Band filling and interband scattering effects in MgB$_2$: C vs Al doping

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We argue, based on band structure calculations and Eliashberg theory, that the observed decrease of $T_c$ of Al and C doped MgB$_2$ samples can be understood mainly in terms of a band filling effect due to the electron doping by Al and C. A simple scaling of the electron-phonon coupling constant $\lambda$ by the variation of the density of states as function of electron doping is sufficient to capture the experimentally observed behavior. Further, we also explain the long standing open question of the experimental observation of a nearly constant $\pi$ gap as function of doping by a compensation of the effect of band filling and interband scattering. Both effects together generate a nearly constant $\pi$ gap and shift the merging point of both gaps to higher doping concentrations, resolving the discrepancy between experiment and theoretical predictions based on interband scattering only.

The high critical temperature of 40 K in the simple binary compound MgB$_2$ (Ref. 1) was an unexpected present of nature to the scientific community. Now, after a few years of intense experimental and theoretical research the main features of superconductivity in this material seem well understood as due to a phonon mediated mechanism with different coupling strengths to the electronic $\sigma$- and $\pi$-bands[2] [3] [4], which leads to the appearance of two distinct superconducting gaps.

Historically, two-band superconductivity is an old topic which has been proposed already shortly after the formulation of the BCS theory. Suhl, Matthias and Walker [5] suggested a model for superconductivity in transition metals considering overlapping $s$- and $d$-bands. At the same time, Moskalenko formulated an extension of BCS theory for multiple bands [6]. In the early 1960 there have been experimental claims for the observation of two-band superconductivity in some transition metals like e.g. V, Nb and Ta [8] and later, in the 1980, in oxygen depleted SrTiO$_3$ [9].

However until now, MgB$_2$ appears to be first system for which multi-band superconductivity has independently been evidenced by several experimental techniques: heat capacity, tunneling spectroscopy, Raman spectroscopy, penetration depth measurements, ARPRES and the analysis of the critical fields [2]. The appearance of multiple gaps had been predicted theoretically [4] based on the electronic structure of MgB$_2$ [5] [10] [11]. The Fermi surface consists of four sheets: Two cylindrical sheets corresponding to quasi two-dimensional $\sigma$-bands and two tubular networks derived from the more three dimensional $\pi$-bands [5]. The phonons, in particular the optical bond-stretching phonon branch along $\Gamma$-A [11], couple about three times stronger to the holes at the top of the $\sigma$-band as compared to the $\pi$-band [4] [11] [12] [13] [14] [15]. Using linear response theory it is possible to calculate from first principles the electron-phonon coupling (Eliashberg function) which is needed as input for Eliashberg theory. The solution of the Eliashberg equations allows for the calculation of the superconducting gaps or thermodynamical properties like specific heat in good agreement with the experiments [14] [15].

As for any anisotropic order parameter, scattering by nonmagnetic impurities should have a pair breaking effect, just as magnetic impurities have in conventional superconductors. Interband impurity scattering should lead to a decrease of $T_c$ and if strong enough to a single (averaged) order parameter [12] [17]. The interband impurity scattering between the $\sigma$- and $\pi$-bands is exceptionally small [18], due to the particular electronic structure of MgB$_2$, so that in the superconducting state, the two gaps in the $\sigma$- and the $\pi$-bands are preserved even in ‘dirty’ samples with a considerably reduced $T_c$ and a broad range of normal state resistivities.

The decrease of $T_c$ has been experimentally demonstrated by a series of substitution experiments in which Mg has been replaced by Al and B by C [19] [20] [21] [22] [23] [24] [25] [26] [27] [28] [29] [30] [31]. Similarly, irradiation with neutrons leads also to a decrease of $T_c$ [32]. Figure 1 shows a compilation of experimental data for the critical temperature $T_c$ versus Al and C doping concentration.

For the two superconducting gaps it has been observed that the $\sigma$ gap decreases with decreasing $T_c$ and approaches the intermediate coupling value of $2\Delta/k_B T_c$ at $T_c \sim 25$ K. In most experimental reports the $\pi$ gap is found to be independent on the $T_c$ of the sample and to remain close to the value of $\sim 2$ meV seen for undoped samples [42].

There have been recent reports by Gonnelli and coworkers [33] [43] which demonstrate a different behavior of the superconducting gaps depending on the type of dopant. For C doped single crystals with composition Mg(B$_{1-y}$C$_y$)$_2$ ($y \leq 0.132$) their point contact spectroscopy measurements show a merging of the $\sigma$ and $\pi$ gaps for the first time [33] [43]. On the other hand, Gonnelli et al. also find that the behavior of Al doping in single crystals with composition Mg$_{1-x}$Al$_x$B$_2$ ($x \leq 0.21$) is quite different. Even samples with very low $T_c$ of about 20 K still exhibit distinct gaps, at critical temperatures for which theoretical calculations based on Eliashberg theory including interband scattering always predict a single order parameter only [44]. Therefore, at present, there is disagreement between experiment and theory.
In the following we will argue that one essential ingredient to understand the behavior of \( T_c \) is the effect of band filling of holes in the \( \sigma \)-band due to electron doping. To understand the different behavior of the two gaps in Al and C doped samples one additionally needs to consider interband scattering. While band filling will decrease the superconducting gaps, interband scattering will decrease the value of the larger gap and increase the smaller one. These two effects may compensate for the smaller \( \pi \) gap and enable us to explain the observed nearly constant value of the small gap.

First, we will focus on the doping dependence of the critical temperature. Figure 1 summarizes experimental results from different groups. \( T_c \) as function of Al and C doping shows very similar behavior if the C doping is scaled by a factor of two as compared to the Al doping. This follows naturally from the definition of the C doping concentration per boron atom, as expressed in Mg\(_{1-x}\)Al\(_x\)(B\(_{1-y}\)C\(_y\))\(_2\), with \( x \) (\( y \)) for the amount of Al (C) doping. The importance of the band filling is already indicated by the horizontal dotted line \( \sim 25 \) K. This value would be the upper limit of \( T_c \) due to the pair breaking effect of interband scattering only. If interband scattering would be the only relevant mechanism no sample should show a \( T_c \) lower than indicated by the horizontal line. This is clearly not the case as shown in Fig. 1.

\( \text{MgB}_2 \) has a total of 0.26 holes; 0.15 holes in both \( \sigma \) bands and the remaining 0.11 holes in the hole \( \pi \)-band. Al and C substitution will both dope electrons and therefore reduce the number of holes. In a rigid band model the electron doping would be defined with respect to the total number of holes in Mg\(_{2}\) and simply corresponds to a shift of the Fermi level. For small doping the \( \sigma \)-band DOS is practically constant as expected from the quasi two-dimensional character of the \( \sigma \)-bands. After adding 0.15 electrons the \( \sigma \) bands become nearly filled and the DOS starts to decrease rapidly. The coupling of the \( \sigma \)-holes to the optical bond-stretching \( E_{2g} \) phonons drives the superconductivity in this material and determines \( T_c \). Therefore, we just scale the band splitted electron-phonon Eliashberg functions \( \alpha_{ij}^2 F \) and the \( \mu^* \)-matrix \( \lambda \) with the the change of the \( \sigma \)- or \( \pi \)-band DOS as function of doping. We use the Eliashberg functions for pure Mg\(_{2}\) calculated from first-principles linear response theory \cite{11}, which have been used successfully to describe the specific heat \cite{12}, tunneling \cite{14} and penetration depth \cite{16}. The dotted line shown in Fig. 1 corresponds to the rigid band scaling. The decrease in \( T_c \) for small doping concentrations is well reproduced and originates from the small \( k_F \) dispersion of the \( \sigma \) bands along the \( \Gamma \)-A line. The \( \sigma \)-band Fermi surfaces are not perfect cylinders but are slightly warped (see Fig. 3, Ref. \cite{15}). For larger doping concentration, \( T_c \) obtained from this simple model decreases faster than observed in experiment. This is not surprising because we used the unperturbed band structure of pure Mg\(_{2}\) not taking into account neither alterations of the bands due to doping nor the change of the phonon frequencies.

To correct for this failure we further calculate the change of the DOS using the virtual crystal approximation (VCA). In order to simulate the doping of Al, we replace the Mg atom with a virtual atom with charge \( Z = xZ_{\text{Al}} + (1 - x)Z_{\text{Mg}} \) and recalculate the electronic band structure self-consistently using the full potential LMTO method \cite{47}. In agreement with \cite{48}, we find a slower decrease of the \( \sigma \)-band DOS. Using the DOS from the VCA to scale \( \alpha_{ij}^2 F \) we solve the Eliashberg equations and obtain a slower decrease of \( T_c \) (dashed line in Fig. 1) in better agreement with the experimental observations. Recent supercell calculations indicate an even slower \( \sigma \)-band filling \cite{49} compared to the VCA.

An additional effect of doping will be the hardening of the \( E_{2g} \) phonon branch which will decrease the electron-phonon coupling \( \lambda \sim 1/\omega^2 \) \cite{10}. In order to take this effect into account we also calculated the \( E_{2g} \)-\( \Gamma \)-point frequency in the VCA using linear response methods \cite{10}. The final result from scaling \( \alpha_{ij}^2 F \) by the DOS and the \( E_{2g} \) phonon frequency is shown by the solid line in Fig 1. The agreement with experiment improved significantly.

Band filling with the corresponding changes in the DOS seems to be sufficient to understand the behavior of \( T_c \) as function of doping. However, this is not sufficient to understand the evolution of the superconducting gaps, because there should be no difference in the behavior between Al and C doping because both are electron dopants. We now argue that the additional ingredient to understand this behavior is interband scattering.
FIG. 2: Upper panel Al doping: Superconducting σ-gap (upper curve and filled symbols) and π-gap (lower curve and open symbols) as function of critical temperature \( T_c \), obtained from the solution of the Eliashberg equations with scaled \( \sigma^2 F \) without interband scattering (solid lines) compared to experimental results (□) \[33\] and (○) \[28\]. Lower panel C doping: The solid lines show the solution of the Eliashberg equations with interband scattering rate 2000 \( \cdot \) cm\(^{-1} \) compared to the experimental results (□) \[33\] and (○) \[28\]. The limiting cases of interband scattering only (dotted lines) or scaling of \( \sigma^2 F \) (dash-dotted lines) are also shown. The dashed straight line indicates the BCS gap relation for \( \Delta/T_c \).

In the upper panel of Fig. 2 we plot the experimental σ- and π-gaps for Al doped crystals as obtained by Gonnelli et al. \[33\] and by Putti et al. \[28\] as function of the critical temperature of the samples. Together with the experimental data we display the results from the solution of the two-band Eliashberg equations without interband scattering but the Eliashberg functions scaled by the change of DOS and phonon frequency as described above.

The agreement with experiment seems to be reasonable. The results by Putti et al. \[28\] show a merging of the gaps for Al-doping, however both gaps have a ratio of \( \Delta/k_B T_c \) somewhat lower than the canonical BCS ratio as indicated by a dashed line in Fig. 2 which casts doubt on this data point. However, it is still premature to give a definite answer because more experimental data for single crystals and high doping concentrations will be required for a complete picture. Based on the available data which show no clear merging of the two gaps, we conclude that the interband scattering in Al doped samples is small, even at high doping concentrations.

The experimental results for C doped single crystals indicate for the first time a merging of the two superconducting gaps, which is a clear manifestation of interband scattering. In the lower panel of Fig. 2 we show the experimental results \[33\] together with our Eliashberg theory calculations. In difference to the previous case we include the interband scattering in our calculations, which will also cause an additional reduction of \( T_c \). Using a simple linear relation of the interband scattering rate to the doping concentration (\( \gamma_{\text{inter}} = 2000 \cdot \) y \( \text{cm}^{-1} \)) we find e.g. for 10-15% C concentration an additional lowering of \( T_c \) of about 6 K.

The two limiting cases (interband scattering only, scaling of \( \alpha^2 F \)) are also shown in the lower panel in Fig. 2. The decrease of the DOS causes a decrease of both gaps, as can be seen from the dash-dotted lines. In contrast the interband scattering will decrease the σ gap and increase the π gap. Both effects can compensate each other resulting in the solid line, which includes the effects of the scaled \( \alpha^2 F \) and interband scattering. This may explain the experimental observation of a nearly constant π-gap as function of doping, which has been a long standing open question.

The difference in the magnitude of the interband scattering for Al and C doping can be easily rationalized. The σ band-orbitals are located in the boron plane and there is not much weight of the σ-bands in the Mg plane. The π-orbitals are also centered at the boron plane, but extend further out towards the Mg plane. For that reason impurities in the boron plane are more effective interband scatterers \[18, 50\]. Therefore interband scattering due to doped C atoms replacing B atoms is much more likely than for Al doping.

In summary, we have shown that the variation in \( T_c \), of Al and C doped samples of MgB\(_2\) can be understood mainly as due to a simple effect of band filling. Al and C are both electron dopants which reduce the number of holes at the top of the σ bands together with a reduction of the electronic DOS. Further, we suggest that the nearly constant π gap as function of doping can be understood due to a compensation of band filling and interband scattering. The compensation of these effects shifts the merging point of both gaps to higher doping concentrations and lower \( T_c \), resolving the discrepancy between experiment and theoretical predictions based on interband scattering only.

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