Strongly interacting $\sigma$-electrons and MgB$_2$ superconductivity

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Abstract

MgB($p^n p^\sigma n$)$_2$ is classified as a system with strongly interacting $\sigma$-electrons and non-correlated $\pi$-electrons of boron ions. The kinematic and Coulomb interaction $V$ between the orbitally degenerated $\sigma$-electrons provide the superconducting state with an anisotropic gap of $s^\ast$-wave symmetry. The critical temperature $T_c$ has a non-monotonic dependence on the distance $r$ between the centers of gravity of $\sigma$- and $\pi$-bands. MgB$_2$ corresponds to $r = 0.085$ eV and $V = 0.45$ eV in our model with flat bands. The derived superconducting density of electronic states is in good agreement with available experimental and theoretical data. The possibilities for increasing $T_c$ are discussed.

Keywords: A. Superconductors; C. Crystal structure and symmetry; D. Electronic band structure; D. Electron correlations

The unprecedented discovery of superconductivity in the simple binary material MgB$_2$ [1] has opened up new avenues to attack the problem of maximizing $T_c$ and the symmetry of the order parameter. In the present paper we present a model to explain the superconducting state in MgB$_2$ which is based on the correlated $\sigma$- and the non-correlated $\pi$-band. The negatively charged boron layers and the positively charged magnesium layers provide a lowering of the $\pi$-band with respect to the $\sigma$-band, as pointed out in Ref. [2] and which was also noticed first in band calculations [3, 4, 5]. Tight-binding estimates show that the bonding $\sigma$-band, close to the Fermi level, is doubly degenerate (it has $E$-symmetry [3, 4, 5]). The quasi-2D $\sigma$-electrons are more localized than the 3D $\pi$-electrons. This leads to an enhancement of the on-site electron correlations in the system of degenerated $\sigma$-electrons. They are taken to be infinite, while the somewhat weaker intersite Coulomb interactions and electron-phonon interactions simply shift the on-site electron energies. After carrying out a fermion mapping to $X$-operators the Hamiltonian becomes:

$$H = \sum_{p,s} t^{(\sigma)}(p) X^s p(X^o p) + V \sum_{i,j} n_{\sigma}(i) n_{\sigma}(j) - r \sum_{i} n_{\pi}(i) + \\
+ \sum_{p,s} \varepsilon_0^{(\pi)}(p) \left[ n^+_s(p) \pi_s(p) + H.c. \right] - \mu \sum_{i} [n_{\sigma}(i) + n_{\pi}(i)].$$

(1)
It is written in the usual notations, where the non-diagonal $X$-operators describe the on-site transitions of correlated $\sigma$-electrons between the one-particle ground states (with spin projection $s = \pm$) and the empty polar electronic states (0) of the boron sites and $\mu$ is the chemical potential. The wide $\pi$-band is shifted with respect to the $\sigma$-band by an energy $r$. This parameter comprises the mean-field $\pi$-electron interactions, the electron-phonon interactions (e.g. the contribution of the strong coupling of $E_{2g}$-phonons with the $\sigma$-electrons [8]) etc. We included in Eq. (1) also the nearest neighbour Coulomb repulsion $V$ of $\sigma$-electrons, which is essential for the low density of hole-carriers present in MgB$_2$. The mutual hopping between $\sigma$- and $\pi$-electrons is assumed to be negligible due to the characteristic space symmetry of the orbitals involved. A schematic view of our model is presented in Fig. 1.

The diagonal $X$-operators ($X^0 \equiv X^\cdot \equiv X^{\cdot \cdot}$) conform to the completeness relation, $X^0 + 4X^s = 1$, and their thermodynamic averages ($\langle X^0 \rangle$, $\langle X^s \rangle$) are the Boltzmann populations of the energy levels of the unperturbed on-site Hamiltonian in (1). Due to the orbital and spin degeneracy the $\sigma$-electrons occupy their one-particle ground state with density $n_\sigma = \frac{3}{4} \langle X^s \rangle$ per boron site. The correlation factor for the degenerated $\sigma$-electrons is

$$f = \langle X^0 + X^s \rangle = 1 - 3 \langle X^s \rangle = 1 - \frac{3}{4} n_\sigma,$$

and it plays an important role in all arithmetics starting from their unperturbed (zeroth order) Green’s function, $D_{\sigma}^{(0)}(\omega) = f / (-i\omega_n - \mu)$, whereas for $\pi$-electrons $D_{\pi}^{(0)}(\omega) = 1 / (-i\omega_n - \mu - r)$. Note that for the conventional Hubbard model the correlation factor in the paramagnetic phase is $1 - n / 2$ (see [9] and Refs. therein). The energy dispersion of both bands, $\xi(p) = ft(p) - \mu$ and $\varepsilon(p) = \varepsilon_0(p) - r - \mu$, are governed by zeros of the inverse Green’s function

$$D^{-1}(\omega, p) = \text{diag} \left\{ D_{\sigma}^{-1}(\omega, p) ; D_{\pi}^{-1}(\omega, p) \right\} = \text{diag} \left\{ \frac{-i\omega_n + \xi(p)}{f} ; -i\omega_n + \varepsilon(p) \right\},$$

which follows from the Dyson equation

$$D^{-1}(\omega, p) = D^{(0)^{-1}}(\omega) + \hat{t}(p),$$

to first order with respect to the tunneling matrix $\hat{t}(p) = \text{diag} \{ t(p) ; \varepsilon_0(p) \}$.

The chemical potential $\mu$ for the MgB$_2$ = Mg$^{++}$B$^-$ $(p^2)^2$ = Mg$^{++}$B$^-$ $(p^\sigma p^\pi r^2)$ system (Eq. (1)) obeys the equation for the total electron density per boron site

$$n_\sigma + n_\pi = 2,$$

with the partial electron densities given by

$$n_{\sigma, \pi} = 2T \sum_{n, p} e^{i\omega_0} D_{\sigma, \pi}(\omega, p) \equiv n_{\sigma, \pi}(r, \mu).$$

The electron densities, Eq. (4), comply with the requirements $0 < n_\sigma < 1$ (due to the correlation factor, Eq. (2), providing the quarter-fold narrowing of the
degenerate $\sigma$-band) and $0 < n_\sigma < 2$. For any energy difference $r$ between the $\sigma$- and $\pi$-bands the chemical potential $\mu$ has to be such that Eq. (3) for the band fillings is satisfied.

From the system of Eqs. (3, 4) for a flat density of electronic states (DOS hereafter) $\rho_{\sigma,\pi}(\varepsilon) = (1/2w_{1,2}) \theta(w_{1,2}^2 - \varepsilon^2)$ with half-bandwidths $w_1$ and $w_2$ for $\sigma$- and $\pi$-electrons, respectively and $\theta(x)$ is the theta function) we derive the chemical potential of the $A_2^+ B(p^{n_\sigma} p^{n_\pi})_2$ systems as

$$\mu = \frac{w_2 - 5r}{5w_1 + 4w_2} w_1.$$  

(5)

The non-correlated $\pi$-electrons play the role of a reservoir for the $\sigma$-electrons. In the energy dispersion $\xi(p)$ for the $\sigma$-electrons, the correlation factor, Eq. (2), can be expressed also via the electron structure parameters $w_1, w_2$ and $r$ as

$$f = \frac{2w_1 + w_2 + 3r}{5w_1 + 4w_2}.$$  

The anomalous self-energy for the $\sigma$-electrons (Fig. 2) is written self-consistently as

$$\Sigma(p) = T \sum_{n,q} \Gamma_0(p, q) \frac{\Sigma(q)}{\omega_n^2 + \xi^2(q) + \Sigma(q)},$$

(6)

where the vertex $\Gamma_0$ is determined by the amplitudes of the kinematic and Coulomb interactions such that $\Gamma_0(p, q) = -2t_q + V(p - q)$. We do not include the other kinematic vertices in $\Gamma_0$ essential for a comparative analysis of the anisotropic singlet and for triplet pairings and the energy band renormalization at a moderate concentration of carriers [9]. In momentum space the Coulomb repulsion between the nearest neighbours (Eq. (1)) reflects the tight-binding symmetry of the boron honeycomb lattice, $\sqrt{3 + 2(1 - \beta)^2}$.

Near the $\Gamma - A$ line of the Brillouin zone the Coulomb vertex can be factorized as

$$V(p - q) = 2\beta t(p) t(q),$$

where the parameter $\beta = V/6t^2$ expresses the Coulomb repulsion for the nearest $\sigma$-electrons and the energy dispersion is $t(p) = 3t(1 - p_x^2 + p_y^2/12)$. Putting the explicit form of the vertex $\Gamma_0$ in Eq. (6), and after summation over the Matsubara frequencies $\omega_n = (2n + 1)\pi T$ one obtains

$$\Sigma(p) = \sum_q t(q) (1 - \beta t(p)) \Sigma(q) \frac{\text{tanh} \sqrt{\xi^2(q) + \Sigma^2(q)}/2T}{\sqrt{\xi^2(q) + \Sigma^2(q)}},$$

(7)

The search for a solution in the form $\Sigma(p) = \Sigma_0 + t(p) \Sigma_1$ converts Eq. (7) for the superconducting critical temperature and the gap in $A_2^+ B^{-2}$ to

$$1 = \sum_p t(p) (1 - \beta t(p)) \frac{\text{tanh} \sqrt{\xi^2(p) + \Sigma^2(p)}/2T}{\sqrt{\xi^2(p) + \Sigma^2(p)}},$$

(8)

with the gap function $\Sigma(p) = [1 - \beta t(p)] \Sigma_0$. 

3
Equalizing the gap function in Eq. (8) to zero, one can derive analytically $T_c$ in the logarithmic approximation for a flat DOS:

$$T_c = \frac{w_1}{5w_1 + 4w_2} \sqrt{(w_1 + w_2 - r)(w_1 + 4r)} \exp \left( -\frac{1}{\lambda} \right),$$

$$\lambda = \frac{(5w_1 + 4w_2)(3 + 5\beta w_1)}{(2w_1 + w_2 + 3r)^3} (w_2 - 5r) \left[ r - \frac{\beta w_1 w_2 - 2w_1 - w_2}{3 + 5\beta w_1} \right].$$

(9)

Under the prefactor in the square root the restrictions for an energy shift $r$ guarantee the assumed volume of the correlated $\sigma$-band, namely $n_\sigma \geq 0$ ($r \leq w_1 + w_2$) and $n_\sigma \leq 1$ ($r \geq -w_1/4 = -t$). $T_c (r)$ is plotted in Fig. 3 for different values of the parameter $\beta$, reflecting the suppression of superconductivity with an increase of the Coulomb repulsion. The critical temperature $T_c$ has a non-monotonic dependence on the mutual position $r$ of the $\sigma$- and $\pi$-bands.

The MgB$_2$ case, $T_c = 40$ K, corresponds to $r = 0.085$ eV and a dimensionless value $\beta w_1 = 8 V/3w_1$.

The superconducting gap equation follows from Eq. (8) taken for $T = 0$

$$1 = \int \rho_{\sigma}(\varepsilon) \varepsilon (1 - \beta \varepsilon) \frac{dz}{\sqrt{\varepsilon^2 + \Sigma_0^2 (1 - \beta \varepsilon)^2}}.$$  

(10)

It defines the anisotropic superconducting order parameter of $s^\ast$-wave symmetry. In contrast to the isotropic $s$-wave gap, the superconducting gap does not coincide with the amplitude $\Sigma_0$ of the gap function and it should be defined by the minimal square root in Eq. (10).

The near-cylindrical hole-like $\sigma$-Fermi surfaces in MgB$_2$ gives room to calculate the superconducting DOS $\rho(E) = \sum_p \delta \left( E - \sqrt{\varepsilon^2 (p) + \Sigma^2 (p)} \right)$, where the gap function (cf. Eq. (10)) is

$$\Sigma = \Sigma_0 (1 - \beta t (p)) = b (1 + a \cos^2 \vartheta),$$

(11)

where $a = \beta w_1 / (12 (1 - \beta w_1))$, $b = \Sigma_0 (1 - \beta w_1)$ and $\vartheta$ is the azimuthal angle. Then the superconducting DOS normalized with respect to the normal DOS is

$$\frac{\rho(E)}{\rho_0(E)} = \frac{1}{\sqrt{E^2 - b^2 (1 + a z^2)^2}} \int_0^1 dz.$$  

(12)

For a Coulomb repulsion such that $\beta w_1 < 1$ the parameter satisfies $a > 0$ and the superconducting DOS becomes

$$\frac{\rho(b < E < (1 + a) b)}{\rho_0(E)} = \frac{\sqrt{E}}{2ab} K(q),$$

$$\frac{\rho(E > (1 + a) b)}{\rho_0(E)} = \frac{\sqrt{E}}{2ab} F \left( \sin^{-1} \sqrt{\frac{ab}{E + (1 + a) b}} q : q \right),$$

(13)

which is expressed in terms of the complete and incomplete elliptic integrals $K$ and $F$, respectively with modulus $q = \sqrt{(E - b)/2E}$. The DOS (13) has cusps at $E = \pm (1 + a) b$. A similar result was obtained in Ref. [10] for a non-specified
parameter $a > 0$. In our case the parameter $a$ is controlled by the in-plane Coulomb repulsion $V$ as the authors of Ref. 9 noted. At $\beta w_1 = 0.92$ the DOS of Eq. (13) (see Fig. 4, inset) reproduces Fig. 1(b) of Ref. 10.

But for our case of an enhanced Coulomb repulsion $\beta w_1 > 1$, we have to take the parameter $a < 0$ in the gap function (11) and the superconducting DOS (Fig. 4) is then given by

$$\rho_{0}(E) = \frac{E}{(E + b)|a|b} F\left(\sin^{-1} \frac{1}{q}; \sqrt{\frac{2E}{E + b}}\right),$$

$$\rho(E > b) = \frac{E}{2|a|b} F\left(\sin^{-1} q; \sqrt{\frac{E + b}{2E}}\right).$$

For our $a < 0$ case the superconducting DOS (14) contains two logarithmic divergencies at $E = \pm b$ and a gap in the energy range $|E| < (1 - |a|) b$. The "gap" ratio is $1/(1 - |a|)$.

Measurements on MgB$_2$ with scanning tunneling spectroscopy 11 and with high-resolution photo-emission spectroscopy 13 revealed the presence of these two gap sizes. From the ratio 3.3 between the two gaps in Ref. 11 we can extract the parameters $|a| \approx 2/3$ and $\beta w_1 \approx 1.14$ (see Eq. (11)), whereas from data of Ref. 12 one can derive $\beta w_1 = 1.21$. A value $\beta w_1 = 1.14$ can be estimated from Ref. 13. Point-contact spectroscopy 14 shows gaps at 2.8 and 7 meV, from which we estimate a Coulomb repulsion parameter $\beta w_1 = 1.16$. The recent study of energy gaps in superconducting MgB$_2$ by specific-heat measurements revealed "gaps" at 2.0 meV and 7.3 meV 15 for which $\beta w_1 = 1.13$, and a gap ratio $3 - 2.2$ 16, for which $\beta w_1 = 1.14 - 1.15$. Measurements of the specific heat of Mg$^{11}$B$_2$ also give evidence for a second energy gap 17. It is worth noticing that earlier Raman measurements 18 have revealed the presence not only of the discussed peak at 110 cm$^{-1}$, but also of an asymmetric peak at 65 - 60 cm$^{-1}$ (see Figs. 1 and 2 in Ref. 18). These results correspond to a gap ratio 0.6 - 0.54, from which we estimate $|a| = 0.41 - 0.45$ (cf. Eq. (14)) and a Coulomb parameter $\beta w_1 = 1.25 - 1.22$ (Eq. (11)). Later Raman measurements 19 established pronounced peaks, corresponding with gaps at 100 cm$^{-1}$ and 44 cm$^{-1}$. From these data one can extract $a = -0.56$ and $\beta w_1 = 1.18$. At $\beta w_1 = 1$ we have gapless like superconductivity. In this case the superconducting DOS is linear with respect to the energy near the nodes of the superconducting order parameter. Then the superconducting specific heat $C_c \sim T^2$ and the NMR boron relaxation rate $\sim T^3$ at low temperatures (for BEDT-TTF organic salts this is shown in Ref. 20). From this point of view it is interesting that the data of Ref. 21 shows a $C_c \sim T^2$ behaviour and a deviation from the exponential BCS behaviour in $T^{-1}(T)$ of $^{11}$B 22 visualized in MgB$_2$.

In summary, we have analyzed the superconducting properties of the material MgB$_2$ within the framework of a correlated model (1). The existing electron-phonon and non-phonon approaches to the superconducting mechanism in MgB$_2$ can be separated in two groups: one pays attention to the $\sigma$-electrons and the other to the $\pi$-electron subsystem. We have taken into account both the correlated $\sigma$- and noncorrelated $\pi$-electrons. Analysis of our results leads to the conclusion that superconductivity occurs in the subsystem of $\sigma$-electrons with degenerate narrow energy bands whereas the wide-band $\pi$-electrons play
the role of a reservoir. Superconductivity is driven by a non-phonon kinematic interaction in the $\sigma$-band. A lot of evidences in favour of two different superconducting gaps can be explained by anisotropic superconductivity with an order parameter of $s^\ast$-wave symmetry, induced by the in-plane Coulomb repulsion. For an enhanced interboron Coulomb repulsion ($\beta w_1 > 1$) the logarithmic divergencies in the superconducting DOS (Eq. 14, Fig. 4) are manifested by a second gap in the experiments. The kinematic mechanism of superconductivity for correlated electrons was first proposed for high-$T_c$-cuprates ([23], see [1] and Refs. therein) as a non-phonon mechanism with correlated hopping ([24], and Refs. therein). In Ref. [25] it was shown that in the strongly correlated limiting case the kinematic mechanism reproduces the result of hole dressed superconductivity. In our approach the electron-phonon coupling is hidden in the parameter $r$. Therefore the pressure and isotope effects can be explained by the dependence of $r(\omega)$ on the phonon modes. From the non-monotonic $T_c$ dependence on $r$ it follows that the MgB$_2$ material is in the underdoped regime (around $r \gtrsim -w_1/4$). For a fictitious system $A^{2+}B_2$, where the two electrons are contributed by atom A, the superconducting critical temperature increases with an $r$ increase. A pressure increase lowers the $\sigma$-band with an $r$ decrease resulting in a negative pressure derivative of $T_c$ in agreement with experiment [26]. The bell shaped curve $T_c(r)$, with the MgB$_2$ position in the underdoped regime, shows a possibility to reach higher $T_c$’s in diboride materials such as $A^{2+}B^-_2$ with an AlB$_2$ crystal structure. We suggest the synthesis of materials with increased $r$-values (e.g. with ”negative chemical pressure”) and optimized smaller interatomic B-B distances in the honeycomb plane.

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References

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature (London) 410, 63 (2001).
[2] J. M. An, W. E. Pickett, Phys. Rev. Lett. 86, 4366 (2001).
[3] D. R. Armstrong, P. G. Perkins, J. Chem. Soc. Faraday II 75, 12 (1979).
[4] N. I. Medvedeva, J. E. Medvedeva, A. L. Ivanovskii, V. G. Zubkov, A. J. Freeman, JETP Lett. 73, 336 (2001).
[5] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, L. L. Boyer, Phys. Rev. Lett. 86, 4656 (2001).
[6] K. Voelker, V. I. Anisimov, T. M. Rice, cond-mat/0103082.
[7] Y. Kong, O. V. Dolgov, O. Jepsen, O. K. Andersen, Phys. Rev. B 64, R020501 (2001).
[8] T. Yildirim, O. Gulseren, J. W. Lynn, C. M. Brown, T. J. Udovic, H. Z. Qing, N. Rogado, K. A. Regan, M. A. Hayward, J. S. Slusky, T. He, M. K. Haas, P. Khalifah, K. Inumaru, R. J. Cava, Phys. Rev. Lett. 87, 37001 (2001).

[9] V. Ivanov, Europhys. Lett. 52, 351 (2000).

[10] S. Haas, K. Maki, cond-mat/0104207 preprint.

[11] C.-T. Chen, P. Seneor, N.-C. Yeh, R. P. Vasquez, C. U. Jung, Min-Seok Park, Heon-Jung Kim, W. N. Kang, Sung-Ik Lee, cond-mat/0104283.

[12] F. Giubileo, D. Roditchev, W. Sacks, R. Lamy, D. X. Thanh, J. Klein, S. Miraglia, D. Fruchart, J. Marcus, Ph. Monod, cond-mat/0105592.

[13] S. Tsuda, T. Yokoya, T. Kiss, Y. Takano, K. Togano, H. Kitou, H. Ihara, S. Shin, cond-mat/0104489.

[14] P. Szabo, P. Samuely, J. Kacmarcik, Th. Klein, J. Marcus, D. Fruchart, S. Miraglia, C. Marcenat, A. G. M. Jansen, cond-mat/0105598.

[15] R. A. Fisher, F. Bouquet, N. E. Phillips, D. G. Hinks, J. D. Jorgensen, cond-mat/0107072.

[16] A. Junod, Y. Wang, F. Bouquet, P. Toulemonde, to appear in: A. Marlikov (Eds.), Studies of High Temperature Superconductors, Vol. 38, Nova Science, New York; cond-mat/0106394.

[17] F. Bouquet, R. A. Fisher, N. E. Phillips, D. G. Hinks, J. D. Jorgensen, Phys. Rev. Lett. 87, 047001 (2001).

[18] X. K. Chen, M. J. Konstantinovic, J. C. Irwin, D. D. Lawrie, J. P. Franck, cond-mat/0104003 version 1 (31 March 2001).

[19] X. K. Chen, M. J. Konstantinovic, J. C. Irwin, D. D. Lawrie, J. P. Franck, cond-mat/0104003 version 2 (21 May 2001).

[20] V. A. Ivanov, E. A. Ugolkova, M. Ye. Zhuravlev, JETP 86 (1998) 395.

[21] Y. Wang, T. Plackowski, A. Junod, Physica C 355, 179 (2001).

[22] A. Gerashenko, K. Mikhailov, S. Verkhovskii, T. D’yachkova, A. Tyutyunnik, V. Zubkov, cond-mat/0102421.

[23] R. O. Zaitsev, V. A. Ivanov, Sov. Phys. Solid State 29, 1475, 1784 (1987); JETP Lett. 46, 140 (1987); V. A. Ivanov, R. O. Zaitsev, Intern J. Mod. Phys. B 1, 689 (1988), ibid. 3, 1403 (1989).

[24] J. E. Hirsch, Phys. Lett. A 282, 392 (2001).

[25] V. A. Ivanov, M. Ye. Zhuravlev, Theor. and Mathem. Physics 86, 215 (1991); Physica C 185, 1587 (1991).

[26] H. Tou, T. Takenobu, T. Ito, Y. Iwasa, K. Prassides, T. Arima, J. Phys.: Condens. Matter 13, L267 (2001).
Figure captions

**Fig. 1** A schematic view of the energy band diagram. The degenerate $\sigma$-electrons are represented by a lower correlated band.

**Fig. 2** The anomalous self-energy $\Sigma(p)$ for $\sigma$-electrons. The solid line is an anomalous Green’s function (cf. Eq. (6)).

**Fig. 3** The non-monotonic dependence of $T_c(r)$ at different magnitudes of the Coulomb repulsion (parameter $\beta w_1$). Here $w_2/w_1 = 8$. MgB$_2$ is marked in the inset with a solid circle positioned at $r = 0.085$ eV and $\beta w_1 = 1.2$ for $w_1 = 1$ eV and $w_2 = 8$ eV.

**Fig. 4** The superconducting DOS, normalized with respect to the normal DOS, for the Coulomb parameter range $\beta w_1 > 1$. At $\beta w_1 = 0.92$, the Maki result is reproduced (inset) (cf. Eq. (13)).
Fig. 1: Ivanov et al.
Fig. 2: Ivanov et al.
Fig. 3: Ivanov et al.
Fig. 4: Ivanov et al.