Competing order parameters for increased T_c in "polytype" multilayer Cu-O systems

Joseph L. Birman*
School of Natural Sciences, Institute for Advanced Study, Princeton, New Jersey 08540
and Department of Electronics, The Weizmann Institute of Science, 76100 Rehovot, Israel

Jian-Ping Lu†
Department of Physics, City College of City University of New York,
Convent Ave. at 138 St., New York, New York 10031
(Received 27 September 1988)

Using a simple phenomenological model with coupled order parameters for polytype multilayer copper oxide systems, it is demonstrated that polytypism can increase T_c. Explicit expressions and results are given for $T_c(N)$ where N is the polytype number ($N=2,3,\ldots,\infty$). Classes of structures investigated are monolayer polytypes such as [-$(CuO_2)_N$-]; bilayer TlO polytypes such as [-(TlOTlO$(CuO_2)_N$-]; and monolayer TlO polytypes; and 1:2:3 polytypes such as [-(CuO_2)-(CuO-$CuO_2)_n$-]. Two types of nearest-layer bilinear coupling were studied: weak link (Josephson) and spin-spin. Polytypism is predicted to increase T_c in all classes; except in one case. For the same N, monolayer TlO polytypes have lower T_c than the bilayer TlO analog. Using reasonable values of parameters we predict a maximum T_c of 140 K in the monolayer and bilayer TlO series.

I. INTRODUCTION

In this work we present results of a "Landau" version of a Ginzburg-Landau theory which has been developed[1] for the copper oxide high-T_c superconductors. We shall give predictions for the dependence of superconducting transition temperature upon "polytypism," i.e., multilayer repeated stacking of planes or layers in different structures.

The physical idea is that there are distinct "active" elements in the structure. To each active element (type of plane, or chain) denoted a in the structure is associated a Ginzburg-Landau order-parameter field $\phi_a(\mathbf{r})$. The fields $\phi_a(\mathbf{r})$ can be different types of superconducting entities, i.e., "planes" and "chains" in 1:2:3 structures, or competing superconducting and normal planes in the TlBa structures. Each of these $\phi_a(\mathbf{r})$ has some distinct "bare" transition temperature T_a^0 in that structure. The $\phi_a(\mathbf{r})$ fields are Josephson (weak link) coupled, and hence compete to be primary order parameters: This produces a shift from the bare temperatures to the observed transition temperature T^*, as well as electrodynamic effects. (In this paper the notation T^* means the predicted transition temperature.)

The full Ginzburg-Landau theory is a generalization to competing order parameters of the work of Lawrence and Doniach, Klemm, Beasely and Luther, Katz, Bulaevski, and others.[2] The free energy in the general Ginzburg-Landau theory[1] is real, gauge invariant, and possesses the relevant space-group symmetry elements of the structure; it is written $F=\int_{(\tau)} f(\mathbf{r})d\tau$ where $f(\mathbf{r})$ is the free-energy density per cell. We may take $f(\mathbf{r})$ as

$$f(\mathbf{r})=\sum_a \left[\alpha_a|\phi_a(\mathbf{r})|^2+\beta_a|\phi_a(\mathbf{r})|^4+\frac{h^2}{2m_a}\left|\left(-i\nabla_a-\frac{2e}{hc}\mathbf{A}_a\right)\phi_a(\mathbf{r})\right|^2\right]+\sum_{a,b}\eta_{ab}\left|\phi_a(\mathbf{r})\exp\left(-\frac{2ei}{hc}\int\mathbf{A}\cdot d\mathbf{l}\right)-\phi_b(\mathbf{r})\right|^2, \tag{1}$$

here η_{ab} is the relevant coupling coefficient; $(\nabla_d,\mathbf{A}_d)$ are the d-dimensional gradient, and appropriate vector potential, $\alpha_a(T)=(\alpha_a'/T_a^0)(T-T_a^0)$, and the weak-link Josephson coupling and bare terms are in gauge-invariant form. This Ginzburg-Landau theory is based on the known crystal structure of several series of high-T_c oxides, and has as its objective to provide a framework for the prediction of electrodynamic effects, such as H_{c2}, vortex structure, etc.

In the simplified Landau version discussed here, the competing order-parameter fields $\phi_a(\mathbf{r})$ are taken spatially homogeneous (thus neglecting terms $\nabla\phi_a$ in the free energy), and also no vector potential $\mathbf{A}$ is present. We are concentrating on the temperature region just near T_c^*. If $T>T_c^*$, all order parameters are zero ("normal" state), while for $T<T_c^*$ some $\phi_a\neq 0$ for minimum free energy. Sufficiently close to T^* terms such as $\beta|\phi_a|^4$ in the free energy are small, and so we neglect them. The original motivation of this work concerned the competition between Cu-O chains and CuO_2 planes (as two active entities) in the 90° or 1:2:3 materials such as $YBa_2Cu_3O_{7-\delta}$. Development of the two series of Bi, and Tl-based mixed copper oxide high-T_c superconducting systems has provided even more interesting classes of materials to which the theory applies with suitable changes, leading to testable predictions. In the homogeneous limit of (1), the free-

energy density is a bilinear form in the spatially independent order parameters:

$$f=\sum_a \alpha_a(T)\,|\phi_a|^2+\sum_{a,b}\eta_{ab}\,|\phi_a-\phi_b|^2 . \tag{2}$$

In this limiting form of the "Lawrence-Doniach" (LD) Josephson interaction[2] the quadratic terms for each active entity are shifted,

$$\alpha_a(T)\,|\phi_a|^2 \rightarrow \sum_b [\alpha_a(T)+\eta_{ab}]\,|\phi_a|^2 ,$$

leading to a first-order "mass" renormalization, or lowering of the bare T_a^0. This is a proximity effect which is a result of taking the interaction as in Eq. (2). However, omitting the diagonal terms $\eta_{ab}(|\phi_a|^2+|\phi_b|^2)$ we can take the free-energy density in another gauge-invariant form. This reduces to terms analogous to the bilinear spin-spin interaction (SS) in magnetic systems

$$f=\sum_a \alpha_a(T)\,|\phi_a|^2+\sum_{a,b}(-)\eta_{ab}\phi_a\phi_b^*+\text{c.c.} \tag{3}$$

A priori there seems no compelling reason[3] to choose either the LD "proximity effect" form (2) or the spin-spin form (3) for the Landau f.

Strictly, the bilinear free energy (2) or (3) cannot be minimized (for minimization the omitted nonlinear terms $\beta_a|\phi_a|^4$ must be included). We can extremize f by solving the linear equations $\partial f/\partial\phi_a=0$. The secular equation resulting is of the form $||(\alpha_a(T)+p\eta_{ab})\delta_{a,b}-\eta_{ab}||=0$ in case (2) [in this case, for finite number of elements (planes) the terms for boundary planes and interior planes differ: $p=2$ for interior and $p=1$ for boundary] and $||\alpha_a(T)-\eta_{ab}||=0$ in case (3). The transition temperature T^* is the largest root. The corresponding form of f (rotated to principal axes) is

$$f=\sum_\lambda A_\lambda(T)\,|\zeta_\lambda|^2 ,$$

and $A_\lambda(T^*)=0$ at the greatest root, while ζ_λ is the eigenvector, i.e., that linear combination of the bare order parameters ϕ_a which first has nonzero amplitude at $T^*=T$.

We now apply this simple idea to several classes of high-T_c copper oxide systems: the TlBa class $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$, a related monolayer TlO class,[4] and the 1:2:3 class typified by $YBa_2Cu_3O_{7-\delta}$.[5] With some modification the model can apply to the 2:1:4 class typified by $La_{2-x}Ba_xCuO_4$;[6] and the BiSr class typified by $Bi_2Sr_2Ca_nCu_{n+1}O_{6+2n}$.[7] In the last named case, other structural features omitted here, such as incommensurate modulation, may be important.

In all the classes we shall take one of the ϕ_a to be the superconducting order parameter of CuO_2 plane, the other ϕ_b will depend on the systems. Here, the objective is to predict the dependence of transition temperature T^* upon order of stacking N or polytypism. To implement this idea, we introduce polytype multilayer models as shown on Figs. 1(a)–1(c). In Fig. 1(a) polytypes of a single active layer are shown; we take this as the CuO_2 layer. In Fig. 1(b) the members of the bilayer TlBa class are shown (shaded layers are TlO, open layers are CuO_2). In Fig. 1(c) we show member of the 1:2:3 class with CuO_2 as open layers and the CuO chain-containing layer interleaved. Modifications needed for the monolayer TlO systems are evident.

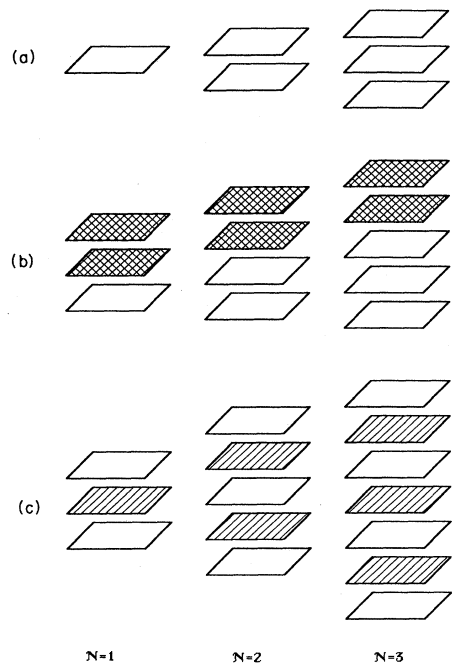

FIG. 1. Model for polytypes of different classes. Polytypes $N=1,2,3$ are illustrated. (a) Monolayer polytypes: The basic layer is taken as a CuO_2 superconducting layer. (b) Polytypes of the bilayer TlO type in the TlBa class. TlO layers are crosshatched, CuO_2 layers as above. For monolayer TlO type, delete one TlO layer and close up. (c) Polytypes of 1:2:3 class. The layers with filament are the layers of CuO chains; the open squares are CuO_2 layers.

II. POLYTYPES OF CuO_2 MONOLAYERS

The CuO_2 plane is a common entity in all classes if we neglect orthorhombicity, and also the "rippling" by which O and Cu ions are slightly noncoplanar, and take a tetragonal model for the CuO_2 array. First make a very simplified ansatz: only the CuO_2 planes are active in determining T^*. Consider polytypes of the basic layer: $-(CuO_2)_N-$ [see Fig. 1(a)]. Further, take only coupling between nearest-neighbor CuO_2 layers $\eta_{ab}=\eta_2\delta_{n,n\pm1}$ and use the SS form Eq. (3). The transition temperature $T^*(N)$ for an N-layer polytype is the maximum eigenvalue of the N-dimensional Jacobi matrix

$$\begin{vmatrix} \alpha(T) & -\eta_2 & 0 & 0 & \cdots \\ -\eta_2 & \alpha(T) & -\eta_2 & 0 & \cdots \\ 0 & -\eta_2 & \alpha(T) & -\eta_2 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{vmatrix}=0 . \tag{4}$$

In (4), $\alpha(T)=(\alpha_p'/T_p^0)(T-T_p^0)$. Both $T^*(N)$ and the eigenvectors can be analytically obtained for $N=2,\ldots,5$. For $N\rightarrow\infty$ we make a "Bloch" ansatz for order parameter ϕ_n at the nth layer $\phi_n=e^{i\theta}\phi_{n-1}$ and it is easy to see that $T^*(\infty)$ occurs for $\theta=0$. For this monolayer polytype sequence the results are of form

$$T^*(N)=T_p^0[1+r_N(\eta_2/\alpha_p')] ,$$

TABLE I. Transition temperature for monolayer polytypes $-(CuO_2)_N-$. The table lists the maximum eigenvalue of the determinant $\Delta_N(T)$, which is the predicted transition temperature $T^*(N)$. The coefficients r_N were found analytically. The experimental data used for illustration are for the bilayer TlO class of materials, as given in Refs. 6 and 8. In this monolayer model, we take $T^*(1)=80$ K $=T_p^0$ for one layer CuO_2; $T^*(2)=110$ K for two layers. Then the coupling constant $\eta_2/\alpha_p'=0.38$. The theory column is our predicted values.

	$T^*(N)=[1+r_N(\eta_2\alpha_p')]T_p^0$	$T^*(N)$ for TlBa class	
Number N	r_N	Experiment	Theory
1	0	80 K	
2	1	110 K	
3	$\sqrt{2}$	125 K	123 K
4	$(1+\sqrt{5})/2$		129 K
5	$\sqrt{3}$		133 K
⋮	⋮		⋮
∞	2		141 K

where T_p^0 is the bare-CuO_2-layer transition temperature for $N=1$; the maximum is $T^*(\infty)$. In Table I the values are given for r_N.

Note that $T^*(N)$ is an increasing function of N, and an important result is that for five layers ($N=5$) one has reached 95% of the maximum ($N\rightarrow\infty$) possible transition temperature, for reasonable values of parameters. A second important result is that the eigenvector for $T^*(N)$ is always a *symmetric* combination of the bare layer order parameters. There is no coupling between symmetric and antisymmetric combinations. In the more general Ginzburg-Landau theory, Josephson phase factors provide such coupling.

Finally, note that if this model is applied to the TlBa and BiSr classes we would take T_p^0 (the bare CuO_2 plane temperature) to be 80 K, which is the value for a single CuO_2 layer, i.e., in 2:0:2:1 there is *one* CuO_2 layer per cell. Then, using the measured temperature of 110 K for two-layer material (2:1:2:2) we obtain $\eta_2/\alpha_p'=0.34$. It follows that $T^*(\infty)$ which we predict as the maximum possible temperature for infinite monolayer sequence is $T^*(\infty)=138$ K for $[2,(N-1),2,N]$ with $N\rightarrow\infty$ (see Table I).

III. POLYTYPES IN Tl-Ba AND Bi-Sr CuO_2 CLASS

At the time of writing several members of the Tl-Ba and Bi-Sr classes have been prepared, their T_c and crystal structures determined.[6,7] These are so-called types 2:0:2:1, 2:1:2:2, 2:2:2:3, and 1:2:2:3 with $T_c=80$, 110, 125, and 110 K, respectively. In this notation, $2(N-1)2N$ identifies a polytype with

$$[\text{-TlO-TlO-BaO-CuO}_2\text{-(Ca-CuO}_2)_N\text{-BaO-}] .$$

In the structural model we now adopt, the layers, e.g., TlO, BaO, CuO_2, Ca are stacked above one another, we ignore the lateral shifts. In this polytype there are $(N+1)$ layers of CuO_2, with a layer of Ca between each, and $N=0,1,2,\ldots$ per cell.

In recent work of relevance to our model, a material with monolayer TlO, composition 1:2:2:3 and $T_c=110$ K was prepared.[8] These authors determined the structure and report it involves identical layering as the 2:2:2:3 material, modulo replacing the bilayer TlO-TlO by the TlO monolayer, and closing up in the z direction. In the framework of polytype models, this permits the conclusion that TlO-TlO interaction is important in this class and suggests a natural generalization of the previous model. We make the following assumptions: (1) Each CuO_2 plane has identical $\alpha_p(T)$. (2) The TlO planes are nonsuperconducting and $\alpha_T=$const. (3) Nonzero coupling between CuO_2-CuO_2, CuO_2-TlO, and TlO-TlO. (The effects of the interleaved BaO and Ca layers are assumed incorporated in the appropriate coupling constants.) (4) We consider a periodic (∞) repeat of the basic polytype cell (defined below). (5) We use the spin-spin form of interaction Eq. (3).

The scheme used for 2:2:2:3, with the layer-layer couplings defined, is

$$\text{-[TlO-}\bar{\eta}_0\text{-TlO-}(\eta_0)\text{-CuO}_2\text{-}(\eta_2)\text{-CuO}_2\text{-}(\eta_2)\text{-CuO}_2\text{-}(\eta_0)\text{-}] .$$

The parameters of the model are bare T_p^0, normalized coupling constants η_0/α', $\bar{\eta}_0/\alpha'$, η_2/α' if we take $\alpha_T'=\alpha_p'=\alpha'$. An infinite periodic array is assumed in the z direction. Since we only take nearest-neighbor couplings the resulting determinant is tridiagonal (not of Jacobi type). We solved analytically for the maximum root $T^*(N)$ for the following members of the bilayer TlO-TlO class: $N=1$ (or TTC), $N=2$ (or $TTCC$), $N=3$ (or $TTCCC$), $N=4$ [or $TT(C)_4$], and $N=\infty$ [or $TT(C)_\infty$], using an obvious notation. We also obtained analytical solutions for the members of the monolayer TlO class $[T(C)_N]$, where $N=3$ (or $TCCC$) is the new 110-K material. Results are presented in Table II. Note that using the observed transition temperatures for materials 2:0:2:1, 2:1:2:2, and 1:2:2:3, we can obtain the parameters needed. Then we calculate $T^*(3)=123$ K for 2:2:2:3 (instead of measured 125 K), as well as $T^*(\infty)\cong 140$ K.

Several points are worth noting about the results. (1) For this model, the bare T_p^0 of CuO_2 will be determined from the measured $T_c^{\exp}$ for TTC, $T_c=80$ K. But now the relation between bare T_p^0 and $T^*(1)=T_c^{\exp}$ (see Table II where various reduced ratios of coupling coefficients are defined) gives $T_p^0<T^*(1)$. We obtain $T_p^0=T^*(1)/(1+2\zeta_2)$ where $T^*(1)$ is the observed transition temperature, which is 80 K for (TTC). Then $T_p^0<80$ K, and in our parameter set $T_p^0\approx 40$ K. (This is the value of T_c^* for $La_{2-x}Ba_xCuO_4$ with a single sheet of CuO_2!) (2) The symmetric combination of order parameters ϕ_a is the eigenvector for maximum root $T^*(N)$. (3) The maximum $T^*(\infty)$ for the $[TT(C)_\infty]$ polytype is predicted at ≈ 140 K. As a check, results for this (TlBa) or (BrSr) class go over to the monolayer polytype case when $\eta_0=\bar{\eta}_0=0$ and $\alpha_T=1$. Essentially the same maximum $T^*(\infty)\cong 140$ K is predicted for the series $[T(C)_\infty]$ of polytypes.

Predictions for other members of the series are also

TABLE II. Transition temperature for polytypes of the TlBa class. The table gives predicted transition temperature $T^*(N)$ for polytypes of bilayer TlO and monolayer TlO members of the TlBa class. Theory column is our predicted values. Experimental values taken from Refs. 6 and 8.

Number	-$[TT(C)_n]$- class $T^*(N)=[1+f^{TT}(N)]T_p^0$			-$[T(C)_N]$- class $T^*(N)=[1+f^{T}(N)]T_p^0$		
N	$f^{TT}(N)$ [a]	Experiment	Theory [b]	$f^{T}(N)$ [c]	Experiment	Theory [b]
1	$2\zeta_2$	85 K	88 K	$4\zeta_3$	NA	56 K
1	a	110 K	112 K	c	85	96 K
3	a	125 K	121 K	c	110 K	112 K
4	a		124 K	c	122 K	120 K
⋮						
∞	$2\zeta_1$		136 K	$2\zeta_1$		136 K

[a]Functions $f^{TT}(N)$ are defined as $f^{TT}(2)=(\zeta_1+\zeta_2)$; $f^{TT}(3)-0.5(\zeta_2+[\zeta_2^2+8\zeta_1^2]^{1/2})$; $f^{TT}(4)-0.5(\zeta_1+\zeta_2+[(\zeta_1-\zeta_2)^2+4\zeta_1^2]^{1/2})$; here $\zeta_1=(\eta_2/\alpha_c')$; $\zeta_2=[\eta_0^2/\alpha_c'(\alpha_T-\bar{\eta}_0)]$. Basic coupling η_2, η_0, $\bar{\eta}_0$, and α_c' and α_T' are defined in the text.

[b]The SS coupling was used in the calculation here. Parameter values are chosen to fit to the known experimental data $T_p^0=40$ K, $\zeta_1=1.2$, $\zeta_2=0.6$, $\zeta_3=0.1$. Predicted values of T^* are shown in the theory columns.

[c]Functions $f^{T}(N)$ are defined as $f^{T}(2)=(\zeta_1+2\zeta_3)$; $f^{T}(3)=\zeta_3+[\zeta_3^2+2\zeta_1^2]^{1/2}$; $f^{T}(4)=(\zeta_1/2+\zeta_3)+[(\zeta_1/2-\zeta_3)^2+\zeta_1^2]^{1/2}$; here $\zeta_3=(\eta_0^2/\alpha_c'\alpha_T)$.

given in Table II. In so far as the (BiSr) series is isostructural, the same predicted sequence of $T^*(N)$ arises. However, incommensurate modulation in (BiSr) may play an important role, not included in the model.

Further observations: The asymptotic (maximum) $T^*(\infty)$ for these series are essentially the same as for the monolayer polytypes (≈ 140 K). The rate of approach to $T^*(\infty)$ differs, with $[TT(C)_N]$ reaching $T^*(\infty)$ more rapidly in N than $[T(C)_N]$. These results use the spin-spin form of coupling as in Eq. (3) (see Table I).

IV. POLYTYPES IN THE 1:2:3 CLASS

The prototype material of this class is $YBa_2Cu_3O_{7-\delta}$. The crystal structure has been carefully determined[9] and the ordered vacancy model is well established. For our model, we also take account of the fact that there is conclusive experimental evidence[10] that replacing Y by rare-earth ions carrying localized magnetic moments does not affect T^*. Thus, we assume that each slice of crystal consisting of the planes between Y ions can be treated in isolation from neighboring slices, the assumed composition being stacked planes in the z direction:

$$\ldots\text{-[-Y-}CuO_2\text{-BaO-CuO-BaO-}CuO_2\text{-]-}\ldots$$

(again neglecting orthorhombicity and the puckering of the CuO_2 planes). We identify two types of active entities as the CuO_2 planes (denoted p as before) and the plane containing parallel filaments of CuO chains (denoted c). Now, the basic assumption is that we have competing chain and plane superconducting order parameters, which produce $T^*=95$ K for the three-layer prototype 1:2:3. For the model, we take couplings between plane and chain (nearest neighbors) and plane and plane (second neighbors), and define the coupling constants via

$$\text{[-}CuO_2\text{-}(\eta_1)\text{-CuO-}(\eta_1)\text{-}CuO_2\text{-]}\,.$$
$$|\longleftarrow\ \eta_2\ \longrightarrow|$$

This is the basic three-layer sandwich [see Fig. 1(c)]. We now assume (1) interaction terms between layers either LD proximity type [Eq. (2)] or SS type [Eq. (3)]; (2) each CuO_2 plane has identical $\alpha_p(T)$ as before, with $\alpha_p(T)=(\alpha_p'/T_p^0)(T-T_p^0)$; (3) the CuO chain layer has $\alpha_c(T)=(\alpha_c'/T_c^0)(T-T_c^0)$. We examined cases $T_c^0>T_p^0$ and $T_p^0>T_c^0$. The coefficients η_1 (and η_2) are assumed to include the effect of exchange coupling via the BaO layer [more specifically, via the O(4) ion].

The general structure of polytype N of the 1:2:3 class is

$$\text{[-}CuO_2\text{-(CuO-}CuO_2)_n\text{-]}\quad\text{with } N=(2n+1)\,,$$

where $n=1$ is the three-layer 1:2:3 case, $n=2$ gives a five-layer polytype, etc. [see Fig. 1(c)]. We use the ansatz that coupling η_1 is present between nearest CuO_2-CuO layers and η_2 between second neighbor CuO_2-CuO_2 layers. Then, the secular determinant is no longer triadiagonal, its structure is illustrated for $n=2$ for SS coupling:

$$\Delta(5)=\begin{vmatrix} x & y & z & 0 & 0 \\ y & x' & y & 0 & 0 \\ z & y & x & y & z \\ 0 & 0 & y & x' & y \\ 0 & 0 & z & y & x \end{vmatrix}=0\,.$$

This form applies in case the interaction is taken as the spin-spin type (3), and then $\alpha_p(T)=x$, $y=-\eta_1$, $z=-\eta_2$, $\alpha_c(T)=x'$. The maximum eigenvalue $T^*(N)$ can be found analytically for $N=3,5$ ($N=2n+1$). A general iterative algorithm relating determinants $\Delta(N)$ of increasing order has been obtained,[11] but for $N\geq 7$ nu-

merical solution is required for the maximum eigenvalue, $T^*(N)$ even after factorizing $\Delta(N)=P[(N-1)/2]Q\times[(N+1)/2]$ where $P(N)$ and $Q(M)$ are polynomials of $N(M)$th degree in T.

In case the LD coupling is used as in Eq. (2) the (1,1) and (N,N) elements in $\Delta(N)$ are replaced by x^0 and the identification is now $x^0=[\alpha_p(T)+\eta_1+\eta_2]$, $x=[\alpha_p(T)+2(\eta_1+\eta_2)]$, $x'=[\alpha_p(T)+2\eta_1]$, y and z are as above.

Detailed results for $T^*(N)$ as function of the parameters depend on whether LD or SS coupling is used, but certain general features are similar. For orientation we begin with the case of the three-layer prototype, and assume $T_c^0>T_p^0$, and consider $\Delta(3)$ for the LD coupling: This form is the limit of the Ginzburg-Landau theory for two superconducting types of order parameter, e.g., chain and plane as suggested by NQR experiments.[12] The transition temperature [maximum root $T^*(3)$] is determined from the equation

$$\Delta(3)=[x'(x^0+z)-2y^2](x^0-z)=0,$$

and an examination shows that the first factor is relevant:

$$x'(T)[x^0(T)+z]-2y^2=0.$$

This equation gives $T^*(3)$ and corresponds to an eigenvector that is a linear combination of ϕ_c for the chain, plus a symmetric superposition of the $\phi_p^+=\phi_p^-$ [+ (−) refers to CuO_2 plane above (below) the CuO chains]. From the definition of x^0 we note that this equation is independent of z (i.e., independent of the CuO_2-CuO_2 second-neighbors couplings η_2). Hence,

$$\{\alpha_c[T^*(3)]+2\eta_1\}\{\alpha_p[T^*(3)]+2\eta_1\}-8\eta_1^2=0,$$

and $T^*(3)$ is directly obtained.

For the polytype with five layers, $\Delta(5)$ factorizes into a quadratic and a cubic (in T) and T^* is determined from the maximum root of

$$xx^0x'-2x^0y^2-xy^2+4y^0z-2x'z^2=0.$$

For normalized coupling parameters η_1 and $\eta_2<1$, it can be shown directly that

$$T^*(5)>T^*(3).$$

Since, in this class we expect $\eta_1>\eta_2$, if we neglect η_2 $(z=0)$ our equation becomes

$$xx'-3y^2=0$$

which evidently gives a larger root $T^*(5)$ than $T^*(3)$. Again the eigenvector corresponding is a symmetric combination of the chain, plus a symmetric combination of plane bare order parameters. For the next polytypes in this class with seven layers, $\Delta(7)$ factorizes and $T^*(7)$ is the maximum root of a fourth-degree equation, which is (taking $z=0$)

$$(xx')^2-4(xx')y^2+2y^4=0$$

or

$$xx'-(2+\sqrt{2})y^2=0.$$

We then find

$$T^*(7)>T^*(5)>T^*(3).$$

With some effort the case $z=0$ can be studied explicitly for a few larger values of N, and

$$T^*(N)>T^*(N-1).$$

For $N\to\infty$, $T^*(\infty)$ with $z=0$ is determined by

$$xx'-4y^2=0.$$

Thus in this case $(T_c^0>T_p^0)$ with LD coupling we obtain

$$T^*(\infty)>\cdots>T^*(N)>T^*(N-1)\cdots>T^*(3).$$

Keeping the LD coupling, and now letting $T_p^0>T_c^0$, we obtain a descending sequence of maximum eigenvalues

$$T^*(3)>\cdots>T^*(N-1)>T^*(N)>\cdots>T^*(\infty)$$

for this case.

For SS coupling we find $T^*(N)$ is an increasing function of N for both $T_p^0>T_c^0$ and $T_p^0<T_c^0$.

Further details and illustrative calculations for the 1:2:3 class are given in the Appendix.

V. SUMMARY AND CONCLUSIONS

In this work we introduced a simple model for the copper oxide high-T_c superconductors based on Ginzburg-Landau theory in the homogeneous or Landau approximation. The model utilized the assumption that in each of the classes of materials considered there are active entities to which an ordered parameter (field) ϕ_a should be assigned. A common active entity in the systems considered is the CuO_2 plane. We assign a superconducting field ϕ_p to each CuO_2 plane present. In the layerlike TlBa (or BiSr) systems we assume there is a second normal order parameter ϕ_T for each TlO plane. The set of order parameters is coupled via nearest-neighbor plane-plane interaction. For the 1:2:3 class we take the second type of parameter to represent assumed superconducting order on the CuO chains and assign to the layer of coupled 1D CuO chains an order parameter ϕ_c (it stands for a layer of coupled parallel chains, i.e., $\phi_c=\sum_m\phi_m$ so ϕ_c is a Bloch sum of individual chain parameters ϕ_m). The planes and chains are coupled bilinearly: plane-plane and plane-chain couplings are included.

In the simplest version of the model we consider polytype or multilayer stacks of identical CuO_2 planes with nearest-neighbor coupling. For more elaborate models to apply to TlBa, and 1:2:3 types of systems, several types of planes are introduced [see Figs. 1(a)–1(c)]. In all these cases, the intermediate layers (e.g., BaO, Ca, etc.) are assumed to play a role by affecting the interlayer coupling constants η_{ab}. The transition temperature T^* is obtained by extremizing the free energy, and is the maximum eigenvalue of a certain determinant for that structure.

Our major results and predictions in the framework of this coupled order parameter model are the following.

(1) Polytypes increase T^* for N increasing (when SS coupling applies) in (a) monolayers -$[CuO_2]_N$; (b) the TlBa classes -[TlO-TlO-$[CuO_2]_N$]- and -[TlO-

$[CuO_2]_N$]-; (c) the 1:2:3 structure -[CuO_2-(CuO-$CuO_2)_n$]- if $T_c^0 > T_p^0$.

(2) Polytypes increase T^* for N increasing (with LD coupling) in the 1:2:3 structure if $T_c^0 > T_p^0$.

(3) Polytypes decrease T^* for N increasing (when LD coupling applies) in the 1:2:3 structure if $T_c^0 < T_p^0$.

(4) In the TlBa classes for reasonable values of parameters, the model accounts for experimental T_c; and 95% of the maximum possible T^* is reached for polytype $N=5$.

(5) The monolayer TlO compounds $[T(C)_N]$ have lower T^* than corresponding bilayer TlO $[TT(C)_N]$.

(6) The maximum possible T^* for the monolayer TlO and bilayer TlO classes is $T^*(\infty) \approx 140$ K.

Note added. After our work was completed, we became aware of other work with some similarity to our model.[13–16]

ACKNOWLEDGMENTS

One of us (J.L.B) wants to thank Professor S. L. Adler for hospitality at the Institute for Advanced Study Princeton and Professor R. Hornreich and his colleagues for the useful comments and warm reception at the Weizmann Institute of Science and support from the Meyerhoff Foundation. Special thanks are due to Professor S. Shtrikman for a discussion which lead to considering *both* LD and SS types of coupling in the model. Discussions with Dr. S. Galam and Dr. J. Malinsky were helpful. J.L.B. wishes to thank Professor A. Aharony for making Ref. 14 available prior to publication and also Dr. S. Theodorakis for sending a copy of his unpublished work and for pointing out Refs. 15. J.-P.L. acknowledges support of the Mina Rees Fund, City University of New York. Partial support by FRAP-PSC-CUNY is also acknowledged.

APPENDIX: ILLUSTRATIVE CALCULATIONS ON 1:2:3 CLASS POLYTYPES

Returning to the general secular determinant $\Delta(N)$ for 1:2:3 class, we now neglect the second-neighbor interaction (take $z=0$). For prototype 1:2:3 in our model, $N=3$ (with the effect of the layers of BaO incorporated into the coupling coefficients η_1 and η_2) and the active entities are planes of CuO_2 (P) and layers of CuO chains (C). The structure is P-C-P. Polytypes of 1:2:3 are as above: P-$(C$-P-$)_n$, so $N=(2n+1)$. The secular determinant $\Delta(N)$ is

$$\Delta(N)=\begin{vmatrix} x & y & 0 & 0 & 0 & \cdots \\ y & x' & y & 0 & 0 & \cdots \\ 0 & y & x & y & 0 & \cdots \\ 0 & 0 & y & x' & y & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 .$$

First consider SS coupling [Eq. (3)] and let $y=-\eta_1$, $x=(\alpha'/T_p^0)(T-T_p^0)$, $x'=(\alpha'/T_c^0)(T-T_c^0)$ and take $\alpha_p'=\alpha_c'=\alpha'$. Let $T_p^0=3T_c^0$. The relevant coupling parameter is η_1/α'. Figure 2 shows $T^*=T_c$ [maximum root of $\Delta(N)$] for $N=3,5,7$ and $N=\infty$, as a function of η_1/α'.

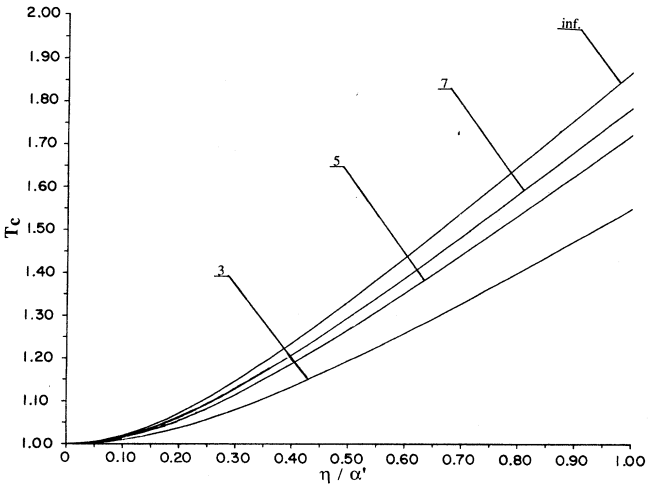

FIG. 2. Superconducting transition temperature $T^*(N)$ as function of reduced coupling parameter η_1/α' for 1:2:3 polytypes with N layers [see Fig. 1(c)]. The system is composed of two types of layers: L_1 and L_2, which are stacked alternately [L_1-L_2-L_1-. . .] total N layers, or if L_1=plane, L_2=chain, then [P-C-P-. . .]. For this figure, $T_p^0=3T_c^0$ and $T_c=T^*(N)$ are given in units of T_p^0 or $T_c^0=3T_p^0$, and T_c is given in units of T_c^0. Spin-spin coupling between nearest layers is assumed. Note $T_c=T^*(N)$ is an increasing function of N (for any η_1/α') reaching 95% of its asymptote $T^*(\infty)$ at $N=5$. Labels on the curves refer to N.

As previously, $N=\infty$ is the periodic repeat case. Results clearly show that $T_c=T^*(N)$ is an increasing function of N, reaching (for $\eta_1<1$) 95% of the maximum possible value $T^*(\infty)$ by $N=5$. All results for T_c are normalized in terms of T_p^0: i.e., at $y=0$ $T^*(N)=T_p^0$ independent of N. Still retaining the SS interaction, let us now take

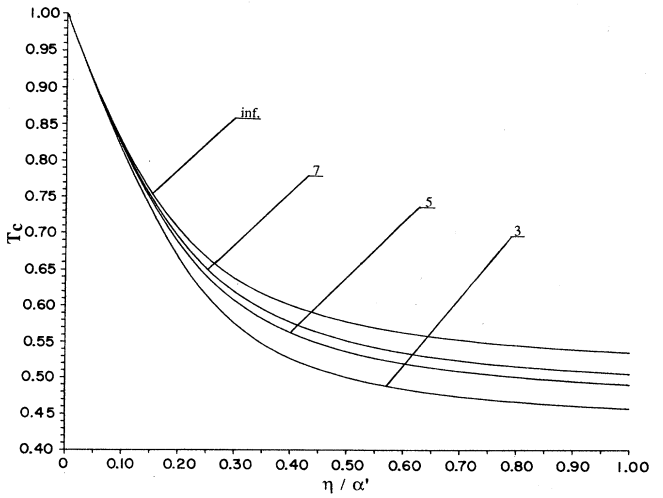

FIG. 3. System as described in Fig. 1(c). Here LD nearest-layer coupling is used [see text Eq. (2)] and $T_c^0=3T_p^0$. Note $T_c=T^*(N)$ is an increasing function of N at any η_1. $T^*=T_c$ is given in units of T_c^0.

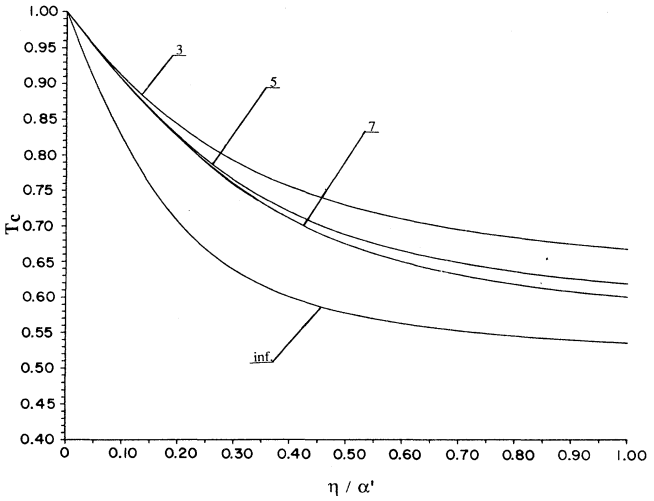

FIG. 4. System as described in Fig. 1(c). Here LD nearest-layer coupling is used [see text Eq. (2)] and $T_p^0=3T_c^0$. Note $T_c=T^*(N)$ is a decreasing function of N at any η_1. $T^*(N)=T_c$ is given in units of T_p^0.

$T_c^0=3T_p^0$. Then Fig. 2 still applies except now $T_c=T^*(N)$ is in units of T_c^0; i.e., at $y=0$ $T^*(N)=T_c^0$ independent of N. Clearly $T^*(N)$ for SS coupling is an increasing function of N.

Now turn to the Lawrence-Doniach coupling (2). Keep nearest-neighbor coupling $y=-\eta_1$. In the secular determinant $\Delta(N)$ the two end diagonal entries are now $\Delta(N)_{11}=\alpha_p(T)+\eta_1=\Delta(N)_{NN}$, while the remaining diagonal entries are $x=\alpha_p(T)+2\eta_1$; $x'=\alpha_c(T)+2\eta_1$. Now let $T_c^0=3T_p^0$. Figure 3 shows $T^*(N)$ for different polytypes as function of reduced coupling strength. To be noted is that $T^*(N)$ is an increasing function of N.

For LD coupling but $T_p^0>T_c^0$, results are shown in Fig. 4. In this case $T^*(N)$ is a decreasing function of N at any η_1/α' to the limit $T^*(\infty)$.

These graphical computations indicate that except for LD coupling in the 1:2:3 structure, with $T_p^0>T_c^0$, polytypism should always increase $T^*(N)$ with N. The maximum value $T^*(\infty)$ can be obtained from the figures for given η_1/α' as a fraction of the bare temperature T_p^0 or T_c^0.

For example, using LD coupling with $T_c^0=200$ K (bare temperature for a layer of 1D chains) and $T_p^0=60$ K (bare temperature for a CuO_2 plane), then from Fig. 3 with $\eta_1\approx\frac{1}{4}$, we would find $T^*(\infty)\approx 134$ K as the maximum in 1:2:3 class. These assignments of T_c^0, T_p^0 follow the original report of Warren *et al.* [12] but have since been retracted [see Pennington *et al.* [12] and Walstedt *et al.*], and assignments are now reversed with $T_p^0>T_c^0$.

*Permanent address: Department of Physics, City College of City University of New York, Convent Avenue at 138 Street, New York, NY 10031. (Correspondence should be sent to this address.)

†Present address: The James Franck Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637.

[1]J. L. Birman (unpublished).

[2]W. E. Lawrence and S. Doniach, in *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, 1970,* edited by E. Kanda (Keigaku, Tokyo, 1971), p. 361; K. Yamagi, Phys. Lett. **38A**, 43 (1972); R. R. Gerhardts, Phys. Rev. B **11**, 2945 (1974); R. A. Klemm, A. Luther, and M. R. Beasley, *ibid.* **12**, 877 (1975); L. A. Turkevich and R. A. Klemm, *ibid.* **19**, 2520 (1979); E. I. Kats, Zh. Eksp. Teor. Fiz. **56**, 1695 (1969) [Sov. Phys. JETP **20**, 897 (1969)]; **58**, 1471 (1970) [**31**, 787 (1970)]; L. N. Bulaevski, *ibid.* **64**, 2241 (1973) [*ibid.* **37**, 1133 (1973)]; **68**, 1278 (1973) [**38**, 634 (1974)].

[3]The form (2) is the limiting case of the LD version of GL theory, the latter having been widely used for various superconductivity properties including the proximity effect. The form (3) emphasizes the purely bilinear interaction. At present it appears most useful to follow both possibilities and decide *a posteriori* which is preferable. J.L.B. acknowledges very useful discussion with Professor S. Shtrikman on this point, leading us to fully explore the SS interaction.

[4]G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[5]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng; L. Gao, Z. J. Haang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[6]A recent summary of properties and structures of the TlBa series with references is given in R. Pool, Science **240**, 146 (1988).

[7]For the Bi Sr series, see H. Maeda *et al.*, Jpn. J. Appl. Phys. **27**, L209 (1988); C. W. Chu *et al.*, Phys. Rev. Lett. **60**, 941 (1988); R. M. Hazen *et al.*, *ibid.* **60**, 1174 (1988); M. A. Subramanian *et al.*, Science **239**, 1015 (1988).

[8]S. S. P. Parkin (unpublished); also see note added in S. S. Parkin *et al.*, Phys. Rev. Lett. **60**, 2539 (1988); Y. Gao *et al.*, Science **241**, 954 (1988); P. Haldar *et al.*, *ibid.* **241**, 1198 (1988).

[9]A recent structure determination with many references is A. Williams *et al.*, Phys. Rev. B **37**, 7960 (1988).

[10]A recent example showing this, along with many relevant references, is Y. Tajima *et al.*, Phys. Rev. B **37**, 7956 (1988).

[11]J. L. Birman and J. S. Birman (unpublished).

[12]W. W. Warren *et al.*, Phys. Rev. Lett. **59**, 1860 (1987); C. H. Pennington *et al.*, Phys. Rev. B **37**, 7944 (1988); R. E. Walstedt *et al.* Phys. Rev. B **38**, 9303 (1988).

[13]J. M. Wheatley, T. C. Hsu, and P. W. Anderson, Nature **333**, 121 (1988).

[14]T. Schneider and D. Baerlswyl, Z. Phys. (to be published).

[15]The monolayer model with SS coupling was previously used by P. R. Antoniewicz and G. E. Fredericks, Solid State Commun. **12**, 23 (1973) for conventional layer superconductors like $NbSe_2$, and criticized by L. N. Bulaevski, Usp. Fiz. Nauk **116**, 449 (1975) [Sov. Phys. Usp. **18**, 514 (1975)]; also see I. O. Kulik, Solid State Commun. **19**, 535 (1976), and later papers.

[16]Similar models have independently been introduced by S. Theodorakis, Phys. Lett. A **132**, 287 (1988); (unpublished); and S. Theodorakis and Z. Tesanovic, Phys. Lett. A **132**, 372 (1988).