# Space−group approach to the wavefunction of a Cooper pair. Application to unconventional superconductors

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Zero–total momentum two–electron wavefunction in crystal space–groups are constructed making use of induced representation method and projection operator technique.Theory is applied to analysis of nodal structure of Cooper pairs in unconventional supercondectors. Theoretical results are compared with experimental data.

## 1  Introduction

The Bardeen–Cooper–Schriffer (BCS) [1] theory of superconductivity provides explanation of this phenomenon in pure metals in terms of electron–phonon interactions and singlet pairing with spherically symmetrical gap without any nodes. Due to the latter fact temperature dependence of physical properties is exponential. Following Anderson [2] we write the pairing function (wavefunction of a Cooper pair) in a following second quantized form:

$$\left\langle C_{k\uparrow}^{\dagger} C_{-k\downarrow}^{\dagger} + C_{-k\uparrow}^{\dagger} C_{k\downarrow}^{\dagger} \right\rangle. \tag{1}$$

Wavefunctions of electrons in each one of two terms are connected terms by time reversal $\theta$. The singlet pairing function is symmetrical with respect to the space inversion. If the pairing potential is spherically symmetrical, the spatial distribution of singlet pairing function is approximated by spherical $s$–, $d$–, etc. functions. The pairing function in conventional or BCS superconductors corresponds to $s$–pairing. The main feature of conventional superconductors is the absence of any points on Fermi surface with vanishing superconducting gap.

After the discovery high temperature superconductivity (HTSC) with $T_c$ of the order $100\,\mathrm{K}$ by Müller and Bednorz [3], it becomes clear that some statements of BCS theory should be reconsidered. Among these are the pairing symmetry, other then totally symmetric and pairing potential other then pure electron–phonon interaction. On the other hand the proper treatment of experimental data on the symmetry of superconducting state may shed some light on the most intriguing scientific problem of physics and chemistry of last two decades: the nature of unconventional superconductivity. The HTSC materials have unusual temperature dependence of resistivity above $T_c$. The resistivity is proportional to $T$ instead of $T^2$ for normal metals. Note that unusual temperature dependence of HTSC material $La_{1.8}Ba_{0.2}CuO_4$ above $T_c$ was obtained some time before the discovery of high $T_c$–superconductivity [4] Specific heat behavior of YBaCuO compounds below $T_c$ is fitted by the $T^2$ dependence, but with some contribution of $T$ term, which is

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proportional to $H^{1/2}$ also presents. This clearly indicates that HTSC materials are unconventional superconductors, i.e. their pairing function is not totally symmetric. Their photoelectron spectra reveal a pronounced trough in the diagonal of the square (see review articles [5,6]). The pairing function in hight $T_c$ superconductors is even and is usually denoted as $d_{x^2-y^2}$, whereas some authors denote it as $d + \mathrm{i}s$ [5].

The existence of line and point nodes in the pairing function results in power–low behavior of many physical properties (e.g. specific heat $C$ and nuclear magnetic resonance (NMR) relaxation rate $1/T_1$). Theoretical considerations (see review [7]) result in following power–lows:

$$C \propto \begin{cases} T^2 & \text{line zeros,} \\ T^3 & \text{point zeros,} \end{cases} \tag{2}$$

$$1/T_1 \propto \begin{cases} T^3 & \text{line zeros,} \\ T^5 & \text{point zeros.} \end{cases} \tag{3}$$

For last two decades, heavy fermion superconductors (HFSC) have revealed a variety of unusual behavior that hint at unconventional superconductivity. Power–low behavior of physical properties of HFSC materials $UPt_3$ [8], $CeCu_2Si_2$ [9] and $UBe_{13}$ [10] indicate line zeros in the energy gap and hence unconventional type of superconductivity. Note that relations (2) and (3) and experimental data are to some extent contradictory. Recent experiments show a significant linear term in heat capacity in HFSC, corresponding to the normal state, however NMR measurements find only cubic term [11]. The transport and thermal properties of heavy–fermion superconductors were explained in terms of the anisotropic order parameter with line or point nodes, i.e. superconducting gap vanishes at point or lines of Fermi surface. The anisotropy and temperature dependence of the magnetic field penetration in the muon spin relaxation experiments indicate that the gap in $UPt_3$ has both line of nodes in the basal plane and axial point nodes [12]. Neutron scattering experiments show antiferromagnetic order in HFSC. The values of $T_c$ of HF superconductors $UPt_3$, $URu_2Si_2$ and $UBe_{13}$ (0.55 K, 1.2 K and 0.8 K respectively) are connected with the temperature of antiferromagnetic transition $T_N$ (5 K, 17.5 K and 8 K respectively the remarkable relation $T_N \sim 10T_c$, indicating intimate relationship between superconductivity and antiferromagnetism [13]. However HFSCs reveal different features of spatial symmetry. The parity of pairing function of antiferromagnetic $CeCu_2Si_2$ is even because the spin susceptibility measured by Knight shift decreases below $T_c$ [14]. On the other hand, the absence of the Knight shift change in $UPt_3$ across the superconducting transition indicates that $UPt_3$ is an odd parity superconductor [15,16]. The splitting of superconducting transition in $UPt_3$ is an extremely unusual phenomena, providing persuasive additional evidence that superconductivity involves non–$s$–pairing [17].

The three triplet (odd) components of Cooper the pair wavefunction corresponding to $M_S = 1, 0, -1$ are written as [2]:

$$\left\langle C^\dagger_{k\uparrow} C^\dagger_{-k\uparrow} - C^\dagger_{-k\uparrow} C^\dagger_{k\uparrow} \right\rangle, \tag{4}$$

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$$\left\langle C_{k\uparrow}^{\dagger} C_{-k\downarrow}^{\dagger} - C_{-k\uparrow}^{\dagger} C_{k\downarrow}^{\dagger} \right\rangle, \tag{5}$$

$$\left\langle C_{k\downarrow}^{\dagger} C_{-k\downarrow}^{\dagger} - C_{-k\downarrow}^{\dagger} C_{k\downarrow}^{\dagger} \right\rangle, \tag{6}$$

Wavefunctions of electrons in formulae (4) and (6) are connected by space inversion $I$. These two formula correspond to ferromagnetic case. On the other hand, wavefunctions in formula (5) are connected by time reversal and correspond to antiferromagnetic case. In point groups with axial symmetry ferromagnetic and antiferromagnetic triplet pairs are independent.

Recently discovered superconductivity in the layered perovskite oxide $Sr_2RuO_4$, i.e. similar to HTSC, is triplet with odd order parameter , i.e. different from HTSC. Despite of a relatively small $T_c = 1.5$ this superconductor attracted much attention due to its unusual physical properties (see a review article [18] ). Muon spin relaxation experiments on $Sr_2RuO_4$ reveal spontaneous appearance of internal magnetic field below $T_c$, indicating time–reversal symmetry breacking [19]. Experimentally obtained horizontal lines of nodes are very surprising for this quasi two–dimensional structure [18].

It was believed for a long time that ferromagnetism and superconductivity cannot coexist. [20]. However recent discovery of superconductivity on the border of itinerant electron ferromagnetism in $UGe_2$ [21] revealed the possibility of magnetically mediated superconductivity. The set of ferromagnetic spin triplet superconductors is continued by $URhGe$ [22] and $ZrZn_2$ [23]. The most surprising from the point of view of symmetry is recently discovered spin triplet superconductor $CePt_3Si$ without of inversion symmetry in crystal space group [24]. In this case two electrons with opposite momenta are connected by time reversal, but it follows from formulae (1) and (5) that this case corresponds to antiferromagnetic pairs.

The nature of unconventional superconductivity is far from understanding. Moreover it was pointed out [6], that HTSCs highlight a major intellectual crisis in the quantum theory of solids, which in the form of one–electron band theory has been very successful for describing metals (like Cu) but has proven inadequate for strongly correlated electron systems.

Superconductivity is a macroscopic quantum effect and experimental data contain direct information on the symmetry of the wavefunction of a Cooper pair. In opens a unique opportunity to apply group theoretical results to experimental data directly. (In contrast to conventional atomic and molecular physics, where group theory is used for basis transformation of self-consistent calculations.) There are 3 group theoretical approaches to the wavefunction of a Cooper pair: point–group approach, unitary–group approach (or $SO(5)$) and space group approach. In the present work following Ginzburg and Landau [25] we consider the wavefunction of a Cooper pair and superconducting order parameter (SOP) to be identical.

The representation of SOP in a point–group approach [26, 27] (see also review articles [5, 7, 28]) is based on the reduction of spherical $s$, $p$, $d$, $f$, etc. functions to the actual point group symmetry. Since the choice of basis functions for any irreducible representation (IR) is not unique the, conclusions of the point group approach on their nodal structure are ambiguous [29]. Consideration of pairing

functions in a strong spin–orbit coupling case results a conclusion that there are no symmetry reasons for the lines of nodes of triplet SOP [27] (Blount theorem). From this point of views the major part of unconventional superconductors, considered above correspond to the exception from the Blount theorem. In the present work we prove the Blount theorem group theoretically and show that violations of Blount theorem are connected with different types of symmetry violations.

An elegant and attractive $SO(5)$ approach [30, 31], which unifies antiferromagnetism and superconductivity by $SO(5)$ continuous group is based on two assumptions. First assumption is the particle–hole symmetry and its fulfilling is based on the details of one–electron band structure. The second one is that the antiferromagnetic order parameter may be constructed from the same electron wavefunctions as the Cooper pair. Let us consider this assumption from the point of view of space–group theory [32].To obtain all possible magnetic symmetries for any space group one should consider all one–dimensional IRs. The group elements whose characters equal to 1 are unitary and that with $-1$ characters correspond to antiunitary elements. The case of $\vec{k} = \vec{b}/2$ (where $\vec{k}$ is the wavevector and $\vec{b}$ is a basis vector reciprocal lattice) corresponds to antiferromagnetic ordering of crystal lattice. It follows from momentum conservation that only electron and hole with momenta $\vec{k} = \vec{b}/4$ can be coupled into the antiferromagnetic order parameter. On the other hand in the theory of superconductivity, due to the inversion symmetry (see formula (1), (4), (5) and (6)) the momentum conservation if fulfilled for any electron wavevector on a Fermi surface.

The space–group approach to the wavefunction of a Cooper pair [33 − 40] is based on the space group irreducible representations [41] and on the induced representation method [32]. It is a direct generalization of Anderson's functions (1), (4), (5) and (6) in $\vec{k} - \vec{k}$ manifold on crystal symmetry. It makes possible straightforward group theoretical analysis of experimental data and construction of two–electron basis directly from one–electron basis functions. In the present work the space group approach to the wavefunction of a Cooper pair is applied to UPt$_3$ (point group $D_{6h}$) and to HTSC materials (point groups $D_{2h}$ and $D_{4h}$).

## 2    Theory

From a unitary IR $t_k$ of a subgroup $H$ one can construct a unitary representation of the whole group $G$ [32]. The structure of this unitary representation (induced representation) depends on the left coset decomposition of the whole group with respect to its subgroup:

$$G = \sum_i s_i H \,, \tag{7}$$

where $i = 1, \ldots, n$ and $n = |G|/|H|$.

The induced representation is defined by the following formula:

$$(t_\kappa \uparrow G)(g)_{i\mu,j\nu} = t_\kappa(s_i^{-1} g s_j)_{\mu\nu} \delta(s_i^{-1} g s_j, H) \,, \tag{8}$$

where: $\delta(s_i^{-1}gs_j, H) = \begin{cases} 1\,, & \text{if } s_i^{-1}gs_j \in H \\ 0\,, & \text{if } s_i^{-1}gs_j \notin H\,. \end{cases}$

Following Ref.[32] we use an up directed arrow for the notation of induction. The indexes $i$ and $j$ in formula denote the block columns and rows of the induced representation matrix and correspond to the single coset decomposition (7). The indexes $\mu$ and $\nu$ number the rows and columns of the "small" IR $t_k$.

In the case of crystal symmetry the induced representation (8) is irreducible representation of a space group, provided the group $H$ is a wave vector $\vec{k}$ group ("little" group) and $t_k$ is its unitary IR (*small* IR) [32,41]. The action of left coset representatives $s_i$ on the wave vector $\vec{k}$ results in all prongs of its star $\left\{\vec{k}\right\}$ In the case of strong spin–orbit coupling the IRs $t_k$ in formula (8) are replaced by double–valued *small* IRs $p_k$ [41].

According to the Pauli exclusion principle the total two–electron wavefunction is antisymmetric with respect to permutation of electronic coordinates. Hence in a weak spin–orbit coupling ($L - S$ scheme) the symmetrized Kronecker square of the spatial part of the wavefunction is combined with antisymmetrized Kronecker square of its spin part (singlet pair), and the antisymmetrized Kronecker square of the spatial part of the wavefunction is combined with the symmetrized Kronecker square of its spin part (triplet pair). In a strong spin-orbit coupling case ($j - j$ scheme) the wavefunction belongs to the antisymmetrized Kronecker square or double–valued IR of the space group. According to Anderson [2] the Cooper pair wavefunction is invariant with respect to lattice translations. Hence it follows the consideration is limited by the centre of a Brillouin zone for two–electron states.

The structure of the Kronecker square of an induced IR may be envisaged by the double coset decomposition of $G$ relative to $H$ which is written [32] as:

$$G = \sum_\sigma H d_\sigma H\,. \tag{9}$$

The sum runs over all distinct double cosets $\sigma$. Corresponding wave vector $\overrightarrow{k}_\sigma$ is defined by the following formula

$$\overrightarrow{k} + d_\sigma \overrightarrow{k} = \overrightarrow{k}_\sigma + \overrightarrow{b}_\sigma\,. \tag{10}$$

The intersection of wave vector groups in the left hand side is written as:

$$M_\sigma = H \cap d_\sigma H d_\sigma^{-1}\,. \tag{11}$$

For each double coset we consider a representation of subgroup $M_\sigma$ defined by the formula:

$$P_\sigma = t_\kappa(m) \otimes t_\kappa(d_\sigma^{-1}md_\sigma)\,, \tag{12}$$

where $m \in M_\sigma$.

For self-inverse double coset, i.e.:

$$Hd_\alpha H = Hd_\alpha^{-1}H\,, \tag{13}$$

there are two extensions of $P_\alpha$ into the subgroup:

$$\tilde{M}_\alpha = M_\alpha + aM_\alpha \,, \tag{14}$$

where $a = d_\sigma h_1 = h_2 d_\sigma$ and $h_1$, $h_2 \in H$.

These extensions corresponding to symmetrized and antisymmetrized parts of Kronecker square are defined in terms of their characters as follows:

$$\chi(P_\alpha^+(am)) = +\chi(t_\kappa(amam)) \,, \tag{15}$$
$$\chi(P_\alpha^-(am)) = -\chi(t_\kappa(amam)) \,, \tag{16}$$

where $m \in M_\alpha$.

The symmetrized and antisymmetrized parts of the Kronecker square of induced representation are written by two following formulae respectively (the Mackey theorem [42] on Kronecker squares):

$$[t_\kappa \uparrow G \otimes t_\kappa \uparrow G] = [q_\kappa \otimes q_\kappa] \uparrow G + \sum_\alpha P_\alpha^+ \uparrow G + \sum_\beta P_\beta \uparrow G \,, \tag{17}$$

$$\{t_\kappa \uparrow G \otimes t_\kappa \uparrow G\} = \{t_\kappa \otimes t_\kappa\} \uparrow G + \sum_\alpha P_\alpha^- \uparrow G + \sum_\beta P_\beta \uparrow G \,. \tag{18}$$

The first items on the right–hand sides of (17) and (18) correspond to the double coset defined by the identity element, $\alpha$ corresponds to self-inverse double cosets and $\beta$ to non-self-inverse double cosets for which $Hd_\beta H \neq Hd_\beta^{-1}H$. In the case of a strong spin–orbit coupling case the possible symmetries of two–electron states are obtained by substituting of double–valued IRs [41] into formula (18).

If the one-electron wavevector $\vec{k}$ belongs to a general point inside a Brillouin zone the two–electron wavevector, defined by formula (10), equals zero for the self-inverse double coset defined by the space inversion. The extended intersection group $\tilde{M}_\alpha$ defined by formula (14) is the group $C_i$ consisting of two elements: $E$ and $I$. This case corresponds to Anderson approach [2]. For single–valued IRs we immediately obtain that $P_\alpha^+$ equals to IR $A_g$ of group $C_i$ and that $P_\alpha^-$ equals to IR $A_u$ of group $C_i$.

These representations are induced into the central extension of the space group (point group). The induced representation can be easily decomposed making use of the Frobenius reciprocity theorem: the number of appearance of the IR $\Gamma_\kappa$ of the whole group in the decomposition of the induced representation $p_k \uparrow G$ equals to the number of appearance of IR $p_k$ in the decomposition of $\Gamma_\kappa$, when it subduced to the subgroup. Making use of Frobenius theorem we obtain two conclusions. Firstly, in agreement with Anderson [2], we obtain that for $\vec{k}$ a general point of a Brillouin zone all even IRs are possible for singlet pairs and all odd IRs are possible for triplet pairs. Secondly, the number of appearance of each IR equals to its dimension. Hence it follows that for one–dimensional IR the result is unique, but for two–dimensional IRs there are two non-equivalent basis functions and one can take any linear combinations. From this point of view experimentally

observed double superconducting transition in UPt$_3$ may be connected with two non-equivalent states corresponding to the same two–dimensional IR. To obtain total wavefunction of a Cooper pair in a weak spin–orbit coupling ($L - S$ scheme) one should multiply the spatial part of the wavefunction by spin singlet function $S^0$ for singlet pair and by spin triplet function $S^1$ for triplet pair.

In strong spin orbital coupling case the representation $P_\alpha^-$ equals to IR $A_u$ of group $C_i$ and even IRs are missing. To obtain all possible pair symmetries the time reversal $\theta$ should be considered. In the absence of magnetic fields the total symmetry of a crystal with Fedorov group $G$ is described by the Shubnikov II (grey) magnetic group:

$$M = G + \theta G \,, \tag{19}$$

where $\theta$ is a time–reversal operation.

The time–reversal symmetry results in additional degeneration for one–dimensional small double–valued IRs [32] i.e. at general points and at the planes of symmetry in a Brillouin zone. To obtain all possible two–electron states one should use induced corepresentation $D(p_k) \uparrow G$ [32] in formula (18).

For $\vec{k}$ a general point in a Brillouin zone the decomposition of corepresentation $P_\alpha^-$ (see formula (16)) contains representations $A_g$ and $3A_u$ of the group $C_i$. The IR $A_g$ corresponds to singlet pair and $3A_u$ correspond to three components of triplet pair.

The superconducting state is usually more ordered then the normal state, i.e. the transition to it is accompanied by the symmetry reduction [43]. One possible way is the time–reversal symmetry violation, i.e. transition from the direct product $\theta \times G$ to ordinary Fedorov group $G$ or to one the Shubnikov group $\theta \times (G - H) + H$ [32, 44]. Total number of different cases of construction of Shubnikov groups is quite large. In order to envisage general trends we consider the simplified case of time reversal symmetry violation and its influence on the nodal structure of superconducting order parameter. Ferromagnetic fluctuations can be approximated as time–reversal symmetry violation. In this case the one–electron states belong to double valued IR of the space group. For $\vec{k}$ a general point of a Brillouin zone we obtain two IRs $A_u$ of group: one for spin up states and one for spin–down state, corresponding to formulae (4) and (6). Two remaining IRs correspond to antiferromagnetic pairs: $A_g$ for singlet pair (1) and $A_u$ for triplet pair (5). Hence we obtain following formula for the character of the possible Cooper pair representation (reducible) in the antiferromagnetic state

$$\chi_{\text{aitif}} = \chi_{\text{normal}} - 2\chi_{\text{ferro}} \,, \tag{20}$$

where $\chi_{\text{normal}}$ and $\chi_{\text{ferro}}$ are obtained respectively by substitution of double valued *small* corepresentation and double–valued IR [41] for the antisymmetrized Kronecker square of induced representation. It should be noted that formula (20) is valid in the case of one–dimensional double–valued small IR for one–electron states, i.e. at general points and at the planes of symmetry in one-electron Brillouin zone.

Making use of formula (20) for a general point in a Brilloun zone we obtain that the Kronecker product decomposition for antiferromagnetic state contains IRs $A_g$

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and $A_u$ of the group $C_i$. Hence it follows that in antiferromagnetic state even and odd Cooper pairs are possible. This general result agrees with the experimental data which show both even and odd symmetry [5] for antiferromagnetic heavy–fermion superconductors $CeCu_2Si_2$ and $UPt_3$ respectively.

The space–group approach to the wavefunction of a Cooper pair makes it possible to investigate the nodal structure of SOP as follows. One should consider the distinct directions and planes of symmetry in a one–electron Brillouin zone and calculate the antisymmetrized Kronecker squares with zero total momenta of double–valued IRs or of double–valued corepresentations. The absence of any IR in this square indicates a node of the SOP of this symmetry. There are two types of nodes. The intersection of the direction of nodes of any IR with the Fermi surface results in the point node. The intersection of the plane of nodes with the Fermi surface results in the line of nodes.

Possible IRs for all states at the plain of symmetry (group $C_{2h}$) are presented in Table 1. In normal state all odd IRs are present and one even IR $B_g$ of the group $C_{2h}$ is absent in the decomposition. Hence, it follows that in this case, only nodes of even order parameter on the planes of symmetry are required by the space–group symmetry and no limitations on odd IRs exist. This statement is in agreement with the Blount [27] theorem according to which it is "vanishingly improbable" for "triplet" superconductors to have curves of vanishing gap on the Fermi surface. If the time–reversal symmetry is violated, the antisymmetrized square of the double–valued IR equals to IR $A_u$ of the group $C_{2h}$. Thus, in the ferromagnetic state, only odd IRs are possible for the SOP on the planes of symmetry. The lack of the second odd IR $B_u$ signifies that some of the odd IRs of the point group are forbidden on the planes. The intersection of the plane with the Fermi surface results in the line node of the odd SOP.

Going over to the antiferromagnetic state we see in Table 1 that one even IR $A_g$ (the same as in normal state) and one odd IR $B_u$ appear in the decomposition. Hence it follows that the symmetry requirements for line nodes of even IRs are the same as in normal state, but the lines of node of odd IRs differ from that in ferromagnetic state.

Hence it follows that the theory is in agreement with the above mentioned experimental data on the SOP symmetry in unconventional superconductors, i.e. antiferromagnetic superconductors may be either even (singlet) and odd (triplet) with lines of nodes.

Another reason for violation of Blount theorem is due to crystal symmetry lower then $O_h$. In the case of $O_h$ symmetry spin function belong to three dimensional IR $T_{1g}$. Following relation is valid for the Kronecker product of the induced IR $\Gamma$ of the whole group:

$$\Gamma \times (P_\alpha^- \uparrow G) = (\Gamma \downarrow \tilde{M}_\alpha \times P_\alpha^-) \uparrow G. \qquad (21)$$

Hence we obtain that for $O_h$ symmetry all odd IRs of the subgroup $C_{2h}$ are possible for triplet pair and Blount theorem is fulfilled. For $D_{4h}$ and $D_{6h}$ symmetry the $M_s = 1$ and $-1$ (or $S_x$ and $S_y$) components belong to IR $E_g$ and $M_s = 0$ (or $S_z$) belong to IR $A_{2g}$. It is natural to expect that due to interactions of spins with

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Table 1.   The decomposition of representations $P_\alpha^-$ and $P_\alpha^+$ for the planes of symmetry (group $C_{2h}$)

| state | character | | | | decompmosition |
|---|---|---|---|---|---|
| | $E$ | $\sigma_h$ | $I$ | $C_2$ | IRs |
| normal | 4 | 0 | $-2$ | 2 | $A_g + 2A_u + B_u$ |
| ferromagmetic | 1 | $-1$ | $-1$ | 1 | $A_u$ |
| antiferromagnetic | 2 | 2 | 0 | 0 | $A_g + B_u$ |
| $P_\alpha^+$ | 1 | 1 | 1 | 1 | $A_g$ |
| $P_\alpha^-$ | 1 | 1 | $-1$ | $-1$ | $B_u$ |
| $P_\alpha^- \times T_{1g} \downarrow C_{2h}$ | 3 | $-1$ | $-3$ | 1 | $2A_u + B_u$ |
| $P_\alpha^- \times E_g \downarrow C_{2h}$ | 2 | $-2$ | $-2$ | 2 | $2A_u$ |
| $P_\alpha^- \times A_{2g} \downarrow C_{2h}$ | 1 | 1 | $-1$ | $-1$ | $B_u$ |

crystal field the energies of spin states $E_g$ and $A_{2g}$ are different and only one of them corresponds to superconducting state. Since not all IRs of group $C_{2h}$ are present in the decomposition for both cases and the lines of nodes appear. Thus another symmetry reason for violation of Blount theorem is the lower crystal symmetry.

To show how the theory works we present the antisymmetrized Kronecker squares of double–valued IRs for group $D_{6h}^4$ (symmetry group of UPt$_3$) in Table 2. According to Anderson [2] only components with zero total momentum (IRs in the $\Gamma$ point of a Brillouin zone) are considered for two–electron states. Starting from the general point of the Brillouin zone where all IRs of both parities are possible we are able to enumerate all directions and planes, where some IR is absent and thus indicate point and line nodes of the SOP. For the lines of symmetry, the Kronecker square depends on the index of the small IR and the symmetry analysis depends on the symmetry of the one–electron state. There are two double valued IRs on the planes of symmetry, but their Kronecker squares are the same. Thus on the planes of symmetry the results of the space–group approach to the SOP do not depend on any choice of basis functions.

The space–group approach makes it possible to find the symmetry of SOP, which corresponds to the experimental data. UPt$_3$ is an antiferromagnetic superconductor with odd SOP, so we limit our consideration of Table 2 to the odd IRs corresponding to antiferromagnetic phase. The experiments of Ref.[12] indicate a line of nodes in the basal plane and hence it follows from the Table 2 that IRs $A_{1u}$, $A_{2u}$ and $E_{2u}$ are appropriate candidates. Experiments [12] also indicate point node (nodes) in vertical direction and IR $A_{1u}$ having lines of nodes in two sets of vertical planes should be excluded. Both remaining IRs $E_{2u}$ and $A_{2u}$ have point nodes in vertical direction and are appropriate candidates. The double superconducting transition in UPt$_3$ is connected with the two–dimensionality. Hence we conclude from the data of Table 2 that there is an agreement with all experimental data for the IR $E_{2u}$ only. Our conclusion is in agreement with the results of other theoretical works (see e.g. [45]).

Table 2.  Possible IRs of Cooper pair of the space group $D_{6h}^4$.

| state | $k(H)$, IR direction $\Delta(C_{6v})$ | IRs of Cooper pair |
|---|---|---|
| all | $p_1, p_2$ | $A_{1g} + A_{1u} + E_{1u}$ |
| | $p_3$ | $A_{1g} + A_{1u} + B_{1u} + B_{2u}$ |
| | planes | |
| Ferromagnetic odd | $\Gamma K M^{1)}$ | $A_{1u} + A_{2u} + 2E_{2u}$ |
| Antiferromagnetic odd | | $B_{1u} + B_{2u} + 2E_{1u}$ |
| Antiferromagnetic even | | $A_{1g} + A_{2g} + 2E_{2g}$ |
| normal | | All IRs except $E_{1g}, B_{1g}$ and $B_{2g}$ |
| Ferromagnetic odd | $\Gamma M L^{2)}$ | $A_{1u} + B_{2u} + E_{1u} + E_{2u}$ |
| Antiferromagnetic odd | | $A_{2u} + B_{1u} + E_{1u} + E_{2u}$ |
| Antiferromagnetic even | | $A_{1g} + B_{2g} + E_{1g} + E_{2g}$ |
| normal | | All IRs except $A_{2g}$ and $B_{1g}$ |
| Ferromagnetic odd | $\Gamma K H^{3)}$ | $A_{1u} + B_{1u} + E_{1u} + E_{2u}$ |
| Antiferromagnetic odd | | $A_{2u} + B_{2u} + E_{1u} + E_{2u}$ |
| Antiferromagnetic even | | $A_{1g} + B_{1g} + E_{1g} + E_{2g}$ |
| normal | | All IRs except $A_{2g}$ and $B_{2g}$ |

[1)] Basal plane
[2)] Vertical plane perpendicular to the lateral face of Brillouin zone
[3)] Vertical plane passing via lateral edge of Brillouin zone

It should be also noted that the analysis of recent experiments on anisotropic magnetization of superconducting UPt$_3$ [46] leaved two possibilities for SOP: $E_{1g}$ and $E_{2u}$. It follows from the Table 2 that the nodal structure of these two IRs is the same, but the assumption of the odd IR $E_{2u}$ is in agreement with Knight shift experiments.

The wavefunction of a Cooper pair for the whole group may be obtained by applying projection operators technique to Anderson functions (1), (4), (5) and (6). We will construct these functions taking symmetry groups $D_{2h}$ and $D_{4h}$ of HTSC materials as an example. Let us denote $\vec{k}_1$ the wave vector chosen in the representation domain of a Brillouin zone. Making use of Kovalev's [41] notation $h_{25}$ for the space inversion the spatial parts of Anderson singlet and triplet functions are written as:

$$\Phi_1^s = \psi_1^1 \psi_{25}^2 + \psi_{25}^1 \psi_1^2 \,, \tag{22}$$
$$\Phi_1^t = \psi_1^1 \psi_{25}^2 - \psi_{25}^1 \psi_1^2 \,, \tag{23}$$

where the superscript of $\psi$ denotes the number of electronic coordinate and subscript of $\psi$ the prong of the $\vec{k}$–vector star.

Acting by $h_2$ (180º rotations around the axis $X$) on the functions (22) and (23)

we obtain two other basis functions:

$$\Phi_2^s = \psi_2^1 \psi_{26}^2 + \psi_{26}^1 \psi_1^2 \,, \tag{24}$$

$$\Phi_2^t = \psi_2^1 \psi_{26}^2 - \psi_{26}^1 \psi_2^2 \,. \tag{25}$$

Note that in Kovalev's [41] notations for $O_h$ group multiplication of pure rotation element by $I$ corresponds to adding 24 to the element number. To construct full basis for $D_{2h}$ group we need also functions $\Phi_3^{s(t)}$ and $\Phi_4^{s(t)}$, which are obtained from $\Phi_1^{s(t)}$ by the action of 180° rotations around the axes $Y$ and $Z$ respectively. In addition, for $D_{4h}$ group the elements $h_{13}$, $h_{16}$ (180° rotations around the axes $(\bar{1}10)$ and $(110)$) and $h_{14}$, $h_{15}$ (90° and 270° counterclockwise rotation around $Z$ axis) are required.

These functions span the space of Anderson functions under the action of all point group operations. Since the space inversion is already included in the basis functions, their total number equals to the half of number of point group operations. The action of pure rotations on the initial vector $\vec{k}_1$ result in a star, whose number of prongs is half of the number of prongs in the the wave vector star. The action of the space inversion on the basis vector corresponding to any prong doesn't change a vector but introduces multiplier $-1$ for the triplet case. Making use of standard projection operator technique and functions $\Phi_{1-4}^{s,t}$ we easily obtain the basis functions for Cooper pairs belonging to all IRs of $D_{2h}$ group. The results are presented in Table 3.

Before going to the projection for $D_{4h}$ group it is useful to remind the following correspondence of IRs in the subduction $D_{4h} \downarrow D_{2h}$ : $A_1$ *and* $B_1 \longrightarrow A_1$, $A_2$ *and* $B_2$ $\longrightarrow B_1$, $E \longrightarrow B_2 + B_3$. The basis functions for one–dimensional IRs of $D_{4h}$ group are immediately obtained by projection operator technique. Since each of IRs $E_{g(u)}$ appear twice in the Kronecker product decomposition, there are two independent basis sets labelled by additional quantum numbers . Bearing in mind the above reduction scheme, we begin with basis sets corresponding to IRs $B_2$ and $B_3$ of group $D_{2h}$ we obtain the remainder results of Table 3. The results for triplet pairs for $D_{4h}$ group pairs are not presented in the Table 3. To obtain wavefunctions of triplet pairs one should replace subscripts $g$ to $u$ in the first column and all superscripts $s$ to $t$ in the second column without changing of the signs.

For $\vec{k}$ a general point in a Brillouin zone all IRs are possible for Cooper pair. But when the $\vec{k}$–vector approaches any mirror plane, the mirror reflection image of $\vec{k}$ also approaches the $\vec{k}$–vector. Total number of states decreases and lines of nodes are eventual. There are two possibilities. If two–electron function is unchanged under the action of the reflection, the function under consideration is nonvanishing on the mirror plane. On the other hand, if the function changes its sign, two mirror counterparts are cancelling on the plane. This corresponds to the line of nodes. Note, that the space inversion changes the sign of the spatial part of the triplet function. Making use of the above rules we can easily obtain nodal structure of basis functions of one–dimensional IRs of groups $D_{2h}$ and $D_{4h}$ presented in Table 3.

Two dimensional IRs appear twice for $\vec{k}$ a general point in a Brillouin zone. In this case a direct analysis of nodal structure of basis functions of Table 3 is required.

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Table 3. Spatial parts of Cooper pair wavefunctions for point groups $D_{2h}$ and $D_{4h}$.

| $D_{2h}$ | | $D_{4h}$ | |
|---|---|---|---|
| IR | pairing function | IR | pairing function |
| $A_{1g}$ | $\Phi_1^s + \Phi_2^s + \Phi_3^s + \Phi_4^s$ | $A_{1g}$ | $\Phi_1^s + \Phi_2^s + \Phi_3^s + \Phi_4^s + \Phi_{13}^s + \Phi_{14}^s + \Phi_{15}^s + \Phi_{16}^s$ |
| $B_{1g}$ | $\Phi_1^s - \Phi_2^s - \Phi_3^s + \Phi_4^s$ | $A_{2g}$ | $\Phi_1^s - \Phi_2^s - \Phi_3^s + \Phi_4^s - \Phi_{13}^s + \Phi_{14}^s + \Phi_{15}^s - \Phi_{16}^s$ |
| $B_{2g}$ | $\Phi_1^s - \Phi_2^s + \Phi_3^s - \Phi_4^s$ | $B_{1g}$ | $\Phi_1^s + \Phi_2^s + \Phi_3^s + \Phi_4^s - \Phi_{13}^s - \Phi_{14}^s - \Phi_{15}^s - \Phi_{16}^s$ |
| $B_{3g}$ | $\Phi_1^s + \Phi_2^s - \Phi_3^s - \Phi_4^s$ | $B_{2g}$ | $\Phi_1^s - \Phi_2^s - \Phi_3^s + \Phi_4^s + \Phi_{13}^s - \Phi_{14}^s - \Phi_{15}^s + \Phi_{16}^s$ |
| $A_{1u}$ | $\Phi_1^t + \Phi_2^t + \Phi_3^t + \Phi_4^t$ | $E_g(B_{2g})$ | $\Phi_{13}^s - \Phi_{15}^s + \Phi_{14}^s - \Phi_{16}^s$ |
| $B_{1u}$ | $\Phi_1^s - \Phi_2^s - \Phi_3^s + \Phi_4^s$ | | $\Phi_1^s - \Phi_2^s + \Phi_3^s - \Phi_4^s$ |
| $B_{2u}$ | $\Phi_1^s - \Phi_2^s + \Phi_3^s - \Phi_4^s$ | $E_g(B_{3g})$ | $\Phi_1^s + \Phi_2^s - \Phi_3^s - \Phi_4^s$ |
| $B_{3u}$ | $\Phi_1^s + \Phi_2^s - \Phi_3^s - \Phi_4^s$ | | $\Phi_{13}^s + \Phi_{15}^s - \Phi_{14}^s - \Phi_{16}^s$ |

The analysis shows that basis functions of IR $E_g(B_{2g})$ vanish in the planes (100) and (001) and that of IR $E_g(B_{3g})$ vanish in the planes (010) and (001). Linear combinations of these basis functions $E_g(B_{2g}) \pm E_g(B_{3g})$ vanish in planes (110) and ($\bar{1}$10) respectively and both vanish in plane (001). Hence it follows that only lines of nodes in basal plane follow unambiguously from the symmetry. It should be noted, that point group approach also results different nodal structure of different two–dimensional IRs [4].

The analysis of broad set of experimental data on the of high–$T_c$ superconductors [5] led the most of the authors to the conclusion of singlet pairing and $A_g$ SOP symmetry in these compounds. Angular resolved photoelectron spectra of high–$T_c$ superconductors [5, 6] reveal a strong trough in the diagonal of $xy$ plane indicating $d_{x^2-y^2}$–pairing with line of nodes. On the other hand some experiments reveal also totally symmetric $s$–pairing without nodes. In many cases an interplay between these two types of pairing [5] both belonging to $A_g$ IR exists. It is seen from Tables 3, that $A_g$ pairing function, obtained group theoretically is noddles and that other IRs have nodes in the coordinate planes only. Hence it follows that nodal structure of high–$T_c$ superconductors is more complex then that which follows from the symmetry only. To explain this one can consider two wave vectors $\vec{k}_\alpha$ and $\vec{k}_\beta$ symmetrical with respect to diagonal of the deformed square. Note, that the orthorombicity $(b-a)/(b+a)$ of YBCuO is about 2 % only [5]. Two types of basis functions of Cooper pairs belonging to $A_g$ IR $\Phi_\alpha^s$ and $\Phi_\beta^s$ are easily obtained from the Table 3 by introducing additional subscripts $\alpha$ and $\beta$. One can suppose that due to the interaction two self-vectors are linear combinations of these basis states:

$$\Phi_s^S = C_\alpha \left( \Phi_{1,\alpha}^S + \Phi_{2,\alpha}^S + \Phi_{3,\alpha}^S + \Phi_{4,\alpha}^S \right) + C_\beta \left( \Phi_{1,\beta}^S + \Phi_{2,\beta}^S + \Phi_{3,\beta}^S + \Phi_{4,\beta}^S \right),$$
(26)

$$\Phi_{x^2-y^2}^S = C_\beta \left( \Phi_{1,\alpha}^S + \Phi_{2,\alpha}^S + \Phi_{3,\alpha}^S + \Phi_{4,\alpha}^S \right) - C_\alpha \left( \Phi_{1,\beta}^S + \Phi_{2,\beta}^S + \Phi_{3,\beta}^S + \Phi_{4,\beta}^S \right).$$
(27)

Both combinations belong to IR $A_g$ of group $D_{2h}$. First one corresponds to the

noddles $s$-pairing and the second to the $d_{x^2-y^2}$–pairing with line of nodes in the diagonal of $xy$- plane. In the limit of zero orthorombic distortion the symmetry group is $D_{4h}$ and $C_\alpha = C_\beta$ , subscripts $\alpha$ and $\beta$ are dropped and the sums in second brackets in right hand sides of (26) and (27) are written as $\Phi_{13}^S + \Phi_{14}^S + \Phi_{15}^S + \Phi_{16}^S$. In this case combination (26) belongs to IR $A_{1g}$ and combination (27) belongs to IR $B_{1g}$ of the symmetry group $D_{4h}$. Hence it follows that the nodal structure of SOP in high–$T_c$ superconductors is defined by hidden symmetry $D_{4h}$.

## 3    Conclusion

The nodal structure of zero–total–momentum two–electron states in crystals with magnetic symmetry is investigated group–theoretically. These states are related to possible Cooper pairs and following general results are obtained for the superconducting order parameter (SOP).

In the normal state (time–reversal symmetry is not violated) in crystals of $O_h$ symmetry lines of nodes for even SOP only are required by the symmetry and there are no symmetry requirements for the lines of nodes for the odd SOP (Blount theorem [27]).

In the ferromagnetic state (where time–reversal symmetry is violated) only odd SOP with line nodes is possible. In crystals with lower point group symmetry ($D_{4h}$ and $D_{6h}$) Blount theorem is also violated and lines of nodes of odd SOP follow from the symmetry.

In the antiferromagnetic state an even SOP with the same nodal structure as the normal state and an odd SOP whose nodal structure differs from that in the ferromagnetic state are possible.

It is shown that the theoretical nodal structure of the $E_{2u}$ SOP for the $D_{6h}^4$ group in the antiferromagnetic case is in agreement with the experimental nodal structure of UPt$_3$.

The new type of basis functions is constructed for high $T_c$ superconductors making use the space–group approach and projection operator technique. It is shown that experimentally observed nodal structure of SOP in high–$T_c$ superconductors follows from the hidden symmetry $D_{4h}$.

## References

[1]  J.L.Bardeen, N.Cooper and J.R.Schriffer: Phys. Rev. **108** (1957) 175.

[2]  P.W. Anderson: Phys. Rev. B **30** (1984) 4000.

[3]  J.G. Bednorz and K.A. Müller: Z. Phys. B **64** (1986) 189.

[4]  I.S. Shaplygin, B.G. Kakhan and V.B. Lasarev: Zh. Neorg. Khim. **26** (1979) 1478.

[5]  C.C. Tsuel and J.R. Kirtley: Rev. Mod. Phys. **72** (2000) 969.

[6] A. Damaschelli, Z. Hussain and Z-X. Shen: Rev. Mod .Phys. **75** (2003) 473.

[7] M. Sigrist and K. Ueda: Rev. Mod. Phys. **63** (1991) 239.

[8] D.J. Bishop, C.M. Varma, B. Batlogg, E. Bucher, Z. Fisk and J.L. Smith: Phys. Rev. Lett **53** (1984) 1009.

[9] D.E. MacLaughlin, Cheng Tien, J.C. Gupta, J. Aarts, F.R. De Boer and Z. Fisk: Phys. Rev. B **30** (1984) 1577.

[10] H.R. Ott, H. Rudiger, T.M. Rice, K. Ueda, Z. Fisk and J.L. Smith: Phys. Rev. Lett. **52** (1984) 1915.

[11] R. Zieve, R. Duke and J.L. Smith: Phys. Rev. B **69** (2004) 144503.

[12] C. Broholm, G. Aeppli, R.N. Kleiman, D.R. Harshman, D.J. Bishop, E. Bucher, D.L. Williams, E.J. Ansaldo and R.H. Heffner: Phys. Rev. Lett. **65** (1990) 2065.

[13] R.N. Kleiman, D.J. Bishop, H.R. Ott, Z. Fisk and J.L. Smith: Phys. Rev. Lett. **64** (1990) 1975.

[14] M.-A. Ozaki and K. Machida: J. Phys. Soc. Jap. **60** (1991) 1452.

[15] H. Tou, Y. Kitaoka, K. Asayama, N. Kimura, Y. Onuki, E. Yamamoto and K. Maezawa: Phys. Rev. Lett. **77** (1996) 1374.

[16] Y. Kohori, T. Kohara , H. Shinai, Y. Oda, T. Kaneko, Y. Kitaoka and K. Asayama: J. Phys. Soc. Jpn. **56** (1987) 2263.

[17] R.A. Fisher, S. Kim, B.F. Woodfield et.al.: Phys. Rev. Lett. **82** (1989) 1411.

[18] A.P. Mackenzie and Y. Maeno: Rev. Mod. Phys. **75** (2003).

[19] G.M. Luke, Y. Fudamoto, K.M. Kojima, et.al.: Nature **394** (1998) 558.

[20] N.F. Berg and J.R. Schriffer: Phys. Rev. Lett. **17** (1966) 433.

[21] S.S. Saxena, P. Agarwal and K. Ahilan: Nature **406** (2000) 587.

[22] D. Aoki et.al.: Nature **413** (2001) 613.

[23] C. Pfleiderer et.al.: Nature **412** (2001) 58.

[24] E. Bauer, G. Hilscher, H. Michor et. al.: Phys. Rev. Lett. **92** (2004) 027003.

[25] V.L. Gunzburg and L.D. Landau: Zh. Exp. Teor. Fiz. **20** (1950) 1964 (in Russian).

[26] G.E. Volovik and L.P. Gor'kov: Sov. Phys. Jetp. **61** (1985) 843.

[27] E.I. Blount: Phys. Rev. B **32** (1985) 2935.

[28] J.F. Annett: Adv. Phys. **39** (1991) 83.

[29] S. Yip and A. Garg: Phys. Rev. B **48** (1993) 3304.

[30] S.C. Zhang: Science **275** (1997) 1089.

[31] E. Demler, W. Hanke and S.-C. Zhang: `cond-mat/0405038`.

[32] C.J. Bradley and A.P. Cracknell: *The Mathematical Theory of Symmetry in Solids. Representation Theory of Point Groups and Space Groups.* Oxford, Clarendon, 1972.

[33] Yu.A. Izyumov, V.M. Laptev and V.N. Syromyatnikov: Int. J. Mod. Phys. **3** (1989) 1377.

[34] V.G. Yarzhemsky: Superconductivity:phys. chem. techn. **3** (1990) 2504 (in Russian).

[35] V.G. Yarzhemsky and E.N. Murav'ev: Sov. Phys. Dokl. **36** (1991) 323.

[36] V.G. Yarzhemsky and E.N. Murav'ev: J. Phys: Cond. Matter **4** (1992) 3525.

[37] V.G. Yarzhemsky: Zeitsch. Phys. B **99** (1995) 19.

[38] V.G.Yarzhemsky: Phys. stat. sol. (b) **209** (1998) 101.

[39] V.G. Yarzhemsky: Int. J. Quant. Chem. Int. J. Quant. Chem. **80** (2000) 133.

[40] V.G.Yarzhemsky: in *Lectures on the Physics of Higly Correlated electron Systems*, p.343–252, Melille, N.Y.2003.

[41] O.V. Kovalev: *Irreducible and Induced Representations and Corepresentations of Fedorov's Groups*, Moscow, Nauka 1986, (in Russian).

[42] C.J. Bradley and B.L. Davies: J. Math. Phys. **11** (1970) 1536.

[43] W.W. Schmidt: *Introduction to the physics of superconductors*, Moscow, MCNMO 2000 (in Russian).

[44] Koptsik: *Shubnikov groups*, Moscow University Publ. 1966 (in Russian).

[45] J.A. Sauls: Adv. Phys. **43** (1994) 113.

[46] S. Schottl, E.A. Schuberth, K. Flachbart, J.B. Kycia, J.I. Hong, D.N. Seidman, W. Halperin and E. Bucher: Phys. Rev. Lett. **82** (1999) 2378.