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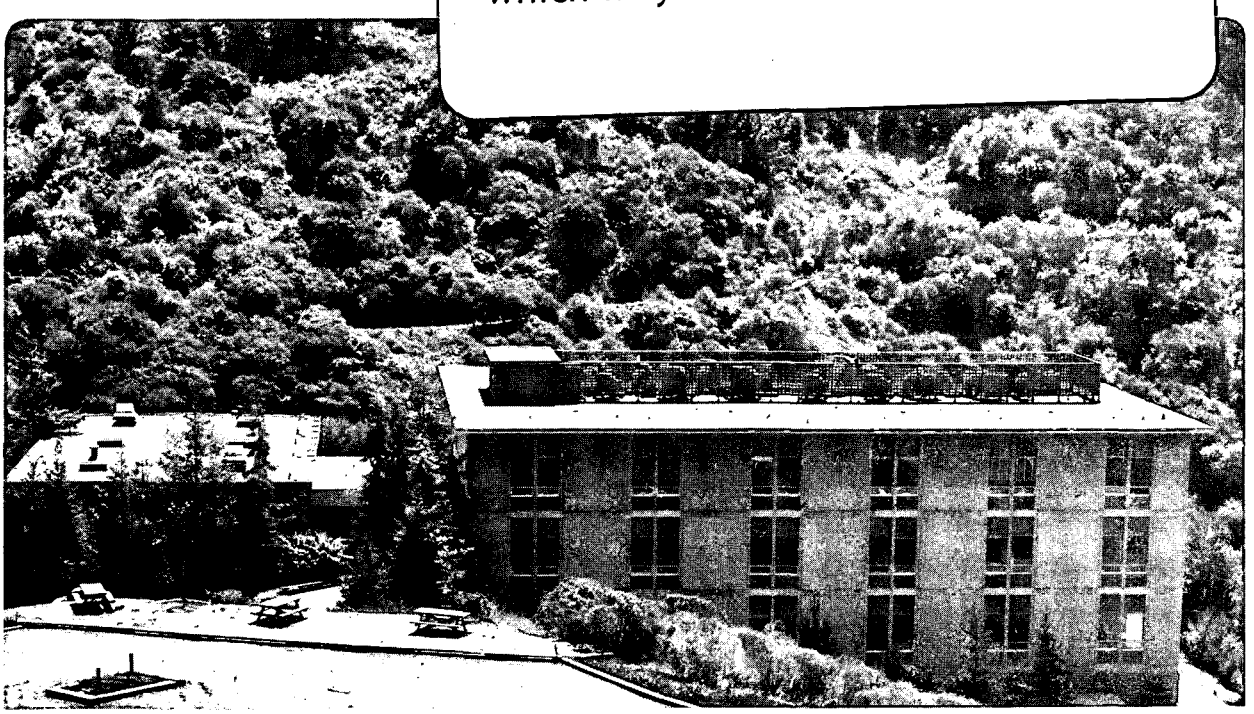

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Ginzburg-Landau Theory of Deformable Superconductors

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ABSTRACT

A Ginzburg-Landau theory is presented for a superconductor that can also sustain a weakly first-order structural phase transition. The distortion and the superconducting order parameters are coupled so that the distorted system tends to favor superconductivity. The equations are solved for a variety of situations. It is found that (A) for some range of the parameters a distorted, superconducting equilibrium bulk could have, when superconductivity is locally destroyed (i.e. by the presence of a magnetic field), an undistorted surface layer, discontinuously superimposed on the bulk; and (B) for a different range of parameters a non-superconducting, undistorted equilibrium bulk can sustain surface super-

conductivity in the presence of a local, surface distortion. The discontinuous changes in the distortion parameter introduce, in effect, an additional coherence length, not calculable from dimensional arguments. The theory should be applicable to the new ceramic high-temperature superconductors, and may serve as a basis for the description of the appearance and disappearance, repeatedly observed, of non-equilibrium very high temperature superconductivity in some oxides.

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I. INTRODUCTION

The 1950 Ginzburg and Landau[1] (GL) phenomenological theory of superconductivity is an extremely useful tool to study spatially dependent effects. It was formulated before the microscopic BCS theory[2], and is independent of the detailed mechanisms responsible for the superconductivity. Although it is based on a somewhat questionable power-series expansion of the free energy in terms of the superconducting order parameter[3], it has a general validity which goes beyond any given mechanism or microscopic property. Its foundations require only a complex order parameter which can sustain a supercurrent, and a gauge-invariant coupling of the parameter to the electromagnetic field. In 1959 Gor'kov[4] showed that the (GL) theory could be derived from the BCS theory, and is valid in for temperatures close to, and below the super-

conducting transition temperature T_c.

The GL theory has been shown to be very successful in describing macroscopic properties of superconductors[3,5], especially in inhomogeneous situations were the ordinary BCS theory is difficult to apply. Examples include the magnetic-field-dependence of the energy gap, and the spatial distribution (flux-line lattice) of magnetic fields, currents and order parameters in a type II superconductor after magnetic field penetration $H_{c1} < H < H_{c2}$. In the original GL theory a pseudowavefunction $\Psi(\vec{r})$ was introduced as a complex order parameter. It was assumed that $|\Psi(\vec{r})|^2$ was proportional to the density of superconducting electrons $n_s(\vec{r})$. The GL theory was then formulated by applying a minimization procedure to an assumed, gauge-invariant expansion of a trial free energy in terms of $|\Psi(\vec{r})|^2$ and the gradient $\vec{\nabla}\Psi(\vec{r})$.

Because of the success and generality of GL theory, it is appealing to apply it to a description of some of the macroscopic properties of the new high T_c oxide superconductors[6–11]. There is not yet a generally accepted microscopic theory of these high-temperature superconductors but, regardless of the underlying mechanism, the GL theory (with its own restricted validity) is certain to be applicable.

The main idea in this contribution is to extend the traditional GL theory by introducing a second, structural order parameter $D(\vec{r})$. In this way the free energy is a function of both $D(\vec{r})$ and $\Psi(\vec{r})$. The new order parameter $D(\vec{r})$ is assumed to be real, and is related to a particular lowering of the crystal symmetry. Therefore, a state with $D(\vec{r}) = 0$, is called a symmetric or undistorted state, whereas a state with $D(\vec{r}) \neq 0$, for which the crystal symmetry is lowered, is called a distorted state. Examples of such transitions are the ferroelectric transitions[12] in. e.g. $BaTiO_3$, the cubic-to-tetragonal transition found[13] in the A15-structure superconductors V_3Si, Nb_3Sn and Nb_3Ge, and the tetragonal to orthorhombic transition[14,15] found in some of the new oxide superconductors (e.g. $La_{2-x}Ba_xCuO_4$, $YBa_2Cu_3O_{7-x}$ and $NdBa_2Cu_3O_{7-x}$).

The very complicated structural and superconducting behavior found in these new materials suggests that the two types of transition may be intimately connected. Although these features cannot be directly explained by the original GL theory, it is an obvious extension of the original idea to include, in a single free-energy expansion, both order parameters and to allow them to couple to each other. There are, in addition, many references in the literature to anomalous properties of the materials at the surface and at grain boundaries[7], as well as reports of metastable superconductivity at very high temperatures[11], which tends to disappear with thermal and/or electrical treatments (which in all probability release local stresses). The theory presented here gives a possible explanation for these phenomena. The explanation is based in the interplay between superconductivity and lattice distortion, and is caused by the coupling between the two order parameters.

II. THE MODEL

In this section an expansion is made of the free-energy function. This is, as mentioned above, a function of both $\Psi(\vec{r})$ and $D(\vec{r})$. Before explicitly writing the expansion, it is important to outline some of the required properties of the system.

The expansion of the free-energy function in the order parameters must satisfy several necessary conditions: (1) it must contain only physically meaningful terms, i.e. all terms must be real; (2) it must contain terms that are compatible with the symmetry of the problem; and (3) the expansion cannot be truncated at "unstable" terms, i.e. the highest order terms kept in the series must be such that the free energy has always a lower bound.

The superconducting transition is known to be of the second order, i.e. one without any latent heat and with a finite discontinuity in the heat capacity at the transition temperature. In light of the discussion above the expansion must be in $|\Psi(\vec{r})|^2$, since Ψ is a complex order parameter. In addition, in order to have a phase transition

the coefficient in front of the $|\Psi(\vec{r})|^2$ term must change sign as a function of the temperature. Furthermore, since the transition is of second order, the term proportional to $|\Psi(\vec{r})|^4$ must always be positive definite. Consequently, it is sufficient in this case to truncate the series at the $|\Psi(\vec{r})|^4$ term. This has been the traditional approach, and the one taken in the original GL paper.

The structural transition, on the other hand, is of a completely different character: (i) its order parameter is real, a "strain" or a "strain tensor"; and (ii) it may be either of the first order (with a latent heat of transformation at the transition temperature) or of second order (no latent heat but a discontinuous specific heat). In this contribution only a scalar strain D is considered, and it is assumed that symmetry considerations restrict the expansion to terms even in D. If both the first- and second-order cases are to be included, the terms proportional to D^2 and to D^4 must change sign for some given values of the controllable parameters (temperature, pressure, etc.)[12]; the expansion must therefore be continued at least up to order D^6. Here it is assumed that that term is positive definite throughout, and the expansion thus truncated there[16].

The interesting effects sought in this contribution arise from the coupling of the two order parameters, Ψ and D. In order to conserve the symmetry discussed above, and to include this coupling, one extra term, proportional to $|\Psi(\vec{r})|^2 D^2(\vec{r})$ is included. The final expansion of the free energy becomes

$$F_{bulk} = -A\ |\Psi|^2 + \tfrac{1}{2}B\ |\Psi|^4 - C\,|\Psi|^2 D^2 + \alpha D^2 - \tfrac{1}{2}\beta D^4 + (1/3)\,\gamma D^6\ . \qquad (2.1)$$

The first two terms are part of the conventional expansion in GL theory[3,5]. The last three terms can be recognized as the conventional expansion used in Landau's theory of second-order phase transitions[12], for systems with symmetry-restricted even powers in D. Finally the third term in (2.1) is the coupling between the two order parameters.

The expansion consist of six terms, with six parameters A, B, C, α, β, and γ. Stability conditions and validity of the expansion restrict B and γ to

$$B > 0 \quad , \quad \gamma > 0\ .$$

These six parameters are in general functions of temperature T, and pressure P, and other variables such as stresses and chemical composition. For the sake of definiteness C and α are taken to be positive quantities. Positive C favors a stable state with broken symmetry ($D \neq 0$) and superconductivity ($\Psi \neq 0$), i.e. the coupling term, for positive C, lowers the free energy when both symmetries are broken. Since the most interesting systems exhibit weakly first-order -- rather than second-order -- phase transitions in the lattice symmetry, the term proportional to D^2 is kept positive, i.e. the parameter α is also positive. Only A and β are allowed to change sign[17]. With this choice of signs the undistorted, normal state, $D = \Psi = 0$ is always locally stable with respect to the distortion, i.e.

$$\left[\frac{\partial^2 F_{bulk}}{\partial D^2}\right]_{\Psi = D = 0} > 0 \ .$$

The uniform, bulk properties of the deformable superconductor are examined first. If C is set equal to zero, i.e. there is no coupling between the two order parameters, the (A, β) parameter plane -- for α, γ, and B fixed, positive constants -- is divided into four quadrants, corresponding to four different equilibrium configurations:

Region I: normal, undistorted state, $\Psi = 0$, $D = 0$;

exists for $A < 0$, $\beta < \beta_0$.

Region II: normal, distorted state, $\Psi = 0$, $D \neq 0$;

exists for $A < 0$, $\beta > \beta_0$.

Region III: superconducting, undistorted state, $\Psi \neq 0$, $D = 0$;

exists for $A > 0$, $\beta < \beta_0$.

Region IV: superconducting, distorted state, $\Psi \neq 0$, $D \neq 0$;

exists for $A > 0$, $\beta > \beta_0$.

The line $\beta = \beta_0$, where

$$\beta_0 = (16\, \alpha\, \gamma / 3)^{1/2} \ , \tag{2.2}$$

separates Region I from Region II, and Region III from Region IV, and corresponds to first-order structural phase transitions, with the parameter D jumping discontinuously

from zero to a minimum value

$$D_0 = \tfrac{1}{2}\,(3\,\beta\,/\,\gamma)^{1/2}\ .$$

The line $A = 0$ separates Region I from Region III, and Region II from Region IV, and corresponds to ordinary second-order superconducting phase transitions; the parameter Ψ is continuous throughout the $(A-\beta)$-plane. The point (a) in that plane, defined by

$$\textit{Point}\ \ (a):\ \ A = 0\ \ ;\ \ \beta = \beta_0\ \ , \tag{2.3}$$

is a singular point, the only one where Region I and Region IV meet -- in fact the only point where all four regions meet.

When the coupling parameter C differs from zero -- i.e. takes a positive, fixed value -- the regions of stability in the $(A-\beta)$-plane change drastically. This is shown in Figure 1 for $C = [B^2\,\alpha\,\gamma\,]^{1/4}$. Region IV has now grown at the expense of the others, and region III is substantially reduced. There are now three singular points, $(a1)$, $(a2)$, and (b), shown in Figure 1, given by the following values of the parameters[18]:

$$\begin{aligned}
&\textit{Point}\ \ (a1):\ \ A = 0\ \ ;\ \ \beta = (16\,\alpha\,\gamma\,/\,3)^{1/2} - C^2\,/\,B\ \ ,\\
&\textit{Point}\ \ (a2):\ \ A = -\,(3\,\alpha\,C^2\,/\,\gamma)^{1/2}\ ;\ \ \beta = (16\,\alpha\,\gamma\,/\,3)^{1/2}\ \ ,\\
&\textit{Point}\ \ (b):\ \ A = \alpha\,B\,/\,C\ \ ;\ \ \beta = -\,C^2\,/\,B\ \ .
\end{aligned} \tag{2.4}$$

Region IV, the superconducting, distorted phase, now has common boundaries with all three other regions. It is separated by a continuous second-order transition from Region II (the normal, distorted phase) at a semi-infinite line starting from point $(a2)$, and given by

$$\begin{gathered}
2\,\gamma\,A = -\,C\,\beta\,[1 + (1 - 4\,\alpha\,\gamma\,/\,\beta^2)^{1/2}\,]\ \ ,\\
\beta > (16\,\alpha\,\gamma\,/\,3)^{1/2}\ \ ;
\end{gathered} \tag{2.5}$$

it is separated from Region I (the normal, undistorted phase) by a discontinuous first-order transition at a finite line connecting point $(a1)$ with point $(a2)$; it is separated from Region III (the superconducting, undistorted phase) either by a discontinuous first-order transition at a finite line connecting $(a1)$ and (b), given by

$$\begin{gathered}
[\,\beta + (C^2\,/\,B)]^2 = (16\,/\,3)\,\gamma\,[\alpha - (A\ C\ /\ B\ )]\ \ ,\\
[-\,C^2\,/\,B\,] < \beta\ < [(16\,\alpha\,\gamma\,/\,3)^{1/2} - C^2\,/\,B\,]\ \ ,
\end{gathered} \tag{2.6}$$

or by a continuous second-order transition at a semi-infinite line of constant A,

$$A = \alpha B / C \quad , \quad \beta < -C^2 / B \quad , \tag{2.7}$$

ending at point (b). The character of the transitions between Region I and Region II, and between Region I and Region III remain unchanged from the $C = 0$ case. The most interesting cases, to be discussed below, appear for parameters close to those of the first-order transition between Regions I and IV, the line in Figure I connecting points (a1) and (a2).

For inhomogeneous systems, with fields present and/or variations in the order parameters, the GL theory has additional contributions to the free energy

$$F = F_{bulk} + F_{gradient,\,field} \quad , \tag{2.7}$$

where the term $F_{gradient,\,field}$ is

$$F_{gradient,\,field} = \frac{1}{2m^*} \left| \left[\frac{\hbar}{i} \vec{\nabla} - \frac{e^*}{c} \vec{A} \right] \Psi \right|^2 + \frac{H^2}{8\pi} + \frac{\hbar^2 \varepsilon^2}{2m^*} \left[\vec{\nabla} D \right]^2 . \tag{2.8}$$

Here m^* is an effective mass, $\hbar$ is Planck's constant divided by 2π, i is the imaginary unit, e^* an elementary charge, c the velocity of light, $\vec{A}$ is the vector potential, H the magnetic field strength. In addition, ε is proportional to the typical length over which D varies (the structural healing length). The first two terms in (2.8) were included in the original GL theory[1,5], the last term is a lattice distortion energy caused by changes in the lattice structure. Healing lengths for structural changes are typically on the order of one lattice parameter, i.e. considerably smaller than all other lengths in the problem (the magnetic-field penetration depth and the superconducting coherence length[5]), and therefore it is appropriate to take the limit $\varepsilon \to 0$. In other words, as compared with Ψ and $\vec{H}$, the distortion parameter D is allowed to change abruptly, with essentially no cost in free energy.

For a superconductor of volume V, the total free energy becomes

$$F_{total} = \int_V \left[F_{bulk} + F_{gradient,\,field} \right] dV \tag{2.9}$$

The equilibrium configuration of the system is that for which the overall free energy attains its global minimum, i.e. the integral (2.9) attains its absolute minimum value. It is the problem of finding such minimum that constitutes the subject of the following section.

III. MINIMIZATION AND RESULTS

For the sake of definiteness, and to illustrate the effects that a coupling of the two order parameters produce, a specific one-dimensional geometry is invoked in this section: a superconducting half-space restricted to $x > 0$. In addition, to make the situation even clearer, the magnetic field is not explicitly included: its main effect is taken into account by requiring, at the surface $x = 0$, a vanishing value of the superconducting order parameter Ψ.

The free energy, the order parameters, and the distances along x can be measured in renormalized units:

$$F = f\ [\alpha^3 / \gamma]^{1/2} \ , \tag{3.1a}$$

$$D = \delta\ [\alpha / \gamma]^{1/4} \ , \tag{3.1b}$$

$$\Psi = \psi\ [\alpha^3 / B^2 \gamma]^{1/8} \ , \tag{3.1c}$$

$$x = \xi\ [\hbar^4 \gamma / 4\, m^2 B^2 \alpha^3]^{1/4} \ ; \tag{3.1d}$$

with the definitions

$$C' = C\ [B^2 \alpha \gamma]^{-1/4} \ , \tag{3.1e}$$

$$A' = A\ [B^2 \alpha^3 / \gamma]^{-1/4} \ , \tag{3.1f}$$

$$\beta' = \beta\ [\alpha \gamma]^{-1/2} \ , \tag{3.1g}$$

the equations (2.9), (2.8) and (2.1) for the dimensionless free energy can be rewritten as

$$f = \int_{\xi=0}^{\xi=\infty} \left[f_{bulk} + \left[\frac{d\psi}{d\xi}\right]^2 + \varepsilon^2 \left[\frac{d\delta}{d\xi}\right]^2 \right] d\xi \ , \tag{3.2}$$

where

$$f_{bulk} = -A'\ |\psi|^2 + \tfrac{1}{2}\ |\psi|^4 - C'\ |\psi|^2 \delta^2 + \delta^2 - \tfrac{1}{2}\ \beta'\ \delta^4 + (1/3)\ \delta^6 \ . \tag{3.3}$$

All quantities in (3.2)-(3.3) are dimensionless.

The remaining variational problem is by no means trivial. Since, as discussed above, the healing length for the distortion parameter δ is of the order of an atomic spacing, i.e. negligible compared with the other lengths in the problem, the correct limit to study is therefore $\varepsilon \to 0$ in (3.2). This limit however allows the distortion δ to have discontinuities in real space; determining whether and where such discontinuities occur is one of the problems to solve. The other order parameter, ψ, must be continuous, although its spatial derivative $\frac{d\psi}{dx}$ may exhibit discontinuous jumps. (It should be noted that in the cases discussed below $\frac{d\psi}{dx}$ is in fact continuous.)

A. Superconducting, distorted bulk with suppressed superconductivity at the surface.

The first problem solved here is for the case when the bulk is in Region IV, i.e. it is in the distorted, superconducting phase. The problem consists of minimizing (3.2)-(3.3) subject to the following boundary conditions:

$$\delta(0) = \delta_{surface} \quad , \tag{3.4a}$$

$$\delta(\infty) = \delta_{bulk} \quad , \tag{3.4b}$$

$$\psi(0) = 0 \quad , \tag{3.4c}$$

$$\psi(\infty) = \psi_{bulk} \quad ; \tag{3.4d}$$

here (3.4c) is an externally imposed boundary condition (e.g. the superconducting order parameter is pushed down to zero at the surface by a strong magnetic field); (3.4b) and (3.4d) are natural (and obvious) boundary conditions; finally (3.4a) is a "natural" undetermined boundary condition -- the total free energy, in particular the surface contribution, must be minimized with respect to $\delta_{surface}$.

The minimization problem can be tackled by the usual methods of classical Lagrangian Mechanics[19]. If the free energy f in (3.3) is considered the Lagrangian; the order parameters, ψ and δ, the degrees of freedom; ε^2, the inverse effective mass corresponding to the δ degree of freedom; $(-f_{bulk})$, the potential; and ξ, the time, the

problem is that of a two-dimensional particle, with an anisotropic mass-tensor, moving in an algebraic (sixth power) potential.

Since ξ does not occur explicit in (3.2)-(3.3), there is a conserved quantity I -- the equivalent to the total energy in the mechanical problem -- given by

$$I = \left[\frac{d\psi}{d\xi}\right]^2 + \varepsilon^2 \left[\frac{d\delta}{d\xi}\right]^2 - f_{bulk} \ . \tag{3.5}$$

It is possible to determine immediately the value of I by noting that deep in the bulk both ψ and δ attain constant values, and that their gradients vanish. Therefore

$$I = - f_{bulk}(\psi_{bulk}, \delta_{bulk}) \ . \tag{3.6}$$

The problem can now be simplified by determining the "trajectory" of the solution in "coordinate" space, i.e. by determining the line in (ψ, δ)-space where the solutions lie. Because of the conserved quantity I, is it possible to use Maupertuis' principle of least action[19]. The action S_0 is

$$S_0 = \int \sqrt{I + f_{bulk}}\, dl \ , \tag{3.7}$$

where

$$(dl)^2 = (d\psi)^2 + \varepsilon^2 (d\delta)^2 \ .$$

Variation of S_0 yields two differential equations

$$2\sqrt{I + f_{bulk}} \frac{d}{dl} \left[\sqrt{I + f_{bulk}} \frac{d\psi}{dl}\right] = \frac{\partial f_{bulk}}{\partial \psi} \ , \tag{3.8a}$$

$$2\varepsilon^2 \sqrt{I + f_{bulk}} \frac{d}{dl} \left[\sqrt{I + f_{bulk}} \frac{d\delta}{dl}\right] = \frac{\partial f_{bulk}}{\partial \delta} \ . \tag{3.8b}$$

In the limit $\varepsilon \to 0$, (3.8b) becomes

$$\frac{\partial f_{bulk}}{\partial \delta} = 0 \ , \quad \text{for} \quad \varepsilon = 0 \ . \tag{3.9}$$

Insertion of (3.3) into (3.9) yields the following solutions

$$\delta = 0 \ , \tag{3.10a}$$

$$\delta^2 = (½) \ [\ \beta' \pm \sqrt{\beta'^2 - 4(1 - C' |\psi|^2)}\ ] \ . \tag{3.10b}$$

This important result establishes that the possible trajectories in (ψ, δ)-space are restricted to three curves. This is a very large simplification, since the solution that gives

the global minimum in the free energy can only jump between these solutions. Also, the natural boundary condition (3.4a), which minimizes the surface free energy, restricts $\delta_{surface}$ to the values spanned by these three curves.

It is now possible to show that it is the *local* free energy density that determines when a discontinuous jump in δ will occurs. With the use of (3.2) and (3.6), the total free energy can be written

$$f = \int_{\psi=0}^{\psi=\psi_{bulk}} \frac{I + 2 f_{bulk}(\psi, \delta)}{\sqrt{I + f_{bulk}(\psi, \delta)}} \, d\psi \ . \tag{3.11}$$

By means of (3.8) this integral can be reduced to one of three different integrals, each a function of only one variable, ψ. And since the integrand is, for each one of the three possibilities, a monotonic function of f_{bulk} (i.e. the integrand never decreases with increasing f_{bulk}), the criterion for minimum global free energy is fulfilled by choosing for each ψ that one of the three branches (3.10) which *locally* yields a minimum of the free-energy density f_{bulk}.

Of the three solutions (3.10), the one in (3.10b) with a minus sign can be discarded, since it always yields a higher free-energy density than the other (3.10b) solution -- that with the plus sign. The problem is now reduced to selecting between (3.10a) and the surviving (3.10b) solutions that which produces the local minimum of f_{bulk} along the path.

If there is, for a particular value of ψ a crossing between the values of the two branches in the integrand of (3.11) -- i.e. a switch between (3.10a) and (3.10b) -- there will be a discontinuity in the parameters. Five quantities remain constant at the discontinuity: ψ, I given by (3.6), the integrand in (3.11), the value of f_{bulk}, and the spatial derivative ($d\psi/d\xi$). Only the variable δ is discontinuous at the switch[20].

For values of the parameters such that the bulk is in Region IV, it is possible to find that subregion for which, when $\psi = 0$ at the surface, a discontinuity in δ will occur. This will happen wherever, in Region IV,

$$\beta' < \beta'_0 = (16/3)^{1/2} \ . \tag{3.14}$$

This line is shown in Figure 2. For $\beta' < \beta'_0$ the value of $\delta_{surface}$ is zero, i.e. the surface is normal and undistorted. Conversely, for $\beta' > \beta'_0$ the value of $\delta_{surface}$ is finite, and the surface is locally normal [as given by (3.4c)] but distorted, even though the distortion is in general smaller than in the bulk. In the first case there is, close to the surface, a discontinuity in the value of δ, which discontinuously jumps from zero to a value close the equilibrium bulk value. The system can be visualized as an undistorted overlayer superimposed to a superconducting, distorted bulk.

The position in real space where the discontinuity takes place can be found by direct integration of (3.5) along the two possible branches, and finding the point where the two values of f_{bulk} cross each other. At the crossover point a discontinuity occurs. Figures 3 and 4 show two examples, corresponding to the two regimes. In Figure 3, where $\beta' > \beta'_0$, there are no discontinuities in δ, and the surface is distorted. In Figure 4, where $\beta' < \beta'_0$, there is a discontinuity in δ near the surface, but ψ and its spatial derivative are continuous throughout. These two figures are for $C'=1$; the corresponding values of of A' and β' are marked in Figure 2.

B. Normal, undistorted bulk with a strained, distorted surface.

The existence in Figures 1 and 2 of a line of discontinuous, first-order transitions between Regions I and IV implies that there is a region of parameter space where both phases are locally stable -- one globally stable, the other metastable. In Region I, where the stable phase is the undistorted, normal state, if the *distorted, superconducting* phase is locally stable, the presence of surface strains of sufficient strength can produce local surface superconductivity that decays exponentially into the bulk. This is only possible in a relatively small curvilinear triangle of the parameter space of Figure 2, with two of the three vertices given by the Points (a1) and (a2), and whose three sides are given by the line separating Region I from Region IV, the line separating

Region I from Region III, and the line

$$[\beta' + C'^2]^2 = 4\,[\,1 - A'\,C'\,]\ , \qquad (3.15)$$
$$A' < 0\ ,\ \beta' < [(16/3)^{1/2} - C'^2]\ .$$

This line is shown in Figure 2.

The problem to solve here is, except for the fact that the parameters must be in the relevant triangle of parameter space, similar to that solved in Section IIIA. It consists of minimizing (3.2)-(3.3), subject now to the new boundary conditions

$$\delta(0) = \delta_{surface}\ , \qquad (3.16a)$$
$$\delta(\infty) = 0\ , \qquad (3.16b)$$
$$\psi(0) = \psi_{surface}\ , \qquad (3.16c)$$
$$\psi(\infty) = 0\ . \qquad (3.16d)$$

In this case (3.16a) is an imposed boundary condition (e.g. the presence of a grain-boundary stress generates a surface strain $\delta_{surface}$); (3.4b) and (3.4d) are the natural (and obvious) boundary conditions; and (3.16c) is a "natural" undetermined boundary condition -- the total free energy, in particular the surface contribution, must be minimized with respect to $\psi_{surface}$.

The solution to this problem follows the same lines described in the previous subsection. In particular there are the three branches described by (3.10). But, since the imposed boundary condition (3.16a) contains an additional parameter, $\delta_{surface}$, the qualitative and quantitative values of the solutions are now functions of four parameters: A', C', β', and $\delta_{surface}$.

If the parameters A', C', and β' are in Region I but the *superconducting, distorted* solution is metastable, an externally imposed surface distortion $\delta_{surface}$ can result in three different kinds of behavior:

(1) for a given range of $\delta_{surface}$ values the surface is locally distorted and relaxes to the undistorted bulk within the (infinitesimally small) atomic-scale healing length of δ; there is no superconductivity anywhere in the sample;

(2) in a different range of $\delta_{surface}$ the surface distortion makes the *superconducting, distorted* state locally favorable, even though the *superconducting, undistorted* state -- were it not for the forced surface distortion -- would be more favorable; the system relaxes to this *superconducting, undistorted* state within an infinitesimal atomic-scale healing length; the superconducting order parameter decays, in turn, exponentially into a *normal, undistorted* bulk within a distance of the order of the superconducting coherence length ξ_0;

(3) in a third range of values of $\delta_{surface}$, the *superconducting, distorted* phase is locally favorable energetically, with its local free energy lower than the *superconducting, undistorted* phase with the same ψ; as a result a *superconducting, distorted* layer of finite thickness is superimposed on the undistorted bulk; a *superconducting, undistorted* region ($\delta = 0$) begins where the local free energies of both phases attain the same value for the common value of ψ; from that point inwards the superconducting order parameter decays into the bulk exponentially with characteristic length ξ_0.

The regions in $\{A', \beta', C', \delta_{surface}\}$ parameter space where these solutions exist can be found by: (i) finding the parameter values for which the distorted superconducting solution (3.10b) exist (there is no induced superconductivity otherwise); (ii) comparing the energy of f_{bulk} for the different possible states, that is the *normal, distorted* state, the *superconducting, distorted* state, and the *superconducting, undistorted* state.

The metastable *superconducting, distorted* solution (3.10b) is only defined for

$$\begin{aligned} &\delta_{\min}^2 > \beta'/2 && -C'^2 < \beta' < 2 \quad , \\ &\delta_{\min}^2 > \beta'/2 + [\,(\beta'/2)^2 - 1]^{1/2} && 2 < \beta' < (16/3)^{1/2} \quad . \end{aligned} \tag{3.17}$$

Therefore $\delta_{surface} > \delta_{\min}$ in order to observe any superconductivity at all. In other words, for $\delta_{surface} < \delta_{\min}$ only case (1) above is obtained.

Comparison of the local energies of the two superconducting states, shows that the *superconducting, distorted* state is energetically favorable for

$$\delta^2 > 3\,\beta'/4 \quad . \tag{3.18}$$

Therefore case (2) may exist only for

$$\delta^2_{surface} < 3\,\beta'/4 \quad ,$$

case (3) only for

$$\delta^2_{surface} > 3\,\beta'/4 \quad .$$

Finally the criterion for the *superconducting, distorted* state to be energetically favorable with respect to the *normal, distorted* state is that the local distortion δ lies between the two roots

$$\delta^2_{roots} = \tfrac{1}{2}\left[(\beta' + 2C'^2) \pm [(\beta' + 2C'^2)^2 - 4(1 - 2A'C')]^{1/2}\right] \quad . \tag{3.19}$$

This result is a function of A', C' and β', in contrast to (3.17) and (3,18), which depend only on β'. The three possible regions of stability are shown in Figure 5 in the ($\delta^2_{surface}$ - β') plane, for $A' = -0.5$ and $C' = 1$. Figure 6 gives an example where the surface is both *superconducting* and *distorted.* The values of the parameters for this example are shown in Figures 2 and 5. It corresponds to case (3) above. It is seen that the superconducting order parameter decreases exponentially into the bulk, with a decay length corresponding to the superconducting coherence length. The distortion δ is non-vanishing over a finite thickness near the surface and decays abruptly (over distance of atomic dimensions) to zero. This distortion, however, is sufficient to induce surface superconductivity in a layer of thickness of the order of the coherence length ξ_0 close to the surface.

IV. CONCLUSIONS

The solution of the GL equations for a system of two -- a superconducting and a distortion -- coupled order parameters gives extremely interesting physical effects. The equations, completely formulated here, were only solved in a few important cases.

Two notable effects were found in different ranges of the parameters. The first effect, valid for a superconducting, distorted ground state with a metastable normal,

undistorted state, exhibits an unusually large magnetostriction: a magnetic field, which depresses the superconductivity, also results in a suppression of the structural deformation. Although this effect was discussed in detail here only in a planar surface and the magnetic field was not explicitly included -- its effect taken into account by a ψ-related boundary condition at the surface -- it should have general validity; in particular it should be of great importance in type II superconductors for fields greater than H_{c1}, where flux penetration produces complicated patterns of field and order parameter distributions. This case in currently under intensive investigation by the authors. It could be of great interest and importance in understanding the behavior of the high temperature oxide superconductors.

A second effect, even more spectacular, takes place for parameters corresponding to a stable normal, undistorted state, whenever the superconducting, distorted state is metastable. In this case the presence of surface and grain boundary stresses may produce local strains which in turn induce surface superconductivity. This phenomenon may be the cause of the observed unstable, *very high temperature* superconductivity obtained in some ceramics[11], which tends to disappear over time (order of days), and is influenced by thermal, mechanical and electrical treatments and history of the sample.

The discontinuous transitions observed in the deformation parameter are a consequence of the competition between two states. Such a discontinuous change takes place over distances that are not easily determined by dimensional or analytical means, and therefore introduce into the problem new and not readily calculable "characteristic lengths".

It is important to emphasize that these systems are very complicated, and the coupling of disparate order parameters open the door to a whole variety of effects, only some of which were examined here. But the theoretical phenomenological model discussed here, even with its richness of structures and phases, is a poor reflection of the complexities found in real three- four- and five-component oxide systems, whose real

macroscopic and microscopic behaviors are still only sketchily known and understood.

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16 First-order transitions for which the power series expansion in D is valid throughout are usually called "weakly first order" transitions; they are the only ones included in this paper.

17 The cases corresponding to negative values of α and C may be of interest for other purposes, but they are not investigated here.

18 It should be noted that for C=0 points (a1) and (a2) coalesce into point (a) given by (3.2), and point (b) moves to infinity.

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20 It is possible to have solutions with discontinuous values of $(d\psi/d\xi)$; they appear when the absolute minimum of the local free energy is in one of the branches (3.10), and that solution ceases to exist -- the discriminant in (3.10b) becomes negative. That type of solution is not present in the cases studied here.

FIGURE CAPTIONS

Figure 1

The regions of stability of the various phases in the β' - A' parameter plane, for $C' = 1$. Region I corresponds to the normal, undistorted phase; region II to the normal, distorted phase; region III to the superconducting, undistorted phase; and region IV to the superconducting, distorted phase. Continuous lines correspond to continuous (second-order) transitions across the boundary. Dashed lines correspond to discontinuous (first-order) transitions. The values of the three singular points ($a1$), ($a2$), and (b) are given in the text.

Figure 2

An enlargement of the graph of Figure 1 in the neighborhood of the three singular points. The crescent with vertices at the singular points (b) and ($a2$) corresponds to the region of metastability of the superconducting, distorted phase (globally stable only in Region IV). The three points marked ($A1$), ($A2$), and (B) correspond to the examples shown in Figures 3, 4 and 6, respectively. In this graph, as in Figure 1, $C' = 1$.

Figure 3

The solution of the GL equations as a function of distance from the surface for parameters corresponding to the point ($A1$) of Figure 2, with the imposed boundary condition $\psi = 0$ at the surface. The surface is at $\xi = 0$. The parameters are $A' = -0.5$, $C' = 1$, and $\beta' = 2.5$. (a) The dimensionless superconducting order parameter $|\psi|$. (b) The dimensionless distortion parameter δ.

Figure 4

The solution of the GL equations as a function of distance from the surface for

parameters corresponding to the point $(A2)$ of Figure 2, with the imposed boundary condition $\psi = 0$ at the surface. The surface is at $\xi = 0$. The parameters are $A' = -0.5$, $C' = 1$, and $\beta' = 2.1$. (a) The dimensionless superconducting order parameter $|\psi|$. (b) The dimensionless distortion parameter δ. Note that there is a discontinuity in δ, and that the sample has a finite undistorted layer induced by the destroyed superconductivity at the surface.

Figure 5

The regions in the parameter plane β' - $\delta^2_{surface}$ corresponding to the various solutions of the GL equations. In this case $A' = -0.5$ and $C' = 1$. The regions correspond to the following cases:

(1) A distorted surface that heals to zero over an atomic distance; no superconductivity anywhere in the sample.

(2) A distorted surface that heals to zero over an atomic distance; surface superconductivity which decays exponentially over a coherence length into a normal bulk.

(3) A finite distorted slab at the surface with an abrupt decay to zero over an atomic distance; surface superconductivity which decays exponentially over a coherence length into a normal bulk.

The point marked (B) corresponds to the case of Figure 6.

Figure 6

The solution of the GL equations for parameters corresponding to the point (B) of Figures 2 and 5, with the imposed boundary condition $\delta = 1.15$ at the surface. The surface is at $\xi = 0$. The parameters are $A' = -0.5$, $C' = 1$, and $\beta' = 1.5$. (a) The dimensionless superconducting order parameter $|\psi|$. (b) The dimensionless distortion parameter δ. Note the appearance of surface-induced superconductivity, which decays exponentially into the bulk. There is a finite distorted slab near the surface, and an abrupt tran-

sition to the undistorted state; the superconducting order parameter, however, is continuous and extends well into the undistorted region.

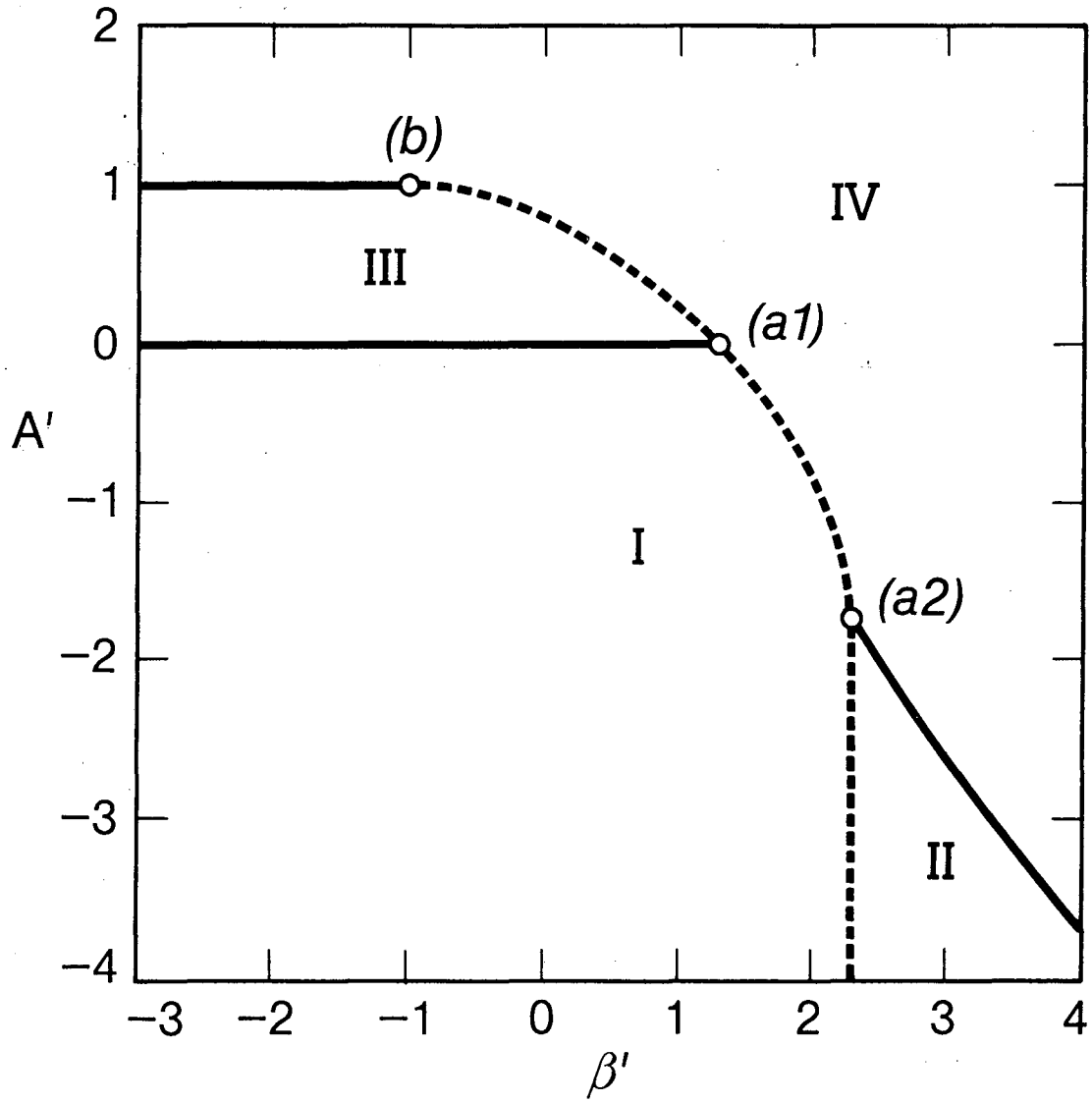

FIGURE 1

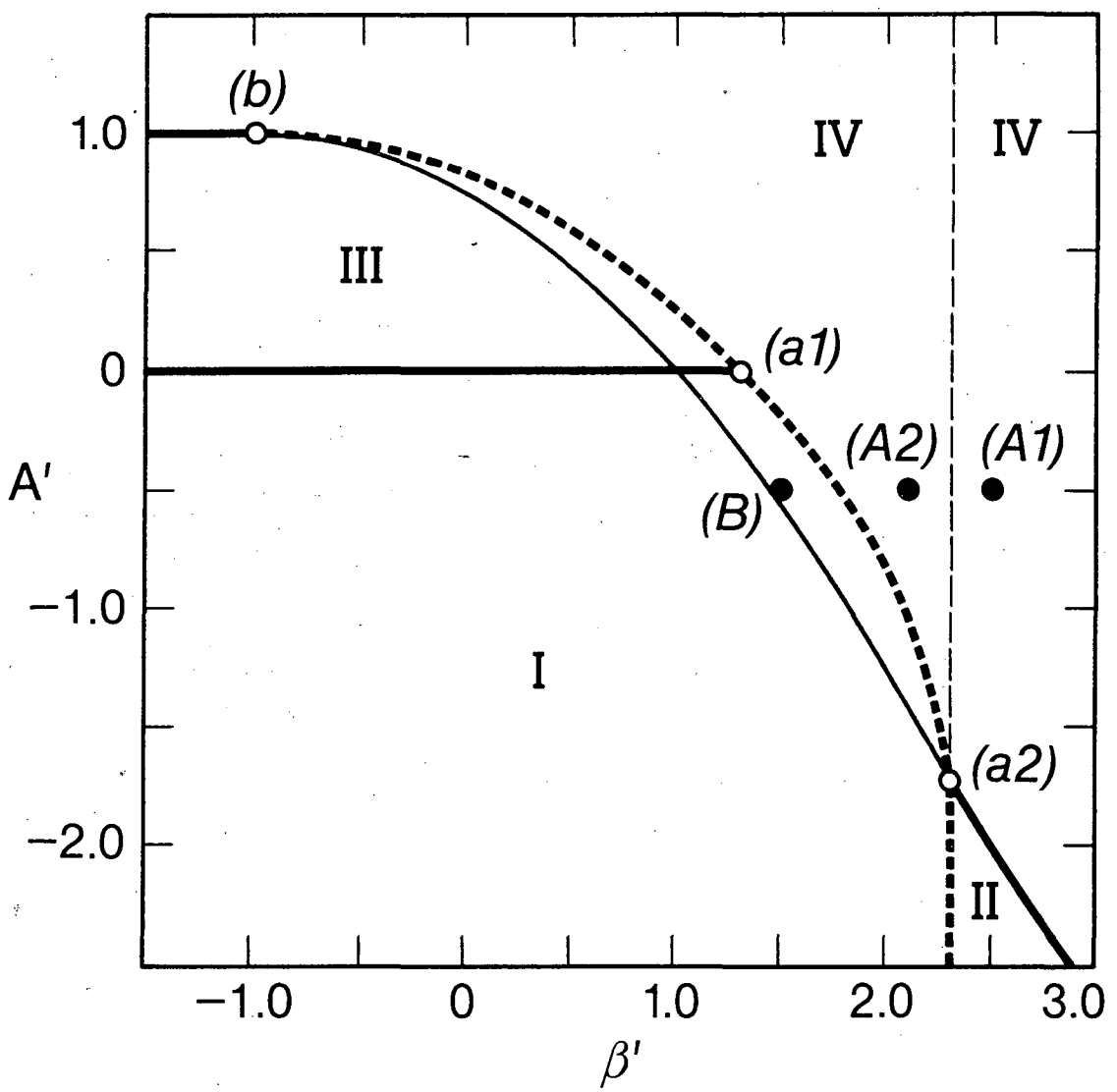

FIGURE 2

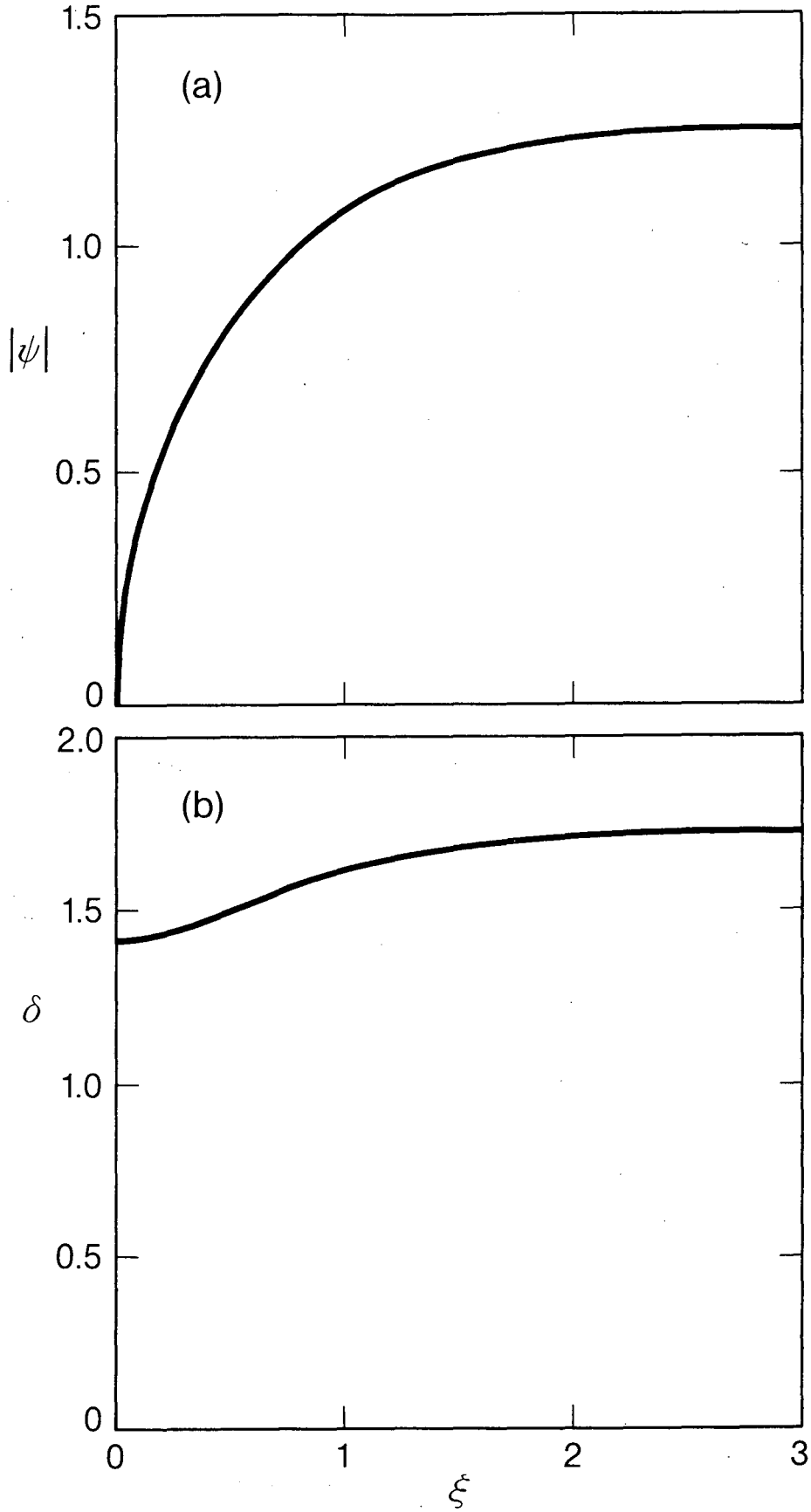

FIGURE 3

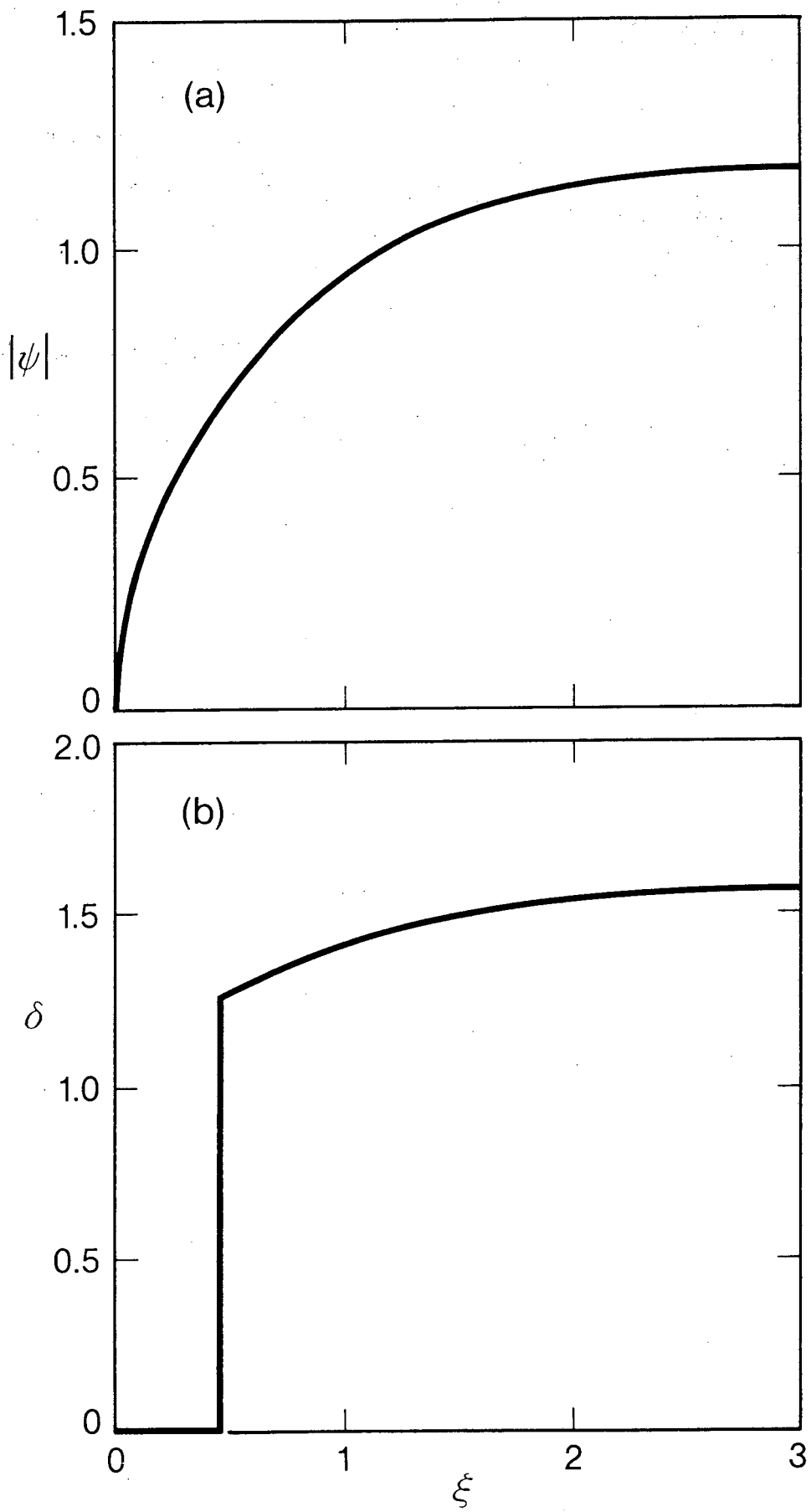

FIGURE 4

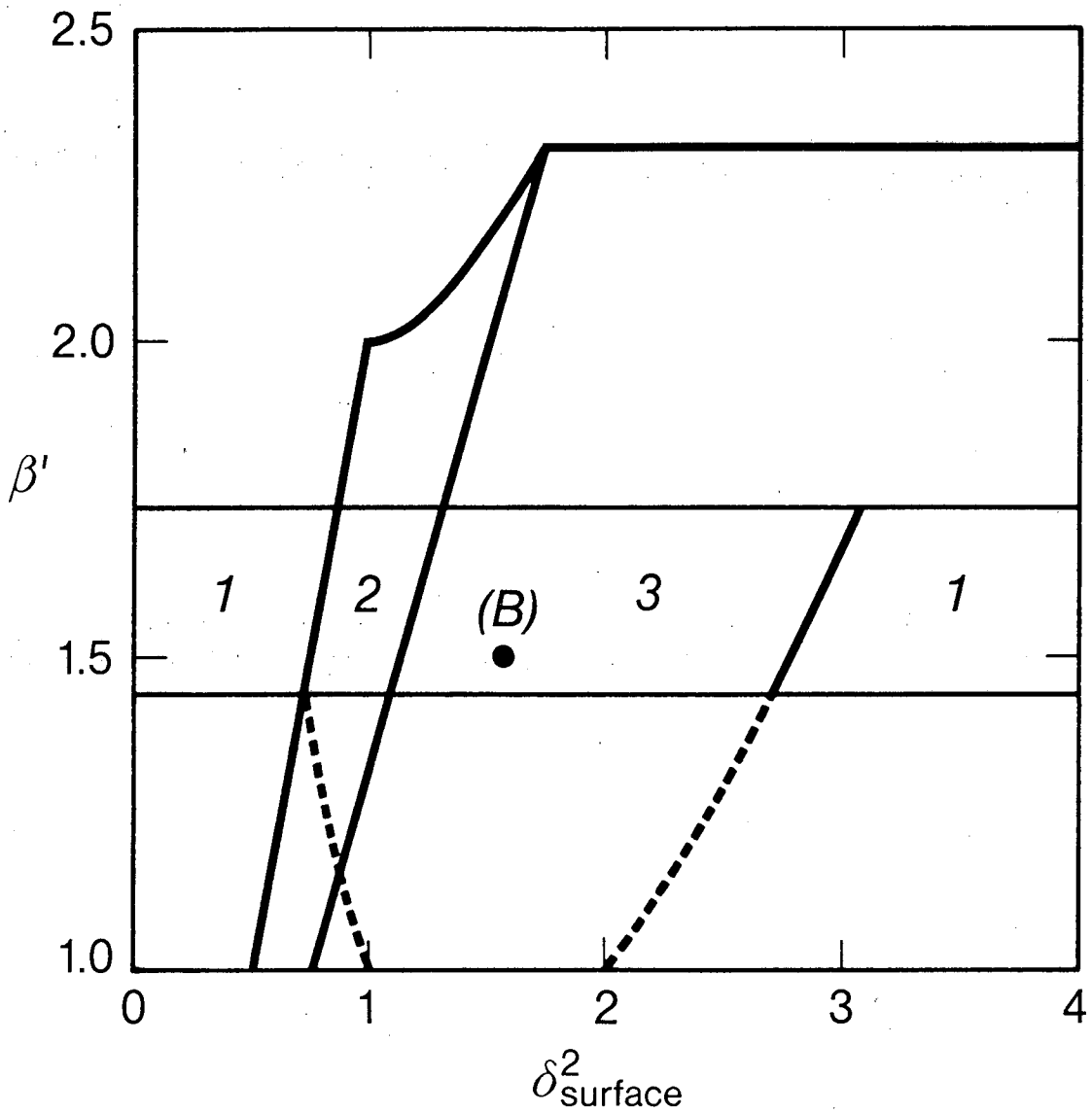

FIGURE 5

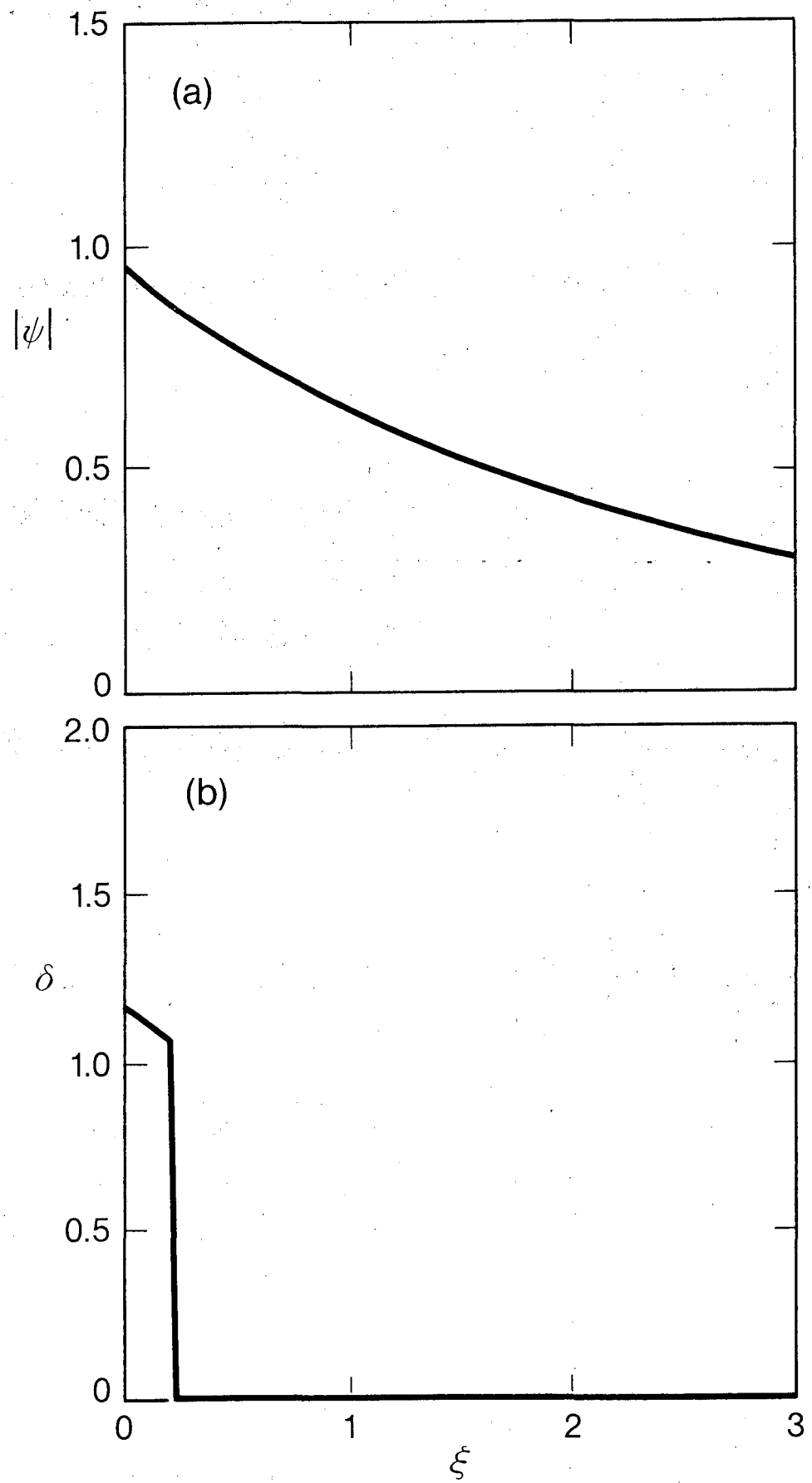

FIGURE 6

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