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Role of interlayer coupling in cuprate high-T_c superconductors

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ABSTRACT: The effect of the interlayer Josephson coupling on the high-T_c superconductors (HTSCs) is re-examined in light of the recent discovery that the critical temperatures, T_c, of the $n = 4$ members of the HTSC homologous series $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$, $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4+\delta}$, and $TlBa_2Ca_{n-1}Cu_nO_{2n+3+\delta}$, are lower than those of the $n = 3$ members of the series. This is in contradiction to the prediction of a Ginzburg-Landau theory that the T_c's of a homologous series of HTSCs would increase monotonically with the number of layers. That theory was based on the assumption that the strengths of the Josephson coupling between the different CuO_2 layers within a homologous series are the same. It is shown that the T_c's of the $n = 4$ member in a series would be lower than those of the $n = 3$ member if the hole concentrations in the interior CuO_2 layers are different from those in the outer layers.

KEYWORDS: high temperature superconductor, Ginzburg-Landau approach, layer effect, Josephson tunnelling

INTRODUCTION

The discovery of 90 K superconductivity in $YBa_2Cu_3O_{7-\delta}$ [1], not the discovery of 35 K superconductivity in a multi-phase $Ba_xLa_{3-x}Cu_5O_{8-y}$ ceramic[2], was the event that excited the whole world. Later studies showed that the 35 K superconductor had the K_2NiF_4 structure[3]. Superconductivity was initially achieved by adjusting the oxygen content so that the copper valency was about 2.2. The reason for the lack of excitement about the 35 K high-T_c superconductor (HTSC) is that at 35 K, liquid helium still has to be used. Shortly after the discovery of the 90 K HTSC, superconductivity at equally high or higher temperatures was seen in some Bi-based[4] and Tl-based[5,6] perovskite structure compounds. Noticing that the critical temperatures, T_c, of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1$, 2, and 3)[4], of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n = 1$, 2, and 3)[5], and of $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ ($n = 2$, 3, and 4)[6] increased monotonically, Wheatley et al[7] proposed that the T_c's of the layered superconductors would increase as more CuO_2 layers are inserted into the homologous series. Toradi et al[8] even conjectured that room temperature superconductivity could be achieved if enough layers were added.

A consensus has developed that the electron-phonon interaction cannot account for the higher T_c's seen in the cuprate HTSCs. This is not true of the '214' superconductors where Weber[9], using a first principle calculation based on the Eliashberg formulism, found that the electron-phonon interaction could lead to a T_c between 30–40 K for the La-Ba-Cu-O ceramic. Also, it is clearly established that superconductivity in two recently discovered superconductors, the fullerene Cs_3C_{60} ($T_c \sim 40$ K[10]) and MgB_2 ($T_c \sim 39$ K[11]), are driven by the electron-phonon interaction. For the higher T_c HTSCs, many exotic mechanisms to explain the superconductivity have been proposed. One of these, the resonant valence bond model of Anderson[12], has attracted much attention. In spite of the tremendous amount of research done on this model, it has not even come close in accounting for the most important feature of the HTSCs, their high T_c's. It was recently pointed out that there is still a lack of a generally accepted mechanism responsible for superconductivity in HTSCs, the same situation as twenty years ago[13].

In the absence of a microscopic theory for HTSCs Birman and Lu[14] and Eab and Tang[15,16] have separately developed phenomenological theories for layered HTSCs based on the Ginzburg-Landau approach. Unlike the earlier conjecture made in Ref. 8, both Birman and Lu, and Eab and Tang predicted that the T_c would reach a maximum value (140 K) for the bismuth series, and as more layers were added there would be a saturation effect. A similar conclusion was reached more recently by Chen et al[17] when they applied the Ginzburg-Landau approach to the homologous $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ series. For this series Chen et al predicted a maximum T_c of 160 K. All three studies predicted a monotonic increase in the T_c's of the homologous series as the number of layers increased.

Recent measurements of the T_c's of the $n = 4$ and 5 members of the Tl series[18,19] and the Hg series[20] show that the T_c's of these members are lower than the T_c's of the $n = 3$ member. Setty and Singh[21] suggested that the drop in the T_c is due to the presence of CuO_2 layers with different doping levels in the HTSCs. The presence of non-equivalent layers is consistent with the actual structure of the cuprate superconductors. The Cu ions in the outer (top and bottom) layers have pyramidal coordination with the O^{2-} ions, while the Cu ions in interior layers have square-planar coordination with the O^{2-} ions. Cu-NMR experiments[22] done on the $n = 3$, 4, and 5 members of the Hg-based series indicated that the local hole doping in the two types of layers are different. Kim et al[23] have recently suggested that the hole concentrations in the interior planes may not be the optimal values needed for superconductivity to occur in these planes. If the hole concentration were such that superconductivity did not occur in the interior layers, then there would only be one order parameter in the $HgBa_2Ca_3Cu_4O_{10+\delta}$ superconductor.

The aim of the present paper is to modify our previous work so that it could yield results more consistent with the recent observations, i.e., the decrease in the T_c as more CuO_2 layers ($n \geqslant 4$) are inserted into a layered HTSC to create the homologous series of superconductors such as $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$. We present the Ginzburg-Landau expressions for the free energies of the $n = 3$ and $n = 4$ members of the homologous series of HTSCs which would more accurately reflect their crystal structure, i.e., the top and bottom CuO_2 layers being different from the interior CuO_2 layers. We then minimize the free energy expressions and obtain a set of equations for the components of the order parameters for the next two members ($n = 3$ and $n = 4$) of the homologous series.

GINZBURG-LANDAU APPROACH

The theory of (second order) phase transitions was developed by Ginzburg and Landau and is based on basic principles of symmetry and not on the exact form of any interactions. In this theory, every phase is characterized by an order parameter which is non-zero when the state is in that phase but becomes zero when the state leaves the phase. The free energy functional is taken to be real, gauge invariant, and possesses the relevant space group symmetry elements of the structure. The extension of the Ginzburg-Landau theory to multi-layer superconductors was done by Lawrence and Doniach[24]. The first extension of the their formulism to HTSCs was by Eab and Tang.[25]

The free energy expressions for the $n = 1$ and 2 members of a homologous series are given in Refs. 14–16. Those for the $n = 3$ and $n = 4$ members are given respectively by

$$F(\varphi_{j,1},\varphi_{j,2},\varphi_{j,3}) = \sum_j \frac{1}{2}\int \mathrm{d}^2 r \left\{ \sum_{k=1}^{3} a_k|\varphi_{j,k}|^2 + b_k g_{ii}\partial_i^2|\varphi_{j,k}|^2 + c_k|\varphi_{j,k}|^4 + \gamma_0(|\varphi_{j,1}-\varphi_{j+1,3}|^2 + |\varphi_{j,3}-\varphi_{j-1,1}|^2) + \gamma_1(|\varphi_{j,1}-\varphi_{j,2}|^2 + |\varphi_{j,2}-\varphi_{j,3}|^2) \right\} \quad (1)$$

and

$$F(\varphi_{j,1},\varphi_{j,2},\varphi_{j,3},\varphi_{j,4}) = \sum_j \frac{1}{2}\int \mathrm{d}^2 r \left\{ \sum_{k=1}^{4} a_k|\varphi_{j,k}|^2 + b_k g_{ii}\partial_i^2|\varphi_{j,k}|^2 + c_k|\varphi_{j,k}|^4 + \gamma_0(|\varphi_{j,1}-\varphi_{j+1,4}|^2 + |\varphi_{j,4}-\varphi_{j-1,1}|^2) + \gamma_1(|\varphi_{j,1}-\varphi_{j,2}|^2+|\varphi_{j,3}-\varphi_{j,4}|^2)+\gamma_2|\varphi_{j,2}-\varphi_{j,3}|^2 \right\} \quad (2)$$

where the summations over j are over the cell layers in the entire superconductor. In the above free energy expansions, $\varphi_{j,k}$ is the kth order parameter in the jth unit layer, a_k and c_k are the coefficients of the first two terms in the even power series expansion of the free energy in terms of the order parameter $\varphi_{j,k}$, and b_j is the measure of the contribution to the free energy due to the non-uniformity of the order parameter. The g_{ii} are introduced to take care of any possible asymmetry of the system. The γ's are the strength of the Josephson coupling between the different layers within the unit cell; γ_0 is the strength of the tunnelling through the charge reservoir layer lying in between the top (lower) and bottom (top) CuO_2 layers in adjacent unit layer cells, γ_1 is the strength of the Josephson coupling between an outside layer and the adjacent middle layer, and γ_2 is the strength of the Josephson coupling between middle layers. The values of γ_i depend on which n is under consideration. If the amount of holes available is not sufficient to make the number of holes in the middle layers take on the optimal values needed for the order parameter for the layer to exist, then the order parameters in the outer layers would not be equivalent to the order parameters in the middle layers.

As was pointed out in Refs. 15 and 16, if the $-b_k g_{ii}\partial_i^2$ are non-definite negative, the uniform solution that gives $b_k g_{ii}\partial_i^2\varphi_{j,k} = 0$ minimizes the free energies, (1) and (2). For these types of solutions, the terms containing the b_i's in free energies drop out. Therefore, the question of whether the b_i's are temperature dependent is unimportant. Due to the inverse symmetry of the structure, the top and bottom CuO_2 layers are identical and so for the $n = 3$ layer HTSCs, $\varphi_{j,1} = \varphi_{j,3}$ while the order parameter for the middle layer can be either the same or different from the order parameter $\varphi_{j,1}$. For the $n = 4$ members, layers 1 and 4 are equivalent and 2 and 3 are equivalent.

In the cases where the order parameters in adjacent layers are not equivalent, it would be reasonable to expect that the strength of the Josephson tunnelling between the first and second and between the second and third CuO_2 layers in the $n = 3$ member would not be the same as the strength of the Josephson coupling between the first and second layer in the $n = 2$ member. For the $n = 4$ members, we would expect that the strength of the coupling between the middle layers would be different from the coupling between the outer and middle layers, i.e., $\gamma_1 \neq \gamma_2$. In the case that there are enough holes available to optimally dope all layers, all the coupling strengths within a homologous series would be the same.

The a_i and c_i are assumed to be of the same form as those found in the standard Ginzburg-Landau theory, i.e., $a_i = \alpha_i(T - T_i^*)$, where T_i^* is the temperature at which an isolated ith CuO_2 layer would go superconducting. The symmetry arguments for the $n = 3$ case give $T_1^* = T_3^* \neq T_2^*$ and $\alpha_1 = \alpha_3 \neq \alpha_2$, and for the $n = 4$ case, $T_1^* = T_4^* \neq T_2^* = T_3^*$ and $\alpha_1 = \alpha_4 \neq \alpha_2 = \alpha_3$. For all layers being equivalent, the inequalities in the above relations become equalities.

The minimization of the free energies is achieved by applying the condition

$$\delta F(\{\varphi\}) = F(\{\varphi + \delta\varphi\}) - F(\{\varphi\}) = 0 \qquad (3)$$

For the case of $n = 1$ and 2, we obtain the same matrix equations obtained in Refs. 14–16. For the $n = 3$ and 4 cases, we obtain

$$\begin{pmatrix} \beta_{101} & \gamma_1 & \gamma_0 \\ \gamma_1 & \beta_{211} & \gamma_1 \\ \gamma_0 & \gamma_1 & \beta_{101} \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \varphi_1 \end{pmatrix} = 0 \qquad (4)$$

and

$$\begin{pmatrix} \beta_{101} & \gamma_1 & 0 & \gamma_0 \\ \gamma_1 & \beta_{211} & \gamma_2 & 0 \\ 0 & \gamma_2 & \beta_{211} & \gamma_1 \\ \gamma_0 & 0 & \gamma_1 & \beta_{101} \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \varphi_2 \\ \varphi_1 \end{pmatrix} = 0 \qquad (5)$$

in which $\beta_{ijk} \equiv a_i - \gamma_j - \gamma_k$.

The expressions for the T_c's are obtained by first setting $a_1 = \alpha_1(T_c - T_1^*)$ and $a_2 = \alpha_2(T_c - T_2^*)$ and then evaluating the determinant equations $\det M = 0$ where the M are the matrices which appear on the left-hand sides of (4) and (5).

In the case of equivalent layers, simple analytical expressions can be obtained. Setting $a_1 = a_2$, $T_1^* = T_2^* = T^*$, $\alpha_1 = \alpha_2 = \alpha$, and $\gamma_1 = \gamma_2$ in (4) and (5), and solving the determinant equations for the $n =$ 1, 2, 3, and 4 members of the homologous series, we obtain

$$a - 2\gamma_0 = 0, \qquad (6)$$

$$a(a - 2(\gamma_0 + \gamma_1)) = 0, \qquad (7)$$

$$a(a - 3\gamma_1)(a - \gamma_1 - 2\gamma_0) = 0, \qquad (8)$$

$$a(a - 2\gamma_1)\big(a^2 - (4\gamma_1 + 2\gamma_0)a + \gamma_1(6\gamma_0 - 2\gamma_1)\big) = 0, \qquad (9)$$

where $a \equiv \alpha(T_c - T^*)$.

Based on the values of T_c given by Chen and Lin[26] for the $n = 1$, 2, and 3 members of each series we have calculated T^*, γ_0/α and γ_1/α, and using these values in (9), we have obtained the T_c's of the 4th member of each of the homologous series (Table 1). Comparing these with the experimentally measured values for the 4th member of three of the series, we find the predicted T_c's are higher than the observed values (Table 1).

CONSEQUENCES OF NON-EQUIVALENT LAYERS

We now consider what would be the consequence of some of the CuO_2 layers in the $n \geqslant 3$ member of a homologous series of layered superconductors not being equivalent. When this happens, the two free energy expressions, (1) and (2), will depend on the six parameters T_1^*, T_2^*, α_1, α_2, λ_1, and λ_2. The outer (top and bottom) CuO_2 layers are the closest to the charge reservoir layers (the HgO layer, in the case of the Hg

Table 1 Observed critical temperatures (T_c) of the first four members of the 4 homologous series (from Ref. 26), the values of the parameters in the Ginzburg-Landau expression for the free energies, and the predicted T_c's for the $n = 4$ members using the Ginzburg-Landau theory for layered superconductors where all layers are equivalent.

Homologous Series	Observed T_c (K)				Parameters (K)			Predicted T_c (K)
	$n = 1$	2	3	4	T^*	γ_0/α	γ_1/α	$n = 4$
$HgBa_2Ca_{n-1}Cu_nO_{2n+2}$	97	127	135	129	90	3.5	15	142.4
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$	90	115	125	116	87.5	1.25	12.5	130.6
$TlBa_2Ca_{n-1}Cu_nO_{2n+3}$	52	107	133.5	127	51	0.5	27.5	145.0
$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$	36	90	110		29	3.5	27	122.3

series). It would be easier to transfer the holes into these layers than into the layers further away. As we have pointed out, NMR experiments have indicated that the hole concentrations in different layers are not the same. Early measurements of the T_c's of the $La_{2-x}Sr_xCuO_4$ superconductors[21] clearly established that the hole concentration in the CuO_2 plane is one of the main factors controlling superconductivity in the cuprate superconductors. It appears that in most high T_c superconductors, the T_c's exhibit an inverted parabolic dependence on the hole concentration, with the highest T_c occurring at the optimal concentration.

Assuming that the optimal hole concentration occurs in the exterior layer, we have $T_1^* > T_2^*$. Inserting $T_2^* = T_1^* - \delta T$ into (4) and (5), fairly simple expressions for the determinants can be still be obtained if we assume $\gamma_1 = \gamma_2$ and $\alpha_1 = \alpha_2$. Evaluating the two determinants and setting them to zero, we obtain

$$a(a - 3\gamma_1)(a - \gamma_1 - 2\gamma_0) + \{(a - \gamma_0 - \gamma_1)^2 - \gamma_0^2\}\alpha\,\delta T^* = 0 \quad (10)$$

and

$$a(a - 2\gamma_1)\big(a^2 - (4\gamma_1 + 2\gamma_0)a + \gamma_1(6\gamma_0 - 2\gamma_1)\big) + \big\{a^3 - (4\gamma_1 + 2\gamma_0)a^2 + (\gamma_0 + \gamma_1)(2\gamma_0 + 5\gamma_1)a - \gamma_1^2(\gamma_1 - 3\gamma_0)\big\}\alpha\,\delta T^* = 0 \quad (11)$$

where only terms up to first order in δT^* have been kept. In the limit $\delta T^* \to 0$, (10) and (11) reduce to (8) and (9), the equations for the T_c's of the 4-layer superconductors in which all the CuO_2 layers are equivalent.

Using the values of T^*, γ_0/α, and γ_1/α (given in Table 1) for the Hg-series, the Tl-series, and the Tl_2-series, we have calculated the T_c's of the 4th member of each series when $T_2^* = T_1^* - \delta T$ is systematically changed. The T_c's were obtained by substituting the numerical values of all the parameters appearing in the determinant of the matrix appearing on the left-hand side of (5) and using MATHEMATICA to solve the $\det M = 0$ equation. We did not use (11) to obtain the T_c's of the fourth member since the equation is linear in δT. On the curves shown in Fig. 1, we have also indicated the values of the observed T_c's (black squares) reported in Ref. 26 for the $n = 4$ members of three of the series (Table 1). The intercepts of the curves with the y-axis are the predicted T_c values of the 4th member of the homologous series. The values of the δT at which the predicted T_c of the 4th member would be the observed T_c are 9.45, 10.82, and 10.45 for the Hg, Tl_2, and Tl series, respectively. In other words, the pair condensations in an isolated interior CuO_2 layers would have to occur at 80.55 K as opposed to a pair condensation temperature in the exterior layer of 90 K for $HgBa_2Ca_3Cu_4O_{10+\delta}$. For the other two superconductors, $Tl_2Ba_2Ca_3Cu_4O_{12+\delta}$ and $TlBa_2Ca_3Cu_4O_{11+\delta}$, the two pairs of condensation temperatures are (77.18 K, 87.18 K) and (40.55 K, 51 K), respectively. The higher value in each pair is the condensation temperature for the exterior layer. Since superconducting $Bi_2Sr_2Ca_3Cu_4O_{12+\delta}$ has not been found, we cannot list an observed T_c for this superconductor.

Another possible reason for the decrease in the T_c's of the 4th member of a homologous series of layered superconductors could be the strength of the Josephson tunnelling between interior layers, γ_2. This parameter does not appear in the expression for the free energy of the three layer members of the homologous series. We now assume that $\gamma_2 \neq \gamma_1$ and that $T_1^* = T_2^*$ and $\alpha_1 = \alpha_2$ and substitute $\gamma_2 = \gamma_1 + \delta\gamma$ into the determinant equation as before. We then systematically vary $\delta\gamma$ and solve for T_c using MATHEMATICA. The values of $\delta\gamma$ needed for the predicted T_c's to agree with the observed T_c's are too large, i.e., γ_2 would have to be negative. We do not consider this to be the cause of the T_c's of the 4th members of the series being lower than those of the 3rd members.

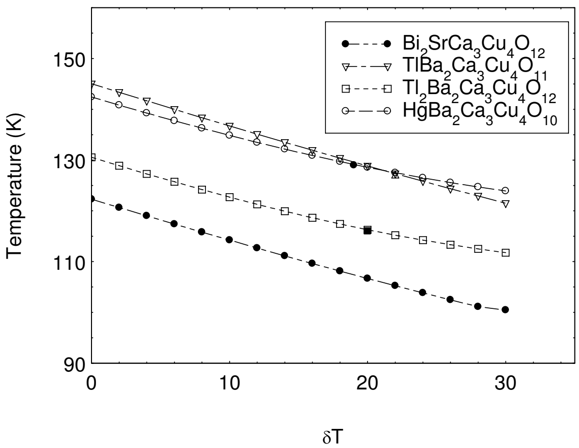

Fig. 1 Predicted dependence of the T_c's of the 4th member of the homologous series on the difference between the pair condensation temperatures in the interior and exterior CuO_2 layers.

We have not attempted to predict the value of the critical temperature of the 5th member of any series. To do this, we would have to include terms containing a fifth order parameter in the Ginzburg-Landau free energy. We would then have five critical temperatures (T_1^*, T_2^*, T_3^*, T_4^*, and T_5^*) at which the ith isolated layer becomes superconducting. Symmetry consideration would require $T_1^* = T_5^*$ and $T_2^* = T_4^*$ with nothing required of T_3^*. It would not be possible to determine both the differences between T_1^* and T_2^* and between T_2^* and T_3^* with only the measured T_c of the fifth member of a homologous series. We would need the T_c of the sixth member. However, as we add additional layers, the structures of the higher members of the homologous series become unstable.

DISCUSSION

As new experimental evidence at odds with the predictions of the current theory in vogue or which indicate that some of the assumptions used in the theory are wrong emerge, the theory needs to be modified. We have done this in this paper. We have shown that that a difference in the hole concentrations in the interior and exterior CuO_2 layers in a four-layer superconductor can account for the difference between the experimental and predicted T_c's of the 4th members of the three series. Since it is not always possible to fabricate ceramics the exact same way each time, there will always be the possibility that the hole concentrations will be different every time. This may account for why Kim et al[20] were able to obtain a 4-layer Tl superconductor having a T_c higher than that of the 3-layer superconductor whereas di Stasio et al[27] obtained a 4-layer Tl superconductor having a T_c lower than that of the 3-layer superconductor.

As a final point, the authors wish to convey their puzzlement over the continued referral to the resonant valence bond model as a viable model for high temperature superconductivity when it has not been able to account for any experimental observation seen in the superconducting phase of HTSCs. The layer model of HTSCs introduced by Birman and Lu[14] and by Eab and Tang[15,16] has been able to account for the layer effect seen in HTSCs.

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