Electron-phonon coupling and two-band superconductivity
of Al- and C-doped MgB$_2$

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Abstract

We have studied the electron-phonon and superconducting properties of the Mg$_{1-x}$Al$_x$B$_2$ and MgB$_{2(1-y)}$C$_{2y}$ alloys within the framework of density functional theory using the self-consistent virtual-crystal approximation. For both alloys, the Eliashberg spectral functions and the electron-phonon coupling constants have been calculated in the two-band model for several concentrations up to $x$(Al)$= 0.55$ and $y$(C)$= 0.175$. We solved numerically the two-band Eliashberg gap equations without considering interband scattering. Using a single parameter for the Coulomb pseudopotential, which was determined for the undoped compound, we were able to reproduce the experimental doping dependence of $\Delta_\sigma$, $\Delta_\pi$, and $T_c$ for both alloys on a quantitative level. In particular, the observed differences in the doping range of superconductivity between Al and C doping indicate a pronounced influence of the doping site, which can be explained naturally in the present approach without the need to invoke interband scattering, suggesting that this factor plays only a minor role.

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I. INTRODUCTION

The discovery of superconductivity in 2001 in the intermetallic compound MgB$_2$, with a critical temperature $T_c \approx 39$ K$^1$, has motivated a lot of theoretical and experimental studies in order to understand the origin and characteristics of the relatively high $T_c$ in this material. It is now generally accepted that MgB$_2$ is a phonon-mediated superconductor, and that the high transition temperature arises due to a combination of several peculiar features in its electronic structure and electron-phonon coupling, which conspire to produce a superconducting state with multiple gaps$^2-10$. Its electronic band structure in the vicinity of the Fermi energy consists of two bonding $\sigma$ bands corresponding to in-plane $s - p_x - p_y$ ($sp^2$) hybridization in the boron layer and two $\pi$ bands (bonding and anti-bonding) formed by hybridized boron $p_z$ orbitals. A substantial part of the electron-phonon coupling has its origin in the interaction of states at the $\sigma$-band Fermi surfaces with one specific phonon mode, the B-B bond stretching mode with $E_{2g}$ symmetry at the $\Gamma$ point$^4,6,11-14$. In addition, MgB$_2$ possesses two distinct superconducting gaps associated with the $\sigma$ and $\pi$ Fermi surfaces. This superconducting state can be described within a multiband version of the Eliashberg theory where the pairing interaction is split into intra- and interband contributions$^{11,15-17}$.

In the search for related compounds with similar outstanding superconducting properties, only a few variants of MgB$_2$ have been found. Among them, two alloy systems could be successfully synthesized based on the partial substitution of Mg by Al$^{18-21}$ and B by C$^{22-26}$, respectively. Both substitutions provide electron doping to the alloy and lead to a reduction of $T_c$. For Mg$_{1-x}$Al$_x$B$_2$ and MgB$_2$$_{2(1-y)}$C$_2$$_y$, loss of superconductivity is found for $x > 0.5^{18,21}$ and $y > 0.15^{22,26}$, respectively. A correlation between the $T_c$ reduction and the filling of the hole-type $\sigma$-bands as a function of Al-doped content was found by first principles calculations within the virtual-crystal approximation$^{27,28}$. In parallel with the reduction of $T_c$ also a decrease of the superconducting gaps $\Delta_{\sigma}$ and $\Delta_{\pi}$ has been observed. For single crystals as well as polycrystals Al doping was found to decrease both $\sigma$ and $\pi$ gaps monotonically, which, however, stay distinguishable even for $T_c$ as low as 10 K ($x \approx 0.32$)$^{29,35}$. These observations indicate that the interband scattering $\Gamma_{\sigma\pi}$ remains small even at high doping levels, and is insufficient to produce a merging of the $\sigma$ and $\pi$ gaps. On contrast, for the C-doped system, contradictory experimental results have been reported with respect to the question
if the superconducting gaps merge as a function of doping\textsuperscript{31,33,36-38}. In all experiments a decrease of both gaps with C doping was observed. There are point-contact tunneling\textsuperscript{36,37}, point-contact spectroscopy\textsuperscript{33} and photoemission spectroscopy\textsuperscript{38} measurements that show a clear difference between the $\sigma$ and $\pi$ gaps at all doping levels. However, there exists also point-contact spectroscopy measurements\textsuperscript{31} that suggest a merging of the gaps at $T_c \approx 17$ K ($y \approx 0.13$). This was then interpreted as a doping-induced increase of the interband scattering $\Gamma_{\sigma\pi}$, which tends to reduce gap anisotropies.

From the theoretical point of view, many investigations have been performed to study the doping dependence of the structural\textsuperscript{27,39}, electronic\textsuperscript{27,40-44}, vibrational\textsuperscript{44-47} and superconducting properties\textsuperscript{41,44,46,48-53} of the Mg$_{1-x}$Al$_x$B$_2$ and MgB$_2(1-y)$C$_{2y}$ systems using different approximations for the simulation of the alloys, like the supercell approach\textsuperscript{39,40,45,47,49}, the rigid band approximation (RBA)\textsuperscript{44}, the virtual-crystal approximation (VCA)\textsuperscript{3,27,43,46}, the coherent potential approximation (CPA)\textsuperscript{41,42,48}, and the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA)\textsuperscript{53}. However, in particular for the supercell and CPA approaches, the studies have been limited to a few Al or C concentrations only, because these calculations are computationally very demanding, especially if one is interested in very low (close to Mg or B) or high (close to Al) concentrations. Additionally, in these approaches the symmetry of the original system is lost, which complicates the interpretation and understanding of experimental results as a function of doping.

In this paper, we present a study of the electron-phonon and superconducting properties of Mg$_{1-x}$Al$_x$B$_2$ and MgB$_2(1-y)$C$_{2y}$ within the framework of density functional theory\textsuperscript{54} using the self-consistent virtual-crystal approximation (VCA)\textsuperscript{27,55-57}. We calculate the electron-phonon (e-ph) properties such as the Eliashberg function, $\alpha_{ij}^2 F(\omega)$, and the e-ph coupling constant, $\lambda_{ij}$, within the two-band model as a function of doping. By solving the two-band Eliashberg gap equations on the imaginary axis we obtain the superconducting gaps, $\Delta_\sigma$ and $\Delta_\pi$, and the value of $T_c$ as a function of $x$ or $y$ for the Mg$_{1-x}$Al$_x$B$_2$ and MgB$_2(1-y)$C$_{2y}$ alloys, respectively. The evolution of these quantities is analyzed and discussed in connection with changes in the electronic and vibrational properties.
II. COMPUTATIONAL DETAILS

The calculations were performed with the mixed-basis pseudopotential method (MBPP)\textsuperscript{58,59}. For Mg/Al and B/C norm-conserving pseudopotentials were constructed according to the Vanderbilt description\textsuperscript{60}. Details of pseudopotentials, basis functions and calculational aspects for ground-state and phonon properties can be found in a previous publication\textsuperscript{28}. The Mg\textsubscript{1-x}Al\textsubscript{x}B\textsubscript{2} and MgB\textsubscript{2(1-y)}C\textsubscript{2y} alloys were modeled in the self-consistent virtual-crystal approximation (VCA)\textsuperscript{27,28,55–57,61–63}. The VCA is implemented within the MBPP method\textsuperscript{58,59} by generating new pseudopotentials with a fractional nuclear charge at the Mg or B site for each \(x\) and \(y\), respectively (Al: \(Z=12+x\) and C: \(Z=5+y\)), and by adjusting the valence charge accordingly\textsuperscript{28}. From our previous results for the electronic and vibrational properties\textsuperscript{28} the screened electron-phonon matrix elements were calculated via density functional perturbation theory\textsuperscript{54,64–66}, which are the key elements of the Eliashberg theory\textsuperscript{67–70}. The calculations employ the PBE version of the generalized gradient approximation (GGA)\textsuperscript{71–73}, and are performed at the optimal lattice parameters for each doping level\textsuperscript{28}. Eliashberg functions for all band combinations where obtained by standard Fourier interpolation of quantities calculated with a dense \(36 \times 36 \times 36\) \(k\)-point mesh and a \(6 \times 6 \times 6\) \(q\)-point mesh. The original four-band Eliashberg functions are projected onto an effective two-band model by averaging over the two \(\sigma\) and the two \(\pi\) bands, respectively. The partial and total Eliashberg functions are given by the following expressions,

\[
\alpha_{ij}^2 F(\omega) = \frac{1}{N_i} \sum_{q\nu} \delta(\omega - \omega_{q\nu}) \sum_{k,k_n} \left| g_{k,i,k_n,j}^{q\nu} \right|^2 \delta(\epsilon_{k,i} - \epsilon_F) \delta(\epsilon_{k_n,j} - \epsilon_F),
\]

\[
\alpha^2 F(\omega) = \frac{1}{N_{tot}} \sum_{ij} N_i \alpha_{ij}^2 F(\omega),
\]

where \(i\) and \(j\) are the band indices \(\sigma\) or \(\pi\), \(N_i\) (\(N_{tot}\)) is the partial (total) electronic density of states at the Fermi level (per atom and spin), and \(g_{k,i,k_n,j}^{q\nu}\) is the e-ph matrix element for scattering of an electron from a Bloch state with momentum \(k\) to another Bloch state \(k_n = k + q\) by a phonon \(q\nu\) (\(\nu\) indicates the branch index and \(\omega_{q\nu}\) is the phonon frequency).

In a similar way, the partial and total e-ph coupling parameters (\(\lambda\)) are expressed as follows,
\[ \lambda_{ij} = 2 \int \frac{d\omega}{\omega} \alpha_{ij}^2 F(\omega), \quad (3) \]

\[ \lambda_{\text{tot}} = \frac{1}{N_{\text{tot}}} \sum_{ij} N_i \lambda_{ij}, \quad (4) \]

Within the two-band model, there are three independent contributions to \( \alpha_{ij}^2 F(\omega) \): two intraband (\( \pi\pi \) and \( \sigma\sigma \)) and one interband \( \alpha_{\pi\sigma}^2 F(\omega) = \frac{N_\pi}{N_\sigma} \alpha_{\sigma\pi}^2 F(\omega) \). With the knowledge of \( \alpha_{ij}^2 F(\omega) \), the two-band Eliashberg gap equations\(^{67-69,74} \) on the imaginary axis were numerically solved in order to obtain the gap values and \( T_c \) for each given Al or C concentration, respectively. This procedure has been previously used in similar studies of undoped MgB\(_2\).\(^{16,50} \)

The solution involves four non-linear coupled equations for the Matsubara gaps \( \Delta_i(i\omega_n) \) and the renormalization functions \( Z_i(i\omega_n) \),

\[ \Delta_i(i\omega_n)Z_i(i\omega_n) = \pi T \sum_{m,j} \left[ \Lambda_{ij}(i\omega_m - i\omega_n) - \mu_{ij}^*(\omega_c) \theta(|\omega_c - |\omega_m||) \right] N_{\Delta 1}^j(i\omega_m), \quad (5) \]

\[ Z_i(i\omega_n) = 1 + \frac{\pi T}{\omega_n} \sum_{m,j} \Lambda_{ij}(i\omega_m - i\omega_n) N_{\Delta 0}^j(i\omega_m), \quad (6) \]

where \( \theta \) is the Heaviside function, and \( \mu_{ij}^* \) is the Coulomb pseudopotential, \( \omega_c \) a cutoff frequency (chosen as \( \omega_c \approx 10 \omega_{\text{max}} \)) and \( \omega_n = \pi T(2n - 1) \), with \( n = 0, \pm 1, \pm 2, \ldots \), is the discrete set of Matsubara frequencies. The pairing interaction is contained in the kernel

\[ \Lambda_{ij}(i\omega_m - i\omega_n) = 2 \int_0^\infty \frac{\omega \alpha_{ij}^2 F(\omega) d\omega}{\omega^2 + (\omega_n - \omega_m)^2}, \quad (7) \]

and we defined the following quantities:

\[ N_{\Delta 1}^j(i\omega_m) = \frac{\Delta_j(i\omega_m)}{\sqrt{\omega_m^2 + \Delta_j^2(i\omega_m)}}, \quad (8) \]

\[ N_{\Delta 0}^j(i\omega_m) = \frac{\omega_m}{\sqrt{\omega_m^2 + \Delta_j^2(i\omega_m)}}, \quad (9) \]

In order to keep the number of adjustable parameter to a minimum, we approximated the Coulomb pseudopotential matrix \( \mu_{ij}^* \), which is a two-by-two matrix in the case of the two-band model, by a diagonal form proposed earlier\(^{75} \) as \( \mu_{ij}^* = \mu_{ij}^0 \delta_{ij} \).\(^{76} \) The gap values were identified with \( \Delta_i(i\omega_1) \), which corresponds to the point on the imaginary axis which is
closest to the real axis. Test calculations solving the Eliashberg equations on the real axis indicated that this approximation is accurate on the level of 1% or better.

III. RESULTS AND DISCUSSION

Based on our previous results for the electronic and vibrational properties, we have calculated the electron-phonon coupling quantities of the two-band model ($\alpha_{ij}^2 F(\omega)$ and $\lambda_{ij}$ with $i,j = \sigma, \pi$) for the ranges $x \leq 0.55$ and $y \leq 0.175$ in the Al- and C-doped systems, respectively.

![Graphs showing the evolution of the Eliashberg function and components](image)

FIG. 1. (Color online) Evolution of the (a) total Eliashberg function and (b) components $\alpha_{ij}^2 F(\omega)$ ($i,j = \sigma, \pi$) for the Mg$_{1-x}$Al$_x$B$_2$ alloy.

In Fig. 1 we show the evolution of the Eliashberg functions, the total spectra and the four components $\alpha_{ij}^2 F(\omega)$ ($i,j = \sigma, \pi$) of Mg$_{1-x}$Al$_x$B$_2$ for six Al concentrations in the superconducting regime ($x = 0.0, 0.1, 0.2, 0.3, 0.4,$ and $0.55$). We observe that for MgB$_2$ ($x = 0$) the largest contribution to the total spectral function comes from the $\sigma\sigma$ component, where the main peak centered at approximately 70 meV corresponds to frequency of the $E_{2g}$-phonon mode. The $\pi\pi$ spectrum has its main contribution from the high-frequency phonon region related to the $B_{1g}$-phonon mode, while the interband contribution, $\sigma\pi(\pi\sigma)$, is concentrated
in the region between 50 and 70 meV. We note that, although the $\sigma\sigma$ part represents the main contribution to the total spectra, the other components cannot be neglected in a proper quantitative description of the e-ph coupling and of the superconducting properties.

FIG. 2. (Color online) Evolution of the (a) total Eliashberg function and (b) components $\alpha^2_{ij}F(\omega)$ ($i, j = \sigma, \pi$) for the MgB$_2(1-y)$C$_2y$ alloy.

From the evolution of spectral functions for Mg$_{1-x}$Al$_x$B$_2$ (Fig. 1) we observe that almost all components are reduced by Al-doping, but the largest changes are exhibited by $\alpha^2_{\sigma\sigma}F(\omega)$. Its main peak shifts to higher frequencies and its area is reduced at the same time until it practically vanishes for $x = 0.55$. This doping level is close to the region where the loss of superconductivity has been observed experimentally ($x \gtrsim 0.5$).$^{18-21}$ The reduction of $\alpha^2_{\sigma\sigma}F(\omega)$ indicates the loss of intraband e-ph coupling between the $\sigma$ states and the bond-stretching phonon modes and has its origin in the continuous filling of the $\sigma$ bands, which is completed at $x_c = 0.57$.$^{28}$ The shift to higher frequencies is due to the hardening of the $E_{2g}$-phonon mode as $x$ increases, a phenomenon discussed previously.$^{28}$ Similar to $\sigma\sigma$, the $\pi\sigma$ interband contribution is also reduced as a function of $x$ and almost disappears at $x = 0.55$. On contrast, the $\sigma\pi$ contribution shows an slight increase around 50 and 70 meV, and the $\pi\pi$ contribution at higher frequencies strengthens slightly with doping, but the position of...
its main peak is almost unaffected. In recent electron tunneling spectroscopy measurements on Al-doped thin films, this general behavior of the Eliashberg function indeed has been observed, supporting our results.

In Fig. 2 we present the results for the Eliashberg functions of MgB$_2$(1$-y$)C$_{2y}$ for six C concentrations in the superconducting region of the alloy ($y =0.0$, 0.05, 0.1, 0.125, 0.15, and 0.175). The different components of $\alpha^2 F(\omega)$ exhibit the same trends with increasing C concentration as those found for the Al-doping. However the shape of the spectra are different and the changes take place at lower concentrations. When comparing the two alloys, one should take into account that the number of doping-induced electrons per unit cell is given by $x$ and $2y$, respectively. Even with this factor of two, the vanishing of the $\sigma\sigma$ and $\sigma\pi$ contributions at $2y \approx 0.35$ occurs at a much smaller doping level than for Al-doping ($x = 0.55$). The dramatic reduction of $\alpha^2_{\sigma\sigma} F(\omega)$ at $y \approx 0.175$ correlates also with the complete filling of the $\sigma$-bands on MgB$_2$(1$-y$)C$_{2y}$.

In Fig. 3 calculated total and partial contributions for $\lambda$ as well as for $N(E_F)$ are shown. For MgB$_2$ the calculated values are $\lambda_{\sigma\sigma} = 0.850$, $\lambda_{\sigma\pi} = 0.196$, $\lambda_{\pi\sigma} = 0.145$, $\lambda_{\pi\pi} = 0.250$, and
\( \lambda_{\text{tot}} = 0.672 \). It is worth mentioning that this \( \lambda_{\text{tot}} \) value is very close to the experimental one by Geerk \textit{et al.} \( \lambda_{\text{eff}} = 0.650 \). \( N(E_F) \) partial contributions for MgB\(_2\) are \( N_\sigma = 0.148 \) states eV\(^{-1}\)/spin and \( N_\pi = 0.200 \) states eV\(^{-1}\)/spin, which are very similar to those calculated earlier by Liu \textit{et al.} \(^{15}\) and Golubov \textit{et al.} \(^{16}\). As seen from Fig. 3, the main contribution to the e-ph coupling (\( \lambda \)) in undoped MgB\(_2\) comes from the \( \sigma \sigma \) component. Among the different contributions of the e-ph coupling, \( \lambda_{\sigma \sigma} \) shows the largest changes on doping with a reduction of \( \approx 75\% \) (comparing the boundary concentrations). The other components also decrease with doping, albeit at different scales, ranging from the nearly constant behavior of \( \lambda_{\sigma \pi} \) and \( \lambda_{\pi \pi} \) to an almost complete vanishing of \( \lambda_{\pi \sigma} \). As a consequence, \( \lambda_{\text{tot}} \) monotonically decreases with doping.

![Graph of partial contributions for MgB\(_2\)](image)

**FIG. 4.** (Color online) Evolution of \( \lambda_{ij}/N_j \) and \( \lambda_{\text{tot}}/N_{\text{tot}} \) as a function of \( x \) and \( y \) for Mg\(_{1-x}\)Al\(_x\)B\(_2\) and MgB\(_{2(1-y)}\)C\(_{2y}\), respectively. Note that \( \lambda_{\pi \sigma}/N_\sigma \equiv \lambda_{\sigma \pi}/N_\pi \).

Doping-induced changes in the coupling constants can arise from changes in the partial density of states or from changes in the e-ph matrix elements. In order to distinguish between these two possibilities, we plotted in Fig. 4 the ratios \( \lambda_{ij}/N_j \) and \( \lambda_{\text{tot}}/N_{\text{tot}} \). Indeed, a relationship \( \alpha_{ij}^2 F(\omega) \sim N_j \) and \( \lambda_{ij} \sim N_j \) can easily be derived from Eq. 1 under the
assumption of momentum-independent e-ph matrix elements. The ratios \( \lambda_{ij}/N_j \) for the interband (\( \lambda_{\sigma\pi}, \lambda_{\pi\sigma} \)) as well as for the intraband \( \lambda_{\pi\pi} \) couplings remain practically constant as a function of doping for both alloys, indicating that the corresponding e-ph matrix elements are approximately independent of doping. However, for the (\( \sigma\sigma \)) intraband coupling, the ratio exhibits a stronger variation with doping, in particular for Al doping, which signals a clear doping dependence of the e-ph matrix elements. In this case, a simple scaling with the partial density of states would be inappropriate to describe the doping dependence of \( \lambda_{\sigma\sigma} \).

![Graph showing temperature dependence of superconducting gaps](image)

FIG. 5. (Color online) Temperature dependence of the superconducting gaps \( \Delta_{\sigma} \) and \( \Delta_{\pi} \) (solid lines) for undoped MgB\(_2\) as obtained from the two-band Eliashberg gap equations. Symbols represent experimental data (\( \blacktriangle \) Gonnelli et al., (○) Iavarone et al., (△) Szabo et al., and (♦) Schmidt et al.). The calculated gap values at \( T \to 0 \) K are \( \Delta_{\sigma} = 7.04 \) meV and \( \Delta_{\pi} = 2.71 \) meV.

To solve the Eliashberg gap equations, we determined the single remaining parameter, the Coulomb pseudopotential \( \mu_0^* \), by the requirement that for undoped MgB\(_2\) the experimental transition temperature of \( T_c = 38.82 \mathrm{K} \)\(^{31,34} \) is reproduced. For a cutoff frequency \( \omega_c = 10\omega_{\text{max}} \)\(^{ph} \), we found \( \mu_0^* = 0.107 \). The resulting temperature dependence of the superconducting gaps is shown in Fig. 5 and compared with available experimental data\(^{7,9,34} \). The gap values for \( T \to 0 \) K are \( \Delta_{\sigma} = 7.04 \) meV and \( \Delta_{\pi} = 2.71 \) meV, respectively, in good agreement with experimental results\(^{8,9,34} \).
The same two-band Eliashberg approach was adopted for the alloys Mg$_{1-x}$Al$_x$B$_2$ and MgB$_{2(1-y)}$C$_{2y}$ keeping $\mu_0^*$ at the obtained value for undoped MgB$_2$. The doping dependence of $\Delta_\sigma$, $\Delta_\pi$, and $T_c$ for both alloys is presented in Fig. 6 and compared with experimental data$^{18,20–26,30–35,37,38}$. The calculations reproduce the experimental trends that both gaps and $T_c$ decrease with increasing Al or C doping. Beside this common feature the two alloys exhibit also striking differences. The first concerns the doping range where superconductivity exists. $T_c$ goes to zero close to the critical concentration for which the $\sigma$-band is completely filled ($x_c$(Al) = 0.57, $y_c$(C) = 0.177)$^{28}$. Thus, superconductivity vanishes significantly faster on C doping than on Al doping, even when taking into account that one should compare doping levels $x = 2y$ as discussed above. The second difference relates to the shape of the $T_c$ versus doping curves. For Al doping, $T_c$ initially drops fast and develops a longer tail,
whereas for C doping $T_c$ is only slowly reduced initially, while it exhibits a steeper drop towards the critical concentration where $T_c$ vanishes. A similar difference in shape is also observed for the larger gap. As both alloys are electron-doped systems, these differences indicate the importance of the doping site for the superconducting properties. As explained in Refs. 27 and 28, the origin of this difference can be traced back to the distribution of the extra charge introduced by doping. In the Al-doped system an important portion of the extra electrons is located in the interplanar region, and only a small fraction in the boron planes. In contrast, for C doping the extra charge mainly remains in the area between the B atoms within the boron plane, exactly in the region of the $\sigma$-bonds. Therefore, the extra charge introduced by C doping is more effective in reducing the number of holes in the $\sigma$-band and has a stronger influence on the phonon frequencies, in particular, on the hardening of the $E_{2g}$ mode. Consequently, C doping leads to a faster decrease of the e-ph coupling and of the superconducting properties as compared to Al doping.

The various experimental data sets for $T_c$ and the gaps plotted in Fig. 6 exhibit a clear spread indicating a large dependence of the superconducting properties on the sample preparation methods and on the physical conditions of the measurement procedure itself. In addition, an accurate determination of the actual doping concentration in these alloys is complicated and far from trivial. Furthermore, there is so far no consensus about the behavior of the gaps for larger C doping. While some experiments suggest a merging of the $\Delta_\sigma$ and $\Delta_\pi$ gap at $y \approx 0.13^{31,34}$, others find two distinct gaps even for the highest doping levels$^{33,37,38}$. Within these experimental uncertainties, our calculations agree quantitatively with the data for both alloys. In particular, the different doping regimes are obtained in a natural way. We recall that our study involved only a single free parameter, $\mu_0^*$, which was fixed for the undoped system and which does not directly affect the doping dependence or the gap anisotropy.

In agreement with experimental data, the present calculation predicts for both alloys a stronger influence of doping on the $\sigma$ gap, which follows approximately the doping dependence of $T_c$. On contrast, the $\pi$ gap remains rather stable and only slowly decreases on doping. This is at variance with a previous ab initio study based on the fully anisotropic gap equations by Choi et al.$^{44}$, where doping was modeled by simply introducing excess electrons. For a moderate doping level of $x = 0.2$ ($y = 0.1$), they found a severe degradation of the $\pi$ gap while the $\sigma$ gap was more robust. This failure of a rigid-band-like type approach
indicates that a more self-consistent site-dependent treatment of the doping is required for a proper description of the superconducting properties in doped MgB$_2$.

Two previous computational studies$^{51,52}$ of the superconducting properties of MgB$_2$ alloys adopted a scaling scheme to describe the doping dependence. The Eliashberg functions for the undoped compound were scaled taking into account the doping dependence of $N(E_F)$ and of the $E_{2g}$ phonon frequency. As such an approach does not discriminate between the doping sites, Kortus et al.$^{52}$ argued that the differences observed for Al and C doping are due to a larger interband scattering for C than for Al doping. The present study, however, demonstrates that the difference between Al and C doping appears naturally within the VCA approach, without the need to introduce another free parameter such as the interband scattering, as long as the influence of doping on the structure and on the lattice dynamics is properly taken into account.

**IV. CONCLUSIONS**

We have performed a first-principles study of the electron-phonon coupling and superconducting properties for the Mg$_{1-x}$Al$_x$B$_2$ and MgB$_2$(1−$y$)C$_{2y}$ alloys as a function of $x$ and $y$, respectively, by combining the self-consistent virtual-crystal approximation and the two-band Eliashberg model. For undoped MgB$_2$, the Eliashberg function possess a main peak at around 70 meV related to the $E_{2g}$-phonon mode coming from the $\sigma\sigma$ contribution, and a sharper peak at 90 meV which originates largely from the $\pi\pi$ contribution, and is related to the $B_{1g}$-phonon mode. The total coupling constant $\lambda_{tot} = 0.67$ agrees with the experimental value of 0.65 as deduced from tunneling measurements. For the alloys we found that $\alpha^2F(\omega)$ depends very sensitively on doping. It exhibits pronounced changes both in shape and in position of its main peaks, which renders any attempt to derive it from the spectrum of undoped MgB$_2$ via scaling procedures very unreliable. The calculated evolution of the Eliashberg functions compare well with recent electron tunneling spectroscopy measurements on Al-doped thin films. The e-ph coupling parameter and its different contributions decrease as a function of doping for both alloys. Although both Al and C dopants donate electrons, the e-ph coupling exhibits a clear dependence on the doping site, which is also reflected in $\alpha^2F(\omega)$. With the Coulomb pseudopotential fixed for the undoped compound, we could reproduce the experimental doping dependence of $\Delta_\sigma$, $\Delta_\pi$, and $T_c$ for both alloys.
The observed differences between Al and C doping, like the doping range of superconductivity, are naturally obtained in the present VCA approach, without the need to invoke other factors, as, e.g., interband scattering. These results emphasize that a quantitative description of the superconducting properties of the two MgB$_2$ alloys require a proper treatment of the doping at least on the level of VCA, and suggest that interband scattering plays only a minor role.

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In some previous works (Refs. 77–79) also an uniform matrix form for the Coulomb pseudopotential matrix has been adopted. It has been demonstrated that this specific form underestimates considerably the value of $\Delta_\pi$ (Ref. 75). However, we tested another form used in previous publications (Refs. 16 and 51) where the diagonal elements are considered to be different between them additionally off-diagonal ones are included, nevertheless they are much smaller than the diagonal ones. Results in Section III were practically the same for both forms, except for a slight reduction of $\Delta_\pi$ by 10%.

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