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ELECTRON AND HOLE-DOPED HIGH-TEMPERATURE SUPERCONDUCTORS: A COMMON CHARGE TRANSFER MODEL

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The discovery of high-Tc superconductivity in electron-doped cuprate compounds is certainly a test for the theories proposed for the hole-doped systems. In this work it is shown that a similar charge transfer mechanism as the one proposed for hole-doped CuO_2 and BiO_3 systems allows pairing of the electrons in the CuO_2 layers. Only the modification of the parameter values, due to the different T' structure without apical O^{-2} ions must be taken into account. The observation of Cu^{1+} ions in $Nd_{2-x}Ce_xCuO_2$ as well as the presence of O_{2p} holes give support to this picture.

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The finding of high -temperature superconductivity (HTS) in $Ln_{2-x}R_xCuO_{4-y}$ (where Ln = Pr, Nd, Sm or Eu and R = Ce, Th)[1-3] strongly motivates to test if the theories proposed for the hole-doped case can also be applied to these electron-doped cuprates. Although more experimental information is necessary to confirm the n-character of these new superconductors some results suggest that this is the case. Here it is shown that an analogous charge transfer (CT) mechanism as the one proposed for the CuO_2[4] and BiO_3[5] systems can give rise to pairing of the electrons added in the CuO_2 layers. The necessary conditions remain the same as in the hole-doped case[5]: proximity of the metal (M = Cu or Bi) and O levels, a gap in the electronic spectrum and important M-O repulsion, with inclusion of longer range Coulomb interactions in the electron-doped systems. We compare the three types of high-Tc superconductors: hole-doped with magnetic and non magnetic metallic ions, and the electron-doped compounds, in the strong coupling limit, and complete the analysis of this latter case with a second order perturbation calculation in the hopping t, with and without screening for the Coulomb interaction.

The charge carriers in the previously known cuprate superconductors were holes. The insulating material was rendered metallic by substitution of a 2^+ aikaline earth by a 3^+ rare earth or by adding oxygen. As emphasized first by Emery[6], it is energetically more favourable for these extra holes to go primarily on the planar O^{-2} sites. Instead, Tokura, Takagi and Uchida[7], starting from semiconducting Ln_2CuO_4, replaced the Ln^{3+} ion by the higher valency Ce ion and removed oxygen by annealing under reducing atmosphere, achieving superconductivity abruptly when the concentration arrives to a critical value. Although they confirmed the electron nature of the carriers deduced from their chemical analysis by the Hall and Seebeck coefficients, they were very cautious about the location of the doped electrons: in the CuO_2 sheets or mainly in the Nd layers; they were not able to rule out this last possibility. The observation by X-ray absorption

measurements by Tranquada et al.[8] of Cu^{1+} in $Nd_{2-x}Ce_xCuO_4$ as well as the report of HTS in $Ln_2CuO_{4-x}F_x$ (Ln = Pr, Nd)[9] seem to give support to the former hypothesis.

As also pointed out by Emery[10] the T' structure of these new materials[1] without apical O^{-2} ions must favour the addition of electrons to fill the Cu 3d holes; we are going to come back to this point in relation to our model parameter values. The observation of O_{2p} holes by Nücker et al.[11] by EELS in $Nd_{2-x}Ce_xCuO_4$ increasing with Ce concentration is in agreement with our CT mechanism; however we must say that as in the case of the hole doped superconductors, they do not find by this experiment[12] clear evidence for Cu^{1+}. Also first Cu 2p XPS core lines failed to identify Cu^{1+} in $Nd_{2-x}Ce_xCuO_4$.[13] New systematic X-ray absorption and core level photoemission measurements in "n-doped" superconducting cuprates, by Asensio et al.[14] show evidence of the presence in the vecinity of the Fermi level of both, electrons in (previously empty, in undoped and doped but not reduced samples) Cu 3d orbitals and, in a lower proportion, of holes in O_{2p} orbitals.

The general Hamiltonian for HTS, proposed for the dynamics of the holes in the CuO_2 layers[4] and three-dimensional BiO_3 compounds[5], that we use now also for the electron-doped case, can be written:

$$H = H_o + H'$$

$$H_o = \sum_{i\sigma} \varepsilon_M n^M_{i\sigma} + \sum_{j\sigma} \varepsilon_p n^p_{j\sigma} + U_M \sum_i n^M_{i\uparrow} n^M_{i\downarrow} + U_p \sum_j n^p_{j\uparrow} n^p_{j\downarrow} + \sum_{k,l\neq k} \sum_{\sigma\sigma'} \sum_{\alpha\beta} G_{kl} n^\alpha_{k\sigma} n^\beta_{l\sigma'} \qquad (1)$$

$$H' = t \sum_{<l,j>\sigma} (c^{M\,+}_{l\sigma} p_{j\sigma} + H.c.)$$

where the first term in H_o represents the energy of the M orbitals ($3d(x^2-y^2)$ if M = Cu, 6s if M = Bi). The second is the energy of the O_{2p} orbitals directed towards their nearest-neighbour M ions. The third and fourth terms describe on-site Coulomb energies: the fifth represents intersite Coulomb repulsion between M and O ions. These last interactions become $\tilde{U}_M$ and $\tilde{G}_{kl}$ when O displacements as observed in BiO_3 compounds, are taken into account ($\tilde{U}_M = U_M > 0$ for the cuprates, $\tilde{U}_M < 0$ for the bismuthates; the detailed expression is given in Ref.5). H' represents the hopping between nearest-neighbour M and O ions (the phases of the atomic orbitals were chosen to have t > 0 for all directions). As correlations are essential, the interaction Hamiltonian H_o is solved exactly and H' included as perturbation. We define:

$$\Delta = \varepsilon_p - \varepsilon_M \qquad ; \quad G_{kl} = \frac{e^2}{r_{kl}} f(r_{kl}) = G_i \qquad (2)$$

where r_{kl} is the distance between M-O, M-M and O-O ions at the k, l positions, these ions being i-th neighbours and $f(r_{kl})$ is an

eventual screening function. For simplicity in many discussions only the nearest-neighbour repulsion G_1 between M and O ions is considered. The crucial role of this term, inducing charge fluctuations due to the unusual covalency of the M-O network in these perovskites has been first remarked by Varma, Schmitt-Rink and Abrahams[15], it has latter been shown that the effective interaction between O holes through such polarization could be attractive, leading perhaps to HTS. Although in the case of the p-type systems this term suffices to have binding of two holes added to the semiconducting compound[4,5], it is well known that longer range Coulomb interactions must also be considered to prevent a local accumulation of charge when the concentration of holes is increased, the inclusion of more terms modifying in turn the pairing conditions. Within the notation of Eq.(1) to dope CuO_2 layers with electrons means to take out Cu 3d holes. In the strong coupling limit it is trivial to see that nearest neighbour Cu^{1+} ions yield repulsion, longer range Coulomb interactions must be then necessarily considered in order to relate two missing holes. We are going to see that in this case a similar CT mechanism allows pairing.

We define the binding energy as the difference between the energy of two paired and two infinitely distant particles (holes or electrons) added to the stoichiometric compound:

$$E_b = E_2 - 2E_1 \qquad (3)$$

The conditions to have pairing but not clustering of a third added particle are then:

$$1)\ E_b < 0 \qquad (4.a)$$

$$2)\ E_2 + E_1 < E_3 \qquad (4.b)$$

Although the kinetic energy will compete against clustering of particles we must verify also this last condition to ensure pairing. We next compare the three different types of high temperature superconductors in the strong coupling limit ($t=0$). The t^2 results for the hole-doped case have been given elsewhere[5] and they do not modify the conclusions.

I) Hole pairing

a) Magnetic case

We start considering the Cu-based oxides for which $\tilde{U}_M$ and $\Delta > 0$. For simplicity we take $\tilde{U}_M$ and $U_p \to \infty$. The undoped semiconducting compound has one hole per Cu site; the antiferromagnetic ground state (in t^4 order) is progressively destroyed with doping by t^2 processes. Here we discuss the 0^{th} order results and then the spin does not take part. Fig.1(a) shows the pairing of O holes by a CT mechanism[4] induced by the nearest-neighbour M-O repulsion G_1. The reordering of the charges lowers the two added-holes energy and condition 1 [Eq. 4(a)] is given by:

$$\Delta < G_1 - 2G_2 + 3G_3 - 4G_4 + 4G_5 - 2G_6 + \ldots \qquad (5)$$

Then when only G_1 is considered, $E_b < 0$ for $\Delta > G_1^{2h} = G_1$. But condition 2 [Eq.4 (b)] inhibiting the clustering of a third added

hole in the empty O site neighbouring the Cu missing hole [site A in Fig. 1(a)], reads:

$$G_1 - G_3 < 2G_2 \qquad (6)$$

longer range terms are compensated. Eq.6 implies that at least G_2 must be included. But then for an unscreened Coulomb potential [$f(r_{kl}) = 1$ in Eq.3], Eq.5 becomes:

$$\Delta < G\,(1 - 2 \times 0.707 + 3 \times 0.5 - \ldots) \qquad (7)$$

and G_3 must also be taken into account in order to verify this inequality. However for the Coulomb potential this term favours the formation of spatially extended strings of Cu^+O^- pairs, as those found by Schüttler.[16] Although G_4 plays against these additional charge transfers, it also kills the pairing. When G_5 and G_8 are included the state with two charge transfers becomes energetically more favourable (see Fig. 2(e) in Rev. 16). As these longer range interactions are considered, more configurations competing in energy appear. Exact diagonalization results for small clusters by Hirsch et al.[17] show how a G_2 interaction weakens the attraction. The interval in which pairing is allowed by the CT mechanism of Fig. 1(a) is drastically reduced but for some parameter values they still have pairing in a very small region, with addition of only G_2, i.e. a certain repulsion between nearest-neighbor O sites.

The shape and range of the potential strongly affect the low energy configurations and the critical value G_c.

b) Non magnetic case

This case has been studied in detail in Refs.5 and 18 in connection with the $BaBiO_3$ based superconductors. In fact, the similar M-O network and the presence of O holes[19] as well as a positive Seebeck effect in $BaPb_{1-x}Bi_xO_3$[20] and in $Ba_{1-x}K_xBiO_3$[21] suggest a common pairing mechanism for these non magnetic systems and the cuprate compounds. Considering that the effect of the observed O displacements is to create negative $\tilde{U}_M$ centers at the Bi sites, giving rise to a charge-ordered instead of an antiferromagnetic insulator for the undoped compound:

$$\tilde{U}_M = U_M - z(2A-B) = U_M - z\,A' < 0 \qquad (8)$$

where z is the coordination number of the M ions and A' the difference between the diagonal energy gain (2A for any displaced O ion) and the loss of elastic energy (B). Defining as $\tilde{G}_i$ the Coulomb interactions in the distorted case, it is straightforward to see that the critical value for pairing G_c also increases with longer range Coulomb interactions, necessary to prevent local accumulation of the added O holes. This conclusion is unchanged in 2 and 3 dimensions, although it is this last case that would correspond to $BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}K_xBiO_3$ systems, for simplicity Fig.1 (b) sketches the pairing of holes in 2 dimensions by a

biexcitonic mechanism and the interactions we consider to prove Eq.4 (a):

$$2\varepsilon_d + 2\Delta + 4A' - U_N + 4G_2 + 2G_3 + 16\tilde{C}_4 - 16\tilde{C}_5 + 8\tilde{C}_6 \ldots < 2(\varepsilon_d + A' + 2\tilde{C}_1 + 4\tilde{C}_4 + 2\tilde{C}_8 + \ldots) \quad (9)$$

this yielding:

$$G_c > \frac{\Delta + A' - U_N/2}{2 - 1.414 - 0.5 + \ldots} \quad (10)$$

for the unscreened Coulomb potential, the inclusion of $\tilde{C}_7$ being necessary to verify Eq.4 (b) in this t = 0 limit:

$$2\tilde{C}_8 < G_3 + 2\tilde{C}_7 \quad (11)$$

Although from band structure calculations it has been suggested[22] that also in this case, doping with electron must lead HTS, the three dimensionality of these systems (each Bi atom having 6 nearest-neighbour O as in the case of cuprates with apical O atoms of the T structure) should play against this possibility.

II) Electron pairing

Although as we have already said, more experimental results still are necessary to confirm the n-character of the carriers in these electron-doped cuprates, we are now going to discuss the pairing of electrons in CuO_2 layers.

We have the same layered structure of Fig. 1(a), with Δ and $\tilde{U}_N > 0$, with one hole at each Cu site for the undoped semiconducting compound. Now instead of adding holes in the O sites, we extract holes from the Cu sites. In the CuO_2 plane there is no other possibility. G_3 is therefore the lowest range interaction relating two Cu ions, but it is straightforward to see that nearest-neighbour Cu^{1+} ions yield repulsion. Fig.2 shows pairing of next nearest neighbour electrons by a CT mechanism analogous to the one proposed for the hole doped case. In the t=0 limit, Eq. 11(a) reads:

$$\Delta < -G_1 + 4G_3 - 2G_4 + 2G_5 - 2G_6 + \ldots \quad (12)$$

Considering again an unscreened Coulomb potential, the inclusion of G_4 is necessary to preserve the lattice stability against CT processes in the undoped system, the critical value up to this term being in this case:

$$G_c^{(0)} > 9.43\,\Delta \quad (13)$$

We must now verify that there is no charge clustering when a third electron is added. Eq.4 (b) requires:

$$-2G_3 + G_6 < 0 \quad (14)$$

i.e. while if only terms up to G_4 are considered there is no energy difference, G_5 yields an energy gain for a distant third added particle. G_6, playing against pairing in both Eqs.12 and 14, must be included with G_5 for an unscreened Coulomb potential as

the values of both interactions are very similar. However, in that case the transfer of the Cu hole in site A to the upper O atom becomes more favourable.

Then considering that Coulomb correlations up to G_4 are important and that longer range ones are completely screened, pairing of electrons is obtained by the CT mechanism as sketched in fig. 2, very similar to the one proposed for the previous cases. However as said before the T'structure of these new compounds, without apical O^{-2} ions must favour the electron doping, in our notation this implies that Δ although positive must be considerable smaller that in the case of the T-phase structure with Cu-O octahedra in the p-type superconductors. This is, to add electrons in a CuO_2 layer is only possible in the Cu sites and it is easier in this new case; the contrary occurs when holes are added in these systems.

We show now how the t = 0 limit results are modified when the hopping term H' is included. In second order perturbation theory:

$$E_1^{(2)} = -\varepsilon_N - 4G_3 - t^2\left\{-\frac{28}{\Delta + G_1 - 4G_3 + 4G_4} + \frac{16}{\Delta - 3G_3 + 4G_4} + \frac{4}{\Delta + G_1 - 3G_3 + 4G_4} + \frac{8}{\Delta + G_1 - 3G_3 + 3G_4} + \frac{8}{\Delta + G_1 - 4G_3 + 3G_4}\right\}$$

$$E_2^{(2)} = \frac{E_A^{(2)} + E_B^{(2)}}{2} - \sqrt{\left[\frac{E_A^{(2)} - E_B^{(2)}}{2}\right]^2 + t^2} \quad (15)$$

where:

$$E_A^{(2)} = -2\varepsilon_N - 8G_3 - t^2\left\{-\frac{50}{\Delta + G_1 - 4G_3 + 4G_4} + \frac{8}{\Delta - 3G_3 + 4G_4} + \frac{6}{\Delta + G_1 - 3G_3 + 4G_4} + \frac{12}{\Delta + G_1 - 3G_3 + 3G_4} + \frac{12}{\Delta + G_1 - 4G_3 + 3G_4} + \frac{2}{\Delta + G_1 - 3G_3 + 2G_4} + \frac{2}{\Delta - 2G_3 + 4G_4}\right\}$$

$$E_B^{(2)} = -2\varepsilon_N + \Delta + G_1 - 12G_3 + 2G_4 - t^2\left\{-\frac{59}{\Delta + G_1 - 4G_3 + 4G_4} + \frac{4}{\Delta - 3G_3 + 4G_4} + \frac{5}{\Delta + G_1 - 3G_3 + 4G_4} + \frac{10}{\Delta + G_1 - 3G_3 + 2G_4} + \frac{1}{\Delta + G_1 - 4G_3 + 3G_4} - \frac{2}{\Delta + G_1 - 2G_3 + 2G_4} + \frac{2}{\Delta - G_1 + G_2 - G_3 + 3G_4} + \frac{1}{\Delta - G_1 - G_3 + 2G_4 + U_p} + \frac{1}{-\Delta - G_1 + G_3 - 2G_4 + U_N} + \frac{2}{\Delta + G_3 - 2G_4} + \frac{1}{\Delta - 2G_3 + G_4} + \frac{1}{\Delta + 2G_4} + \frac{2}{\Delta + G_1 - 3G_3 + 2G_4} + \frac{2}{\Delta + G_2 - 2G_3 + 2G_4}\right\}$$

$E_2^{(2)}$ taking into account the energies of two next-nearest-neighbour Cu electrons without and with CT. Fig.3 shows how for Coulomb interactions up to G_4 the hopping helps electron pairing. Fig.4 shows the same second order perturbation calculation when a straight-line potential is considered. In this case G_2 is increased by the hopping.

To conclude, assuming that correlations are of essential relevance, we have shown in the strong correlation limit, that a CT mechanism yields pairing of the electrons in the CuO_2 layers.

The recent observation[14] of Cu^{1+} ions in the superconducting samples and simultaneously of O holes in a lower proportion gives support to this picture. Also the fact that the amount of electron doping is larger than the Ce concentration (in a 3/2 ratio)[24] is in agreement. Of course this is just a simplified ionic approach to these complex systems, and parameters and results must be modified -we expect only quantitatively- by hopping, hybridization and other terms present in the real case.

Although similar, the polarized structure for Cu electrons is not identical to the one binding pairs of O holes, i.e. there is no exact electron-hole symmetry. On the other hand the different structure of both types of superconducting cuprates (T' and T) must also imply changes in the parameter values, that seem to be more restricted in this new case. This agrees with the experimental results that seem to point out differences in the details of the pairing in both cases. As an example, although the antiferromagnetic order of the CuO_2 layers in the parent compound is progressively destroyed with electron doping[24] as in the case of hole doping, the sudden appearence of the superconductivity contrasts with the linear behaviour of Tc with the hole concentration[25] The coherence length of these new "eventually" n-doped cuprates[26] is larger than the one observed for the p-type superconductors, as obtained in this calculation [compare Figs.2 and 1 (a)].

The necessary conditions to have electron pairing remain the same of Ref.5 for hole doped cuprates and bismuthates: proximity of the metal and O levels, a gap in the excitation spectrum and important M-O repulsion, with inclusion of longer range Coulomb energies in this new case. Although more experimental results are necessary, it is satisfactory to have a common theory for all types of high-Tc superconductors.

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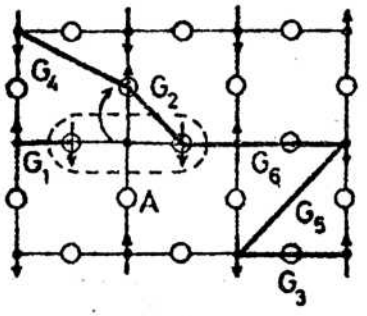
Figure captions

Fig. 1 - Charge rearrangement when two holes are added to the insulating parent compound. a) Cu oxides plane structure, b) Bi oxides case. Also indicated interactions discussed in the text.

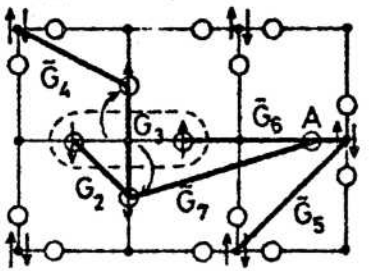
Fig. 2 - Same as in Fig. 1 (a) but when two electrons are added. Site A: energetically most favourable location for the clustering of a third added particle.

Fig. 3 - Binding energy for a pair of electrons considering a Coulomb potential up to G_4 as a function of G_1, for U_d, $U_p \to \infty$, and indicated values of t/A.

Fig. 4 - Same as Fig. 3 for a straight-line potential between $G_1 = G$ and $G_8 = 0$.



(a)



(b)

Fig. 1

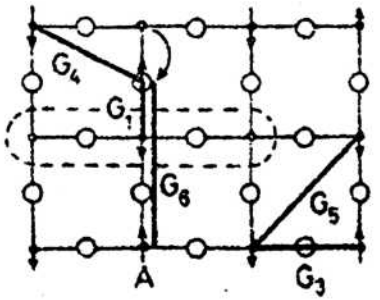
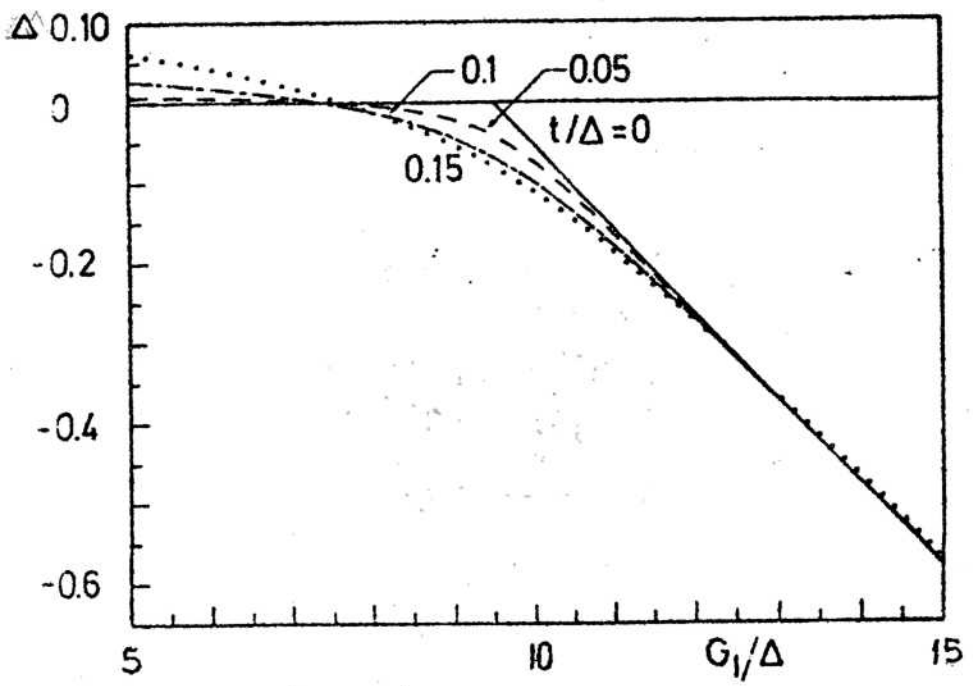


Fig. 2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0
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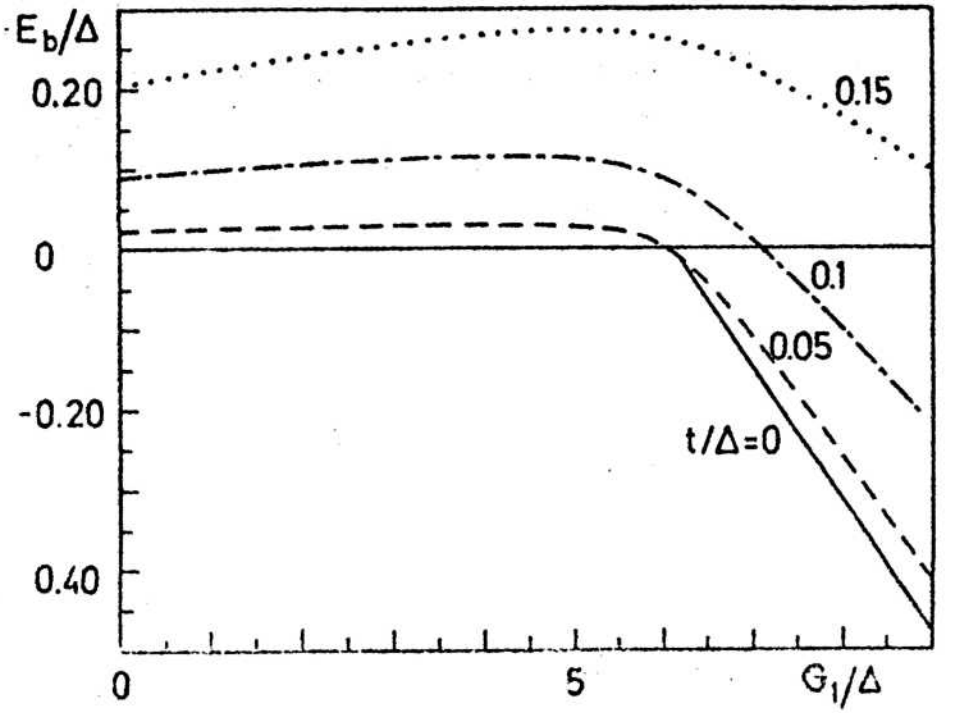
-0.4
-0.6
0.1
0.05
t/Δ=0
0.15
5
10
G_1/Δ
15

Fig. 3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0.20
0
-0.20
0.40
0.15
0.1
0.05
t/Δ=0
0
5
G_1/Δ

Fig. 4