High $T_c$ superconductivity in MgB$_2$ by nonadiabatic pairing

E. Cappelluti$^1$, S. Ciuchi$^2$, C. Grimaldi$^3$, L. Pietronero$^{1,4}$, and S. Strässler$^3$

$^1$Dipart. di Fisica, Università di Roma “La Sapienza”, Piazzale A. Moro, 2, 00185 Roma, and INFN UdR Roma1, Italy
$^2$Dipart. di Fisica, Università dell’Aquila, v. Vetoio, 67010 Cappito-L’Aquila, and INFN UdR l’Aquila, Italy
$^3$Ecole Polytechnique Fédérale de Lausanne, IPR-LPM, CH-1015 Lausanne, Switzerland
$^4$Istituto di Acustica “O.M. Corbino”, CNR, Area di Ricerca Tor Vergata, Roma, Italy

The evidence for the key role of the $\sigma$ bands in the electronic properties of MgB$_2$ points to the possibility of nonadiabatic effects in the superconductivity of these materials. These are governed by the small value of the Fermi energy due to the vicinity of the hole doping level to the top of the $\sigma$ bands. We show that the nonadiabatic theory leads to a coherent interpretation of $T_c = 39$ K and the boron isotope coefficient $\alpha_B = 0.30$ without invoking very large couplings and it naturally explains the role of the disorder on $T_c$. It also leads to various specific predictions for the properties of MgB$_2$ and for the material optimization of these type of compounds.

The field of high-$T_c$ superconductivity is living an exciting time. New techniques provide in fact the possibility to explore physical regimes that were previously inaccessible and superconducting materials which were often regarded as “conventional” BCS ones, as the fullerenes, have proven to be real high-$T_c$ compounds. In this context the magnesium diboride MgB$_2$, which was recently found to be superconductor with $T_c = 39$ K, is a promising material. The question is to assess whether MgB$_2$ is one of the best optimized BCS materials or its superconducting properties stem from a novel mechanism of pairing and can be further improved in MgB$_2$ or in related compounds. In this Letter we would like to discuss some theoretical and experimental evidences that in our opinion point towards an unconventional type for the superconductivity, which we identify with the nonadiabatic framework.

MgB$_2$ is often regarded in literature as a conventional BCS-like superconductors, whose properties could be well described by the standard Migdal-Eliashberg (ME) theory. The high value of $T_c$ is thus ascribed to the high frequency B-B phonon modes in the presence of an intermediate or strong electron-phonon (el-ph) coupling $\lambda$. LDA calculations find in fact $\lambda \approx 0.7 - 0.9$ which, all together with the representative phononic energy scale $\omega_{ph} \approx 650 - 850$ K, is in principle able to account for the large value of $T_c$ in MgB$_2$ [3,4]. However this picture is shaken by a series of facts. First, recent reflectance data are not consistent with a value of $\lambda$ strong enough to give $T_c = 39$ K [10]. Second, the experimental determination of the total isotope effect on $T_c$ reported a boron isotope coefficient $\alpha_B = 0.30$ and a negligible magnesium isotope effect [11]. Preliminary indications suggest that this value of $\alpha$ cannot be explained by the LDA estimates of $\lambda \approx 0.7 - 0.9$, but requires a much larger coupling $\lambda \approx 1.4$ [11]. We have solved numerically the Eliashberg equations to reproduce the experimental value of the isotope coefficient. We consider a rectangular Eliashberg function $[\alpha^2 F(\omega) = \text{const. for } 650 \text{ K} \leq \omega \leq 850 \text{ K}]$ as well as a simple Einstein spectrum with frequency $\omega_0$.

The limiting values $\omega_0 = 650$ K and $\omega_0 = 850$ K of the Einstein model can be thus considered respectively as lower and upper bounds of a realistic Eliashberg function. In Fig. 1 we show the critical temperature $T_c$ as function of $\lambda$ for fixed value of $\alpha = 0.30$. The corresponding needed Coulomb pseudopotential varies in the range $\mu^* \approx 0.28 - 0.30$ and does not depend on the specific Eliashberg function. We can see that a quite strong el-ph coupling is required to reproduce both $T_c = 39$ K and $\alpha = 0.30$ with $\lambda$ ranging from 1.4 to 1.7. These values of $\lambda$ and $\mu^*$ are thus even larger than the estimations of Ref. [11], confirming and reinforcing the discrepancy between LDA results and the ME analysis of the experimental data (see also Ref. [12]). Note that, contrary to cuprates and fullerenes, electronic correlation is not expected to play a significant role in MgB$_2$, and LDA calculations should be considered quantitatively reliable.

This analysis therefore points towards a more complex framework to understand superconductivity in MgB$_2$. An useful insight, in our opinion, comes from a comparison of the electronic structure of MgB$_2$ and graphite.

![Graph](https://via.placeholder.com/150)

**FIG. 1.** Critical temperature $T_c$ as function of $\lambda$ for fixed value of boron isotope effect $\alpha_B = 0.30$. Solid line corresponds to the rectangular Eliashberg function, grey region represents the solutions spanned by the Einstein model with frequency $650 \text{ K} \leq \omega_0 \leq 850$ K. The dashed line marks the value $T_c = 39$ K.
These two compounds are indeed structurally and electronically very similar. A main difference is the relative position of the $\sigma$ and $\pi$ bands with respect to the chemical potential $\mu$. In undoped graphite the Fermi energy cuts the $\pi$ bands just at the $K$ point, where the density of states (DOS) vanishes. Doping graphite with donors or acceptors, however, shifts the chemical potential $\mu$ of $\approx \pm 1$ eV providing metallic charges in the system and a finite DOS $\sigma$. This situation, on the other hand, is naturally accounted in MgB$_2$, where $\mu$ lies well below the $\pi$-band crossing at the $K$ point and even crosses the two $\sigma$ bands (see Fig. 2 where a pictorial sketch of the band structure is drawn). Note that in the conventional ME context the only electronic relevant parameter is just the DOS at the Fermi level $N(0)$. From this point of view the difference between the superconducting properties of MgB$_2$ with $T_c = 39$ K and intercalated doped graphite with $T_c$ up to $0.55$ K at ambient pressure is hard to justify since both the materials show similar $N(0)$. Such a comparison suggests that the origin of the high-$T_c$ phase in MgB$_2$ should be sought among the features which differentiate MgB$_2$ from doped graphite.

A similar impasse was encountered in the ME description of superconductivity in fullerenes, which also share many similarities with graphite. Even there, LDA estimates of the el-ph coupling $\lambda$ were insufficient to account for the high $T_c$ and for the small isotope effect. Such a discrepancy has been explained in terms of opening of nonadiabatic channels which, under favourable conditions fulfilled in fullerenes, can effectively enhance the superconducting pairing $\text{[4]}$. A key role is played by the small Fermi energy $E_F$ that in fullerenes is of the same order of the phonon frequency, violating the adiabatic assumption ($\omega_{\text{ph}} \ll E_F$). In this situation Migdal’s theorem $\text{[13]}$, on which conventional ME theory relies, breaks down. The proper inclusion of the nonadiabatic contributions follows the framework of Ref. $\text{[4]}$ and leads to a new set of equations for superconductivity $\text{[17]}$:

$$Z(\omega_n) = 1 + \frac{T_c}{\omega_n} \sum_{\omega_m} \Gamma Z(\omega_n, \omega_m, Q_c) \eta_m,$$  \hspace{1cm} (1)

$$Z(\omega_n)\Delta(\omega_n) = T_c \sum_{\omega_m} \Gamma_{\Delta}(\omega_n, \omega_m, Q_c) \frac{\Delta(\omega_m)}{\omega_m} \eta_m,$$ \hspace{1cm} (2)

where $\eta_m = 2 \arctan\{E_F/|Z(\omega_m)|\}$, $Z(\omega_n)$ is the renormalization function and $\Delta(\omega_n)$ is the superconducting gap function in Matsubara frequencies. The breakdown of Migdal’s theorem strongly affects the “on-diagonal” $\Gamma_Z$ and the “off-diagonal” $\Gamma_{\Delta}$ el-ph kernels which include now vertex and cross contributions $\text{[4]}$:

$$\Gamma_Z(\omega_n, \omega_m, Q_c) = \lambda D(\omega_n - \omega_m)[1 + \lambda P(\omega_n, \omega_m, Q_c)],$$

$$\Gamma_{\Delta}(\omega_n, \omega_m, Q_c) = \lambda D(\omega_n - \omega_m)[1 + 2\lambda P(\omega_n, \omega_m, Q_c)] + \lambda^2 C(\omega_n, \omega_m, Q_c) - \mu,$$

where $D(\omega_n - \omega_m)$ is the phonon propagator and $\mu$ the dynamically unscreened Coulomb repulsion, to be not confused with the chemical potential. The vertex and cross functions, $P(\omega_n, \omega_m, Q_c)$ and $C(\omega_n, \omega_m, Q_c)$, represent an average of the nonadiabatic diagrams over the momentum space probed by the el-ph scattering, parametrized by the quantity $Q_c$.

In the nonadiabatic context outlined above, the role of the $\sigma$ bands in MgB$_2$ acquires a new and interesting perspective. Indeed the Fermi energy of these bands $E_F^\sigma$ is also quite small, $E_F^\sigma \approx 0.4 - 0.6$ eV $\text{[4]}$, leading to $\omega_{\text{ph}}/E_F^\sigma \sim 0.1 - 0.2$. These values, together the sizable $\lambda \approx 1$, point towards a similar size of the vertex corrections $\lambda \omega_{\text{ph}}/E_F \sim 0.1 - 0.2$ and nonadiabatic channels induced by the breakdown of Migdal’s theorem can be therefore expected to be operative. In this situation it is clear that the use of conventional ME framework can lead to inconsistent results and a nonadiabatic approach is unavoidable. The scenario we propose is the following:

- MgB$_2$ can be described as a multiband system with two conventional ME bands $\pi$ (with large $E_F^\pi > 3$ eV) and two nonadiabatic bands $\sigma$ ($E_F^\sigma \approx 0.4 - 0.6$ eV).
- $\pi$ bands can be in good approximation can be considered as conventional. They could possibly contribute to the dynamical screening of $\mu^*$ and to the static screening (Thomas-Fermi like) of the long-range el-ph interaction. They can also lead to the opening of a smaller superconducting gap in the $\pi$ bands which does not probed directly nonadiabatic effects.
In previous studies we showed that the vertex function $\omega$ where electronic correlation.
positive in the whole region of the vertex function will be enlarged and will
high-frequency diabatic) channels of el-ph interactions. Origin of the
vertex function is strongly dependent on the position of the chemical potential. In particular for almost filled band
systems, as MgB$_2$, the vertex structure becomes shapeless and positive (solid lines). In such a situation the contri-
tribution of the nonadiabatic vertex function is positive in the whole momentum space, and nonadiabatic chan-
nels are expected to enhance $T_c$ regardless the amount of electronic correlation. This trend is shown in Fig. 3c
where the enhancement of $T_c$ due to nonadiabatic vertex corrections is reported. The calculation of $T_c$ follows
a procedure similar to the one employed in Ref. [14], where the vertex and cross functions are replaced by their re-
pective averages over the momentum transfer and by setting $\omega_n - \omega_m = \omega_0$. Note how, as $\mu$ moves towards the
top of the band (panel b), $T_c$ gets significantly enhanced by the opening of nonadiabatic channels already for val-
ues of $\lambda$ consistent with the LDA calculations. Similar results were reported within the infinite dimensions ap-
proximation [22].

It should be noted that the almost 2D character is an important ingredient for having a substantial value of $T_c$
because the density of states remains finite at the band edge [1]. A 3D parabolic hole doped band would in fact
lead to a DOS proportional to $\sqrt{|\mu|}$, which vanishes as $\mu$ goes to zero. Additional effects can moreover arise from
an intrinsic momentum modulation of the el-ph interaction. Low values of hole doping would in fact enlarge the
screening length leading to an el-ph interaction peaked at small momentum transfer. A similar argument was
proposed for instance in relation to copper oxides [23] and, in principle, it could explain the reflectance data in MgB$_2$ [10]. Both the argumentations can of course hold true and coexist in MgB$_2$, explaining the high-$T_c$ super-
conductivity in this material as effect of a nonadiabatic el-ph pairing.

We would like to stress that, once $\sigma$ bands are accepted to play a key role in the superconducting pair-
ing of MgB$_2$, nonadiabatic effects are unavoidably present due to the smallness of their Fermi energy. The onset
of nonadiabatic channels can thus provide a natural ex-
planation for the inconsistency between the theoretical values of $\lambda$ calculated by LDA technique ($\lambda \simeq 0.7 - 0.9$)
and the high value $\lambda \gtrsim 1.4$ needed to reproduce experimental data $T_c = 39$ K and $\alpha = 0.30$.

Signatures of a nonadiabatic interaction can be found however in other anomalous properties of MgB$_2$. The
analysis of these features can provide further independent evidences for the nonadiabatic pairing and suggest
precise experimental tests.

**Impurities and chemical doping.** A remarkable

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**FIG. 3.** (a) Momentum structure of the vertex function for a parabolic 2D hole-like band. Different curves correspond to different hole-fillings shown in panel (b). (c) Estimate of the enhancement of $T_c$ for the nonadiabatic vertex theory with respect to the ME one.

- High-$T_c$ superconductivity is mainly driven by $\sigma$-band states. The peculiar feature of such bands is the smallness of the Fermi energy which induces new (nonadiabatic) channels of el-ph interactions. Origin of the high-$T_c$ superconductivity is the effective enhancement of the superconducting pairing as long as vertex corrections result positive $[P(\omega_n, \omega_m, Q_c) > 0]$.

As seen in the last item, an important element in this scenario is the overall sign of the nonadiabatic effects, which governs the enhancement or the suppression of $T_c$. In previous studies we showed that the vertex function $P$ roughly obeys the simple relation [18][19]:

\[
\begin{cases}
  P > 0 & v_F q / \omega \lesssim 1 \\
  P < 0 & v_F q / \omega \gtrsim 1
\end{cases}
\]  

where $\omega$ is a generic exchanged energy involved in the scattering of order of $\omega_{ph}$, and $v_F$ is the Fermi velocity. In fullerene compounds, the strong electronic correlation favours the small $q$ momentum el-ph coupling $[v_F q / \omega \lesssim 1]$ [20] probing therefore the positive part of the vertex function $P$.

In MgB$_2$ the situation is deeply different. In fact the nonadiabatic regime in MgB$_2$ is related to the closeness of the Fermi level to the top of the 2D $\sigma$-bands, and the non trivial dependence of the momentum-frequency structure of $P$ on the filling has thus to be taken into account [21]. To this regard, Eq. (2) is very helpful to illustrate this point since, for parabolic hole bands, $v_F \propto \sqrt{|\mu|}$ where $\mu$ is the chemical potential with respect to the top of the band. As $\mu$ is made smaller, the positive region of the vertex function will be enlarged and will eventually cover the whole momentum space. Hence, in MgB$_2$ the nonadiabatic vertex diagrams are intrinsically positive in the whole momentum space regardless any electronic correlation.

In Fig. 3 we show the numerical calculation of the

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\[
\sigma
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reduction of $T_c$ upon radiation-induced disorder has recently been observed in MgB$_2$ \cite{22}, in contrast with Anderson’s theorem. This kind of reduction in a $s$-wave superconductor has been shown to be one of the characteristic features of a nonadiabatic pairing \cite{23}, as seen for instance in fullerenes \cite{26}. The experimentally observed reduction of $T_c$ can be therefore a further evidence of nonadiabatic superconductivity. Similar conclusions can be drawn by the analysis of the chemical substitutional doping in MgB$_2$. In fact, both electron \cite{27} and hole \cite{28} doped materials show a lower $T_c$ than the pure stoichiometric MgB$_2$. It is clear however that the contemporary suppression of $T_c$ upon electron or hole doping can not be understood in terms of band filling. We suggest a much more plausible scenario, namely that the stoichiometric disorder induced by chemical substitution to be mainly responsible for the reduction of $T_c$, with band filling as a secondary effect. Again, since nonmagnetic ion substitution does not break time reversal symmetry and Anderson’s theorem in ME theory, a nonadiabatic pairing appears as a natural explanation. To test this picture the comparison with some completely substituted compounds would be interesting.

**Isotope effects.** The detection of isotope effects on various quantities receives a crucial importance in the nonadiabatic framework since it directly probes the nonadiabatic nature of el-ph interaction. In particular it has been shown that nonadiabatic effects give rise to a finite isotope effect on quantities which in conventional ME theory are expected to not show it, for instance the effective electron mass $m^* \left[29\right]$ and the spin susceptibility $\chi \left[30\right]$. The actual discovery of an anomalous isotope effects on these or other quantities represents therefore a precise prediction of the nonadiabatic theory which could be experimentally checked.

**New high-$T_c$ materials.** Interesting suggestions can come from the proposed nonadiabatic scenario in regard to material engineering and superconductivity optimization. According the analysis above discussed, a crucial difference between low-$T_c$ doped graphite and high-$T_c$ MgB$_2$ is the upward shift of the $\sigma$ bands and their consequent cutting of the Fermi level. The study of the relative position of the $\sigma$ bands with respect of the $\pi$ bands, and of both of them with respect to the chemical potential approaches therefore extremely interesting. In particular we would suggest that high-$T_c$ superconductivity could be achieved in MgB$_2$-like materials when Fermi level is lower but very close to the top of the $\sigma$ bands. On the contrary we predict no high-$T_c$ superconductivity in the same family if compounds when i) Fermi level does not cross the $\sigma$ bands, ii) or where the Fermi level is very distant from the top of the $\sigma$ bands ($E_F > 1$ eV) and the system looses its nonadiabatic nature. Theoretical calculations which can stimulate material engineering in this sense are in progress. A potential candidate would be the hole doped graphite as long as Fermi level could be lowered to cut the underneath $\sigma$ bands or the $\sigma$ bands arisen by electrostatic effects. High level of chemical doping by acceptor intercalation was for long time unsuccessful in graphite as well as in C$_{60}$ since such compounds resulted unstable \cite{13}. The recent discoveries of superconductivity at $T_c = 35$ K in graphite-sulphur compounds \cite{31} and at $T_c = 117$ K in FET hole-doped fullerenes \cite{2} could thus both arise from the unifying framework of the nonadiabatic superconductivity. We thus encourage renewed work along these lines.

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