Superconducting (SC) states of high-$T_c$ cuprates are known to have $d_{x^2-y^2}$-wave symmetry.\cite{1,2} Since the pair wave function of such an unconventional SC state has strong angular dependence, the effects of the presence of surfaces, impurities are different from those in conventional $s$-wave superconductors. For example, it is possible to break the time-reversal symmetry ($T$) near a surface or a Josephson junction by inducing the second component of the SC order parameter (OP)\cite{3,4,5,6,7,8,9,10,11,12,13} with a nontrivial phase difference between the two OPs. In the case of a Josephson junction it may occur when the surface has [110] orientation, because the second SCOP induced by the tunneling process can have phase difference $\pm \pi/2$ leading to a $T$-breaking state.\cite{22} For a [110] surface faced to a vacuum the necessary condition to break $T$ seems to be that the bare transition temperature ($T_c$) of the second OP is positive.\cite{7,10,11,12,14}

In this paper we examine the possibility to have a $T$-breaking surface state near the [110] surface of a $d_{x^2-y^2}$-wave superconductor when the bare $T_c$ of the additional OP is negative, namely, the second OP will not occur in the bulk even at zero temperature. We take an $s$-wave SCOP as the second component, since $d_{x^2-y^2}$-wave and extended $s$-wave symmetries are natural candidates for superconducting states in the models with nearest-neighbor interactions (e.g., the $t-J$ model). We will show that this kind of $T$-violation is possible, and that both the SCOPs and the magnetic field (vector potential) should be treated self-consistently in order to describe this situation correctly. It also turns out that the $T$-violation may occur for a relatively small GL parameter $\kappa$ (i.e., of the order of 10), when $T_c$ of the second OP is negative. Then the present mechanism may not be relevant to the $T$-violation in hole-doped cuprates in which $\kappa \sim 100$. However, we expect the surface states of electron-doped cuprates may be described by the present theory, because some of the latter systems have much smaller $\kappa$ values.\cite{15,16}

## II. Ginzburg-Landau Equation

We consider a superconductor with tetragonal symmetry and assume only a $d_{x^2-y^2}$-wave SCOP, $\Delta_d$, is present in the bulk. An $s$-wave SCOP, $\Delta_s$, is taken into account as a possible second component when $\Delta_d$ is suppressed near the surface. For such a system the Ginzburg-Landau (GL) free energy is given as

$$
\mathcal{F} = \int d\mathbf{r} \left[ \sum_{\mu=d,s} \left( \alpha_\mu |\Delta_\mu|^2 + \frac{\beta_\mu}{2} |\Delta_\mu|^4 + K_\mu |D\Delta_\mu|^2 \right) + \gamma_1 |\Delta_d|^2 |\Delta_s|^2 + \frac{\gamma_2}{2} (\Delta_d^2)^2 + (\Delta_s^2)^2 \right] + K_{ds} \left\{ (D_\gamma \Delta_d)(D_\gamma \Delta_s)^* - (D_\gamma \Delta_d)(D_\gamma \Delta_s)^* + c.c \right\} + \frac{1}{8\pi} (\nabla \times \mathbf{A})^2
$$

where $\mathbf{A}$ is the vector potential and $D = \nabla - (2\pi i/\Phi_0) \mathbf{A}$ is the gauge invariant gradient with $\Phi_0 = hc/2e$ being the magnetic flux quantum. Coefficients $\alpha_\mu (\propto T - T_{cp})$, $\beta_\mu$, $K_\mu$, $\gamma_1$, $\gamma_2$ and $K_{ds}$ are real, and we assume $T_{cd} > 0$, while $T_{cs}$ can be both positive and negative. The $\gamma_2$ is one of the terms which determine the relative phase of OPs, $\phi_{ds} (\equiv \phi_d - \phi_s)$: $\Delta_{\mu} = |\Delta_{\mu}| \exp(i\phi_{\mu})$. We take $\gamma_2 > 0$, because this choice would lead to the $(d \pm is)$-state ($\phi_{ds} = \pm \pi/2$) instead of the $(d \pm s)$-state ($\phi_{ds} = 0, \pi$). In the former case the nodes of the $d$-wave state are removed and the more condensation energy can be gained. It is also to be noted that $\gamma_1 \pm 2\gamma_2$ is positive in usual weak-coupling model, since two OPs compete each other. Now we rewrite $\mathcal{F}$ in the dimensionless unit to
see the parameter dependence of the model more clearly,

\[ \mathcal{F} = \frac{H_2^2 \xi_3^2}{4\pi} \int dr \left[ -|\eta_d|^2 + \frac{1}{2}|\eta_d|^4 + |\tilde{D}\eta_d|^2 \right. \\
+ \tilde{a}_s|\eta_s|^2 + \frac{\tilde{b}_s}{2}|\eta_s|^4 + \tilde{K}_s|\tilde{D}\eta_s|^2 \\
+ \tilde{\gamma}_1 |\eta_d|^2 |\eta_s|^2 + \tilde{\gamma}_2 \left( |\eta_d|^2 |\eta_s|^2 + (|\eta_d|^2)^2 \right) \\
+ \tilde{K}_{ds} \left( (\tilde{D}_x \eta_d)(\tilde{D}_x \eta_s) + (\tilde{D}_y \eta_d)(\tilde{D}_y \eta_s) + \text{c.c.} \right) \\
+ \left. (\nabla \times \mathbf{a})^2 \right], \]

where \( \eta_{d,s} = \Delta_{d,s}/\Delta_0 \) with \( \Delta_0 = \sqrt{|\alpha_d|/\beta_d} \) being the bulk d-wave OP. \( \mathbf{r} \) was rescaled using the coherence length for the d-wave OP, \( \xi_d = \sqrt{K_d/|\alpha_d|} \), as \( \mathbf{r} \to r/\xi_d \), and \( \tilde{D} \equiv \nabla - i\mathbf{a}/\kappa \). Here \( \mathbf{a} = A/(\sqrt{2}\pi d_{xy}) \), and the magnetic field is measured in units of \( \sqrt{2}H_c \), where \( H_c = \sqrt{4\pi\alpha_d^2/\beta_d} \) is the thermodynamic critical field. \( \kappa = \lambda_d/\xi_d \) is the GL parameter with \( \lambda_d = \phi_0/(2\sqrt{2}\pi d_{xy}) \) the penetration depth for the bulk d-wave superconductor. The parameters in Eq.(2) are defined as \( \tilde{a}_s = a_s/|\alpha_d|, \tilde{b}_s = b_s/|\beta_d|, \tilde{K}_s = K_s/K_d \), \( \tilde{\gamma}_1 = \gamma_1/|\beta_d|, \tilde{\gamma}_2 = \gamma_2/|\beta_d| \) and \( \tilde{K}_{ds} = K_{ds}/K_d \).

Usually the surface effect is described by the second-order surface GL free energy, \( \mathcal{F}_{ds} = \int dS \sum_{\mu,\nu=d,s} g_{\mu\nu}|\eta^*_\mu|\eta^*_\nu \), where integration is carried out on the surface. Using the symmetry argument we find \( g_{ds} = g_{sd} = g_0 \cos 2\theta \) where \( \theta \) is the angle between the surface and the crystal a-axis with \( g_0 \) being a constant. This term could also determine \( \phi_{ds} \), and it leads to the \((d \pm s)\)-state in the case of a [100] surface \((\theta = 0)\), since the \( \tilde{\gamma}_2 \) term is higher order than the \( g_{ds} \) term. However, \( g_{ds} \) vanishes for a [110] surface \((\theta = 45^\circ)\) which we consider in the following. The \( g_{\mu\nu} \) term will represent the suppression of \( \eta_{d,s} \) near the surface. Instead of using \( g_{ds} \) we impose the condition \( \eta_d = 0 \) at the [110] surface, because the \( d_{x^2-y^2} \)-wave SCOP should vanish there. Since the s-wave SCOP is only little affected by the presence of the surface, we take \( g_{ss} = 0 \). (In numerical calculations we have checked that taking small positive \( g_{ss} \) will not change the results qualitatively.)

In order to consider the [110] surface we transform the coordinate system, \((x, y, z) \to (\tilde{x}, \tilde{y}, z) \). Here \( x \) is parallel to the crystal a \((b) \) axis \((z \) is parallel to the surface), and \( \tilde{x} \) and \( \tilde{y} \) axes are perpendicular and parallel to the surface, respectively. (See Fig.1.) In the free energy density only the \( \tilde{K}_{ds} \) term is changed under this transformation to

\[ \frac{2\tilde{K}_{ds}}{\kappa} \tilde{a}_s \text{Im}(|\eta_s^*| \partial_{\tilde{z}} |\eta_d| - |\eta_d| \partial_{\tilde{z}} |\eta_s^*|) \]

where we have assumed that the system is uniform along the surface, and the gauge freedom was taken as \( \mathbf{a} = a_g(\tilde{x})\mathbf{e}_g \).

The expression for the supercurrent is obtained by varying the electronic part of \( \mathcal{F} \) \((i.e., \) except the last term\) with respect to \( \mathbf{a} \). Since the surface is faced to the vacuum, the \( \tilde{x} \) component, \( j_{\tilde{x}} \), should obviously vanish. (We have numerically checked that \( j_{\tilde{x}} \) actually vanishes.) The \( \tilde{y} \) component, \( j_{\tilde{y}} \), and that in the the dimensionless unit, \( j_{\tilde{y}} \), are given as

\[ j_{\tilde{y}} = j_{\tilde{y}}/\left( \sqrt{2}H_c \right) \\
= -\frac{1}{4\pi} \left[ \tilde{a}_s \left| \eta_d \right|^2 + \tilde{K}_s |\eta_s|^2 \right] + \frac{1}{\kappa} \text{Im} \left[ |\eta_s^*| \partial_{\tilde{z}} |\eta_d| - |\eta_d| \partial_{\tilde{z}} |\eta_s^*| \right] \]

III. SURFACE STATE AND SPONTANEOUS CURRENT

We numerically solve the problem by employing the quasi-Newton method to minimize the free energy \( \mathcal{F} \) under the condition \( \eta_d(\tilde{x} = 0) = 0 \). We minimize \( \mathcal{F} \) with respect to all variables, i.e., \( \eta_d, \eta_s \) and \( a_g \). Note that the Maxwell’s equation is taken into account in this procedure, and we call this as ”fully self-consistent calculation”. For the sake of comparison we will also show the results by treating only \( \eta_s \) and \( \eta_s \) self-consistently.

First let us consider the case of \( \tilde{a}_s < 0 \) \((i.e., T < T_c) \). In this case, we would get finite \( \eta_s \) if \( \eta_d \) were absent. However, for \( T_{cd} > T_{cs} \) the stability condition for \( \eta_s \) in the bulk is given as \( \tilde{a}_s + (\tilde{\gamma}_1 - 2\tilde{\gamma}_2) |\eta_d|^2 < 0 \), so the transition temperature of \( \eta_s \) is lower than the bare one, \( T_{cs} \), and \( \eta_s \) would be totally suppressed if \( T_{cd} \gg T_{cs} \). Near the surface or impurities the situation can be different. There \( \eta_s \) may be finite because the dominant SCOP, \( \eta_d \), is suppressed. In Fig.2 the spatial variations of the SCOPs near the surface are shown. \( \eta_s \) gets finite near the surface while \( \eta_d \) is suppressed. The relative phase \( \phi_{ds} \) will be determined by \( \tilde{\gamma}_2 \) and \( \tilde{K}_{ds} \) terms, and the former favors \( \phi_{ds} = \pm \pi/2 \) as mentioned. From Eq.(3) we see that the \( \tilde{K}_{ds} \) term also favors \( \phi_{ds} = \pm \pi/2 \), and \( a_g \) will be spontaneously generated. (We take \( \eta_d \) to be real and \( a_g = 0 \) in the bulk, \( i.e., \tilde{x} \to \infty \).) Numerical calculations show that \( \eta_d \) is real for all \( \tilde{x} \), and that \( \phi_{ds} = \pm \pi/2 \) where \( \eta_s \) is finite. This indicates that a \( T \)-violating \((d + s)\)-wave surface state with a spontaneous magnetic field \( b_z \)
the magnetic field is not treated self-consistently, because
fully self-consistent calculation but not in the case where
contributions from only the spatial variations of SCOPs
x(= 0) corresponds to the surface faced to the vacuum. (a)
integration of the Maxwell’s equation with the boundary condition
b2(±∞) = 0 leads to \( \int_{-\infty}^{\infty} dz j_\beta(\hat{x}) = 0 \), implying that the
averaged current should vanish. This is the case for the
fully self-consistent calculation but not in the case where
the magnetic field is not treated self-consistently, because
of the absence of the screening effect in the latter.

Next we consider the case of \( \tilde{\alpha}_s > 0 \), i.e., \( T > T_{cs} \).
Note that \( T_{cs} \) may be negative, in which case \( \eta_s \) will not
occur in the bulk at \( T = 0 \) even when \( \eta_d \) is absent. The
results for the SCOPs are depicted in Fig.4. (Here the
GL parameter is taken to be \( \kappa = 16 \).) It is seen that finite
Im(\( \eta_s \)) is obtained, though we naively expect \( \eta_s = 0 \).
This is because the \( \tilde{K}_d \) term couples \( \partial_2 \Re(\eta_d) \) bilinearly
to \( a_\beta \Im(\eta_a) \). It may induce the state with Im(\( \eta_a \)) \( \neq 0 \)
and \( b_2 \neq 0 \), but the state with \( \eta_a = 0 \) and \( b_2 = 0 \) may also be
a self-consistent solution. Numerical calculations show
that the former one has the lower energy, and thus the
time-reversal symmetry is violated spontaneously. Here
\( |\tilde{\alpha}_s| \), \( \tilde{\beta}_s \) and \( \tilde{K}_s \) were taken to be much smaller than those
in Fig.2. Otherwise the \( T \)-violation will not occur, becaus
these terms cost the energy for \( \tilde{\alpha}_s > 0 \) and the
energy gain is solely coming from the \( \tilde{K}_d \) term. The
spatial variations of \( b_z \) and \( j_\beta \) are shown in Fig.5.

In the case of \( \tilde{\alpha}_s > 0 \), the results with or without treating
the vector potential self-consistently are completely
different. If we do not take into account the \( a_\beta \) term,
\( \eta_s \) will never appear, since there is no mechanism to de-
rive finite \( \eta_s \). Thus neither the spontaneous current nor
the spontaneous field can occur. It implies that the \( T \-
violation near the surface cannot be described in this kind
of simplified treatment for the superconductors in which
the second SCOP has negative \( T_c \).

In order to see the dependence on \( \kappa \) we show the results
for a larger \( \kappa \) (\( \kappa = 19 \)) in Fig.6 and 7. It is seen that |\( \eta_s \)|,
|\( b_2 \) and |\( j_\beta \)| are much smaller than those for \( \kappa = 16 \).
This \( \kappa \) dependence can be understood as follows. \( \eta_d \) is
suppressed in the region near the surface (\( \hat{x} \lesssim \xi_d \)), and
\( \eta_s \) and \( a_\beta \) would be finite there if \( T \) is broken. On the
other hand the magnetic field \( b_z \) would be finite in the
region \( \hat{x} \lesssim \lambda_d \). When \( \kappa \) is large, the loss of energy due

\( (= \partial_x a_\beta \) and a supercurrent \( j_\beta \) occurs near the surface.
The spatial distributions of \( b_z \) and \( j_\beta \) are presented in
Fig.3.

In order to see the role played by the vector potential,
we investigate the same problem by setting \( a_\beta = 0 \)
ev-erywhere. Namely we treat only SCOPs self-consistently.
When \( a_\beta \) is set to zero, the spontaneous current \( j_\beta \) has
contributions from only the spatial variations of SCOPs
(i.e., the last line of Eq.(4)), and we calculate the mag-
netic field from \( j_\beta \) using Maxwell’s equation, \( j_\beta(\hat{x}) = \)
\(- 1/\mu \partial_0 j_\beta(x) \). For \( \tilde{\alpha}_s < 0 \), the results for the SCOPs look
similar as in the fully self-consistent calculations. The \( T-
breaking \( (d + i\beta) \)-state occurs as shown in Fig.2. On the
contrary, the behaviors of \( b_z \) and \( j_\beta \) are different in that
\( j_\beta \) always has the same sign, and that \( b_z \) is a monotonous
function of \( \hat{x} \). These results are not correct even qual-
itatively as well as in a quantitative sense. Integration
of the Maxwell’s equation with the boundary condition
\( b_z(\pm \infty) = 0 \) leads to \( \int_{-\infty}^{\infty} dz j_\beta(\hat{x}) = 0 \), implying that the
averaged current should vanish. This is the case for the
fully self-consistent calculation but not in the case where
the magnetic field is not treated self-consistently, because
of the absence of the screening effect in the latter.
to finite $b_z$ in the large region ($\xi_d \lesssim \tilde{x} \lesssim \lambda d$) overwhelms the energy gain coming from the $K_{ds}$ term which acts only in the small region $\tilde{x} \lesssim \xi_d$. Thus for large $\kappa$ the $T$-violation is not favored. If the larger value of $K_{ds}$ is taken, the $T$-breaking state can occur for larger $\kappa$. But the natural assumption seems to be $K_{ds} \leq K_d$ ($K_{ds} \leq 1$), so that the $T$-violation may occur for $\kappa$ of the order of 10. (On the contrary the $T$-violation may occur for much larger $\kappa$ in the case of $\tilde{\alpha}_s < 0$, because the energy can be gained by not only $K_{ds}$ but also $\tilde{\alpha}_s$ term.) It implies that the present mechanism may not be relevant to hole-doped cuprates in which $\kappa \sim 100$, but it may describe the surface states of electron-doped cuprates which have smaller $\kappa$.

If we assume $H_c = 1T$, the maximum values of $|B_z|$ and $|J_y|$ are $2.5 \times 10^{-1}T$ and $3.7 \times 10A/cm^2$, respectively, for $\kappa = 16$. For $\kappa = 19$ they are $8.6 \times 10^{-2}T$ and $1.2 \times 10A/cm^2$, respectively. These values rapidly decrease as $\kappa$ increases, and the $T$-breaking state disappears as $\kappa$ exceeds 19 for the parameters used here. If we compare these values with experiments, it should be noted that surface roughness will reduce $|B_z|$ and $|J_y|$, because $T$-violation is most favored in the case of $\theta = 45^\circ$ (When $\theta \neq 45^\circ$, $g_{ds}$ will be finite and the $T$-violation is not favored.)

IV. SUMMARY

We have examined the role played by the vector potential concerning the occurrence of surface states with spontaneously broken $T$ in $d_{x^2-y^2}$-wave superconductors. It has been known that the $T$-breaking state may naturally appear if the bare $T_c$ of the additional OP is positive. For the Josephson junction composed of $d_{x^2-y^2}$-wave and other superconductors, tunneling may induce second component of SCOP and thus $T$ may be broken. In these cases the $T$-breaking states may be described without treating the vector potential self-consistently. In this paper it was shown that the surface state of a $d_{x^2-y^2}$-wave superconductor may break $T$ even when the bare $T_c$ of the second SCOP is negative. However, to describe this situation correctly not only the SCOPs but also the vector potential must be treated on an equal footing. In the present mechanism the $T$-violation may occur for rather small values of the GL parameter $\kappa (\lesssim 20)$, so that it may not be relevant to hole-doped cuprates. We expect the present theory may be used to describe the surface states of electron-doped high-$T_c$ cuprates, because their $\kappa$ are much smaller than those of hole-doped systems.

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