( yz \), and \( 3z^2-r^2 \) symmetry components. We find that the band with \( 3z^2-r^2 \) symmetry is the narrowest of all the d bands. Thus, a half-filled \( 3z^2-r^2 \) band is more likely to induce exchange splitting than the other bands. In the case of Mn the minority \( 3z^2-r^2 \) band is nearly half-filled, resulting in an exchange-split d band. Our calculations show that the centers of the \( d \) ↑ and the \( d \downarrow \) bands are separated by 0.114 Ry leading to the Stoner exchange integral \( \text{I} = \frac{d\uparrow-\downarrow}{m} \) to be 0.062 Ry/\( \mu_B \). However, in the case of Fe the additional one electron fills up the minority \( 3z^2-r^2 \) band, as can be seen from Fig. 2, thereby making Fe nearly non-magnetic in MgB2. In addition, following the prescription of Liechtenstein et al. [49], we have calculated the on-site Heisenberg exchange interaction \( J_0 \). The values of \( J_0 \) for Mn and Fe alloys are found to be 0.7292 mRy and 0.0001 mRy respectively, confirming Mn to be magnetic and Fe to be nearly non-magnetic in MgB2.
solved into three non-degenerate $xy$, $yz$, and $3z^2-1$ symmetry components. The inset in the bottom panel shows the spin polarized, d-projected DOS of bcc Fe, resolved into two non-degenerate $xy(yz, zx)$ (dashed line) and $3z^2 - 1(x^2 - y^2)$ (solid line) symmetry components. In the inset figure, the $x$-axis corresponds to energy ranging from $-0.4$ Ry to $0.2$ Ry, while the $y$-axis represents the DOS from $0$ to $12$ state/Ry/atom for both spins. The dashed vertical line through energy zero represents the Fermi energy. Note that the DOS in the figure corresponds to per transition-metal atom.

It is instructive to compare the DOS of Fe in Mg$_{0.95}$Fe$_{0.05}$B$_2$ with that of bcc Fe as shown in the inset of Fig. 2, where the d-projected DOS of bcc Fe has been resolved into two non-degenerate $xy(yz, zx)$ and $3z^2 - 1(x^2 - y^2)$ symmetry components. The calculated magnetic moment of bcc Fe is found to be $2.24 \, \mu_B/\text{atom}$. The significant changes in the DOS of Fe involve $x^2 - y^2$ and $3z^2 - 1$ symmetry components. Due to the change in local symmetry, as one goes from bcc Fe to hexagonal Mg$_{0.95}$Fe$_{0.05}$B$_2$, the narrow $x^2 - y^2$ band of bcc Fe hybridizes with the $Bp_x(y)$ bands of Mg$_{0.95}$Fe$_{0.05}$B$_2$ and gets broadened as shown in Fig. 2. The effects of hybridization on the B $p_{x(y)}$ DOS can be seen in Fig. 1 in the form of a hump around $0.14$ Ry below the Fermi energy. On the other hand, the filling up of the minority $3z^2 - 1$ band by the extra electron results in an inward movement of the band by $0.15$ Ry, making magnetism unsustainable in Mg$_{0.95}$Fe$_{0.05}$B$_2$.

Many of the superconducting properties of MgB$_2$ can be directly related to its normal state electronic structure. In particular, an understanding of how the additions of Mn and Fe impurities affect the electronic states over the entire BZ can be very useful in this regard. In Fig. 3 we show the spin polarized, k-resolved Bloch spectral density $A_B(E, k)$ for Mg$_{0.95}$Mn$_{0.05}$B$_2$ and Mg$_{0.95}$Fe$_{0.05}$B$_2$ alloys at $\Gamma$, $A$, $M$, $H$, $K$, and $L$ points of the hexagonal BZ. As expected, the differences between majority and minority $A_B(E, k)$ are much more for Mg$_{0.95}$Mn$_{0.05}$B$_2$ alloys than for Mg$_{0.95}$Fe$_{0.05}$B$_2$ alloys over the entire BZ. New states, predominantly d in character are seen to form just below $E_F$ at $\Gamma$ and $K$ points. The disorder-induced broadening of the doubly degenerate $Bp_\sigma$ states located between $-0.05 < E < +0.05$ at $\Gamma$ and $Bp_\pi$ states just above $E_F$ at $M$ point can be seen clearly. At $M$ point, the lowest lying peak is characteristic of the s band, while the next two peaks correspond to the $p_x$ bands. We find that the $p_x$ bands at $M$ point in ordered MgB$_2$ are relatively far apart in comparison to the Mn and Fe substituted systems. A change in the dispersion of bands is expected to affect the three dimensionality of the Fermi surface [47] of the substituted materials (a detailed comparison will be published elsewhere). We also note that in transition-metal diborides, such as TaB$_2$ and others, a strong metal d hybridization with the B p bands is observed in $A-L-H$ plane of the BZ [50,51]. However, in the case of Mn and Fe impurities, the d bands are narrower and only the states that are close to $E_F$ are affected.

In summary, we have carried out density-functional-based electronic structure calculations to study the effects of Mn and Fe substitutions on the $\sigma$ and $\pi$ bands of MgB$_2$. The self-consistent calculations for Mg$_{0.95}$Mn$_{0.05}$B$_2$ and Mg$_{0.95}$Fe$_{0.05}$B$_2$ alloys show that Mn forms a local magnetic moment of $1.84 \, \mu_B/\text{atom}$ while Fe tends to remain feebly magnetic with a local magnetic moment of $0.04 \, \mu_B/\text{atom}$. Further, the k-resolved Bloch spectral density of states at $\Gamma$, $A$, $M$, $H$, $K$, and $L$ points of the hexagonal Brillouin zone show that for Mn substituted alloys the $\sigma$ bands of MgB$_2$ are hybridized with the Mn d bands and undergo modifications.
when compared to its Fe counterparts. Given that pσ and pπ orbitals are responsible for superconductivity in MgB₂, Mn impurities could, therefore, act as strong magnetic scattering centers leading to pair-breaking effects. In contrast, the Fe impurities in MgB₂ are nearly non-magnetic with essentially no pair-breaking effects.

Acknowledgements

One of us (PJTJ) would like to thank Dr. Andrei Ruban for providing the KKR-ASA code. Discussions with Dr Igor Mazin on the electronic structure properties of MgB₂ are gratefully acknowledged.

References