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IV.1

SYMMETRY OF HIGH-T_c SUPERCONDUCTORS

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Abstract: The symmetry classification of superconducting states is reviewed. Based on purely symmetry considerations, a simple proof is given for the enhancement of $d_{x^2-y^2}$ superconductivity at the surface of cuprate materials. A novel method to study mixed superconducting phases is introduced.

1. INTRODUCTION

In the last two decades, important discoveries in the field of superconductivity [1] have reopened the question of what is the symmetry of the superconducting state. In this contribution, after a brief historical introduction, the classification of superconducting states will be reviewed. Some consequences of the symmetry of the state will be then discussed, especially in view of the recent interest in the symmetry of high-T_c superconductors. Finally, a novel approach particularly useful for mixed symmetry states will be introduced.

In 1957, Bardeen, Cooper and Schriffer proposed a microscopic theory of superconductivity [2]. This theory was isotropic (s-wave pairing). In 1958, Bogoliubov [3] and Valatin [4] introduced a transformation that made the treatment of superconductivity simpler (quasi-particle transformation). Still in 1958, Anderson [5] addressed the same problem by introducing the algebra of SU(2) to describe the properties of the system (quasi-spin algebra). In the same year, Bohr, Mottelson and Pines applied BCS theory to

the study of atomic nuclei and found evidence for s-wave pairing in nuclei [6]. The symmetry of the superconducting state was enlarged by Anderson and Morel in 1961 [7] and by Balian and Werthamer in 1963 [8] (p-wave pairing). Up to the late 60's, BCS theory based on s-wave pairing was used both in condensed matter systems and in atomic nuclei. However, beginning in the early 70's it become apparent that other types of symmetry play a role. It is convenient at this stage to separate rotational invariant systems from point group invariant systems. For rotationally invariant systems, the symmetry group to be described in Sect.2 is $G \equiv O(3)$. In 1973 Leggett [9] proposed p-wave pairing to describe properties of ^3He and in 1974 Arima and Iachello [10] proposed a combination of s- and d-wave pairing to describe properties of atomic nuclei. For point group invariant systems, the symmetry group is $G \equiv$ *Point group*. In 1979, Steglich et al. [11] discovered superconductivity in heavy fermion materials. Some of the point groups relevant to these materials are D_{4h}, O_h and D_{6h}. Finally, in 1986 the discovery of high-T_c superconductivity in cuprate materials with point group D_{4h} by Bednorz and Müller [1] brought the question of the symmetry of the superconducting state back to the forefront of physics.

An excellent account of the symmetry of superconducting states is given in the review article of Sigrist and Ueda [12]. In the first part of this contribution, this article will be followed and consequences of symmetry on the surface of cuprate materials will be derived. In the second part of the contribution, a novel approach to the study of mixed superconducting phases will be introduced and its connection to the Ginzburg-Landau approach briefly discussed.

2. PAIRING HAMILTONIAN

The starting point for the study of the symmetry of the superconducting state is the pairing Hamiltonian. For applications to condensed matter systems it is convenient to write this Hamiltonian in momentum space

$$H = \sum_{\vec{k},s} \varepsilon\left(\vec{k}\right) a^{\dagger}_{\vec{k},s} a_{\vec{k},s} + \frac{1}{2} \sum_{\vec{k},\vec{k}',s_1,s_2,s_3,s_4} \upsilon_{s_1,s_2,s_3,s_4}\left(\vec{k},\vec{k}'\right) a^{\dagger}_{-\vec{k},s_1} a^{\dagger}_{\vec{k},s_2} a_{-\vec{k}',s_3} a_{-\vec{k}',s_4} \quad . \tag{1}$$

Here $\varepsilon(\vec{k})$ is the single particle energy and $\upsilon(\vec{k},\vec{k}')$ the interaction. The symmetry of the superconducting state can be derived from that of the Hamiltonian. In general, the symmetry group $\mathcal{G}$ is the direct product

$$\mathcal{G} \equiv G \otimes SU_s(2) \otimes \mathcal{T} \otimes U(1) \tag{2}$$

where for point group invariant systems G = *Point group*, while for rotational invariant systems $G = O(3)$. The group $SU_s(2)$ describes ordinary spin, while $\mathcal{T}$ is the time-reversal group and U (1) the gauge group. In this article, the discussion will be limited to G, which will be called the intrinsic group.

By introducing gap functions $\Delta_{S_1S_2}(\vec{k})$, H can be approximated by a one-particle Hamiltonian

$$\begin{aligned}\tilde{H} = & \sum_{\vec{k},s} \varepsilon\left(\vec{k}\right) a^{\dagger}_{\vec{k},s} a_{\vec{k},s} \\ & + \frac{1}{2} \sum_{\vec{k},s_1,s_2} [\Delta_{s_1,s_2}\left(\vec{k}\right) a^{\dagger}_{\vec{k},s_1} a^{\dagger}_{-\vec{k},s_2} - \Delta^{*}_{s_1,s_2}\left(-\vec{k}\right) a_{-\vec{k},s_1} a_{\vec{k},s_2}].\end{aligned} \tag{3}$$

The Bogoliubov transformation

$$a_{\vec{k},s} = \sum_{s'} \left(u_{\vec{k},ss'} \alpha_{\vec{k},s'} + \upsilon_{\vec{k},ss'} \alpha^{\dagger}_{-\vec{k},s'} \right) \tag{4}$$

brings this Hamiltonian in an even simpler form, in terms of quasi-particle operators $\alpha_{\vec{k},s}$ and quasi-particle energies, $E_{\vec{k},s}$.

3. CLASSIFICATION OF SUPERCONDUCTING STATES

A complete classification of superconducting states is given in the review paper of Sigrist and Ueda [12], both for triplet and singlet pairing. Since it appears that in high-T_c superconductors one has singlet pairing, only this case will be discussed in this article. We are interested here in obtaining a basis for the representations of the group $\mathcal{G}$ of Eq.(2).

For rotational invariant systems, the group $G \equiv O(3) = SO(3) \otimes \mathcal{P}$,where $\mathcal{P}$ is the parity operation. Leaving aside time-reversal and gauge groups and noting that $S = 0$ (singlet states), we are led to consider the classification of the representations of $O(3)$. These are labeled by the integer number $\ell = 0, 1, 2,...$ The parity is $(-)^{\ell}$ and can be omitted.
We thus have

$$D(\mathcal{G}) = D_{\ell}(G) \otimes D_S(SU_s(2)) \otimes D_T(T) \otimes D_{\varphi}(U(1)) \tag{5}$$

The basis functions for the intrinsic group G are the polynomial harmonics in momentum space,

$$k^{\ell} Y_{\ell m}\left(\hat{k}\right). \tag{6}$$

[The spherical harmonics $Y_{\ell m}(\hat{k})$ are a basis for the representations of $SO(3)$. Here the polynomial harmonics are used to construct the basis states in the following tables.] For singlet pairing, only positive parity harmonics are of importance. The lowest positive parity harmonics are given in Table 1 (real form). For studying surface phenomena, we also need negative parity harmonics. The lowest negative parity harmonics are given in Table 2 (real form).

Table IV:1:1. Real forms of the lowest ($\ell \leq 4$) positive parity harmonics. $P_m^{\ell}(\theta)$ are the associated Legendre polynomials

$\ell = 0$	P_0^0
$\ell = 2$	$k^2 P_m^2(\theta) \begin{cases} \cos m\varphi \\ \sin m\varphi \end{cases}$
$\ell = 4$	$k^4 P_m^4(\theta) \begin{cases} \cos m\varphi \\ \sin m\varphi \end{cases}$

Table IV:1:2. Real forms of the lowest ($\ell \leq 3$) negative parity harmonics.

$\ell = 1$	$kP_m^1(\theta) \begin{cases} \cos m\varphi \\ \sin m\varphi \end{cases}$
$\ell = 3$	$k^3 P_m^3(\theta) \begin{cases} \cos m\varphi \\ \sin m\varphi \end{cases}$

For point group invariant systems, the intrinsic group is *G = Point group*. The construction of the basis for these systems is a standard group theoretical problem. For the groups D_{4h}, D_{6h} and O_h it was done by Hamermesh many years ago [13]. I report here only the case of $G \equiv D_{4h}$. For positive parity one has Table 3. For negative parity one has Table 4.

The representations here are labelled by the group theoretical notation [13] A_1, A_2, B_1, B_2, E. The first four are one dimensional, while the representation E is two dimensional. For $\ell \geq 3$, some representations are contained twice and the situation is slightly more complicated. In condensed matter physics, it has become customary to label the representations with the letter Γ [14]. When both positive and negative parity states are considered also the parity label is added, Γ^+ and Γ^-. The conversion between the two notations is $A_1 \rightarrow \Gamma_1$, $A_2 \rightarrow \Gamma_2$, $B_1 \rightarrow \Gamma_3$, $B_2 \rightarrow \Gamma_4$, and $E \rightarrow \Gamma_5$.

For high-T_c superconductors it appears that only s- and d-wave pairing is important. It appears also that superconductivity is in the CuO planes (x-y plane). Restricting the classification to two-dimensions one has Table 5. Here in the last column, the notation often used in high-T_c superconductivity is also indicated. Also a star is placed on the representation Γ_1 originating from $\ell = 2$ to distinguish it from that originating from $\ell = 0$, although both transform in the same way under D_{4h}. Another notation is "extended s-wave".

Table IV:1:3. Construction of the positive parity basis ($\ell \leq 2$) for the group D_{4h}.

$\ell = 0$	A_1	P_0^0	1
$\ell = 2$	A_1	$k^2 P_0^2(\theta)$	$k_z^2; k_x^2 + k_y^2$
	A_2	–	–
	B_1	$k^2 P_2^2(\theta)\sin 2\varphi$	$k_x^2 - k_y^2$
	B_2	$k^2 P_2^2(\theta)\cos 2\varphi$	$k_x k_y$
	E	$k^2 P_1^2(\theta)\begin{cases}\cos\varphi \\ \sin\varphi\end{cases}$	$\begin{cases}k_y k_z \\ k_z k_x\end{cases}$

Table IV:1:4. Construction of the negative parity basis ($\ell \leq 1$) for the group D_{4h}.

$\ell = 1$	A_1	–		–
	A_2	$kP_0^1(\vartheta)$		k_z
	B_1	–		–
	B_2	–		–
	E	$kP_1^1(\vartheta)$	$\begin{cases}\cos\varphi \\ \sin\varphi\end{cases}$	$\begin{cases}k_x \\ k_y\end{cases}$

4. CONSEQUENCES OF SYMMETRY: QUASI-PARTICLE SPECTRUM

An immediate consequence of symmetry is the nature of the quasi-particle spectrum. The density of states $\rho(\omega)$ can be calculated from the knowledge of the quasi-particle energies. For singlet states $E_{k,\pm} = E_k$, with

$$E_k = \left(\varepsilon^2(\vec{k}) + \Delta^2(\vec{k})\right)^{1/2} . \tag{7}$$

In ordinary superconductors (s-wave pairing), $\Delta(\vec{k}) = \Delta_0$, and

$$\rho(\omega) = \begin{Bmatrix} 0 & \omega < \Delta_0 \\ N(0) \quad \dfrac{\omega}{\sqrt{\omega^2 - \Delta_0^2}} & \omega > \Delta_0 \end{Bmatrix}. \tag{8}$$

As an example of unconventional pairing consider the polar state in p-wave pairing. The density of states is given here by

$$\rho(\omega) = \begin{Bmatrix} N(0)\frac{\pi}{2}\frac{\omega}{\Delta_0} & \omega < \Delta_0 \\ N(0)\ \frac{\omega}{\Delta_0}\arcsin\frac{\Delta_0}{\omega} & \omega > \Delta_0 \end{Bmatrix}. \tag{9}$$

In general, for rotational invariant systems, the gap function can be expanded into polynomial harmonics

$$\Delta(\vec{k}) = \Delta_0 \sum_{\ell m} c_{\ell m} k^{\ell} Y_{\ell m}(\hat{k}) \tag{10}$$

Table IV:1:5. Restriction of the basis to two-dimensions.

$\ell = 0$	Γ_1	1	s
$\ell = 2$	Γ_{1*}	$k_x^2 + k_y^2$	s_*
	Γ_3	$k_x^2 - k_y^2$	$d_{x^2-y^2}$
	Γ_4	$k_x k_y$	d_{xy}

while, for point group invariant systems, it can be expanded into Γ_i's

$$\Delta(\vec{k}) = \Delta_0 \sum_i c_i \Gamma_i(\vec{k}) \tag{11}$$

In two dimensions, and point group D_{4h}, the expansion is

$$\Delta(\vec{k}) = \Delta_0 \left[c_1 \Gamma_1(\vec{k}) + c_3 \Gamma_3(\vec{k}) + c_4 \Gamma_4(\vec{k}) \right]. \tag{12}$$

It is convenient to introduce polar coordinates, k and φ, as in Fig. 1. The expansion becomes then, for k independent gaps, i.e. dropping the factor k^2 in Γ_3 and Γ_4,

$$\begin{aligned} \Delta(\varphi) &= \Delta_0 \left[c_1 + c_3 \cos 2\varphi + c_4 \sin 2\varphi \right] \\ &\equiv \Delta_0 f(\varphi) \\ 0 \le \varphi &\le \frac{\pi}{2}. \end{aligned} \tag{13}$$

If only $c_3 \neq 0$, the gap has a line of nodes at $\varphi = \pi/4$. One can introduce the quantity

$$\rho(\omega, \varphi) = \begin{Bmatrix} 0 & \omega < \Delta_0 f(\varphi) \\ N(0) \quad \dfrac{\omega}{\sqrt{\omega^2 - \Delta_0^2 f(\varphi)^2}} & \omega > \Delta_0 f(\varphi) \end{Bmatrix} \tag{14}$$

and obtain the total density of states by

$$\rho(\omega) = \frac{1}{\pi/2} \int_0^{\pi/2} \rho(\omega, \varphi) d\varphi. \tag{15}$$

The dependence of $\rho(\omega)$ as $\omega \to 0$ is reflected in the behavior of several physical quantities as a function of temperature.

Since the density of states depends on the symmetry of the gap, any measurement sensitive to $\rho(\omega)$ will give information on the symmetry of the gap. An example is ARPES measurements [15]. The photoemission intensity can be written as

$$I(\omega) = \int w(\omega - \omega')S(\omega')\rho(\omega')d\omega', \tag{16}$$

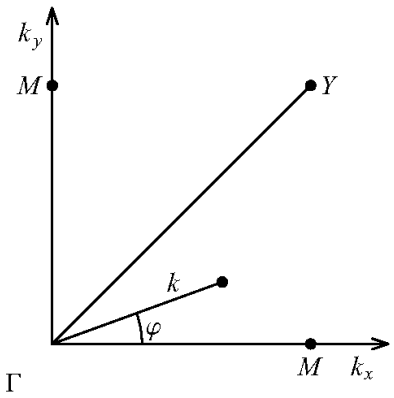

Figure IV:1:1. Choice of coordinates for expansion of the gap function

where the weight function depends on the energy resolution of the apparatus and can be taken as a Lorentzian

$$w(\omega - \omega') = \frac{\gamma^2}{(\omega - \omega')^2 + \gamma^2} \tag{17}$$

with width at half-maximum γ and $S(\omega)$ is the sensitivity of the instrument. Recent ARPES measurements [16] appear to indicate that in high-T_c superconductors the symmetry of the gap is $d_{x^2-y^2}$. However, ARPES measurements are sensitive only to the surface, of the order of 10× lattice

constants. The question then arises on whether or not the symmetry of the gap is uniform throughout.

5. SURFACE VERSUS BULK

In 1974, Ambegaokar et al. [17] noted that anisotropic superconductivity is strongly influenced by a boundary within the range of its coherence length. They noted that in superfluid ^3He (p-wave superconductor) the internal angular momentum of the Cooper pairs always turns perpendicular to the vessel wall of the confining fluid. In an independent devolopment, in 1974 Arima and the author [10] introduced a model of atomic nuclei seen as liquid drops with s- and d-wave pairing. By analyzing the spectra of several atomic nuclei they concluded that some nuclei (Sn,Pb,...) are characterized by purely s-wave pairing while others (Sm,Gd,..;Pt,Os,...) are characterized by a mixture of s-and d-wave, with the bulk being only s-wave and the surface being a mixture of s- and d-wave, in fact mostly d-wave [18]. It thus appears that anisotropic pairing in rotational invariant systems with a surface is strongly influenced by the presence of a boundary. Recently, Müller has suggested that the same situation occurs in high T_c superconductors [19].

The arguments of Ambegaokar et al. are based on the introduction of a coordinate dependent gap

$$\Delta_{s_1 s_2}(\hat{k},\vec{r}) = \sum_m \eta_m(\vec{r})\Delta_m(\hat{k}), \tag{18}$$

where $\eta_m(\vec{r})$ are coordinate dependent order parameters, and on the solution of the appropriate integral equation. A much simpler argument can be given by pure symmetry considerations which are particularly appropriate for systems with point group symmetry. Consider a surface S with normal $\vec{n} \equiv (n_x, n_y, n_z)$ and couple the vector $\vec{n}$ to the order parameter. For rotational invariant systems, the normal vector $\vec{n}$ belongs to the vector representation $D_{\ell=1}(G)$. From Table 4 one can see that it belongs to the representations $\Gamma_2^- \oplus \Gamma_5^-$ of D_{4h}. When coupled to a representation Γ of the order parameter it induces terms of the type

$$D^d \otimes \Gamma^* \otimes \Gamma. \tag{19}$$

The power of D's must be even $d = 2, 4, \ldots$ since a vector has negative parity and the coupling terms must be of positive parity. Also the total product in (19) must transform as the scalar representation Γ_1. Sigrist and Ueda have analyzed all possible coupling terms. For two-dimensional systems, the coupling terms can be written as in Table 6. [The extended s-wave s_* couples in the same way as s and it has been omitted]. For a vector in the x direction $\vec{n} \equiv (1, 0, 0)$, Fig.2, or in the y direction $\vec{n} \equiv (0, 1, 0)$, one obtains the important result that, apart from a uniform contribution g_1, only the $d_{x^2-y^2}$ representation is affected by the boundary in the amount g_3. For $g_3 > 0$ the surface produces an enhancement of d-wave pairing at the boundary. This result does not depend on details of how the boundary interacts, but only on its symmetry properties. It makes the suggestion of Müller [19] very plausible and makes point group invariant systems very similar to rotational invariant systems [20]. Returning to the integral equation of Ambegaokar et al., one can make reasonable models of how the order parameter changes with x. One such a model is that in which

$$\eta_{\Gamma_3} \propto \eta_0 \left[1 - \tanh \frac{x - x_0}{\xi} \right] \tag{20}$$

where ξ is of the order of the correlation length, and x_0 is the location of the boundary.

Table IV:1:6. Invariant couplings with a surface with normal $\vec{n} \equiv (n_x, n_y)$ in two-dimensions.

Γ_1	$g_1\left(n_x^2 + n_y^2\right)$	s
Γ_3	$g_1\left(n_x^2 + n_y^2\right) + g_3\left(n_x^2 - n_y^2\right)^2$	d_{x^2-}
Γ_4	$g_1\left(n_x^2 + n_y^2\right) + g_3 n_x^2 n_y^2$	d_{xy}

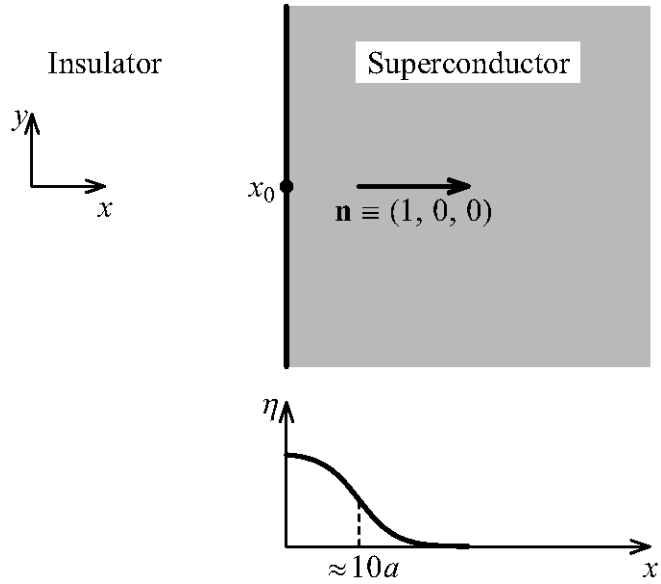

Figure IV:1:2. Geometry of the insulator-superconductor boundary discussed in the text, together with a model of the order parameter, Eq.(20).

6. BEYOND MEAN FIELD

A global phenomenological description of high-T_c superconductors is made difficult by the possibility of several almost degenerate phases and by boundary effects arising from the presence of anisotropic gap. The treatment of the same problem in atomic nuclei suggests two methods for dealing with this problem: the method of interacting bosons introduced by Arima and the author [18] and the method based on the Ginsburg-Landau formulation reported by Sigrist and Ueda [12].

In the method of interacting bosons, one introduces boson creation, $\Gamma_i^\dagger$, and annihilation, Γ_i, operators satisfying boson commutation relations

$$\left[\Gamma_i, \Gamma_j^\dagger\right] = \delta_{ij}, \quad \left[\Gamma_i, \Gamma_j\right] = \left[\Gamma_i^\dagger, \Gamma_j^\dagger\right] = 0. \tag{21}$$

These boson operators are related to those introduced in [20] as shown in Table 7. They transform under D_{4h} as the representation indicated by the appropriate letter. [An extended s-wave Γ_{1*} can also be introduced.] One then constructs the Hamiltonian by expanding it into bilinear products of creation and annihilation operators, with the constraint that H must transform as the representation Γ_1 of D_{4h}

$$\begin{aligned} H = & \varepsilon_1 \Gamma_1^\dagger \Gamma_1 + \varepsilon_3 \Gamma_3^\dagger \Gamma_3 + \varepsilon_4 \Gamma_4^\dagger \Gamma_4 \\ & + u_{1111} \Gamma_1^\dagger \Gamma_1^\dagger \Gamma_1 \Gamma_1 + u_{3333} \Gamma_3^\dagger \Gamma_3^\dagger \Gamma_3 \Gamma_3 + u_{4444} \Gamma_4^\dagger \Gamma_4^\dagger \Gamma_4 \Gamma_4 \\ & + u_{1133} \left(\Gamma_1^\dagger \Gamma_1^\dagger \Gamma_3 \Gamma_3 + \Gamma_3^\dagger \Gamma_3^\dagger \Gamma_1 \Gamma_1 \right) + u_{1144} \left(\Gamma_1^\dagger \Gamma_1^\dagger \Gamma_4 \Gamma_4 + \Gamma_4^\dagger \Gamma_4^\dagger \Gamma_1 \Gamma_1 \right) \\ & + u_{3344} \left(\Gamma_3^\dagger \Gamma_3^\dagger \Gamma_4 \Gamma_4 + \Gamma_4^\dagger \Gamma_4^\dagger \Gamma_3 \Gamma_3 \right) \end{aligned} \tag{22}$$

This is done by using the multiplication rules for D_{4h}, for example,

$$\Gamma_3 \otimes \Gamma_3 = \Gamma_1 . \tag{23}$$

The Hamiltonian is then diagonalized in the basis

$$B : \Pi_i \left(\Gamma_i^\dagger \right)^{N_i} |0\rangle \tag{24}$$

with $N = N_1 + N_3 + N_4$. This basis is spanned by the representations of the group $U(3)$. It has been shown recently [21], that even if $N \sim 20$ the solutions are very close to the limit $N \to \infty$. Within this approach, space anisotropy can be taken into account by making $\varepsilon = \varepsilon(\vec{r})$ and $u = u(\vec{r})$. In addition one can easily discuss the case in which the coefficients depend on an external parameter, such as doping, $\varepsilon = \varepsilon(c)$ and $u = u(c)$. If both effects are present

$$\begin{aligned} \varepsilon &= \varepsilon(\vec{r}, c), \\ u &= u(\vec{r}, c). \end{aligned} \tag{25}$$

The values of ε and u will depend on the material. Diagonalization of the Hamiltonian will produce wave functions of the type

$$|\Psi\rangle = \sum_{N_1,N_3,N_4} \alpha_{N_1,N_3,N_4} \left(\Gamma_1^\dagger\right)^{N_1} \left(\Gamma_3^\dagger\right)^{N_3} \left(\Gamma_4^\dagger\right)^{N_4} |0\rangle \tag{26}$$

with

$$\alpha_i = \alpha_i\left(\vec{r}, c\right), \tag{27}$$

as advocated by Müller. With these wave functions one can evaluate the expectation values of the number operators

$$v_i = \langle\Psi| \frac{N_i}{N} |\Psi\rangle \tag{28}$$

Table IV:1:7. Boson operators in the method of interacting bosons.

$s-boson$	$s^\dagger$	$\Gamma_1^\dagger$
$d_{x^2-y^2}-boson$	$\left(d_-^\dagger + d_+^\dagger\right) = d_3^\dagger$	$\Gamma_3^\dagger$
$d_{xy}-boson$	$\left(d_-^\dagger - d_+^\dagger\right) = d_4^\dagger$	$\Gamma_4^\dagger$

which give the composition of the superconducting state in terms of the representations Γ_1, Γ_3, Γ_4.

A major question however is how to construct the phase diagram of mixed systems. In order to do that, one needs to enlarge the boson space, by introducing an auxiliary boson, Γ_0, that transforms as the representation Γ_1, and represents pairs in the normal phase. The Hamiltonian becomes

$$H = \sum_{i=0,1,3,4} \varepsilon_i \Gamma_i^\dagger \Gamma_i^\dagger + \sum_{i<j=0,1,3,4} u_{iijj} \left(\Gamma_i^\dagger \Gamma_i^\dagger \Gamma_j \Gamma_j + \Gamma_j^\dagger \Gamma_j^\dagger \Gamma_i \Gamma_i\right) \tag{29}$$

and is diagonalized in the basis $\mathcal{B}$ with $N = N_0 + N_1 + N_3 + N_4$. The study of phase transitions for this system has been extensively investigated. One introduces coherent states [22]

$$|N, \eta_i\rangle = \left(\Gamma_0^\dagger + \sum_{i=1,3,4} \eta_i \Gamma_i^\dagger\right)^N |0\rangle \tag{30}$$

that depend on the (generally complex) order parameter η_i. By evaluating the expectation value of the Hamiltonian in the state (30) one obtains the energy functional

$$F(\eta_i) = \langle N, \eta_i \mid H \mid N, \eta_i \rangle. \tag{31}$$

Minimization with respect to η_i gives the equilibrium values. A study of the equilibrium values and their derivatives with respect to the coupling constants ε, u gives then the phase diagram [18]. If temperature dependence needs to be studied, it can be done by making the coupling constants ε, u temperature dependent.

An alternative method is to start directly from the Ginzburg-Landau approach [12]. In this method, one introduces (in general complex) order parameters η_i, as in Table 8, and expands the free energy in powers of the order parameters. For real order parameters and up to quartic terms one obtains

$$F(\eta_i) = \sum_{i=1,3,4} A_i(T)\eta_i^2 + \sum_{i<j=1,3,4} \beta_{ij}\eta_i^2\eta_j^2 \tag{32}$$

Table IV:1:8. Order parameters in the Ginzburg-Landau approach.

s	Γ_1	$\eta_1 \mid e^{i\varphi 1}$
$d_{x^2-y^2}$	Γ_3	$\eta_3 \mid e^{i\varphi 3}$
d_{xy}	Γ_4	$\eta_4 \mid e^{i\varphi 4}$

where the notation of Sigrist and Ueda has been used. The coefficient of the second order term is temperature dependent and written as

$$A_i(T) = a' \frac{T}{T - T_{c,i}} \tag{33}$$

where $T_{c,i}$ is the critical temperature for phase Γ_i. The coefficients are material dependent and they may also depend on external parameters such as doping, c. The Ginzburg-Landau theory is equivalent to the method of interacting bosons.

7. CONCLUSIONS

In this article, the symmetry of superconducting phases for two-dimensional systems with D_{4h} intrinsic group has been discussed. An important result has been obtained by purely symmetry arguments namely that $d_{x^2-y^2}$ symmetry is enhanced at the surface due to boundary effects, making the recent suggestion of Müller very plausible. Finally a novel method has been introduced that allows a detailed phenomenological study of the phase structure of cuprate materials, including

(i) Anisotropy in momentum space, $\vec{k}$
(ii) Anisotropy in coordinate space, $\vec{r}$ and
(iii) Mixing of two or more almost degenerate superconducting phases.

By applying these methods to the analysis of experiments, it should be possible to understand whether or not:

(i) cuprate superconductors are anisotropic in momentum space and what is their symmetry type (s- versus d-wave)
(ii) cuprate superconductors are anisotropic in coordinate space (surface versus bulk)
(iii) different superconducting phases are mixed.

The remaining important aspect is how to derive these properties from a microscopic theory. In this respect, particularly interesting is the interacting boson-fermion model described at this workshop by Micnas [23]. This model is an extension of the method discussed above to mixed systems of bosons and fermions [24]. A symmetry analysis of this system will be presented elsewhere.

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