Nonadiabatic superconductivity in MgB<sub>2</sub> and cuprates

A.S. Alexandrov

Department of Physics, Loughborough University, Loughborough LE11 3TU, UK

The Fermi energy, \( E_F \), of newly discovered high-\( T_c \) superconductor MgB\(_2\) and cuprates is estimated from the measured London penetration depth using a parameter-free expression. \( E_F \) of MgB\(_2\) and more than 30 lanthanum, yttrium and mercury-based cuprates appears to be about or below 100 meV, depending on doping. There is every evidence that the remarkable low value of \( E_F \) and the strong coupling of carriers with high-frequency phonons is the cause of high \( T_c \) in all newly discovered superconductors. Taking into account that the carriers mainly reside on oxygen in cuprates, on boron in magnesium diboride, and on carbon in doped fullerenes, these superconductors form what is essentially nonadiabatic ‘metallic’ oxygen, boron and carbon, respectively. The boron isotope effect on the carrier mass in magnesium-diboride similar to the oxygen isotope effect on the supercarrier mass observed by Guo-meng Zhao et al. in cuprates is predicted.

One of the common features of all newly discovered high-temperature superconductors \((T_c \geq 30K)\) is a strong coupling of carriers with optical phonons, as follows from the experimental values of their static and high-frequency dielectric constants [4], other optical probes [5, 6], isotope effect [3, 4], photoemission [5], tunneling [7], and first-principles band structure calculations. Hence, it is natural to expect that the Migdal-Eliashberg [8] BCS-like approach to coupled system of electrons and phonons would account for their normal state and superconducting properties. The approach is based on “Migdal’s theorem” [9], which showed that the contribution of the diagrams with ‘crossing’ phonon lines (so called ‘vertex’ corrections) is small if the parameter \( \lambda \omega/E_F \) is small \((h = k_B = c = 1)\). Neglecting the vertex corrections, Migdal calculated the renormalized electron mass as \( m^* = m(1 + \lambda) \) (near the Fermi level) [10] and Eliashberg later extended the Migdal theory to describe the BCS superconducting state at intermediate values of the electron-phonon (BCS) coupling constant \( \lambda \) [11] by breaking the gauge symmetry. The same theory, applied to phonons, yields the renormalized phonon frequency \( \tilde{\omega} = \omega(1 - 2\lambda)^{1/2} \) with an instability at \( \lambda = 0.5 \). Because of this instability, both Migdal [9] and Eliashberg [11] restricted the applicability of their approach to \( \lambda \leq 1 \). It was then shown that if the adiabatic Born-Oppenheimer approach is properly applied to a metal, there is only negligible renormalization of the phonon frequencies of the order of the adiabatic ratio, \( \omega/E_F \ll 1 \) at any value of \( \lambda \). The conclusion was that the standard electron-phonon interaction could be applied to electrons for any value of \( \lambda \), but it should not be applied to renormalize the characteristics of the phonons [3]. As a result, many authors used the Migdal-Eliashberg theory with \( \lambda \) much larger than 1 (see, for example, Ref. [12]).

However, starting from the infinite coupling limit, \( \lambda = \infty \) and applying the inverse “1/\( \lambda \)” expansion technique [1] it was shown [12] that a many-electron system collapses into small (nonadiabatic) polaron regime at \( \lambda \geq 1 \) almost independently of the adiabatic ratio. This regime is beyond the Migdal-Eliashberg theory. It cannot be reached by summation of the standard Feynman-Dyson perturbation diagrams with the translation-invariant Green’s functions even including all vertex corrections, because of the broken translational symmetry, as first discussed by Landau [13] for a single electron and by us [12] for the many-electron system. In recent years quite a few numerical and analytical studies have confirmed this conclusion [14, 15] (and references therein). Of course, if the coupling is not very strong \((\lambda < 1)\) and the adiabatic ratio is sufficiently small, \( \omega/E_F \ll 1 \), one can apply the standard Feynman-Dyson perturbation technique including the vertex corrections to the vertex function [16, 17]. If one or both of these two conditions is not satisfied then the nonadiabatic polaron theory of superconductivity [18] is more appropriate.

Here I show that the adiabatic ratio in all novel superconductors is of the order or even larger than unity for most essential optical phonons. Consider recent high-temperature superconductor MgB\(_2\) [19]. The crystal structure of magnesium-diboride contains planes of magnesium and graphite-like planes of boron atoms. First-principles band structure calculations [20, 21] show that magnesium donates its outer electrons to boron layers like copper donates its electrons to oxygen in cuprates, and alkali metals to carbon in doped C60. The band structure is quasi-two-dimensional with two generate hole pockets [21] and the bare (LDA) Fermi energy about 0.55 eV. Applying the parabolic approximation for the band dispersion one obtains the renormalized Fermi energy as

\[
E_F = \frac{\pi n_d d}{m_i},
\]

where \( d \) is the interplane distance, and \( n_i, m_i^* \) are the density of holes and their effective mass in each of two bands \((i = 1, 2)\), renormalized due to the electron-phonon (and electron-electron) interaction. One can express the renormalized band-structure parameters through the in-plane London penetration depth at \( T = 0 \), measured experimentally:

\[
\lambda_{\parallel}^{-2} = 4\pi e^2 \sum_i \frac{n_i}{m_i^*}.
\]
As a result, one obtains the parameter-free expression for the “true” Fermi energy as

\[ E_F = \frac{d}{4ge^2 \lambda_H^4}, \]

where \( g \) is the degeneracy of the spectrum \( (g = 2 \) in MgB\(_2\)). The same expression applies in cuprates because of the two-dimensional character of their band structure. However, the degeneracy \( g \) in cuprates may depend on doping. In underdoped cuprates one expects 4 hole pockets inside the Brillouin zone (BZ) due to the Mott-Hubbard gap. If the hole band minima are shifted with doping to BZ boundaries, all their wave vectors would belong to the stars with two or more prongs. The groups of the wave vector for this stars have only 1D representations. It means that the spectrum will be degenerate with respect to the number of prongs which has the star, i.e \( g \geq 2 \). The only exception is the minimum at \( \mathbf{k} = (\pi, \pi) \) with one prong and \( g = 1 \). Hence, in the cuprates the degeneracy is \( 1 \leq g \leq 4 \).

Generally, the ratios \( n/m \) in Eq.(1) and Eq.(2) are not necessary the same. The ‘superfluid’ density in Eq.(2) might be different from the total density of delocalized carriers in Eq.(1). However, in a translationally invariant system they must be the same. This is true even in the extreme case of a pure two-dimensional superfluid, where quantum fluctuations are important. One can, however, obtain a reduced value of the zero temperature superfluid density in the dirty limit, \( l \ll \xi(0) \), where \( \xi(0) \) is the zero-temperature coherence length. The latter was measured directly in cuprates as the size of the vortex core. It is about 10 Å or even less. On the contrary, the mean free path was found surprisingly large at low temperatures, \( l \approx 100-1000 \) Å. Hence, I believe that all novel superconductors, including MgB\(_2\) are in the clean limit, \( l \gg \xi(0) \), so that the parameter-free expression for \( E_F \), Eq.(3), is perfectly applicable.

Parameter-free estimate of the Fermi energy, \( E_F \), obtained by using Eq.(3), is presented in the Table. It becomes clear that the Fermi energy in magnesium diboride and in more than 30 cuprates is about 100 meV or even less, in particular, if the degeneracy \( g \geq 2 \) is taken into account. That should be compared with the characteristic phonon frequency, which can be estimated as the plasma frequency of boron or oxygen ions,

\[ \omega = (4\pi Z^2 e^2 N/M)^{1/2}. \]

With \( Z = 1, \ N = 2/V_{cell}, \ M=10 \) a.u. one obtains \( \omega \approx 69 \) meV for MgB\(_2\), and \( \omega=84\)meV with \( Z = 2, \ N = 6/V_{cell}, \ M=16 \) a.u. for YBa\(_2\)Cu\(_3\)O\(_6\). Here \( V_{cell} \) is the volume of the (chemical) unit cell. The estimate agrees well with the measured phonon spectra [10][11]. As established experimentally in cuprates [11], the high-frequency phonons are strongly coupled with carriers. The parameter-free expression, Eq.(3), does not apply to doped fullerenes with their three-dimensional energy structure. However, it is well established that they are also in the nonadiabatic regime [12].

The low Fermi energy (Table), \( E_F \ll \omega \) is a serious problem within the Migdal-Eliashberg approach. In the framework of this BCS-like approach (largely independent of the nature of coupling) the critical temperature is fairly well approximated by McMillan’s formula (see in e.g. Ref. [10]),

\[ T_c = \frac{\omega}{1.45 \exp \left[ -\frac{1.04(1+\lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right]} \],

which works well for simple metals and their alloys. There are no general restrictions on the BCS value of \( T_c \) if the dielectric function formalism is properly applied. Allen and Dynes [44] found that in the strong-coupling limit \( \lambda \gg 1 \) the critical temperature might be as high as \( T_c \approx \omega^{1/2}/2\pi \). Nevertheless, applying this kind of theory to novel superconductors is problematic. Since the Fermi energy is small and phonon frequencies are high, the Coulomb pseudopotential \( \mu^* \) is of the order of the bare Coulomb repulsion, \( \mu^* \approx \mu \approx 1 \) because the Tolmachev-Morel-Anderson logarithm is ineffective. Hence, to get experimental \( T_c \) with Eq.(5), one has to have a strong coupling, \( \lambda \gg 1 \). However, one cannot increase \( \lambda \) without accounting for the polaron collapse of the band. As discussed above, this happens at \( \lambda \approx 1 \) for uncorrelated polarons, and even for a smaller value of the bare electron-phonon coupling in strongly correlated models [17]. Of course, one can argue [17], that a renormalized value of the coupling \( \lambda - \lambda/(1-2\lambda) \) appears in Eq.(5), rather than a bare \( \lambda \) because of the familiar Migdal’s softening of the phonon spectrum. That leaves some room for high \( T_c \) in the region of the applicability of the Eliashberg theory (i.e. \( \lambda \lesssim 0.5 \)). However, even in this region the non-crossing diagrams cannot be treated as vertex corrections because \( \omega/E_F \geq 1 \), since they are comparable to the standard terms.

To conclude, I have shown that MgB\(_2\) and cuprates are in the nonadiabatic regime, where the Migdal-Eliashberg theory is inappropriate. The interaction with optical high-frequency phonons should be treated within the multi-polaron theory [34] based on the canonical Lang-Firsov transformation. The renormalized Fermi energy is one order of magnitude lower than the bare (LDA) Fermi energy in MgB\(_2\), which corresponds to ca 2 phonons dressing a hole [9]. The ‘bare’ phonon dressing might be even stronger because the electron correlations undress polarons, as argued by Hirsh [10]. Nevertheless, the ground state of MgB\(_2\) might yet be a (polaronic) BCS/Fermi liquid [13] if the interaction with these phonons is not so strong that the bipolaron (real-space) pairs would form. Then, as in the case of doped fullerenes [12], the interaction with low-frequency phonons (\( \omega \ll E_F \)) could be accounted for within the framework of the Migdal-Eliashberg approach. While the Fermi surface topology
is not changed in the canonical transformation, there is a qualitative difference between the ordinary Fermi liquid and the nonadiabatic polarons. In particular, the renormalized (effective) mass of electrons is independent of the ion mass $M$ in ordinary metals (where the Migdal approximation is believed to be valid), because $\lambda$ does not depend on the isotope mass. However, the polaronic mass $m^*$ will depend on $M$. This is because the polaron mass $m^* = m \exp(A/\omega)$, where $m$ is the band mass in the absence of the electron-phonon interaction, and $A$ is a constant. Hence, there is a large isotope effect on the carrier mass in polaronic metals, in contrast to the zero isotope effect in ordinary metals. Recently, this effect has been experimentally found in cuprates and manganites. I anticipate the same effect in MgB$_2$. Also the optical conductivity of polarons is different from that in ordinary electrons. In particular, there is a substantial non-Drude polaron mid-infrared conductivity at the expense of the Drude contribution. On the other hand the nonadiabatic polaron $dc$ conductivity has a metallic character if the temperature is below the characteristic optical phonon frequency. Its magnitude and temperature dependence are determined by the coupling with low-frequency phonons alone (like in usual metals) because there is no scattering off high-frequency phonons bound with the carriers into coherent (Glauber) polaronic states.

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| Compound | $T_c$ (K) | $\lambda_{H,ab}$ | $d$ (Å) | $gE_F$ (meV) |
|----------|----------|------------------|--------|-------------|
| $La_{1.8}Sr_{0.2}CuO_4$ | 36.2 | 2000 | 6.6 | 112 |
| $La_{1.76}Sr_{0.24}CuO_4$ | 27.5 | 1980 | 6.6 | 114 |
| $La_{1.76}Sr_{0.24}CuO_4$ | 20.0 | 2050 | 6.6 | 106 |
| $La_{1.85}Sr_{0.15}CuO_4$ | 37.0 | 2400 | 6.6 | 77 |
| $La_{1.9}Sr_{0.1}CuO_4$ | 30.0 | 3200 | 6.6 | 44 |
| $La_{1.75}Sr_{0.25}CuO_4$ | 24.0 | 2800 | 6.6 | 57 |
| $YBa_2Cu_3O_7$ | 92.5 | 1400 | 4.29 | 148 |
| $YBaCuO(2\%Zn)$ | 68.2 | 2600 | 4.29 | 43 |
| $YBaCuO(3\%Zn)$ | 55.0 | 3000 | 4.29 | 32 |
| $YBaCuO(5\%Zn)$ | 46.4 | 3700 | 4.29 | 21 |
| $YBa_2Cu_3O_{6.7}$ | 66.0 | 2100 | 4.29 | 66 |
| $YBa_2Cu_3O_{6.57}$ | 56.0 | 2900 | 4.29 | 34 |
| $YBa_2Cu_3O_{6.92}$ | 91.5 | 1861 | 4.29 | 84 |
| $YBa_2Cu_3O_{6.88}$ | 87.9 | 1864 | 4.29 | 84 |
| $YBa_2Cu_3O_{6.84}$ | 83.7 | 1771 | 4.29 | 92 |
| $YBa_2Cu_3O_{6.79}$ | 73.4 | 2156 | 4.29 | 62 |
| $YBa_2Cu_3O_{6.77}$ | 67.9 | 2150 | 4.29 | 63 |
| $YBa_2Cu_3O_{6.74}$ | 63.8 | 2022 | 4.29 | 71 |
| $YBa_2Cu_3O_{6.7}$ | 60.0 | 2096 | 4.29 | 66 |
| $YBa_2Cu_3O_{6.65}$ | 58.0 | 2035 | 4.29 | 70 |
| $YBa_2Cu_3O_{6.6}$ | 56.0 | 2285 | 4.29 | 56 |
| $HgBa_2CuO_{4+\delta}$ | 70.0 | 2160 | 9.5 | 138 |
| $HgBa_2CuO_{4.055}$ | 78.2 | 1610 | 9.5 | 248 |
| $HgBa_2CuO_{4.053}$ | 78.5 | 2000 | 9.5 | 161 |
| $HgBa_2CuO_{4.066}$ | 88.5 | 1530 | 9.5 | 274 |
| $HgBa_2CuO_{4.096}$ | 95.6 | 1450 | 9.5 | 305 |
| $HgBa_2CuO_{4.097}$ | 95.3 | 1650 | 9.5 | 236 |
| $HgBa_2CuO_{4.1}$ | 94.1 | 1580 | 9.5 | 257 |
| $HgBa_2CuO_{4.101}$ | 93.4 | 1560 | 9.5 | 264 |
| $HgBa_2CuO_{4.101}$ | 92.5 | 1390 | 9.5 | 332 |
| $HgBa_2CuO_{4.105}$ | 90.9 | 1560 | 9.5 | 264 |
| $HgBa_2CuO_{4.108}$ | 89.1 | 1770 | 9.5 | 205 |
| $MgB_2$ | 39 | 1400 | 3.52 | 122 |

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