HIGH $T_c$ SUPERCONDUCTIVITY IN DIBORIDES BY MICRO-STRAIN AND FERMI LEVEL TUNING

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It is shown that the process of $T_c$ amplification in diborides occurs in a particular region of the ($\rho, \varepsilon$) phase diagram, where $\rho$ is the charge density and $\varepsilon$ is the micro-strain in the metallic boron plane. The $T_c(\rho, \varepsilon)$ shows that the superconducting phase occurs while the chemical potential is tuned near the “shape resonance” of the diboride superlattice and the micro-strain is in a critical range. The range of the high $T_c$ phase is determined by the modulation amplitude $\Delta_{\text{shape}}$ of the shape resonance energy due to the zero-point lattice vibrations $\Delta u_{\text{rms}}(\varepsilon)$, pointing towards an electronic or vibronic pairing mechanism. It has been discussed that the McMillan’s formula breaks down for the diborides.

High $T_c$ cuprate superconductors are at the border between a BCS condensate and a Bose condensate. One characteristic difference between a Bose condensate and a BCS condensate is that the BCS pairing in the weak coupling involves particles in a narrow energy range around $E_F$ (i.e. within a cutoff energy $\omega_0$ around the chemical potential). Most of the expected deviation from the BCS scheme are expected for the limit of a small $E_F$ or for a very high cutoff energy $\omega_0$ ($\omega_0/E_F > 1$) that is a case of a dilute electron gas where $r_s > 10$ or for a very strong electron–electron interaction giving a conduction band narrowing.

In the high $T_c$ cuprates there are two candidates as mediators for the pairing: spin fluctuations ($\omega_0 = 150$ meV) or longitudinal optical phonons ($\omega_0 = 70$ meV) giving $\omega_0/E_F \sim 0.1$–0.3 taking the Fermi level at optimum doping from photoemission data. The high $T_c$ is usually associated with a strong coupling regime well beyond the weak coupling approximation of the standard BCS theory that works for low $T_c$ 3D intermetallic compounds. In the cuprates the strong coupling regime has been associated by the majority of theoretical proposals with the proximity to a Mott–Hubbard insulator with $U/W > 1$ ($U$ is the Coulomb repulsion and $W$ is the bandwidth) where an insulating antiferromagnetic phase occurs with vanishing Fermi energy. The hole doping $\delta$ has been used as the physical parameter measuring the distance from the Mott–Hubbard insulator at $\delta = 0$. 

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For intermetallics with $T_c$ in the range 10–23 K the critical temperature is generally interpreted in the frame of the strong coupling approximation given by the McMillan’s formula\cite{1,2} where the pairing effective attraction $V_h$\cite{3} is proportional to $(D/\omega_0)^2$ where the deformation potential $D = \Delta V_{q,\nu}/\Delta u_{rms}$ where $\Delta u_{rms}$ is the amplitude of the zero-point lattice vibrations and $\Delta V_{q,\nu}$ is the associated variation of the electronic energy. An increasing electron–phonon interaction is characterized by a softening of the phonon energy and an increasing energy width of the phonon frequency. The electron–phonon coupling $V_h$ is related with the deformation potential. A correlation has been recognized between higher $T_c$ and stronger degree of lattice instability in intermetallics by the experimental work of Matthias\cite{4} and Testardi.\cite{5} The empirical rule says that the increasing of $T_c$ in 3D metal is obtained by driving the system toward a lattice instability with the softening of phonon modes $\omega_0$ and increasing density of states $D(E_F)$ that implies an increasing electron–phonon coupling.

There is growing evidence that high $T_c$ in cuprates and the large electron–phonon interaction is driven by the lattice misfit with the intercalated rocksalt layers, that has been measured by the lattice micro-strain induced in the CuO$_2$ plane.\cite{6,7} At an optimum value of the micro-strain $\varepsilon \sim 4\%$ of the Cu-O bond a large amplitude of the zero-point lattice vibrations has been measured. Moreover the process for $T_c$ amplification in this metallic heterostructure at the atomic limit (MEHAL) requires the tuning of the Fermi level at a “shape resonance”.\cite{8,9} Therefore the highest $T_c$ occurs in a particular range in the so called “Bianconi plot” where the critical temperature is plotted as a function of micro-strain and charge density.\cite{6}

The recent discovery of 39 K superconductivity in MgB$_2$\cite{10} (see Fig. 1) has been interpreted by many authors in terms of an extreme case of a BCS superconductor with a electron–phonon coupling $\lambda = 1$ and $\mu^* = 0.1$\cite{11} or $\lambda = 1.5$ and $\mu^* = 0.25$.\cite{12}

It has been shown that the high $T_c$ phase occurs in solid solution Al$_{1-x}$Mg$_x$B$_2$, going from AlB$_2$ to MgB$_2$, with variable Mg content. It has been pointed out that

![Fig. 1. High $T_c$ superconductivity time line. The maximum critical temperature $T_c$ reached in 2001 in metallic heterostructures at the atomic limit.](image_url)
High $T_c$ Superconductivity in Diborides

Fig. 2. Superconducting critical temperature $T_c$ in Al$_{1-x}$Mg$_x$B$_2$ samples as a function of the number of holes per unit cell in the $\sigma$ sub-band (panel a) and as a function of the tensile micro-strain in the boron layers $\varepsilon = (a_0 - a)/a_0$, where $a_0 = c/1.075$. The dashed line shows the charge density where the Fermi level is tuned to the “shape resonance” i.e. the 2D to 3D cross-over of the Fermi surface of the $\sigma$ sub-band.

Fig. 3. Plot of the micro-strain versus the number of holes in the $\sigma$ sub-band in diborides. The “high $T_c$” regime appears in the dashed region while the “low $T_c$” regime is in the dotted region. The dashed line shows the charge density where the Fermi level is tuned to the “shape resonance” i.e. the 2D to 3D cross-over of the Fermi surface of the $\sigma$ sub-band.

The high $T_c$ in these diborides$^{13-18}$ occurs at the 2D–3D cross-over of the Fermi surface of the boron $\sigma$ sub-band and the tuning of the micro-strain at an optimum value for the pairing mechanism as it is shown in Fig. 2. Therefore the high $T_c$ phase appears by tuning the Fermi in critical region of holes in the $\sigma$ sub-band and micro-strain as it is shown in Fig. 3.

The softening of the $E_{2g}$ mode shown in Fig. 4 is in agreement with an increasing Debye Waller factor at zero temperature in diffraction data. By assuming a deformation potential $D = 13$ eV/Å$^{11}$ it is possible to obtain the modulation am-
Fig. 4. Energy of the $E_{2g}$ phonon mode measured by micro-Raman as a function of the tensile micro-strain of the boron lattice.

Fig. 5. Shift of the Fermi level ($E_F$) relative to the Energy ($E_c$) of the “shape resonance” i.e. the critical point at the point ($E_f - E_c$) (filled dots) as a function of the number of the holes per unit cell in the $\sigma$ sub-band. The top of the $\sigma$ sub-band is indicated by the dashed line ($E_A - E_c$). It is determined by the dispersion in the $c$ axis direction of the $\sigma$ sub-band that decreases with the expansion of the $c$ axis. The shaded area is defined by the amplitude $\Delta_{\text{shape}}$ of the energy modulation of the critical point at $E_c$ due to the zero point amplitude of the $E_{2g}$ phonon mode.

In order to test the generic assumption that $T_c$ in MgB$_2$ follows the BCS prediction we have calculated $T_c$ using the McMillan’s formula and it has been compared with the experimental data in Fig. 6 as a function of the ratio $E_t/\omega_0$. Clearly the
Fig. 6. Critical temperature $T_c(\text{exp})$ (filled dots) of $\text{Al}_{1-x}\text{Mg}_x\text{B}_2$ as a function of adiabatic ratio $E_f/\omega_0$ compared with the calculated $T_c(\text{BCS})$ using the McMillan’s formula. (Striped line): The ratio between the experimental critical temperature and the calculated one. (Dashed line): using the McMillan Formula increases in the nonadiabatic region.

Fig. 7. Effective interaction (open dots) extracted by the experimental inversion of the McMillan formula compared with the expected variation of $V_h$ due to the variation of the phonon frequency (solid line) in Fig. 4. The factor $f = V_h(\text{exp})/V_h(\text{theory})$ is also shown (filled dots).

calculated $T_c$, for a different set of $1 < \lambda < 1.5$ and $0.1 < \mu^* < 0.25$, is in disagreement with the experiment showing the breakdown of the Migdal–Eliashberg theory for the diborides as it was already found in fullerene.

In order to understand the deviation of the calculated $T_c$ from the experimental data we have inverted the McMillan’s formula to get the effective electron–phonon interaction needed to explain the data. We have plotted $V_h$ as function of the adiabatic parameter $E_f/\omega_0$ in Fig. 7.

$$V_h = \frac{U_c + 1.04(g/N(0))}{1 - 0.62N(0)U_c - 1.04g}$$
Fig. 8. The effective coupling electronic \( g \) for the pairing mediated by virtual electronic excitations extracted by the simple relation \( T_c = E_f \exp(-1/g_{\text{electronic}}) \) where the Fermi energy of the holes in the \( \sigma \) sub-band \( E_{\sigma} = E_{\Lambda} - E_F \).

with

\[
g = \frac{-1}{\ln(1.45T_c/\omega_0)}, \quad U_c = \frac{V_c}{1 + N(0)V_c \ln(E_f/\omega_0)}
\]

where \( \omega_0, T_c \) are measured directly and \( E_f \) and \( N(0) \) are calculated in agreement with experimental data. \( V_c = 0.6 \) eV has been obtained from \( \mu^* = 0.11 \) for MgB\(_2\). The result in Fig. 7 shows also the variation of \( V_h \) (theory) normalized to the value for MgB\(_2\) with the expected variation due to the variation of \( \omega_0 \) and assuming a constant deformation potential.

There are two possible interpretations for the breakdown of the McMillan’s formula to predict the variation of \( T_c \) in diborides.

The deviation can be assigned to vertex corrections\(^{12,19} \) in the electron–phonon pairing mechanism with decreasing the adiabatic ratio \( E_f/\omega_0 \). From the results in Fig. 7 we can extract the factor \( f = V_h(\text{exp})/V_h \) (theory) that is plotted in Fig. 7. This factor gives the increase of the net effective attractive interaction with decreasing \( E_f/\omega_0 \) in the range \( 1 < E_f/\omega_0 < 10 \).

The second possible interpretation is that the pairing is not due to an electron–phonon mechanism but to an electronic excitations driven by the large energy modulation of electronic states. In this later case the critical temperature is not given by the McMillan’s formula but the pre-factor is the Fermi energy\(^{20} \) therefore we can extract an effective electron–electron coupling strength from the formula:

\[
g_{\text{electronic}} = \frac{-1}{\ln(T_c/E_f)}.
\]

The superconducting critical temperature scales as the Fermi temperature \( T_c = (0.4/k_t\xi_0)T_l \), with \( k_t\xi_0 = 90^{17} \) for \( E_f/\omega_0 > 4.2 \). In this range the Fermi surface is 2D-like. The effective coupling \( g_{\text{electronic}} \) is plotted as a function of \( E_f/\omega_0 \) in Fig. 8.
In summary, we have found the breakdown of the McMillan’s formula for diborides. The results point toward a large correction of the electron–phonon interaction approaching the antiadiabatic limit or toward an electronic or vibronic pairing mechanism.

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