Space-Group Approach to the Wavefunction of a Cooper Pair: Nodal Structure and Additional Quantum Numbers for Sr$_2$RuO$_4$ and UPt$_3$

V.G. Yarzhemsky[1,2,*]

[1]*Kurnakov Institute of General and Inorganic Chemistry, 31 Leninsky, 119991, Moscow, Russia*

[2]*Moscow Institute of Physics and Technology (State University), Dolgoprudny, 9 Institutsky per., 141700, Moscow Region, Russia*

Abstract: Induced representation method and Mackey theorem on symmetrized squares were applied to construct zero-total-momentum two-electron states in solids, corresponding to Cooper pairs in unconventional superconductors. In this approach the structure of two-electron states depends on the position of one-electron wave vector in a single-electron Brillouin zone. It is shown, that the decomposition of total two-electron basis set results in repeating multidimensional irreducible representations. It is obtained, that in order to label repeating irreducible representation two additional quantum numbers are required: irreducible representation of wave vector group for symmetry planes and directions and quantum numbers on an intermediate group for a general point in a Brillouin zone. Theoretical results are applied to unconventional superconductors UPt$_3$ and Sr$_2$RuO$_4$.

INTRODUCTION

Many of experimental results on unconventional superconductors are connected with the symmetry and the nodal structure of SOP (superconducting order parameter) [1-4], which was considered making use of point-group and space-group approaches. In Ginzburg-Landau theory of superconductivity SOP is considered to be identical with the wavefunction of a Cooper pair [5]. In the present work we will use the term pair or Cooper pair for two-electron states in solids, and the term SOP for experimental data on superconductors or their model representation. The main symmetry requirement for a Cooper pair is its zero total momentum. Hence, it follows that in general case two electrons in a Cooper pair have opposite k- vectors. According to Pauli Exclusion Principle, spatial parts of singlet and triplet pairs for k- a general point in a Brillouin zone may be represented by two following formulae:

$$\psi_k^s = \varphi_k(r_1)\varphi_{-k}(r_2) + \varphi_k(r_2)\varphi_{-k}(r_1) \qquad (1)$$

$$\psi_k^t = \varphi_k(r_1)\varphi_{-k}(r_2) - \varphi_k(r_2)\varphi_{-k}(r_1) \qquad (2)$$

It was shown, that for a general k- vector spatial part of singlet pair is even and that of triplet pair is odd

[6]. In a point group approach [6-9] the basis functions for Cooper pair were constructed making use of polynomial functions belonging to IRs (irreducible representations) of point groups. It was shown, that the results of this approach are ambiguous, since they depend on the choice of basis functions [10]. Nevertheless these functions are useful for the representation of experimental data on SOP.

In a strong spin-orbit coupling the SOP of triplet superconductors is represented as a direct product of spin-triplet function and a vector representing spatial part of Cooper pair wavefunction in k-space. For example, Balian-Werthamer [11] state for triplet ^{3}He state, corresponding to isotropic gap, is written as:

$$\mathbf{d}(\mathbf{k}) = \hat{x}\,k_x + \hat{y}k_y + \hat{z}k_z \qquad (3)$$

where $\hat{x}$, $\hat{y}$ and $\hat{z}$ stand for three components of triplet spin and k_i stand for the three components of the wave vector in isotropic space. Note, that in the case of crystal solids this representation is model, since exact wavefunctions in solids are represented by the stars of k-vector [12-14].

Experimental nodal structures of SOP of unconventional superconductors UPt$_3$, and Sr$_2$RuO$_4$ are quite complex. The anisotropy and temperature dependence of the magnetic field penetration in the muon spin relaxation experiments indicate that the gap in UPt$_3$ (point group D_{6h}) has both line of nodes in the

*Address correspondence to this author at the Kurnakov Institute of General and Inorganic Chemistry, 31 Leninsky, 119991, Moscow, Russia;
Tel: +7 495 954 22 30; Fax: +7 495 954 12 79;
E-mail: vgyar@igic.ras.ru

basal plane and axial point nodes. Following model functions were proposed to fit experimental results for UPt_3 [15]:

$$\Psi(E_{2u}) = k_z \begin{pmatrix} k_x - k_y \\ 2k_x k_y \end{pmatrix} \qquad (4)$$

$$\Psi(E_{1g}) = k_z \begin{pmatrix} k_x \\ k_y \end{pmatrix} \qquad (5)$$

It was obtained that the anisotropy and the anomalies in the temperature dependence of the transverse ultrasound attenuation is explained only by an E_{2u} order parameter [16].

Basis functions for Sr_2RuO_4 (point group D_{4h}) include $\hat{x}$ and $\hat{y}$ spin components for one-dimensional IRs and $\hat{z}$ spin component for two-dimensional IRs [17]. For example, B_{2u} and E_u functions are written as [17]:

$$\Psi(B_{2u}) = \hat{x}k_y + \hat{y}k_x \qquad (6)$$

$$\Psi(E_u) = \hat{z}\left(k_x \pm ik_y\right) \qquad (7)$$

A more broad set of model functions for the SOP of Sr_2RuO_4 is presented in a review [18].

An alternative approach (*i.e.* a space-group approach) to the wavefunction of a Cooper pair [19-30] is based on the exact symmetry of one electron states in solids [12-14] and Mackey theorem on symmetrized squares [31], which was adopted to space groups by Bradley and Davies [32]. In the present work the equations for construction of two-electron states in solids possessing exact permutation and spatial symmetry are presented. Particular emphasis has been placed on complete symmetry classification of two electron states by additional physical quantum numbers. It is shown, that there are three essential quantum numbers for Cooper pairs: the labels of IRs of k-vector group H, IRs space group G at Γ- point and IRs of intermediate group F. The examples of application of the technique to unconventional superconductors UPt_3 and Sr_2RuO_4 are considered.

MATERIALS AND METHODS

In present work the induced representation method [13, 14] and Mackey theorem on symmetrized squares [31, 32] were used to construct exact two-electron

states in solids. It was shown that direct application of Mackey theorem to one-electron states results in Cooper pair wavefunction [19].

The one-electron functions in solid state belong the IRs which are defined by the k-vector group H (little group) and its IRs D^k (small IRs). Let there be a left coset decomposition of a space group G with respect to H:

$$G = \sum_i s_i H \qquad (8)$$

Then the induced representation, defined by following formula is an IR of the space group G [12-14]:

$$D^k \uparrow G(g)_{i\lambda,j\mu} = D^k(g_i^{-1}gg_j)_{\lambda,\nu}\delta(g_i^{-1}gg_j, H) \qquad (9)$$

Where:

$$\delta(g_i^{-1}gg_j, H) = \begin{cases} 1, \text{ if } g_i^{-1}gg_j \in H \\ 0, \text{ if } g_i^{-1}gg_j \notin H \end{cases} \qquad (10)$$

According to general rules of quantum mechanics the wavefunction of two fermions is a direct (Kronecker) square of single-electron states. For two equivalent fermions the Kronecker square is decomposed into symmetrized and antisymmetrized parts which are combined with singlet and triplet spin parts respectively.

To envisage the structure of Kronecher square of induced representation one needs the double coset decomposition of the space group G with respect to the wave vector group H:

$$G = \sum_\sigma H d_\sigma H \qquad (11)$$

For each double coset we consider a group $M_\sigma = H \cap d_\sigma H d_\sigma^{-1}$ and its representation given by the formula:

$$P_\sigma = D^k(m) \times D^k(d_\sigma^{-1}md_\sigma) \qquad (12)$$

Note, that M_σ is the intersection of little groups of vectors k and $k_\sigma = d_\sigma k$. The wave vector of the representation P_θ is given by the relation:

$$k + d_\sigma k = k_\sigma + b \qquad (13)$$

Where b is a vector of reciprocal lattice. The actual

procedure of symmetrization (antisymmetrization) depends on the type of double coset in (11). The self-inverse double coset coincides with double coset, defined by the inverse element, *i.e.*:

$$Hd_\alpha H = Hd_\alpha^{-1} H \qquad (14)$$

For self-inverse double coset there are two possibilities to extend representation (12) on the extended group $\tilde{M}_\alpha = M_\alpha + aM_\alpha$, whose characters are as follows:

$$\chi\left(P_\alpha^+\right) = \chi\left(D^k(amam)\right) \qquad (15)$$

$$\chi\left(P_\alpha^-\right) = \chi\left(D^k(amam)\right) \qquad (16)$$

Where $a = d_\alpha h_1 = h_2 d_\alpha, \ h_1, h_2 \in H$

According to Mackey theorem [31] the symmetrized (square brackets) and antisymmetrized (curly brackets) parts of Kronecker square are given by two formulae respectively:

$$\left[D^k \uparrow G \times D^k \uparrow G\right] = \left[D^k \times D^k\right] \uparrow G + \sum_\alpha P_\alpha^+ \uparrow G + \sum_\beta P_\beta \uparrow G \qquad (17)$$

$$\left\{D^k \uparrow G \times D^k \uparrow G\right\} = \left\{D^k \times D^k\right\} \uparrow G + \sum_\alpha P_\alpha^- \uparrow G + \sum_\beta P_\beta \uparrow G \qquad (18)$$

First items in r.h.s. of (17) and (18) correspond to double coset, defined by the identity element. This may take place in the center of a Brillouin zone (k=0) and at some points at the surface of a Brillouin zone (k=b/2). In these cases the symmetrization is fulfilled by standard group theoretical methods. In the case of nonsymmorphic space groups the formula for symmetrized and antisymmetrized characters respectively are written as:

$$\chi\left[D^k(h) \times D^k(h)\right] = \frac{\chi^2(D^k(h)) + \omega(h,h)\chi\left(D^k(h^2)\right)}{2} \qquad (19)$$

$$\chi\left\{D^k(h) \times D^k(h)\right\} = \frac{\chi^2(D^k(h)) - \omega(h,h)\chi\left(D^k(h^2)\right)}{2} \qquad (20)$$

Where multipliers $\omega(h,h)$ belong to a factor system of projective representation [12]. It was shown [28] that for nonsymmorphic space groups direct connection between multiplicity and parity of a Cooper pair wavefunction [6-9] may be violated.

The sums in second items in r.h.s. of (17) and (18) run over self-inverse double cosets. For k a general point in a Brillouin zone the self-inverse double coset, defined by space inversion corresponds to Cooper pairing. In the case of superconductors without inversion center for the plane of symmetry one can use 180° rotation about the axis perpendicular to this plane to construct pair wavefunction.

The last sums in r.h.s. of (17) and (18) run over not self-inverse double cosets, *i.e.* $Hd_\beta H \neq Hd_\beta^{-1} H$. In this case possible spatial symmetries of singlet and triplet two-electron states are the same. These eventual two-electron states are not related to the Cooper pairs.

For k a general point in a Brilluin zone formulas (12), (15) and (16) result in IRs A_g and A_u of group $\tilde{M}_\alpha$ for symmetrized and antisymmetrized squares respectively. Hence it follows that in agreement with [6] all even IRs are possible for singlet pairs and all odd IRs are possible for triplet pairs. Making use of Frobenius reciprocity theorem (see *e.g.* [14]) one obtains that the frequency of appearance of each representation equals to its dimension. Therefore it follows from Mackey theorem, that two-dimensional and three-dimensional IRs appear twice and thrice respectively, and their basis functions are not defined uniquely. In this case one can choose additional quantum numbers, corresponding to the IRs of some intermediate subgroup [29].

RESULTS AND DISCUSSION

At the planes of symmetry inside the Brillouin zone one-electron wave functions are characterized by intrinsic quantum number – the label of IR of group C_s, consisting of identity element and plane reflection. The analysis for the planes of symmetry is presented in Table **1**.

Table 1: Possible Symmetries of Singlet and Triplet Two-Electron States at the Planes of Symmetry Perpendicular to Quantization Z-Axis

	E	σ_h	I	C_2	IR
Singlet P_I^+	1	1	1	1	A_g
Triplet, spineless P_I^-	1	1	-1	-1	B_u
Triplet OSP $A_g \times P_\alpha^-$	1	1	-1	-1	B_u
Triplet ESP $B_g \times P_I^-$	1	-1	-1	1	A_u

Results of calculations according to Mackey theorem on the symmetry planes do not depend on the

intrinsic quantum number. It is seen from Table **1**, that IR B_g is absent for singlet pair and IR A_u is absent for triplet case. It is clear, that further induction into the whole group will result not all even IRs for singlet case and not all odd IRs for triplet case. The intersection of any symmetry plane with Fermi surface results a line. If IR responsible for Cooper pairing is forbidden on the plane, there is a line of nodes of SOP. Hence it follows that some lines of nodes follow from Mackey theorem. Triplet spin is usually considered within the point group. To obtain the total wavefunction of a Cooper pair one can use the following theorem of induced representation method:

$$\Gamma \times \left(D^k \uparrow G \right) = \left[\left(\Gamma \downarrow H \right) \times D^k \right] \uparrow G \qquad (21)$$

where Γ is IR of G, corresponding to spin wavefunction.

Let us consider D_{4h} group and a symmetry plane perpendicular to spin quantization z- axis. In this case triplet spin function splits into E_g, (basis functions $\hat{x}$ and $\hat{y}$) corresponding to ESP (equal spin pairing) states and A_{2g} corresponding to OSP (opposite spin pairing) states. When reducing according to formula (21) E_g and A_{2g} to the subgroup $\tilde{M}^\alpha = C_{2h}$, we obtain $2B_g$ and A_g respectively.

It seen from Table **1** that all odd IRs of C_{2h} group are possible for total wavefunction of a Cooper pair. Consequently there are no symmetry limitations on odd IRs of the whole group at this plane. This statement corresponds to Blount theorem [7]. However, it is natural to expect that only one type of pairs, say OSP, exists at superconductor under consideration. In this case triplet OSP pairs of A_u symmetry on the plane are forbidden and some odd IRs of the whole group will have nodes at this plane. Thus it was shown, that some violations of Blount theorem [7] appear due to axial

symmetry reduction, which splits three-dimensional spin function into one-dimensional and two-dimensional parts. Note that we considered group theoretical lines of nodes only, but in general case some physical reasons for the lines of nodes of triplet SOP may also exist.

Table **2** shows possible symmetries of triplet pairs in D_{4h} symmetry for the planes and directions in k-space in three approximations: spineless, OSP and ESP for quantization on z-axis. On the planes of symmetry the wave vector group includes a reflection operation and one-electron wavefunction acquires a label A or A'. In the case of Sr_2RuO_4 the solid state wavefunction may be represented as projections of atomic wavefunctions on IRs of the space group. In this approach the intrinsic quantum number on the planes of symmetry becomes very essential. The d_{z^2} functions are symmetrical and are projected on $A \uparrow G$ only. The reflection in diagonal plane changes the sign of $d_{x^2-y^2}$ and this function is projected on $A' \uparrow G$ on diagonal planes and on $A \uparrow G$ on coordinate planes. Similarly, atomic function d_{xy} is projected on $A' \uparrow G$ on coordinate plane and on $A \uparrow G$ on diagonal plane.

Let us consider as an example the results for triplet pairs in spineless case, *i.e.* when the pair is constructed according to Pauli exclusion principle case, but the spin wavefunction is not taken into account It is seen from Table **2**, that on the planes the symmetry of pair doesn't depend on the intrinsic quantum number (A or A'), but nevertheless this quantum number is the important characteristic of the electrons in a Cooper pair. On vertical coordinate planes IRs A_{1u} and B_{1u} are forbidden, on vertical diagonal planes IRs A_{1u} and B_{2u} are forbidden and on basal plane all one-dimensional IRs are forbidden. It should be noted, that for k a general point in a Brillouin zone IR E_u appears twice in

Table 2:   Symmetry of Triplet pairs in D_{4h} Symmetry

Planes	IR of H	Spinless	OSP	ESP
[100],[010]	A, A'	A_{2u}, B_{2u}, E_u	A_{1u}, B_{1u}, E_u	$2E_u+A_{1u}+A_{2u}+B_{1u}+B_{2u}$
[110],[-110]	A, A'	A_{2u}, B_{1u}, E_u	A_{1u}, B_{2u}, E_u	$2E_u+A_{1u}+A_{2u}+B_{1u}+B_{2u}$
[001]	A, A'	$2E_u$	$2E_u$	$2(A_{1u}+A_{2u}+B_{1u}+B_{2u})$
directions				
[001]	A_1, A_2, B_1, B_2	A_{2u}	A_{1u}	E_u
[001]	E	$A_{2g}+A_{2u}+B_{1u}+B_{2u}$	$A_{1g}+A_{1u}+B_{1u}+B_{2u}$	E_g+3E_u
[100]	A_1, A_2, B_1, B_2	E_u	E_u	$A_{1u}+A_{2u}+B_{1u}+B_{2u}$
[110]	A_1, A_2, B_1, B_2	E_u	E_u	$A_{1u}+A_{2u}+B_{1u}+B_{2u}$

the decomposition of the whole two-electron basis, but on vertical planes of symmetry IR E_u appears only ones. Going over to the vertical symmetry axis we see that the result depends on the label of IR in one-electron space. It is interesting to note that on C_{4v} axis for two-dimensional small IR E, one even IR A_{2g} appears for triplet pairs in addition to three odd IRs A_{2u}, B_{1u} and B_{2u}.

Since two-dimensional IR E_u appears twice in total basis decomposition in general *k*-point, its basis set is not unique. Complete classification of basis for multidimensional IRs may be done making use of transitivity of induction theorem [14, 29], which means that the two ways of induction of IR P^k from a subgroup *M* directly into *G* and via an intermediate subgroup *F*, result in equivalent representations:

$$P^k \uparrow G \propto \left(P^k \uparrow F \right) \uparrow G \tag{22}$$

The induced representation in the left hand side of (22) is decomposed onto the IRs Γ^q of the whole group:

$$P^k \uparrow G = \sum_q f_{kq} \Gamma^q \tag{23}$$

The decomposition in the r.h.s. of (22) consists of two steps. The decomposition for the first induction is written as:

$$P^k \uparrow F = \sum_q f'_{ki} \Phi^i \tag{24}$$

Finally, when inducing each one of IRs Φ^i into *G* we obtain:

$$\Phi^i \uparrow G = \sum_q f''_{iq} \mathrm{T}_q \tag{25}$$

According to the transitivity of induction theorem the frequencies in (23), (24) and (25) are connected by the relation:

$$f_{kq} = \sum_i f'_{ki} f''_{iq} \tag{26}$$

If frequencies f'_{ki} and f''_{iq} do not exceed unity, every repeating IR acquires unique additional quantum number - index of IR of intermediate subgroup. This index becomes a good quantum number if the intermediate group is physically meaningful.

Two-electron basis set at general point in one-electron Brillouin zone is shown in Figure **1**. Singlet and triplet basis functions are constructed according to formulae (1) and (2) respectively. Since the space inversion is included in basis functions, their number is the half of the number of vectors in a star of *k*-vector. In Figure **1a**) ψ_1 corresponds to a general k_1-point and in Figure **1b**) ψ_1 corresponds to a *k*-vector on the plane of symmetry and the number of function is two times less. However, in the latter case each basis function has intrinsic quantum number – the label of C_s group. Other basis functions are obtained by the action of symmetry elements on the ψ_1. Following Kovalev [12] notations for cubic group are used: $h_4 = C_{2z}$, $h_{14} = C_{4z}$, $h_{15} = C^3_{4z}$, $h_{26} = \sigma_x$, $h_{27} = \sigma_y$, $h_{37} = \sigma_{-xy}$ and $h_{40} = \sigma_{xy}$. In this notations h_1 are h_{25} are an indentity element and a space inversion. For the element with number equal or less 24 multiplications by h_{25} results in adding 24 and for the elements with numbers larger 24 and less 48
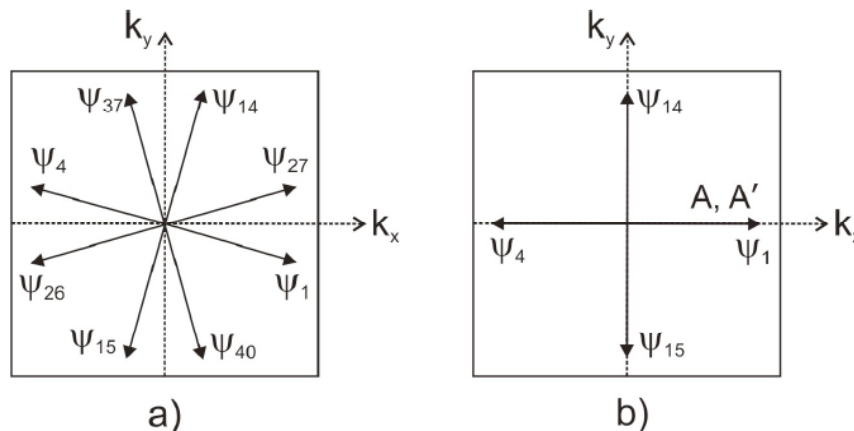

Figure 1: Two-electron basis set for D_{4h} group: **a**) general *k*-point and **b**) *k* at the vertical coordinate plane. The basis functions are defined in formulae (1) and (2) for singlet and triplet cases respectively. Note, that all vectors have some nonzero projection on z-axis, which is the same for all vectors.

multiplications by h_{25} results in subtraction 24. Making use of these rules the parity of basis functions is immediately verified:

$$h_{25}\psi_{27}^t = h_{25}\big(\varphi_{27}(r_1)\varphi_3(r_2)-\varphi_{27}(r_2)\varphi_3(r_1)\big) = $$
$$\big(\varphi_3(r_1)\varphi_{27}(r_2)-\varphi_3(r_2)\varphi_{27}(r_1)\big) = \psi_3^t = -\psi_{27}^t \qquad (27)$$

It is clear from formula (27) that the action of space inversion on triplet two-electron function may be represented by subtracting (adding) 24 from its number or multiplying by -1.

Functions belonging to IRs of point group D_{4h} are easily obtained making standard projection operator technique [33] and the results are presented in Table **3**.

Going over to the vertical planes of symmetry we see from Figure **1 b**) that the number of basis functions is two times less. When going to the plane [010] there are two possibilities: functions ψ_1^t and ψ_{27}^t in linear combination belonging to any IR can merge or cancel. The first case corresponds to nodeless structure and the second to node on the plane of symmetry. Thus if the action of plane reflection operator doesn't change the coefficients of ψ_1^t and ψ_{27}^t in linear combination, there are no nodes on the plane [010]. If the signs in linear combinations are changed, there is a node on this plane. This property of the spinless wavefunctions of Table **3** is immediately verified making use of group multiplication rules presented in [12] and relation (27). One directly obtains nodal structure of one dimensional functions, which coincides with nodal structure, obtained in Table **2** group-theoretically.

For two dimensional IR E_u there are different possibilities. When projecting on IR E_u in standard (x,y) basis, the function of the first row is nodal at [100] plane and the second function is nodal on the [010] plane. It follows from above considerations that at general k-point E_u appears twice in decomposition of the whole basis and at vertical coordinate planes E_u appears ones. The technique of intermediate subgroups and additional quantum numbers makes possible to construct nodeless and nodal on these planes basis sets as follows. In our case the intermediate group is the pair symmetry group C_{2h} on one of the vertical coordinate planes. It is seen from Table **1**, that the symmetry of triplet pair function on the plane is B_u. Hence it follows than if the basis function of any IR transforms as B_u at the plane, it is nodeless at this plane. On the other hand, if the function transforms as A_u it is nodal. We project firstly on IRs A_u or B_u of symmetry group of the plane [010]. The first basis is nodal on the plane and the second is nodeless. Further induction results in nodal and nodeless functions respectively on the plane [100] also. In the case of IR

E_u three types of basis functions are presented. E_u^α corresponds to standard (x,y) basis and nodes of the first and second rows are on different coordinate planes. The E_u^β basis has nodes on vertical coordinate planes and basis functions E_u^β are nodeless on vertical coordinate planes. Nodal and nodeless functions for diagonal vertical planes may be obtained by similar way and are not shown in the Table **3**.

Table 3: **Spatial Parts of Triplet Wave Functions for D_{4h} Group. Basis Function ψ_1 Corresponds to Arbitrary Wave Vector k_1 in a Brillouin Zone in one-Electron Space and is Built According to Formula (2) (Superscript t is Dropped). Other Basis Functions are Obtained by the Action of Half of the Elements of Group D_{4h} on the First One. (See Figure 1 a)**

IR	Wavefunction	Nodes
A_{1u}	$\psi_1+\psi_4+\psi_{14}+\psi_{15}-\psi_{26}-\psi_{27}-\psi_{37}-\psi_{40}$	all planes
A_{2u}	$\psi_1+\psi_4+\psi_{14}+\psi_{15}+\psi_{26}+\psi_{27}+\psi_{37}+\psi_{40}$	[001]
B_{1u}	$\psi_1+\psi_4-\psi_{14}-\psi_{15}-\psi_{26}-\psi_{27}+\psi_{37}+\psi_{40}$	[100],[010]
B_{2u}	$\psi_1+\psi_4-\psi_{14}-\psi_{15}+\psi_{26}+\psi_{27}-\psi_{37}-\psi_{40}$	[110],[-110]
E_u^α	$\psi_1+\psi_{27}-\psi_4-\psi_{26}$ $\psi_{14}+\psi_{37}-\psi_{15}-\psi_{40}$	[100] [010]
E_u^β	$\psi_1-\psi_{27}+\psi_4-\psi_{26}$ $\psi_{14}-\psi_{37}+\psi_{15}-\psi_{40}$	[100] [010] [100] [010]
E_u^γ	$\psi_1+\psi_{27}+\psi_4+\psi_{26}$ $\psi_{14}+\psi_{37}+\psi_{15}+\psi_{40}$	No nodes No nodes

Standard projection operator techniques [33] makes possible to construct triplet functions with spin by similar way. When starting with three basis functions $\hat{x}\psi_1$, $\hat{y}\psi_1$ and $\hat{z}\psi_1$, and projecting on the rows of odd IRs one easily obtains the examples presented in Table **4**. Nodal structure for one-dimensional IRs can be estimated making use of Table **2**. Note that $\hat{x}\psi_1$ and $\hat{y}\psi_1$ functions correspond to ESP case and $\hat{z}\psi_1$ OSP case and that operators of groups D_{4h} and D_{6h} don't mix OSP and ESP states. Nodal structure of two-dimensional IRs is also not uniquely defined by the label of IR of the whole group.

The difference between the functions of Table **4** and model functions of formulae (3)- (7) (see also Refs. [6-9]) should be particularly emphasized. In a model representation of formulae (3)-(7) the k- vector in continuous space is defined by three-dimensional

Table 4:   **Some Examples of Total Triplet Wavefunctions of Cooper Pairs for D_{4h} Symmetry. $\hat{x}$, $\hat{y}$ And $\hat{z}$ Stand for the Three Components of Triplet spin. For Definition of Spatial Parts See Heading of Table 3 and Figure 1a)**

IR	Wavefunctions
B_{2u}	$\hat{z}\psi_1 + \hat{z}\psi_4 - \hat{z}\psi_{14} - \hat{z}\psi_{15} - \hat{z}\psi_{26} - \hat{z}\psi_{27} + \hat{z}\psi_{37} + \hat{z}\psi_{40}$
B_{2u}	$\hat{y}\psi_1 - \hat{y}\psi_4 - \hat{x}\psi_{14} + \hat{x}\psi_{15} + \hat{y}\psi_{26} - \hat{y}\psi_{27} - \hat{x}\psi_{37} + \hat{x}\psi_{40}$
B_{2u}	$\hat{x}\psi_1 - \hat{x}\psi_4 + \hat{y}\psi_{14} - \hat{y}\psi_{15} + \hat{x}\psi_{26} - \hat{x}\psi_{27} + \hat{y}\psi_{37} - \hat{y}\psi_{40}$
E_u^β	$\hat{z}\left(\psi_1 + \psi_{27} + \psi_4 + \psi_{26}\right)$ $\hat{z}\left(\psi_{14} + \psi_{37} + \psi_{15} + \psi_{40}\right)$
E_u^β	$\hat{x}\psi_1 + \hat{x}\psi_{27} - \hat{x}\psi_4 - \hat{x}\psi_{26}$ $-\hat{y}\psi_{14} + \hat{y}\psi_{37} + \hat{y}\psi_{15} - \hat{y}\psi_{40}$

vector (k_x, k_y, k_z) and the nodal structure is represented by constructing different polynomial functions of these components. In a space-group approach the vector k_1 is defined in a basis domain of a Brillouin zone [13] and the other components of basis set shown in Figure **1**, are obtained by the action of left coset representatives in the decomposition of G with respect $\tilde{M}_\alpha$ on k_1. (For k_1 inside the Brillouin zone $\tilde{M}_\alpha = H + IH$.) The nodes of SOP appear when vector k_1 is reaching symmetry points and directions in actual Brillouin zone.
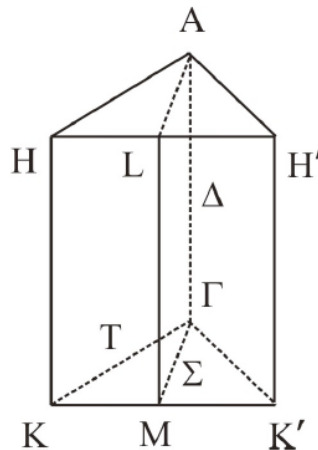

Figure 2: Brillouin zone for the D_{6h} group.

Recent experiment on UPt$_3$ resulted that polar Kerr effect appears only below the lower of the two zero-field superconducting transition temperatures. These results provide evidence for broken time-reversal symmetry in the low-temperature superconducting

phase of UPt$_3$, implying a complex two-component order parameter for superconductivity in this system [34]. Small angle neutron scattering measurements indicate a linear temperature dependence of the London penetration depth - characteristic of nodal structure of the order parameter. Theoretical analysis of this work is consistent with odd parity chiral states [35]. Hence it follows that even IRs should be discarded from the consideration. Experimental data on UPt$_3$ can be viewed as line of nodes in basal plane and point node in ΓA direction [21].

Table **5** shows group theoretical analysis on the planes and lines of symmetry in D_{6h} symmetry group for odd IRs. Starting with spinless case we see that IR E_{2u} is absent on basal plane. IR E_{2u} is also absent in ΓA direction if one-electron states belong to one-dimensional IR of wave vector group C_{6v}. One the hand, if one-electron states belong to two-dimensional IR E_1(or E_2) in ΓA direction, the antisymmetrized square contains IR E_{2u}. Hence it follows that in vertical direction the node of IR E_{2u} depends on intrinsic quantum number – the label of one-electron IR. It should be noted, that in this case possible wavefunctions of triplet pairs include even IR. In OSP case IR E_{1u} possess the same nodal structure and may be a candidate for SOP symmetry. The $B_{1u}+B_{2u}$ model was also proposed for UPt$_3$ [36]. It is seen from Table **5**, that in ESP case IRs B_{1u} and B_{2u} have line nodes in basal plane and in vertical direction if one-electron states belong to one-dimensional small IRs.

CONCLUSION

Eugene Wigner wrote: *I do not believe that the subject of the reduction of direct products of representations has been exhausted* [37]. The results of the present work on the reduction of Kronecker squares of one-electron wavefunctions in solids based on Mackey theorem support his assertion. It is shown that the part of this Kronecker square corresponding to double coset, defined by space inversion, can be related to Cooper pairs. The analysis of symmetrized and antisymmetrized squares resulted in two essential features of Cooper pair wavefunction at general point and at symmetry planes and directions of a Brillouin zone (one-electron). For k a general point the number of appearance of any IR in total basis decomposition equals to its dimension. To classify basis functions of repeating IRs additional quantum numbers, *i.e.* labels of IRs of intermediate group are proposed. When choosing the planes of symmetry for intermediate group, the intermediate quantum numbers for nodal and nodeless wavefunctons are obtained for two-dimensional IRs. The intrinsic quantum number of a

Table 5:   Symmetry of Triplet pairs in D_{6h} Symmetry. Notation According to Figure 2

Planes	IRs of H	spinless	OSP	ESP
ΓML	A, A'	$A_{2u}+B_{2u}+E_{1u}+E_{2u}$	$A_{2u}+B_{1u}+E_{1u}+E_{2u}$	$A_{1u}+A_{2u}+B_{1u}+B_{2u}+2E_{1u}+2E_{2u}$
ΓKH	A, A'	$A_{2u}+B_{1u}+E_{1u}+E_{2u}$	$A_{2u}+B_{2u}+E_{1u}+E_{2u}$	$A_{1u}+A_{2u}+B_{1u}+B_{2u}+2E_{1u}+2E_{2u}$
ΓKM	A, A'	$B_{1u}+B_{2u}+2E_{1u}$	$B_{1u}+B_{2u}+2E_{1u}$	$2A_{1u}+2A_{2u}+4E_{2u}$
directions				
$\Gamma\Sigma$	A_1, A_2, B_1, B_2	$B_{2u}+E_{1u}$	$B_{1u}+E_{1u}$	$A_{1u}+A_{2u}+2E_{2u}$
ΓT	A_1, A_2, B_1, B_2	$B_{1u}+E_{1u}$	$B_{2u}+E_{1u}$	$A_{1u}+A_{2u}+2E_{2u}$
ΓA	A_1, A_2, B_1, B_2	A_{2u}	A_{1u}	E_{1u}
ΓA	E_1, E_2	$E_{2u}+A_{2u}+A_{2g}$	$E_{2u}+A_{1u}+A_{1g}$	$E_{1u}+B_{1u}+B_{2u}+A_{1u}+A_{1g}$

Cooper pair, *i.e.* the label of small IR of the wave vector group, appears at the planes of symmetry. This quantum number is useful to label repeating IRs of the whole group appearing on the planes and lines of symmetry. It is also obtained that the direct connection between multiplicity and parity of a Cooper pair wavefunction [6-9] is violated for two-dimensional IRs in one-electron space. The examples of applications of the obtained tables of antisymmetrized Kronecker squares to the interpretation of experimental data on Sr_2RuO_4 and UPt_3 are presented.

REFERENCES

[1]   Schmitt-Rink S, Miyake K and Varma CM. Transport and thermal properties of heavy-fermion superconductors: a unified picture. Phys Rev L.ett 1986; 57: 2575-4.
http://dx.doi.org/10.1103/PhysRevLett.57.2575

[2]   Bonalde I, Yanoff BD, Salamon MB, Van Harlingen DJ, Chia EM, Mao ZQ et al. Temperature dependence of the penetration depth in Sr2RuO4: evidence for nodes in the gap function. Phys Rev Lett 2000; 85: 4775-4.
http://dx.doi.org/10.1103/PhysRevLett.85.4775

[3]   Matsuda Y, Izawa K and Vekhter I. Nodal structure of unconventional superconductors probed by angle resolved thermal transport measurements. J Phys Condens Matter 2006; 18: R705-47.
http://dx.doi.org/10.1088/0953-8984/18/44/R01

[4]   Norman MR. The challenge of unconventional superconductivity. Science 2011; 332(6026): 196-5.
http://dx.doi.org/10.1126/science.1200181

[5]   Ginzburg VL and Landay LD. On the theory of superconductivity. Zh. Exp. Teor. Fiz 1950; 20: 1064-19 (in Russian).

[6]   Anderson PW. Structure of "triplet" superconducting energy gap. Phys Rev B 1984; 30: 4000-3.
http://dx.doi.org/10.1103/PhysRevB.30.4000

[7]   Blount EI. Symmetry properties of triplet superconductors. Phys Rev B 1985; 32: 2935-10.
http://dx.doi.org/10.1103/PhysRevB.32.2935

[8]   Volovik, GE and Gor'kov LP. Superconducting classes in heavy fermion systems. Sov Phys JETP 1985; 61: 843-12.
http://dx.doi.org/10.1070/PU1985v028n09ABEH003997

[9]   Sigrist M and Ueda K. Phenomenological theory of unconventional superconductivity. Rev Mod Phys 1991; 63: 239-73.
http://dx.doi.org/10.1103/RevModPhys.63.239

[10]   Yip S and Garg A. Superconducting states of reduced symmetry: General order parameters and physical implications Phys Rev B. 1993; 48, 3304-5.
http://dx.doi.org/10.1103/PhysRevB.48.3304

[11]   Balian R and Werthamer NR. Superconductivity with pairs in a relative p wave Phys. Rev 1963; 131: 155-13.
http://dx.doi.org/10.1103/PhysRev.131.1553

[12]   Kovalev OV. Irreducible representations of the crystallographic space groups: irreducible representations, induced representations and corepresentations. New York: Gordon & Breach 1993.

[13]   Bradley CJ and Cracknell AP. The mathematical theory of symmetry in solids. Representation theory of point groups and space groups. Oxford: Clarendon 1972.

[14]   Altman SL. Induced representations for crystals and molecules. New York Academic Press, 1977.

[15]   Sauls JA. Theory for the Superconducting Phases of UPt3 J Low Temp Phys 1994; 95: 153-16.
http://dx.doi.org/10.1007/BF00754932

[16]   Graf MJ, Yip SK and Sauls JA. Identification of the orbital pairing symmetry in UPt3. Phys Rev B 2000; 62, 14393-10.
http://dx.doi.org/10.1103/PhysRevB.62.14393

[17]   Rice T M and Sigrist M. Sr2RuO4: an electronic analogue of 3He? J Phys Condens Matter 1995; 7: L643-6.
http://dx.doi.org/10.1088/0953-8984/7/47/002

[18]   Mackenzie AP and Maeno Y. The superconductivity of Sr2RuO4 and the physics of spin-triplet paring. Rev of Mod Phys 2003; 75: 657-56
http://dx.doi.org/10.1103/RevModPhys.75.657

[19]   Yarzhemsky VG and Murav'ev EN. Space group approach to the wavefunction of a Cooper pair D2h and D4h. J Phys Cond. Matter 1992; 4: 3525-8.

[20]   Yarzhemsky VG. Wavefunction of a Cooper pair in crystals of and symmetry Zeitsch Phys B Cond Matter 1995; 99: 19-5.

[21]   Yarzhemsky VG. Space-Group Approach to the Nodal Structure of Superconducting Order parameter in UPt3 Phys stat. sol (b) 1998; 101: 209-7.

[22]   Yarzhemsky VG. Space-Group Approach to the Nodal Structure of Superconducting Order parameter in Ferromagnetic and Antiferromagnetic Materials. IntJ Quant Chem 1999; 80: 133-8.
http://dx.doi.org/10.1002/1097-461X(2000)80:2<133::AID-QUA9>3.0.CO;2-B

[23] Yarzhemsky VG and Nefedov VI. Symmetry of two-electron states in unconventional superconductors Inorg. Materials. 2005; 41:1247-9.
http://dx.doi.org/10.1007/s10789-005-0295-6

[24] Yarzhemsky VG and Nefedov VI. Crystal Symmetry and the Structure of Two-Electron States in High-Temperature Superconductors. Doklady Physics 2005; 50 (10): 494-5.
http://dx.doi.org/10.1134/1.2123295

[25] Yarzhemsky VG and Nefedov VI. Group theoretical treatment of photoelectron spectra of high-Tc superconductors. Hidden symmetry and color pairs. Philosophical Magazine Letters 2006; 86: 733-10.
http://dx.doi.org/10.1080/09500830600990325

[26] Yarzhemsky VG and Nefedov VI. Structure of triplet states in magnetic crystals. Doklady Physics 2007; 52 (2), 85–5.
http://dx.doi.org/10.1134/S1028335807020048

[27] Yarzhemsky VG and Nefedov VI. Time-reversal symmetry violation and the structure of the superconducting order parameter of PrOs4Sb12. Physics Solid State 2009; 51: 448-8.
http://dx.doi.org/10.1134/S1063783409030020

[28] Micklitz T and Norman M. Odd parity and line nodes in nonsymmorphic superconductors. Phys Rev B 2009; 80: 100506 (R)-4.

[29] Yarzhemsky VG. Nodal quantum numbers for two-electron states in solids. Few-body systems 2012; 53: P499-6.
http://dx.doi.org/10.1007/s00601-012-0438-7

[30] Yarzhemsky VG and Izotov AD. Electronic structure and the structure of the order parameter in high-Tc superconductors based on copper oxides and iron pnictides. Inorg Materials 2014; 50: 907-5.
http://dx.doi.org/10.1134/S0020168514090179

[31] Mackey GW. Symmetric and anti symmetric Kronecker squares and intertwining numbers of induced representations of finite groups Am J Math 1953; 75: 387-19
http://dx.doi.org/10.2307/2372459

[32] Bradley CJ and Davies BL. Kronecker products and symmetrized squares of irreducible representations of space groups. J Math Phys 1970; 11: 1536-17.
http://dx.doi.org/10.1063/1.1665292

[33] Hamermesh M. Group Theory and Its Application to Physical Problems New York: Adison-Wesley, 1964.

[34] Schemm ER, Gannon WJ, Wishne CM, Halperin WP and Kapitulnik A. Observation of broken time-reversal symmetry in the heavy-fermion superconductor UPt3 Science 2014; 345 (6193): 190-4.

[35] Gannon WJ, Halperin WP, Rastovski C, Schlesinger KJ, Hlevyack J, Eskildsen MR et.al. Nodal gap structure and order parameter symmetry of the unconventional superconductor UPt3. New J Phys 2015; 17: 023041-9.
http://dx.doi.org/10.1088/1367-2630/17/2/023041

[36] Machida K and Ozaki Ma. Superconducting double transition in a heavy-fermion material UPt3. Phys Rev Lett 1991; 66: 3293-4.
http://dx.doi.org/10.1103/PhysRevLett.66.3293

[37] Wigner EP. Symmetry principles in old and new physics. Bull Amer Math Soc 1968; 74: 793-23.
http://dx.doi.org/10.1090/S0002-9904-1968-12047-6