BCS Theory for Binary Systems with 2D Electrons

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MgB$_2$ is considered as a binary system with 2D electrons. The classic BCS theory is applied to this system. The transition temperature ($T_c$) is found to be relatively high, because 2D electrons are more capable of moving with the atoms, on top of other special features of this system to enhance the electron-phonon interaction. This system may also shed light on the nature of superconductivity in cuprates.

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There is little doubt that MgB$_2$ ($T_c = 39$K) is a conventional superconductor [1]. The isotope effect is found to be strong, and the energy gap is also of the conventional type [2, 3]. Unsolved is the mystery about $T_c$ which seems to be either above or at the limit suggested by the theory of Bardeen, Cooper and Schrieffer (BCS) for phonon-mediated superconductivity [3]. Therefore it is of current interest to apply the BCS theory to MgB$_2$, taking the special features of this compound into consideration, to see if a proper $T_c$ would arise.

MgB$_2$ features alternating B and Mg rings [1]. Energy band calculation reveals that superconductivity in MgB$_2$ is driven by the 2D bounding $\sigma$ bands [3]. We consider a simple model of alternating layers of light and heavy atoms, to which electrons pertain (Fig. 1). These electrons are more capable of moving with the atoms, compared with free electrons, to enhance the electron-phonon interactions. These interactions may take place either within the same atom layer (intra-layer coupling), or between neighboring layers (inter-layer coupling). The intra and inter-layer couplings may join force to raise $T_c$ still further.

Our simple model might help us to understand cuprates, regardless of the nature of the pairing mechanism. In cuprates atoms are also layered, with electrons pertaining to the atom layers [4]. The intra and inter-layer couplings are in competition: if none dominate then both are suppressed. This leads to a forbidden zone of doping, where the inter-layer coupling is stronger than the coupling within the heavy atom layers, but weaker than that within the light atom layers, so that superconductivity vanishes, reminiscent of the observation by Moodenbaugh et al. in La$_{2-x}$Ba$_x$CuO$_4$ [6]. Careful doping may leave singlet pairs inside the forbidden zone, triplet pairs outside: $p$-wave pairing is possible in the BCS theory, and indeed in a large number of candidate theories, where $p$-wave symmetry is not intrinsically favored [6].

We apply the BCS theory to our binary system. The derivation is simple in principle but involved technically. Second quantization is actually based on the assumption that, despite its statistical nature, the displacement of a particle in a crystal is the exact replica of the displacement of its neighbors, save a phase factor, which serves as a parameter to categorize particle displacement into groups known as Fourier components. The operation to add or take away a component is symbolized by the creation or destruction operator. In this respect there is little difference between normal metals and our binary system. Phonons (atom displacements) have long been treated in complex systems [10]. We treat electrons with the understanding that proper wave functions can be found to reflect the physics of 2D electrons: they pertain to the atom layers, and their wave functions overlap with those in neighboring layers. When $T > 0$ we find the following ensemble average of electron energy

$$W = \sum_{i=1}^{2} \sum_{k} \epsilon_k \left[ f_k^{i} + h_k^{i} (1 - 2 f_k^{i}) \right]$$

$$- \sum_{i,j=1}^{2} \sum_{k,k'} V_{k,k'}^{(ij)} \left[ h_k^{i} (1 - h_k^{i}) \right]^{1/2} (1 - 2 f_k^{i})$$

$$\times \left[ h_{k'}^{j} (1 - h_{k'}^{j}) \right]^{1/2} (1 - 2 f_{k'}^{j})$$

(1)

Fig. 1 Crystal of light (wt. $M_1$ in layer 1, open circles) and heavy (wt. $M_2$ in layer 2) atoms, $a$, $b$ and $c$ are lattice constants, $M_1/M_2 = 0.7$, $a = b = 0.5c$. The antinodes of $\psi_k^{(1)}$ and $\psi_k^{(2)}$ are in layer 1 and 2, respectively. Values of $V$ are in an arbitrary unit.
Here $\mathbf{k}$ is the wave vector to specify the electron state, $\epsilon_{\mathbf{k}}$ state energy relative to the Fermi level, $\hbar \kappa$ occupation probability of state $\mathbf{k}$, $f_{\mathbf{k}}^{(i)}$ excitation probability of the ground pair at states $\mathbf{k}$ and $-\mathbf{k}$, and $i$ and $j$ indicate atom layers. Following BCS we associate $\mathbf{k}$ and $-\mathbf{k}$ with spin $\uparrow$ and $\downarrow$ respectively unless stated otherwise. We have

$$V_{\mathbf{k},\mathbf{k}'}^{(i,j)} = \sum_{l=1}^{6} \frac{2\hbar \omega_{kl} M_{l}^{(i,j)}(\mathbf{k},\mathbf{k}')}{(\hbar \omega_{kl})^{2} - (\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}^{(l)}/2)^{2}}$$

where $\omega_{kl}$ is the phonon frequency, $\kappa = \mathbf{k} - \mathbf{k}'$ phonon vector, $l$ identifies phonon branches. We have 2 atoms in the primitive cell, giving 6 branches in each polarization. However, transverse phonons do not interact with electrons so that Eq. (2) involves just 6 branches (3 of them optic). The matrix element $M_{l}^{(i,j)}$ measures the strength of electron-phonon interaction, which couples electrons as long as their wave functions overlap: the coupling may take place either within the same atom layer ($i = j$) or between neighboring layers ($i \neq j$). We have $M_{l}^{(i,2)} = M_{l}^{(2,i)}$, so that $V_{\mathbf{k},\mathbf{k}'}^{(i,2)} = V_{\mathbf{k}',\mathbf{k}}^{(2,i)}$.

In the binary system the entropy of the electron ensemble is

$$S = -4k_B \sum_{\mathbf{k}} \left[ \frac{1}{2} f_{\mathbf{k}}^{(1)} + \frac{1}{2} f_{\mathbf{k}}^{(2)} \right] \ln \left( \frac{1}{2} f_{\mathbf{k}}^{(1)} + \frac{1}{2} f_{\mathbf{k}}^{(2)} \right) + \left( 1 - \frac{1}{2} f_{\mathbf{k}}^{(1)} - \frac{1}{2} f_{\mathbf{k}}^{(2)} \right) \ln \left( 1 - \frac{1}{2} f_{\mathbf{k}}^{(1)} - \frac{1}{2} f_{\mathbf{k}}^{(2)} \right)$$

where the factor 4 indicates the degree of degeneracy: at the same energy level there can be 2 electrons in each of the 2 atom layers. We have assumed the same density of states in both atom layers, otherwise the factor 1/2 in Eq. (3) must be adjusted. We minimize the free energy $F = W - TS$ with respect to $f_{\mathbf{k}}^{(i)}$ and find

$$\sum_{\mathbf{k}',\mathbf{k}''} V_{\mathbf{k}',\mathbf{k}''}^{(1,1)} \frac{\Delta_{1}(1 - 2f_{\mathbf{k}}^{(1)})}{2(\Delta_{1}^{2} + \epsilon_{\mathbf{k}''}^{(l)})^{1/2}} + \sum_{\mathbf{k}',\mathbf{k}''} V_{\mathbf{k}',\mathbf{k}''}^{(1,2)} \frac{\Delta_{2}(1 - 2f_{\mathbf{k}}^{(2)})}{2(\Delta_{2}^{2} + \epsilon_{\mathbf{k}''}^{(l)})^{1/2}} = \Delta_{1}$$

$$\sum_{\mathbf{k}',\mathbf{k}''} V_{\mathbf{k}',\mathbf{k}''}^{(1,2)} \frac{\Delta_{1}(1 - 2f_{\mathbf{k}}^{(1)})}{2(\Delta_{1}^{2} + \epsilon_{\mathbf{k}''}^{(l)})^{1/2}} + \sum_{\mathbf{k}',\mathbf{k}''} V_{\mathbf{k}',\mathbf{k}''}^{(2,2)} \frac{\Delta_{2}(1 - 2f_{\mathbf{k}}^{(2)})}{2(\Delta_{2}^{2} + \epsilon_{\mathbf{k}''}^{(l)})^{1/2}} = \Delta_{2}$$

which are counterparts of the BCS self-consistent equation, $\epsilon_{\mathbf{k}}/(\Delta_{1}^{2} + \epsilon_{\mathbf{k}}^{(l)})^{1/2} = 1 - 2f_{\mathbf{k}}^{(i)}$. We also minimize $F$ with respect to $f_{\mathbf{k}}^{(i)}$ and find

$$\Delta_{1}^{2} + \epsilon_{\mathbf{k}}^{(l)} = \frac{\Delta_{1}^{2}^{2} + \epsilon_{\mathbf{k}}^{(l)}}{f_{\mathbf{k}}^{(1)} + f_{\mathbf{k}}^{(2)}}$$

where $i = 1$ or $2$, i.e. $\Delta_{1} = \Delta_{2} = \Delta$, which leads through Eqs. (4), (5) and the familiar BCS algorithm to

$$V_{11} \sum_{\mathbf{k}} \frac{1 - 2f_{\mathbf{k}}^{(1)}}{2(\Delta_{1}^{2} + \epsilon_{\mathbf{k}}^{(l)})^{1/2}} + V_{12} \sum_{\mathbf{k}} \frac{1 - 2f_{\mathbf{k}}^{(2)}}{2(\Delta_{1}^{2} + \epsilon_{\mathbf{k}}^{(l)})^{1/2}} = 1$$

$k$ runs over a range where $-\hbar \omega < \epsilon_{\mathbf{k}} < \hbar \omega$, $\omega$ being the average phonon frequency, $V_{ij} = \langle \psi_{\mathbf{k},\mathbf{k}'}^{(i,j)} \rangle_{AV}$ matrix element averaged over the above range of $k$. We find from Eqs. (6) and (7) that

$$\sum_{\mathbf{k}} \frac{1 - 2f_{\mathbf{k}}^{(1)}}{2(\Delta_{1}^{2} + \epsilon_{\mathbf{k}}^{(l)})^{1/2}} = \frac{V_{12} - V_{22}}{V_{12} - V_{11}V_{22}}$$

$$\sum_{\mathbf{k}} \frac{1 - 2f_{\mathbf{k}}^{(2)}}{2(\Delta_{1}^{2} + \epsilon_{\mathbf{k}}^{(l)})^{1/2}} = \frac{V_{12} - V_{11}V_{22}}{V_{12} - V_{11}V_{22}}$$

We have assumed $M_{2} > M_{1}$ (Fig. 1) so that $V_{22} < V_{11}$ (to be justified later). When $V_{22} < V_{12} < (V_{11}V_{22})^{1/2}$, the right hand side of Eq. (8) becomes negative, which means $f_{\mathbf{k}}^{(1)} > 1/2$ must hold at least for some states. This not only violates the nature of $f_{\mathbf{k}}^{(1)}$ but also leads to a contradiction: $\Delta$ may become so large that Eqs. (6) and (7) cannot balance. Similarly, we find from Eq. (9) that $(V_{11}V_{22})^{1/2} < V_{12} < V_{11}$ is not allowed. Apparently

$$V_{22} < V_{12} < V_{11}$$

is a forbidden zone: if the inter-layer coupling is stronger than the coupling within the heavy atom layers, but weaker than that within the light atom layers, then superconductivity is suppressed. Outside this forbidden zone we can add Eqs. (6) and (7) together and find through Eq. (8) that

$$\int_{0}^{\hbar \omega} \frac{die}{(\Delta^{2} + \epsilon^{(l)}_{\mathbf{k}})^{1/2}} \tanh \left( \frac{(\Delta^{2} + \epsilon^{(l)}_{\mathbf{k}})^{1/2}}{2k_{B}T} \right) = \frac{1}{N(0)V}$$

where the summation over $k_{\mathbf{k}}$ has been converted into integration, $N(0)$ is the density of states at the Fermi surface. Eq. (12) is formally identical to the familiar BCS equation with

$$V = \frac{V_{12} - V_{11}V_{22}}{V_{12} - (V_{11} + V_{22})/2}$$

which is the counterpart of the BCS average matrix element $\langle \langle \psi_{\mathbf{k},\mathbf{k}'} \rangle \rangle$

Now we evaluate $V_{\mathbf{k},\mathbf{k}'}^{(i,j)}$ in Eq. (2). At this point we have to be more specific about the electron wave functions. For simplicity, we consider super-positions of two Bloch functions:

$$\psi_{\mathbf{k},\sigma}^{(1)} \propto \exp[i(k_{x}x + k_{y}y)] \cos(\pi z / c)$$

$$\psi_{\mathbf{k},\sigma}^{(2)} \propto \exp[i(k_{x}x + k_{y}y)] \sin(\pi z / c)$$

where $\mathbf{k} = xk_{x} + yk_{y}$ is a 2D wavevector, $\sigma$ spin, $c$ lattice constant in the $c$-direction. Both $\psi^{(1)}$ and $\psi^{(2)}$
have the same Bloch energy, and \( \sigma = \uparrow \) or \( \downarrow \), so that our electron wave functions are of quadruple degeneracy, consistent with the factor 4 in Eq. (3). Furthermore \( \psi^{(1)} \) and \( \psi^{(2)} \) are orthogonal to each other: they are proper base functions for second quantization.

Both \( \psi^{(1)} \) and \( \psi^{(2)} \) are traveling waves in the \( a-b \) plane but standing waves in the \( c \)-direction: they are mobile only in 2D. Apparently \( \psi^{(1)} \) pertains to layer 1 (its anti-nodes are in that plane) whereas \( \psi^{(2)} \) pertains to layer 2 (Fig. 1). It is implied that electron waves overlap with those in the neighboring layer, but not with those in the next neighboring layer (there is a node in between). It appears that \( \psi^{(1)} \) and \( \psi^{(2)} \) are the leading and perhaps dominating terms of the electron configuration in a real binary system: dispersions arising from Eqs. (2), where the matrix \( \begin{pmatrix} 3 \sin x & \sin y \\ \sin y & -3 \sin x \end{pmatrix} \) and \( \begin{pmatrix} 3 \sin x & \sin y \\ \sin y & -3 \sin x \end{pmatrix} \) are comparable when the valency is relatively small. This arises from Eq. (2), where the matrix \( \begin{pmatrix} 3 \sin x & \sin y \\ \sin y & -3 \sin x \end{pmatrix} \) and \( \begin{pmatrix} 3 \sin x & \sin y \\ \sin y & -3 \sin x \end{pmatrix} \) are traveling waves in the plane but standing waves in the \( c \)-plane. Hence, the wave vectors of the electron states \( \psi^{(1)} \) and \( \psi^{(2)} \) differ by \( \pi/M \). In a binary alloy with free electrons, which is considered as one of the long-standing mysteries associated with high \( T_c \) cuprates [12]. It was found that in \( La_{2-x}Ba_xCuO_4 \) \( T_c \approx 25K \) when \( x = 0.09 \) and \( x = 0.15 \), whereas \( T_c \approx 5K \) between these two maxima [7]. According to energy band calculation, in \( LaBaCuO_4 \) the Fermi surface is crossed by the CuO band and two O_2 bands: superconducting carriers are in atom layers which on average have two different masses. Perhaps \( LaBaCuO_4 \) could be modeled as a binary system, which falls into the forbidden zone when the valancy is adjusted into a proper value through doping.

Anomalous suppression of superconductivity: which is considered as one of the long-standing mysteries associated with high \( T_c \) cuprates [12]. It was found that in \( La_{2-x}Ba_xCuO_4 \) \( T_c \approx 25K \) when \( x = 0.09 \) and \( x = 0.15 \), whereas \( T_c \approx 5K \) between these two maxima [7]. According to energy band calculation, in \( LaBaCuO_4 \) the Fermi surface is crossed by the CuO band and two O_2 bands: superconducting carriers are in atom layers which on average have two different masses. Perhaps \( LaBaCuO_4 \) could be modeled as a binary system, which falls into the forbidden zone when the valancy is adjusted into a proper value through doping.

Spin triplet pairs: which may arise when spin singlet pairs fall into the forbidden zone. Specifically, while \( V_{12} < V_{11} \) holds for singlet pairs (inside the forbidden zone, suppressed), \( V_{12} > V_{11} \) may hold for triplet pairs (allowed), because \( V_{11} \) declines faster than \( V_{12} \) when the pair symmetry changes, due to the stronger effect of the exchange term on \( V_{11} \), which arises from intra-layer couplings, where electron waves overlap to a greater extent, compared with the inter-layer coupling. It is interesting that magnetic excitations are observed in \( YBa_2Cu_3O_7 \) and \( Bi_2Sr_2CaCu_2O_8 \) [3]. According to Yin et al. these excitations may not be attributed to the normal state properties of cuprates, because the excitation intensity decreases continuously with increasing temperature, and vanishes above \( T_c \) [3, 14]. Furthermore, magnetic excitations are observable only when doping is optimized [3]. Perhaps these cuprates may also be modeled as a
binary system, where careful doping may drive singlet pairs into the forbidden zone, leaving triplet pairs out. It is difficult to dope MgB$_2$, so that singlet pairs cannot be discriminated: the energy gap must be of the BCS type [3].

In conclusion, the BCS theory may explain the relatively high transition temperature of MgB$_2$ which, according to Bud’ko et al., nearly double the previous record for a nonoxide and non-C60-based compound [2]. We find that in a binary system with 2D electrons $V$ can increase 2-3 times (Fig. 1). According to Yin et al. many experimental observations in cuprates are commonly fit with a phenomenological model that derives from the original BCS theory, characterized by a gap equation corresponding to a presumed symmetry of the order parameter, with an adjustable dimensionless coupling constant, and a given Fermi surface [14]. We find that in our binary system the $p$-wave symmetry may arise in a natural manner from the BCS theory. This may help us to develop a microscopic theory for cuprates. In this letter we have used the original BCS theory, where damping and retardation are ignored with negligible effect [15]. This effect is likely to be similar, whether the superconductor is a normal metal, or a binary system with 2D electrons. Therefore our major conclusion, i.e. $V$ can be 2-3 times larger in the later case, is likely to stand. In future we would like to improve our results by taking damping and retardation into consideration.

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