Band Filling and Interband Scattering Effects in MgB_2: Carbon versus Aluminum Doping

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We argue, based on band structure calculations and the 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 λ by the variation of the density of states as a 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 π gap as a function of doping by a compensation of the effect of band filling and interband scattering. Both effects together generate a nearly constant π 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.

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The high critical temperature of 40 K in the simple binary compound MgB_2 [1] was an unexpected present from 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 to be well understood as due to a phonon mediated mechanism with different coupling strengths to the electronic σ and π bands [2–5], which leads to the appearance of two distinct superconducting gaps.

Historically, two-band superconductivity is an old topic which was proposed shortly after the formulation of BCS theory. Suhl, Matthias, and Walker [6] suggested a model for superconductivity in transition metals considering overlapping s and d bands. At the same time, Moskalenko *et al.* formulated an extension of BCS theory for multiple bands [7]. In the early 1960s, there were experimental claims of the observation of two-band superconductivity in some transition metals, such as, e.g., V, Nb, and Ta [8], and later, in the 1980s, in oxygen depleted $SrTiO_3$ [9].

MgB_2 appears to be the first system for which multiband superconductivity has been independently evidenced by several experimental techniques: heat capacity, tunneling spectroscopy, Raman spectroscopy, penetration depth measurements, angle-resolved photoemission spectroscopy, and the analysis of critical fields [2]. The appearance of multiple gaps has 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 σ bands and two tubular networks derived from the more three-dimensional π bands [5]. The phonons, in particular, the optical bond-stretching phonon branch along Γ-A [11], couple about 3 times stronger to the holes at the top of the σ band as compared to the π band [4,11–15]. Using linear response theory it is possible to calculate from first principles the electron-phonon coupling (Eliashberg function) which is needed as input for the Eliashberg theory. The solution of the Eliashberg equations allows for the calculation of the superconducting gaps or thermodynamical properties, such as 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 [14,16,17]. The interband impurity scattering between σ and π 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 σ and the π 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 [19–31]. 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 σ gap decreases with decreasing T_c and approaches the intermediate coupling value of $2\Delta/k_BT_c$ at $T_c \sim 25$ K. In most experimental reports, the π gap is found to be independent of the T_c of the sample and to remain close to the value of $\sim$2 meV seen for undoped samples [33].

There have been recent reports by Gonnelli and co-workers [34,35] that 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 spectros-

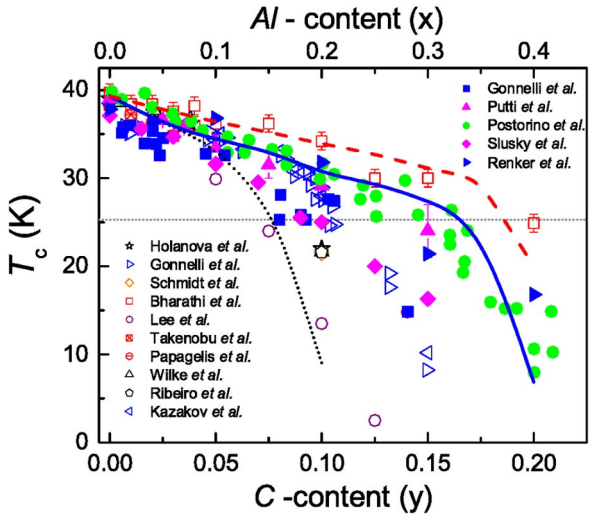

FIG. 1 (color online). Critical temperature T_c as a function of Al (solid symbols) and C (open symbols) versus doping concentration defined as $Mg_{1-x}Al_x(B_{1-y}C_y)_2$. Al doping: (■) [34], (▲) [28], (●) [26], (◆) [44], (▶) [45]; C doping: (☆) [46], (▷) [34], (◇) [30], (□) [47], (○) [48], (⬠, ⊠) [29,49], (△) [50], (⊜) [31], (◁) [51]. The lines present estimates based on Eliashberg theory with different levels of approximation: dotted line with DOS from rigid band model, dashed line with DOS from VCA, and solid line with DOS and phonon renormalization from VCA. The horizontal dotted line is the lower limit for interband scattering only.

copy measurements show a merging of the σ and π gaps for the first time [34,35]. On the other hand, Gonnelli *et al.* also found that the behavior of Al doping in single crystals with composition $Mg_{1-x}Al_xB_2$ ($x \leq 0.21$) is quite different. Even samples with very low T_c of about 20 K still exhibit distinct gaps. Calculations based on the Eliashberg theory including interband scattering predict at these T_c a single order parameter only [36]. 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 σ 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 π 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 a function of Al and C doping shows very similar behavior if the C doping is scaled by a factor of 2 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 ~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.

MgB_2 has a total of 0.26 holes: 0.15 holes in both σ bands and the remaining 0.11 holes in the hole π 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 MgB_2 and would simply correspond to a shift of the Fermi level. For small doping the σ-band density of states (DOS) is practically constant, as expected from the quasi-two-dimensional character of the σ bands. After adding 0.15 electrons the σ bands become nearly filled and the DOS starts to decrease rapidly. The coupling of the σ 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 split electron-phonon Eliashberg functions $\alpha^2_{ij}F$ [14] and the μ^* matrix [37] with the change of the σ- or π-band DOS as a function of doping. We use the Eliashberg functions for pure MgB_2 calculated from first-principles linear response theory [11], which have been used successfully to describe the specific heat [14], tunneling [36], and penetration depth [38].

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_z dispersion of the σ bands along the Γ-A line. The σ-band Fermi surfaces are not perfect cylinders but are slightly warped (see Fig. 3, Ref. [5]). 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 MgB_2 not taking into account either alterations of the bands due to doping or 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 $Z = xZ_{Al} + (1-x)Z_{Mg}$ and recalculate the electronic band structure self-consistently using the full potential linear muffin-tin orbitals method [39]. In agreement with [40], we find a slower decrease of the σ-band DOS. Using the DOS from the VCA to scale $\alpha^2_{ij}F$, 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 σ-band filling [41] 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 $\lambda \sim 1/\omega^2$ [10]. In order to take this effect into account we also calculated the E_{2g}-Γ-point frequency

in the VCA using linear response methods [39]. The final result from scaling $\alpha^2_{ij}F$ by the DOS and the E_{2g} phonon frequency is shown by the solid line in Fig. 1. The agreement with experiment improved significantly. Similar conclusions for Al-doped samples only have been obtained recently in [42].

Band filling with the corresponding changes in the DOS seems to be sufficient to understand the behavior of T_c as a 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.

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.* [34] and by Putti *et al.* [28] as a 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 with the Eliashberg functions scaled by the change of the DOS and phonon frequency as described above.

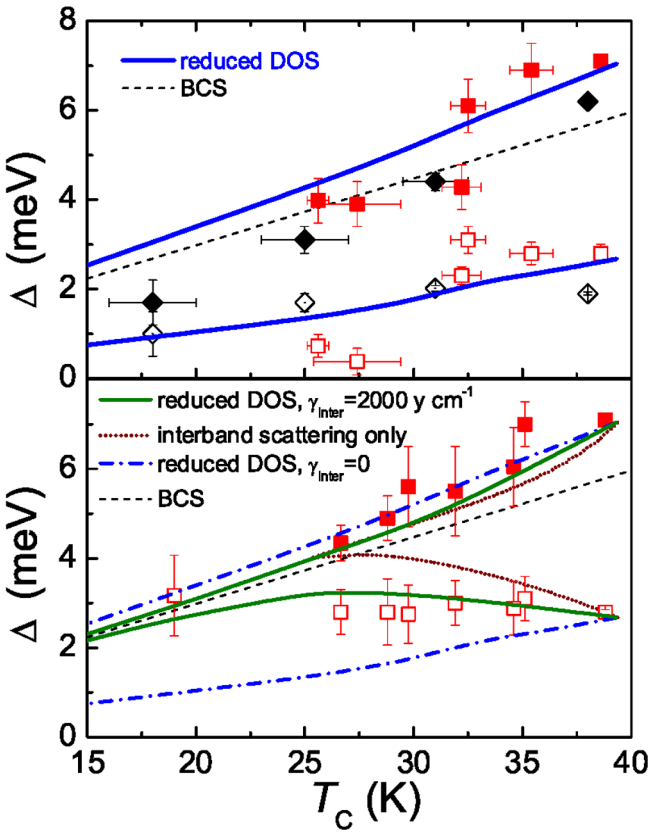

FIG. 2 (color online). (Upper panel) Al doping: Superconducting σ gap (upper curve and solid symbols) and π gap (lower curve and open symbols) as a function of critical temperature T_c obtained from the solution of the Eliashberg equations with scaled $\alpha^2_{ij}F$ without interband scattering (solid lines) compared to experimental results (□) [34] and (◇) [28]. (Lower panel) C doping: The solid lines show the solution of the Eliashberg equations with interband scattering rate $2000y$ cm^{-1} compared to the experimental results (□) [34,35]. The limiting cases of interband scattering only (dotted lines) or scaling of $\alpha^2_{ij}F$ (dash-dotted lines) are also shown. The dashed straight line indicates the BCS gap relation for Δ/T_c.

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 Δ/k_BT_c somewhat lower than the canonical BCS ratio, as indicated by the dashed lines 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 [34] together with our Eliashberg theory calculations. In contrast 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 ($\gamma_{\text{inter}} = 2000y$ 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 and scaling of $\alpha^2_{ij}F$) 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 $\alpha^2_{ij}F$ and interband scattering. This may explain the experimental observation of a nearly constant π gap as a 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 bond 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 [18,43]. 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 a 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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