High T_c Superconductivity in MgB_2 by Nonadiabatic Pairing

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The evidence for the key role of the σ 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 σ 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 types of compounds.

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The field of high-T_c superconductivity is experiencing an exciting time [1]. 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 [2]. In this context the magnesium diboride MgB_2, which was recently found to be a superconductor with $T_c = 39$ K [3], is a promising material. The issue is to assess whether MgB_2 is one of the best optimized BCS materials or whether 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 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 superconductor, 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 λ. Local density approximation (LDA) calculations find in fact $\lambda \simeq 0.7-0.9$ which, all together with a representative phononic energy scale $\omega_{ph} \simeq 650-850$ K, is in principle able to account for the large value of T_c in MgB_2 [4–8]. However this picture is shaken by a series of facts. First, recent reflectance data are not consistent with a value of λ strong enough to give $T_c = 39$ K [9,10]. 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 α cannot be explained by the LDA estimates of $\lambda \simeq 0.7-0.9$ but requires a much larger coupling $\lambda \simeq 1.4$ [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 $650 \leq \omega \leq 850$ K] as well as a simple Einstein spectrum with frequency ω_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 a function of λ for a fixed value of $\alpha = 0.30$. The corresponding needed Coulomb pseudopotential varies in the range $\mu^* \simeq 0.28-0.30$ 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 λ ranging from 1.4

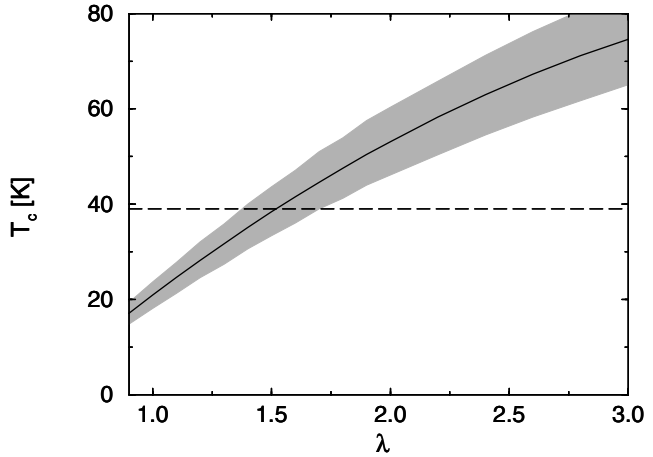

FIG. 1. Critical temperature T_c as a function of λ for a fixed value of boron isotope effect $\alpha_B = 0.30$. The solid line corresponds to the rectangular Eliashberg function; the grey region represents the solutions spanned by the Einstein model with frequency $650 \leq \omega_0 \leq 850$ K. The dashed line marks the value $T_c = 39$ K.

to 1.7. These values of λ and μ^* 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. A useful insight, in our opinion, comes from a comparison of the electronic structure of MgB_2 and graphite. These two compounds are indeed structurally and electronically very similar. The main difference is the relative position of the σ and π bands with respect to the chemical potential μ. In undoped graphite the Fermi energy cuts the π bands just at the K point, where the density of states (DOS) vanishes. Doping graphite with donors or acceptors, however, shifts the chemical potential μ of $\simeq \pm 1$ eV providing metallic charges in the system and a finite DOS [13]. This situation, on the other hand, is naturally accounted in MgB_2, where μ lies well below the π-band crossing at the K point and even crosses the two σ 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.

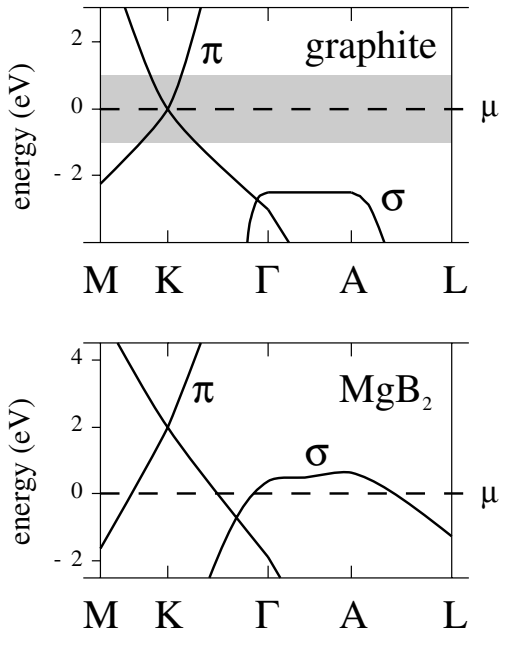

FIG. 2. Schematic band structure of graphite (top panel) and MgB_2 (bottom panel). The grey region in the top panel indicates the doping region achieved by chemical intercalation of graphite (± 1 eV).

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 λ 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 favorable conditions fulfilled in fullerenes, can effectively enhance the superconducting pairing [14]. 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 ($\omega_{ph} \ll E_F$). In this situation Migdal's theorem [15], on which conventional ME theory relies, breaks down. The proper inclusion of the nonadiabatic contributions follows the framework of Ref. [16] and leads to a new set of equations for superconductivity [17]:

$$Z(\omega_n) = 1 + \frac{T_c}{\omega_n} \sum_{\omega_m} \Gamma_Z(\omega_n, \omega_m, Q_c) \eta_m , \qquad (1)$$

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

where $\eta_m = 2 \arctan\{E_F/[Z(\omega_m)\omega_m]\}$, $Z(\omega_n)$ 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" Γ_Z and the "off-diagonal" Γ_Δ el-ph kernels which include now vertex and cross contributions [16]:

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

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

where $D(\omega_n - \omega_m)$ is the phonon propagator and μ is the dynamically unscreened Coulomb repulsion, not to be 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 σ bands in MgB_2 acquires a new and interesting perspective. Indeed the Fermi energy of these bands E_F^σ is also quite small, $E_F^\sigma \sim 0.4$–0.6 eV [5], leading to $\omega_{ph}/E_F \sim 0.1$–0.2. These values, together with the sizable $\lambda \sim 1$, point towards a similar size of the vertex corrections $\lambda\omega_{ph}/E_F \sim 0.1$–$0.2$ and nonadiabatic channels induced by the breakdown of Migdal's theorem can therefore be expected to be operative. In this situation it is clear that the use of a conventional ME framework can lead to inconsistent results and a nonadiabatic approach is unavoidable. The scenario we propose is the following:

(i) MgB_2 can be described as a multiband system with two conventional ME bands π (with large $E_F^\pi > 3$ eV) and two nonadiabatic bands σ ($E_F^\sigma \sim 0.4$–0.6 eV).

(ii) π bands can be in good approximation and can be considered as conventional. They could possibly contribute to the dynamical screening of μ^* 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 π bands which does not directly probe nonadiabatic effects.

(iii) High-T_c superconductivity is mainly driven by σ-band states. The peculiar feature of such bands is the smallness of the Fermi energy which induces new (nonadiabatic) channels of el-ph interactions. The origin of the high-T_c superconductivity is the effective enhancement of the superconducting pairing as long as vertex corrections become 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]:

$$\begin{cases} P > 0 & v_F q/\omega \lesssim 1\,, \\ P < 0 & v_F q/\omega \gtrsim 1\,, \end{cases} \tag{3}$$

where ω is a generic exchanged energy involved in the scattering of order of ω_{ph}, and v_F is the Fermi velocity. In fullerene compounds, the strong electronic correlation favors 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 considerably different. In fact, the nonadiabatic regime in MgB_2 is related to the closeness of the Fermi level to the top of the 2D σ bands, and the nontrivial dependence of the momentum-frequency structure of P on the filling has thus to be taken into account [21]. To this regard, Eq. (3) is very helpful to illustrate this point since, for parabolic hole bands, $v_F \propto \sqrt{|\mu|}$, where μ is the chemical potential with respect to the top of the band. As μ 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 of any electronic correlation.

In Fig. 3 we show the numerical calculation of the momentum structure (panel a) of the vertex function $P(\omega_n, \omega_m, Q)$ ($Q = q/2k_F$) for different hole fillings of a 2D parabolic holelike band (panel b). In panel a, the exchanged energy $\omega_n - \omega_m$ has been set equal to $\omega_0/2$, where ω_0 is an Einstein phonon representing the characteristic phonon energy scale. The structure 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 contribution of the nonadiabatic vertex function is

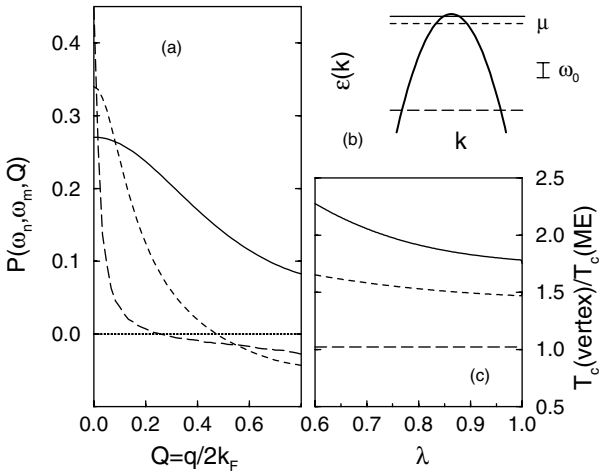

FIG. 3. (a) Momentum structure of the vertex function for a parabolic 2D holelike band. Different curves correspond to different hole fillings shown in panel (b). (c) Estimate of the enhancement of T_c for the nonadiabatic vertex theory with respect to the ME one.

positive in the whole momentum space, and nonadiabatic channels are expected to enhance T_c regardless of 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. [19], where the vertex and cross functions are replaced by their respective averages over the momentum transfer and by setting $\omega_n - \omega_m = \omega_0$. Note how, as μ moves towards the top of the band (panel b), T_c gets significantly enhanced by the opening of nonadiabatic channels already for values of λ consistent with the LDA calculations. Similar results were reported within the infinite dimensions approximation [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 [5]. A 3D parabolic hole-doped band would in fact lead to a DOS proportional to $\sqrt{|\mu|}$, which vanishes as μ 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 [9,10]. Both the arguments can of course hold true and coexist in MgB_2, explaining the high-T_c superconductivity in this material as an effect of a nonadiabatic el-ph pairing.

We stress that once σ bands are accepted to play a key role in the superconducting pairing 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 explanation for the inconsistency between the theoretical values of λ calculated by the

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 reduction of T_c upon radiation-induced disorder has recently been observed in MgB_2 [24], in contrast with Anderson's theorem. This kind of reduction in an s-wave superconductor has been shown to be one of the characteristic features of a nonadiabatic pairing [25], as seen, for instance, in fullerenes [26]. The experimentally observed reduction of T_c can therefore be 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 [27] and hole-doped [28] 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 cannot be understood in terms of band filling. We suggest a much more plausible scenario, namely, that the stoichiometric disorder induced by chemical substitution is 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^* [29] and the spin susceptibility χ [30]. The actual discovery of 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 to the analysis discussed above, a crucial difference between low-T_c doped graphite and high-T_c MgB_2 is the upward shift of the σ bands and their consequent cutting of the Fermi level. The study of the relative position of the σ bands with respect to the π bands, and of both of them with respect to the chemical potential appears therefore extremely interesting. In particular, we suggest that high-T_c superconductivity could be achieved in MgB_2-like materials when the Fermi level is lower but very close to the top of the σ bands. On the contrary we predict no high-T_c superconductivity in the same family of compounds when (i) Fermi level does not cross the σ bands or (ii) where the Fermi level is very distant from the top of the σ bands ($E_F > 1$ eV) and the system loses its nonadiabatic nature. Theoretical calculations which can stimulate material engineering in this sense are in progress. A potential candidate is hole-doped graphite as long as the Fermi level can be lowered to cut the underneath σ bands or the σ bands arisen by electrostatic effects. A high level of chemical doping by acceptor intercalation was for long time unsuccessful in graphite as well as in C_{60} since such compounds became unstable [13]. The recent discoveries of superconductivity at $T_c = 35$ K in graphite-sulfur compounds [31] and at $T_c = 117$ K in field effect hole-doped fullerenes [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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