Abstract: Sr$_2$RuO$_4$ and Fe-pnictide superconductors belong to the same point group symmetry $D_{4h}$. Many experimental data confirm odd pairs in Sr$_2$RuO$_4$ and even pairs in Fe-pnictides, but opposite conclusions also exist. Recent NMR results of Pustogow et al., which revealed even Cooper pairs in Sr$_2$RuO$_4$, require reconsideration of symmetry treatment of its SOP (superconducting order parameter). In the present work making use of the Mackey–Bradley theorem on symmetrized squares, a group theoretical investigation of possible pairing states in $D_{4h}$ symmetry is performed. It is obtained for $I4/mmm$, i.e., space group of Sr$_2$RuO$_4$, that triplet pairs with even spatial parts are possible in $E_u$ direction and in points $M$ and $Y$. For the two latter cases pairing of equivalent electrons with nonzero total momentum is proposed. In $P4/nmm$ space group of Fe-pnictides in point $M$, even and odd pairs are possible for singlet and triplet cases. It is shown that even and odd chiral states with angular momentum projection $m = \pm 1$ have nodes in vertical planes, but $E_g$ is nodal, whereas $E_u$ is nodeless in the basal plane. It is also shown that the widely accepted assertion that the parity of angular momentum value is directly connected with the spatial parity of a pair is not valid in a space-group approach to the wavefunction of a Cooper pair.

Keywords: nodal superconductors; chiral superconductors; pnictide superconductors Sr$_2$RuO$_4$; Cooper pair symmetry

1. Introduction

Pnictide superconductors [1] and Sr$_2$RuO$_4$ [2] have been characterized in a great number of experiments [3,4] whose results are in some cases mutually excluding, and no consensus is currently achievable. The absence of changes in the Knight shift in the $^{17}$O NMR spectrum on passing through $T_c$ confirms oddness of the SOP (superconducting order parameter) of Sr$_2$RuO$_4$ [5]. Phase-sensitive measurements indicate that the phase of the SOP in Sr$_2$RuO$_4$ changes by $\pi$ under inversion and confirmed the odd nature of pairing [6]. Odd superconductivity in Sr$_2$RuO$_4$ is also in agreement with the results of penetration measurements [7,8]. A slight increase in the spin susceptibility originating from the Ru-4d electrons in superconducting state of Sr$_2$RuO$_4$ was connected with a triplet pairing [9]. However, a dramatic increase in $T_c$ from 1.5 K to 3.5 K and increase in $H_{c2}$ (by a factor of 20) in strained samples of Sr$_2$RuO$_4$ [10] was connected with singlet phase.

A reduction in $^{17}$O Knight shift observed for all strain values and temperatures $T < T_c$ [11,12] suggests even SOP and singlet pairs, which were represented by even chiral function:

$$E_g: \mathbf{d}(\mathbf{k}) = d_{2x} \pm i d_{2y}. \quad (1)$$

On the other hand, for the unstrained samples the reduction in Knight shift of approximately 50% is not inconsistent with helical states of $A_{1u}$ or $B_{1u}$ symmetry, which were written as [11]

$$A_{1u}(B_{1u}): \mathbf{d}(\mathbf{k}) = \hat{x}k_x \pm \hat{y}k_y \quad (2)$$
where $\hat{x}$ and $\hat{y}$ stand for the components of triplet spin in the ESP (equal spin pairing) case, and $k_x$ and $k_y$ represent the continuous wavevector. However, by means of the NMR spectroscopy of normal state $\text{Sr}_2\text{RuO}_4$ under uniaxial stress and corresponding density-functional calculations, it was demonstrated that there are two different effects associated with the strain-induced the enhancement of the DOS associated with the $\gamma$-band FS (Fermi surface) passing the $Y$ point of the BZ (Brillouin zone), and a substantial Stoner enhancement [13]. The enhancement of the DOS through the Stoner factor boosts ferromagnetic spin fluctuations, which favors triplet states and seems to disfavor singlet pairing [13]. Thus, the singlet or triplet nature of pairing in $\text{Sr}_2\text{RuO}_4$ is still under debate.

Nevertheless, there is no doubt about other unusual properties of this superconductor. The results of $\mu$SR (muon spin relaxation) experiments on superconducting $\text{Sr}_2\text{RuO}_4$ indicate the presence of spontaneous internal magnetic fields, i.e., TRSB (time-reversal symmetry breaking) [14]. More recent $\mu$SR experiments established splitting between $T_c$ and temperature of TRSB, which rules out any mechanism based on interaction of magnetic fluctuations and conventional superconductivity [15]. Observed Kerr rotation below $T_c$ implies TRSB [16] and is consistent with the SOP of the form [17]:

$$E_a : \mathbf{d}(\mathbf{k}) = \hat{x}(k_x \pm ik_y),$$

where $\hat{z}$ stands for the component of triplet spin vector in OSP (opposite spin pairing case). The measurements of the specific heat resulted in lines of gap minima or zeros in planes $[\pm 1, \pm 1, 0]$ and $[\pm 1, \mp 1, 0]$ [18]. High-resolution inelastic neutron scattering measurements and random phase approximation calculations suggest horizontal line nodes [19]. The results of angle-resolved study of ultrasonic attenuation in $\text{Sr}_2\text{RuO}_4$ suggest that the gap function has nodes in vertical or horizontal planes [20]. Thermal conductivity measurements on single crystals of $\text{Sr}_2\text{RuO}_4$ revealed vertical line nodes of SOP [21]. Recent results of sound velocity experiments are compatible with two-component $d$-wave SOP [22]. The authors [20–22] noticed the inconsistency between chiral $p$-wave or $d$-wave superconductivity and vertical line nodes. However, it was shown that group theoretical vertical line nodes are inherent to real and complex forms of $E_a$ SOP [23]. Recent field-angle-dependent specific-heat measurements [24] revealed the presence of horizontal line nodes in the gap consistent with SOP of (1) structure. Chiral even SOP nodeless in the basal plane was represented in polynomial form as

$$E_g : \mathbf{d}(\mathbf{k}) = d_{x^2−y^2} \pm id_{xy}.$$  

Transport properties of the planar and corner Josephson junctions formed between $\text{Sr}_2\text{RuO}_4$ and Nb revealed time-reversal invariant superconductivity, with most probably helical $p$-wave symmetry [25]. Using the results of resonant ultrasound spectroscopy measurements, the structure of SOP $d_{x^2−y^2} \pm s_{xy}(\hat{x}^2−\hat{y}^2)$ was proposed [26]. Thus, the above-mentioned model representations of SOP in $\text{Sr}_2\text{RuO}_4$ [11,17,22] reflect experimental features, but the inconsistency between their theoretical nodal structure [11,17] and experimental data on vertical line nodes in the chiral case [18,20,21] exists.

The electron band structure of pnictide superconductors is quite unusual resulting in some unconventional features of their SOP. According to the calculations the FS of pnictides consists of two electronic parts: $\alpha$ and $\beta$ near $\Gamma$ point and a hole part $\gamma$ near $M$ point($b/2, b/2, 0$) [27]. The results of scanning tunneling microscopy on Fe(Se,Te) single crystals indicate that the sign is reversed between the hole and the electron FS pockets ($s$-wave), favoring the unconventional pairing mechanism associated with spin fluctuations [28]. ARPES (angle-resolved photoelectron spectroscopy) investigations of NdFeAsO$_{0.5}$F$_{0.1}$ detected some angular fluctuations of gap at $\beta$ FS, but the results do not exclude $p$-wave or $d$-wave pairing states with nodes of the gap [29]. ARPES of Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ revealed nodeless superconducting gaps of different values, opening simultaneously at the bulk $T_c$ on all three observed FS sheets [30]. The results are consistent with the SOP
of s-wave symmetry, although the authors cannot rule out the possibility of nontrivial relative phases between the pairing order parameters on the different FS sheets. ARPES with laser excitation showed that KFe$_2$As$_2$ ($T_c = 3.4$ K) is an s-wave superconductor with unusual multigap structure, i.e., internal and external FS have no zeroes, whereas octet point nodes are located on the middle FS at an angular distance 5$^\circ$ from coordinate axes, and $A_{1g}$ gap symmetry was suggested [31]. However, tunneling conductance spectra of stoichiometric FeSe crystalline films in their superconducting state revealed evidence for a gap function with nodal lines, manifesting symmetry breaking from $C_4$ to $C_2$ [32]. Summarizing experimental results of combinatorial microwave measurements, it was concluded that LiFeAs has nodeless gaps with moderate anisotropy and that BaFe$_2$As$_1$-$x$P$_x$$_2$ has highly anisotropic gaps containing at least one line-nodal gap [33]. A constant Knight in $^{75}$As in NMR investigation of a single crystal of superconducting LiFeAs was considered as a sign of triplet pairing [34]. In addition, the observed anomalous hysteresis at high fields is compatible with the existence of chiral gap wave functions similar to the forms (4) or (5) [35]. Making use of $\mu$SR, symmetry analysis and first principles band structure calculation chiral $d$-wave SOP was proposed for weakly correlated pnictide compound LaPt$_3$P [36].

Both types of compounds Sr$_2$RuO$_4$ and Fe-pnictides have the same $D_{4h}$ point group symmetry, but belong to different space groups: $I4/mmm$ ($D^{17}_{4h}$, 139) and $P4/nmm$ ($D^{7}_{4h}$, 129), respectively, and the symmetry analysis of pair symmetry inside the BZ is the same for them. The BZs for these space groups are presented in Figure 1.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** 1/8 parts of BZ for two space groups of $D_{4h}$ symmetry (a) $I4/mmm$ ($D^{17}_{4h}$), (b) $P4/nmm$ ($D^{7}_{4h}$).

Representations of experimental data (1)–(4) are based on phenomenological point group approach [17,37,38], in which possible SOP functions are obtained by reduction of spherical harmonics to a point group. According to Anderson ansatz [39] wavefunction of a singlet pair is even and that of a triplet pair is odd. It was shown, making use of the space-group approach to the wavefunction of a Cooper pair, that this direct relation between multiplicity and parity of a pair is violated in symmetrical points and directions in a BZ [40,41]. Since the spherical functions are taken for the representation of SOP in phenomenological approaches, it was assumed that singlet pairs have even value of angular momentum $l$ and triplet pairs have odd value of angular momentum [42]. It should be noted that in a general case, for each IR (irreducible representation) $D^{(l)}$ of a rotation group $R_3$ there are even $D^{(l+)}$ and odd $D^{(l-)}$ extensions on the rotation group with space inversion $R_3 + IR_3$ [43]. Hence, the direct relation between the parity of angular momentum value and the spatial parity of pair function is a consequence of the basis function choice, but not of the symmetry requirements. Usually the accepted formula (4) for triplet chiral states is nodeless in vertical planes, but making use of the space-group approach the examples of p-wave SOP with group-theoretical vertical lines of nodes were
obtained [23]. Recent results on even nature of the SOP in Sr$_2$RuO$_4$ [11] require also investigations of vertical nodes of singlet chiral states. It was mentioned that the concept of $s$-wave, $p$-wave, etc., has to be taken with a grain of salt because of the presence of a crystalline lattice that breaks translational symmetry [44]. By virtue of the fact that there are many experimental results on the symmetry of SOP of Sr$_2$RuO$_4$ and Fe- pnictides, which apparently contradict with each other and with model representation, its group theoretical analysis independent on the models is required.

In the present work the space group theory [45] for one-electron states, Anderson ansatz [39] and Mackey–Bradley theorem [46,47] for two-electron states, are used to investigate spatial structures of singlet and triplet pairs in distinct points of a BZ. Symmetrical ansatz [39] and Mackey–Bradley theorem [46,47] for two-electron states, are used to investigate spatial structures of singlet and triplet pairs in distinct points of a BZ. Symmetrical points in a BZ are identified, where direct connection between multiplicity and parity of a pair function is violated. Even and odd chiral states with angular momentum projection $m = \pm 1$ are built, and their nodal structure is investigated.

2. Symmetry of Two-Electron States

One-electron states in a crystal with symmetry group $G$ are labeled by the wavevector $k$, its symmetry group $H$ (little group) and the index $\kappa$ of small IR $D^{\kappa \kappa}$ of $H$ [45]. For brevity the second index for one-electron states will be dropped. The IR of the space group is an induced representation $D^e \uparrow G$ [45]. In a general point of a BZ the dimension of IR $D^e \uparrow G$ equals the number $n$ of point group elements of $\hat{G}$ (central extension of $G$). Two-electron space is a Kronecker square of this space, and its dimension in a general $k$– point equals to $n^2$. This space can be easily decomposed into physically different parts making use of double coset decomposition of $G$ with respect to $H$ [46,47]:

$$G = \sum_\delta H_d \delta H.$$

(6)

The double coset representatives $d_\delta$ denote different terms in a Kronecker square $D^e \uparrow G \times D^e \uparrow G$ decomposition. The notation $\times$ for direct (Kronecker) product is used throughout. For each double coset $\delta$ a representation $P^\pm_\delta$ is considered, whose character is written as:

$$\chi(P^\pm_\delta(m)) = \chi\left(D^e(d_\delta^{-1} md_\delta) \times D(m)\right),$$

(7)

where $m \subset M_\delta = H \cap d_\delta^{-1} H d_\delta$. For self-inverse double cosets, i.e., if $H d_\delta H = H d_\delta^{-1} H$ there are two extensions of $P^\pm_\delta$ on group $M_\kappa = M_\kappa + a M_\kappa$:

$$\chi(P^+_{\kappa a}(am)) = +\chi(D^e(amam)),$$

(8)

and

$$\chi(P^-_{\kappa a}(am)) = -\chi(D^e(amam)),$$

(9)

where the coset representative $a$ is chosen from the relation:

$$ah = \bar{h}a, \ h, \bar{h} \subset H$$

(10)

According to the Mackey–Bradley theorem [46,47] symmetrized (superscript $+$) and antisymmetrized (superscript $-$) parts of a Kronecker square are written as:

$$(D^e \uparrow G \times D^e \uparrow G)^\pm = (D^e \times D^e)^\pm \uparrow G + \sum_\alpha P^\pm_{\kappa a} \uparrow G + \sum_\beta P^\pm_{\kappa b} \uparrow G$$

(11)

The symmetrization (antisymmetrization) in the first item is performed by standard point group technique, sum in the second item runs over self-inverse double cosets, and the sum in the third item runs over not self-inverse double cosets, i.e., if $H d_\delta H \neq H d_\delta^{-1} H$.

Total momentum of a pair is written as:

$$K = \vec{k} + d_a \vec{k} + \vec{b},$$

(12)
where \( \vec{b} \) is a reciprocal lattice vector. In the case of Cooper pairs the double coset representative \( d_a \) is a space inversion \( I \), and in some symmetrical points on the surface of a BZ \( d_\alpha \) is an identity element \( E \). It should be noted that since in a space-group approach one-electron wavefunction is multidimensional, there are states of two equivalent electrons with nonzero total momentum \( K \). Some such states will be considered later on.

According to the Pauli exclusion principle, the symmetrized square of a spatial part of the wavefunction corresponds to a singlet pair and antisymmetrized square corresponds to a triplet pair. For \( K = 0 \) the induced representation \( D^\pm_\alpha \uparrow \hat{G} \) is a reducible representation of a point group \( \hat{G} \). The frequency \( f^\pm_{\alpha,\kappa} \) of appearance of any IR \( \Gamma^\alpha \) of \( \hat{G} \) in the decomposition of induced representation \( D^\pm_\alpha \uparrow \hat{G} \) is given by Frobenius reciprocity theorem [45], i.e., by the formula:

\[
f^\pm_{\alpha,\kappa} = \frac{1}{|M|} \sum_{m \in M} \chi^\ast(\Gamma^\alpha(m))\chi(D^\pm_\alpha(m)) \tag{13}
\]

Inside the BZ in the majority of cases (but not in all) the spatial part of a singlet pair is even and spatial part of a triplet pair is odd. If IR \( D^2 \) is two-dimensional, in the left coset defined by the identity element antisymmetrized square \( D^2 \) is also considered. It is seen in Table 1 that in direction \( \alpha \) and in point \( M \) is a \( D_{4h} \) group (see Figure 1b), and IRs are projective [50]. In the case of projective IRs symmetrized (antisymmetrized) characters in the first item in r.h.s. of formula (11) are written as [41, 49]:

\[
\chi[(D^K(\bar{g}) \times D^2(\bar{g}))-\chi^\ast(D^\ast(\bar{g})) \pm \omega(\bar{g}, \bar{g})\chi(D^\ast(\bar{g}^2))], \tag{14}
\]

where \( \omega(\bar{g}, \bar{g}) \) stands for the factor system of projective representation.

In addition, it may be derived from formula (11) that a usually accepted assertion that triplet (singlet) pairs have odd (even) angular momentum value is violated. For example, consider \( O_h \) group and \( k \) a general point in a BZ. In this case all even (odd) IRs appear in the decomposition for singlet (triplet) pairs with frequencies equal to their dimensions. Consider IR \( T_{1g} \) for a singlet pair and \( T_{2u} \) and \( E_u \) for triplet pairs. It is known that the even spatial part of the wavefunction of atomic term \( ^2P \) transforms as \( T_{1g} \) in \( O_h \) symmetry. In addition, the odd spatial part of atomic term \( ^3P \) splits in crystal field into \( T_{2u} \) and \( E_u \). Hence, it follows that the angular momentum \( l = 1 \) should be assigned to a singlet pair of \( T_{1g} \) symmetry, and the angular momentum \( l = 2 \) should be assigned to eventual pairs of \( T_{2u} \) and \( E_u \) symmetry.

The decompositions of symmetrized and antisymmetrized squares of IRs of the space group \( I4/mmm \) are presented in Table 1. The notations of points in a BZ are according to Figure 1. The results for points inside the BZs for groups \( I4/mmm \) and \( P4/nmm \) are the same and differ on their surfaces. The important point \( M \) for group \( P4/nmm \) is also considered. It is seen in Table 1 that in direction \( \Lambda \), even IR \( A_{2g} \) appears in the decomposition of antisymmetrized square of \( E \uparrow G \). Additionally, \( A_{1u} \) appears in the decomposition of symmetrized square of \( E \uparrow G \). Hence, it follows that in this case triplet pair with spatial part \( A_{2g} \) and singlet pair with spatial part \( A_{1u} \) are possible. In point \( Z \), where \( H = D_{4h} \) double coset defined by the identity element results in zero total momentum of a pair. In this case, spatial parts of singlet and triplet pairs are even. However, since Sr₂RuO₄ is almost a two-dimensional superconductor, these examples unlikely correspond to pairing in it, and we consider symmetry points in basal plane. Because the space inversion is an element of group \( D_{2h} \) of the wavevector \( M \) of \( I4/mmm \) BZ, the left coset defined by the space inversion is absent. Since all IRs of \( D_{2h} \) are one-dimensional, in the left coset defined by the identity element antisymmetrized square vanishes, and only singlet pairs are possible. Hence, in this case triplet Cooper pairs are forbidden by symmetry.
Table 1. Possible IRs of singlet and triplet pairs for group $14/mmm (D_{4h}^7)$ depending on the wavevector in a BZ (see Figure 1a) and IR of wavevector group $H$. Double coset representatives and the pair’s wavevectors $K$ are presented in last two columns. The results for point $M$ of group $P4/nmm (D_{4h}^7)$ are also included. Since, in a general point of a BZ all even IRs are possible for singlet pairs and all odd IRs are possible for triplet pairs, the absence of any IR on line (plane) corresponds to a point node (line of nodes).

| $k$ | IR($H$) | Singlet Pair | Triplet Pair | $d_a$ | $K$ |
|-----|---------|--------------|--------------|-------|-----|
| Planes |
| [100], [010] | all | $A_{1g} + B_{1g} + E_g$ | $A_{2u} + B_{2u} + E_u$ | $l$ | $\Gamma$ |
| [001] | all | $A_{1g} + A_{2g} + B_{1g} + B_{2g}$ | $2E_u$ | $l$ | $\Gamma$ |
| [110], [110] | all | $A_{1g} + B_{2g} + E_g$ | $A_{2u} + B_{1u} + E_u$ | $l$ | $\Gamma$ |
| lines |
| $\Sigma$ | all | $A_{1g} + B_{1g}$ | $E_u$ | $l$ | $\Gamma$ |
| $\Delta$ | all | $A_{1g} + B_{2g}$ | $E_u$ | $l$ | $\Gamma$ |
| $\Lambda$ | $A_i, B_i$ | $A_{1g}$ | $A_{2g}$ | $l$ | $\Gamma$ |
| $\Lambda$ | $E$ | $A_{1g} + B_{1g} + B_{2g} + A_{1u}$ | $A_{2u} + B_{1u} + B_{2u} + A_{2g}$ | $l$ | $\Gamma$ |
| points |
| $Z$ | $A_i, B_i$ | $A_{1g}$ | $-$ | $E$ | $(0,0,\pi) = \Gamma$ |
| $Z$ | $E$ | $A_{1g} + B_{1g} + B_{2g}$ | $A_{2g}$ | $E$ | $(0,0,\pi) = \Gamma$ |
| $M$ | $A_i, B_i$ | $A_{1g} + B_{2g}$ | $-$ | $E$ | $(\pi,\pi,0) = \Gamma$ |
| $M$ | $A_{1g(u)}, B_{1g(u)}$ | $A_{1g}$ | $B_{2g}$ | $C_{2y}$ | $K_s = (0,\pi,0)$ |
| $M$ | $B_{2g(u)}, B_{2g(u)}$ | $B_{1g}$ | $A_{2g}$ | $C_{2y}$ | $K_s = (0,\pi,0)$ |
| $M$ | $1)$ | $t_{1g}, t_{2g}$ | $A_{1g} + B_{2g} + B_{2u}$ | $A_{1u}$ | $E$ | $\Gamma$ |
| $M$ | $1)$ | $t_{3g}, t_{4g}$ | $A_{1g} + B_{2g} + A_{2u}$ | $B_{1u}$ | $E$ | $\Gamma$ |
| $Y$ | $A_i, B_i$ | $A_{1g} + B_{1g}$ | $E_u$ | $-$ | $E$ | $K_s = (0,\pi,0)$ |
| $Y$ | $A_i, B_i$ | $A_{1g} + B_{1g} + E_g$ | $-$ | $E$ | $K_s = (0,\pi,0)$ |
| $Y$ | $A_i, B_i$ | $A_{1g} \uparrow G + B_{2u} \uparrow G$ | $B_{1g} \uparrow G + B_{3u} \uparrow G$ | $\sigma_d$, $K_M$ |

1) Point $M$ of BZ of group $P4/nmm$; 2) Two-dimensional projective IRs, notations of $s$ [50].

However, in point $M$ of $14/mmm$ BZ nontrivial triplet and singlet pairs are possible. Let us consider double coset defined by the rotation $C_{2y}$ (see Figure 2a). In this case the relation (12) results in a two-electron wavevector $K = (0, \pi, 0)$, whose group is $D_{4h}$. In this case IRs of singlet and triplet pairs are different, but they all are even. However, in this case translations by some lattice vectors result in a phase factor $-1$, and this state does not correspond to the definition of a Cooper pair completely. Nevertheless, since many other symmetries in topological superconductors are broken, this unusual case may be considered in the theories of unconventional superconductivity.

In point $Y$ IRs and double coset, defined by the space inversion are the same as for direction $\Sigma$ (see Table 1), consequently possible pair functions are the same also. Though there is a non-trivial wavevector relation, corresponding to double coset, defined by $\sigma_d$ (see Figure 2b). It is seen in Figure 2b), that in this case two-electron state in $M$ has a star, consisting of two prongs. Since space inversion is an element of the wavevector group, this state is characterized by a parity. However, this state is also not completely symmetrical with respect to lattice translation, and some lattice translations result in a phase factor $-1$,
The results for point \( M \) of group \( P4/nmm \) are also included in Table 1. In this case small IRs are projective \([50]\), and formula (14) results in mixing of even and odd IRs in singlet and triplet cases (see also \([49]\)).

3. Nodal Structure and Chirality of Cooper Pair Wavefunction

General group theoretical results of the previous section may be envisaged by introducing a Cooper pair basis set as follows. According to Anderson ansatz \([39]\) for \( k \) a general point in a BZ spatial parts of singlet and triplet pairs are written by the two following formulas, respectively:

\[
\psi^s_k = \psi_k(r_1)\psi_{Ik}(r_2) + \psi_{Ik}(r_1)\psi_k(r_2) \tag{15}
\]

and

\[
\psi^t_k = \psi_k(r_1)\psi_{Ik}(r_2) - \psi_{Ik}(r_1)\psi_k(r_2), \tag{16}
\]

where \( r_1 \) and \( r_2 \) denote electron coordinates, and \( Ik \) represents the action of the space inversion on \( k \). According to the space-group representation theory \([45]\) the one-electron state in crystal is represented by the wavevector star \( \{k\} \), consisting of \( |\hat{G}| \) prongs. When acting by left coset representatives in the decomposition of \( |\hat{G}| \) relative to \( C_i \) on basis functions (15) or (16) one obtains total basis set for singlet or triplet Cooper pair, whose dimension equals to \( |\hat{G}|/2 \). One can choose pure rotation subgroup \( \hat{G}' \) of \( \hat{G} \) or any other subgroup of index 2, which contains only one of the two elements connected by the space inversion. Singlet (triplet) functions form a basis of induced representation \( P_\kappa \pm I \uparrow \hat{G}' \) of \( \hat{G} \). The projection of this reducible basis, sets on the rows of IR \( \Gamma^q \) of the whole group may be obtained making use of the standard projection operator technique \([43]\), i.e., making use of formula:

\[
\Psi^q_i = \frac{|\Gamma^q|}{|\hat{G}'|} \sum_{h_n \in \hat{G}'} \Gamma^q_{in}(h_n)h_n\psi_k. \tag{17}
\]

In the case of \( D_{4h} \) group there are eight basis pair functions for the singlet case and eight functions for the triplet case. Taking three rotations about the \( z \) axis (\( C_1 = C_{4z}, \ C_2 = C_{2z}, \) and \( C_3 = C_{4z}^3 \)) and four reflections in vertical planes (\( \sigma_1 = \sigma_y, \ \sigma_2 = \sigma_{2y}, \ \sigma_3 = \sigma_x, \) and \( \sigma_4 = \sigma_{xy} \)) as left coset representatives, one obtains reducible Cooper pair basis set for a general \( k \)-point in a Brillouin zone, shown in Figure 3. Basis functions \( \psi^s_k \) or \( \psi^t_k \) are obtained by the action of left cost representatives \( h_i \) on the functions \( \psi^s \) or \( \psi^t \) (see formulas (15) and (16)). Note that in Figure 3 all vectors have the same nonzero \( k_z \) projection.
For one-dimensional IRs the linear combinations of the basis set are unique, and Table 1 defines their nodal structure completely. The nodal structure of two-dimensional IRs depends on additional quantum numbers and was considered for triplet pairs elsewhere [23]. It was also shown that chiral basis functions for triplet pairs constructed making use complex form of IR $E_g$ [50] have vertical nodes. However, chiral even functions were not considered in a framework of a space-group approach, and one of the aims of the present work is to consider such states. On vertical planes each one of the two-dimensional IRs appear as ones. It follows from formula (13) that for $k$ a general point in a BZ $E_u$ and $E_g$ appear twice for triplet and singlet cases, respectively. Hence, it follows that for each vertical plane, two-dimensional IRs may be nodal or nodeless.

Chiral forms of IRs $E_g$ and $E_u$ on $C_4$ subgroup [50] are presented in Table 2. Since IRs are characterized by parity, their matrices for all $C_{4hi}$ groups can be easily obtained. It can be easily verified that direct product $A_{2g} \times E_{g(u)}$ equals to $E_{g(u)}$. Consequently, there are two extensions of these matrices on the left coset defined by $\sigma_1$, labeled by the sign of the left coset representative as a superscript. The matrices of element $\sigma_1$ with corresponding superscripts are also presented in Table 2.

Table 2. Matrices $D$ of IRs $E_g$ and $E_u$ for the rotation subgroup $C_4$ elements ($C_1 = C_{4z}$, $C_2 = C_{2x}$, $C_3 = C_{3z}$) and two forms of matrix for the left coset representative $\sigma_1 = \sigma_y$.

\[
\begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
\begin{pmatrix}
i & 0 \\
0 & -i
\end{pmatrix}
\begin{pmatrix}
-1 & 0 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
i & 0 \\
0 & i
\end{pmatrix}
\begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}
\begin{pmatrix}
0 & -1 \\
-1 & 0
\end{pmatrix}
\]

The pairs’ functions of $E_g$ and $E_u$ symmetry constructed from the basis set shown in Figure 3 making use of projection operators (17) are presented in Table 3. It is seen from Table 3 that the basis functions $\psi_{C_1}$, $\psi_{C_2}$ and $\psi_{C_3}$ of the first row of $E_{g(u)}$, obtained by the action of $\pi/2$, $\pi$ and $3\pi/2$ rotations on the initial function $\psi_{g(u)}$, acquire phase factors $i$, $-1$ and $-i$, respectively, i.e., correspond to magnetic quantum number $m = 1$. Basis functions of the second row, obtained by the action of the same rotations on the function $\psi_{g(u)}$, acquire phase factors $-i$, $-1$ and $i$ and correspond to magnetic quantum number $m = -1$. In the Ginzburg–Landau theory the SOP is identified with the wavefunction of a Cooper pair, which includes all pairs in the condensate. In the space-group approach this general
pair function is obtained when the electron wavevector $k$ runs in the sector $0 \leq \theta \leq \pi/4$ (see Figure 3), and other sectors are brought about by left coset representatives. Suppose, that there is a phase winding $e^{i\mu\theta}$ in the first sector. It is natural to suppose that due to topological reasons $\mu = m$. In this case the functions in the sectors labeled by odd numbers in Figure 3 may be considered as possessing angular momentum projection $m = 1$. It is clear that reflection $\sigma_1$ changes the direction of phase winding in sector 8 relative to sector 1, and the functions of even sectors possess angular momentum projection $m = -1$. In this technique the basis functions and their phases in the other sectors are obtained group theoretically by the action of left coset representatives.

Table 3. Pair functions for two-dimensional IRs $E_8$ and $E_6$ of group $D_{4h}$. $\psi^{(f)}$ is a pair function corresponding to Anderson ansatz [39] in a basis domain of a BZ (see formulas (15) and (16) for singlet and triplet cases, respectively). The other functions are obtained by the action of point group elements on $\psi^{(f)}$ (see Figure 3). The superscript corresponds to the sign of matrix of left coset representative $\sigma_1$ (see Table 2).

| IR $^1$ | Pair Function $^2$ | Nodal Planes |
|---------|---------------------|-------------|
| $E_{8,1}^+$ | $\psi^r + i\psi_{C1} - \psi_{C2} - i\psi_{C3}$ | [100][001] |
| $E_{8,-1}^+$ | $\psi^r - i\psi_{C1} + \psi_{C2} + i\psi_{C3}$ | [010], [001] |
| $E_{6,1}^+$ | $\psi^r - \psi_{C1} + \psi_{C2} + i\psi_{C3}$ | [010] |
| $E_{6,-1}^+$ | $\psi^r + \psi_{C1} - \psi_{C2} + i\psi_{C3}$ | [010] |

$^1$ Superscript denotes additional label (see text), and last subscript denotes the row of IR that corresponds to magnetic quantum number $m$. $^2$ Notation of group elements according to Figure 3.

Basis functions of two rows of two-dimensional IRs are localized at different sectors in $k$-space and meet at vertical planes, where interference of pair functions occurs. In order to envisage such interference, the wavefunctions of pairs in a finite number of points were represented by normalized sum of real and imaginary Gaussians. Within the sectors the phases at neighboring points almost coincide, and constructive interference takes place. At the boundaries of the sectors, both constructive and destructive interference of the wavefunctions is possible. When squaring modulus of the complex function at every point we obtain the structure of SOP in the plane normal to the $k_z$-axis. Nodal structures of IRs $E_{8}^+$ and $E_{6}^+$, obtained by this numerical method presented in Figure 4, have nodes in plane [100] and deepen in diagonal planes. Figure 5 shows the same for $E_{8}^-$ and $E_{6}^-$, where line of nodes is in plane [010]. Nodes in vertical coordinate planes are defined by additional quantum number, i.e., the sign of matrix $\sigma_1$ (see Table 2). Nodes and deeps in diagonal vertical planes are the result of phase differences between two complex functions. In order to envisage the origin of these peculiarities, the phases of basis functions with $m = 1$ and $m = -1$ for $E_{8}^+ (u)$ and $E_{8}^-(u)$ are presented in Figures 6 and 7, respectively. Due to the same choice of left coset representative (denoted by superscript “+” or “−”) the results for $E_{8}^+$ and $E_{6}^+$ with the same superscripts coincide, and subscripts are dropped in Figures 6 and 7. In Figure 6 near the positive direction of $x$-axis the phases of functions $E_{8}^+$ at $\theta = \delta$ and $E_{8}^-$ at $\theta = -\delta$ are the same ($\delta$ denotes small positive angle) and the phase $-2\pi$ was added to the function $E_{8}^-$ for convenience. On a clockwise path from $\theta = 360^\circ - \delta$ to $\theta = 90^\circ$ the phase winding of $E_{8}^+$ function is $3/2\pi$, and the total phase is $-\pi/2$. The phase winding on the counter-clockwise of the function $E_{8}^+$ on the path from $\theta = \delta$ to $\theta = 90^\circ$ is $\pi/2$. Thus, the total phase difference is $\pi$, and interference is destructive at $\theta = 90^\circ$. Similar estimation at $\theta = 45^\circ$ results in phases of the first and second function $\pi/4$ and $-\pi/4$, respectively.
respectively, resulting in constructive interference of real parts, destructive interference of imaginary parts and deep (not node) of SOP. Figure 7 shows the $E^-$ case in which reflection $\sigma_1$ changes the phase, and the interference pattern is rotated by $90^\circ$. Note that a similar interference pattern was obtained for complex odd IR $E_u$ without phase winding [23].

Figure 4. SOP of chiral $E^+_{g}$ and $E^+_{u}$ pair functions (see Table 3) Note that $E^+_{g}$ is nodal and $E^+_{u}$ is nodeless in basal plane.

Figure 5. SOP of chiral $E^-_{g}$ and $E^-_{u}$ pair functions (see Table 3). Note that $E^-_{g}$ is nodal and $E^-_{u}$ is nodeless in basal plane.

Figure 6. Phases of two basis functions of IR $E^+_{g(u)}$. Superscript + corresponds to the superscript of matrix $D^{+}(\sigma_{1})$ (see Table 2) Subscripts in figure correspond to magnetic quantum numbers.
work are similar to commonly used chiral functions (1), (4) and (5), and it is important (see also Table 2). Continuing to apply the method of projection operators, we pass to the

d
The function

follows that application of the standard projection operator technique [43] and chiral form of IR (see Table 2). Thus, we obtain the function with

m

element

σ

are required [52]. Consider the application of the technique of the present work to the structures of multi-dimensional IRs, additional quantum numbers, specifying the matrix, nodes and nonunitary structure. It should be noted that authors of these models did not

5. Discussion

Thus, even and odd two-dimensional complex IRs have one vertical nodal plane [100] or [010]. The nodal and nodeless planes are interchanged when multiplying by characters of IR \(A_{2g}\), so the vertical nodal planes of \(E_g\) and \(E_u\) are topologically unstable according to the definition of Kobayashi et al. [51]. The basis functions of \(E_g\) and \(E_u\) symmetry in chiral representations have angular momentum projection \(m = \pm 1\). The essential difference between the structures of \(E_g\) and \(E_u\) appears in the basal plane (see Table 1), where \(E_u\) is nodeless, and nodes of \(E_g\) are topologically stable.

4. Weak Spin-Orbit Coupling

In a weak spin orbit coupling case total pair function is a direct product of its spin and spatial parts. In \(D_{4h}\) symmetry OSP spin function \(\hat{z}\) belongs to IR \(A_{2g}\). Multiplication of \(E_u\) by \(A_{2g}\) results in \(E_u\) also. Since characters of \(A_{2g}\) equal \(-1\) for all elements of the left coset with respect to \(C_{4h}\), it follows that such a multiplication results in an interchange of \(E_u^+\) and \(E_u^-\) cases. The ESP spin functions \(\hat{x}\) and \(\hat{y}\) belong to \(E_g\) in its standard form. In chiral representation of \(E_g\) [50] its basis triplet spin functions are linear combinations \(S_1^1 = (\hat{x} + i\hat{y})/\sqrt{2}\) and \(S_{-1}^1 = (\hat{x} - i\hat{y})/\sqrt{2}\). Decomposition of direct product \(E_g \times E_u\) results in the states \(A_{1u} + B_{1u} + A_{2u} + B_{2u}\), which are similar to helical states (2), (3). Multiplication of the \(E_g\) spin part by the spatial part belonging to any odd one-dimensional IR results in \(E_u\), which corresponds to chiral OSP state. In the case of \(\text{Sr}_2\text{RuO}_4\) singlet spin state of \(A_{1g}\) symmetry and triplet OSP state of \(A_{2g}\) symmetry are considered. Thus, in \(D_{4h}\) symmetry total functions of chiral singlet and triplet OSP pairs belong to IRs \(E_g\) and \(E_u\), respectively.

5. Discussion

Group theoretical basis functions with topological phase winding of the present work are similar to commonly used chiral functions (1), (4) and (5), and it is important to establish the reasons for the appearance of significant differences, namely vertical line nodes and nonunitary structure. It should be noted that authors of these models did not consider matrices, whose basis is formed by these functions. However, to define nodal structures of multi-dimensional IRs, additional quantum numbers, specifying the matrix, are required [52]. Consider the application of the technique of the present work to the functions (1). It is immediately verified that reflection \(\sigma_y\) interchanges two functions (1). The function \(d_{2x} + id_{2y}\) is a good basis function for phase winding in the first sector with \(m = 1\). In addition, the action of rotational elements of \(C_{4z}\) on this function result in the same phase factors as elements of the first row and first column of \(E_g\) in chiral form [50] (see also Table 2). Continuing to apply the method of projection operators, we pass to the element \(\sigma_y\), which transforms the function \(d_{2x} + id_{2y}\) into \(d_{2x} - id_{2y}\) and interchanges rows of IR (see Table 2). Thus, we obtain the function with \(m = -1\) in the 8 sector. Hence, it follows that application of the standard projection operator technique [43] and chiral form of IR \(E_g\) [50] to the first of functions (1) results in the same phase structure as shown in

Figure 7. Phases of two basis functions of IR \(E_{g(u)}^-\). Superscript \(\mp\) corresponds to the superscript of matrix \(D^{-}(\sigma_2)\) (see Table 2) Subscripts in figure correspond to magnetic quantum numbers.
Figures 6 and 7 and, consequently, the same nodal structure, as obtained in the present work in a space-group basis set. It should be noted that according to the Mackey–Bradley theorem, two-dimensional IRs appear twice in a total two-electron basis decomposition. It is immediately verified that multiplication of $E_g$ by $B_{1g}$ results in $E_g$ also, but the magnetic quantum numbers are swapped. Thus, starting projection on the first row from $d_{z^2} - i d_{xy}$ we obtain that functions with $m = -1$ are in the first row of matrix $E_g$ and in odd sectors in $k$-space (see Figure 2). In this case a total phase structure is opposite to that shown in Figures 6 and 7. Hence, it follows that the sum of these two basis sets results in nodeless and unitary (i.e., probabilities of $m = 1$ and $m = -1$ are equal in all $k$-space) SOP structures. However, since experimental results indicate that SOP of Sr$_2$RuO$_4$ is chiral, nodal and nonunitary, we may conclude that this case corresponds to one chiral two-dimensional IR considered in the present work. The structure (4) is similar to (1), but the chiral model form (5), which is also written as $B_{1g} + iB_{2g}$, consists of two different IRs and has no group theoretic analog.

Since the primary detected odd spatial parity [5,6] of unconventional superconductor Sr$_2$RuO$_4$ is under debate [11,13], the establishing of a connection between parity and multiplicity is very essential. In the present work, making use of Anderson ansatz [39] and the Mackey–Bradley theorem [46,47], possible pair symmetries on the dependence of the wavevector $k$ in a BZ are obtained for symmetry group $D_{4h}$. In the majority of cases the wavefunction of a singlet pair is even, and that of a triplet pair is odd (see Table 1). Since in the space-group theory one-electron states are characterized by a wavevector star [45,47], possible pair symmetries with the certain parity may also include states with nonzero total momentum $K$. In point $M$ for $14/nmm$ group, in the case of pairing of electrons $k_M$ and $C_{2y}k_M$, possible symmetries of singlet pairs are $A_{1g} + B_{1g}$ and of triplet pairs are $A_{2g} + B_{2g}$. The wavevector $K$ of these states equals $(0, \pi, 0)$. These states are not completely translation invariant, i.e., some lattice transitions result in a phase factor 1, but some translations result in a phase factor $-1$. In addition, for $k$ in point $Y$ there are pair states denoted as $A_{g} \uparrow G$ and $B_{2u} \uparrow G$ for singlet case and $B_{1g} \uparrow G$ and $B_{3u} \uparrow G$ for triplet case. These pairs are not translation invariant, but characterized by parity. In addition to the symmetries broken in unconventional superconductors such two-electron states represent another possibility, i.e., pairs states with partially broken translation symmetry. Thus, triplet pairs in $14/nmm$ symmetry, being odd in general points of a BZ, may exhibit even spatial part in some symmetrical points of a BZ. Hence, it follows that recent experiments [11] manifesting the contribution of even pairs in Sr$_2$RuO$_4$ may be explained in a triplet pairing scenario. The even triplet pairing and odd singlet pairing cases are referred to as odd frequency pairing [53].

In point $M$ for non-symmorphic space group $P4/nmm$ in addition to the standard relation between multiplicity and parity of a Cooper pair, singlet odd pairs and triplet even pairs are possible.

Chiral states constructed making use of the complex form of IRs $E_{g(u)}$ [50] have a nodal plane in one of the vertical coordinate planes and deeps in diagonal planes. The position of the vertical nodal plane depends on an additional quantum number—the sign of matrix for reflection $\sigma_y$. In these states the basis functions connected by rotations about the $k_z$ axis acquire phase factors corresponding to magnetic quantum numbers $m = \pm 1$. When adding a continuous gauge phase $e^{i\theta}$ in the range $0 \leq \theta \leq \pi/4$ one obtains total phase winding group theoretically. The transformations of $E_g$ and $E_u$ pairs by rotations of the $C_4$ subgroup are the same. This assertion is in agreement with the general conclusion of the present work, that parity and angular momentum of a pair are not connected with each other. For example, in $O_h$ symmetry singlet pairs of $T_{1g}$ symmetry are possible, but it is also the symmetry of $3P$ term of $p^2$ configuration with angular momentum $l = 1$. This result differs from the assertion of phenomenological approaches based on spherical functions, that even (odd) values of momentum correspond to even (odd) inversion symmetry. However the present result does not contradict with general group theory [43]. Phenomenological chiral functions (1) and (4) arise from spherical function in $k$-space and are nodeless in
vertical planes. Group theoretical chiral functions have vertical lines of node and deeps and agree with experimental results [20–22]. Thus, the only robust difference between nodal structures of $E_g$ and $E_u$ states is nodal structure in the basal plane.

6. Conclusions

Making use of the Mackey–Bradley theorem on symmetrized squares and Anderson ansatz for the Cooper pair, group theoretical investigation of possible pairing states in $D_{4h}$ symmetry was performed. It was obtained that for non-symmorphic group $P4/mmm$ of Fe-pnictide superconductors at point $M$ of a BZ, odd singlet and even triplet pairs are possible. It was also obtained that triplet pairs with an even spatial part are possible in $k_z$ direction and in points $M$ and $Y$ of a BZ for the space group $I4/mmm$. For the two latter cases, pairing of equivalent electrons with total pair momentum in symmetry points of BZ other than $I$ is proposed. Thus, the recent results [11–13], which revealed even features of previously considered as odd SOP of $Sr_2RuO_4$, may be explained by the presence of triplet pairs with even spatial structure in some points of a BZ. It was shown that even and odd chiral states with angular momentum projection $m = \pm 1$ have nodes and deeps in vertical planes, which corresponds to the experimental data. The only robust difference between nodal structures of $E_g$ and $E_u$ takes place in the basal plane, where $E_g$ is nodal and $E_u$ is nodeless.

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