Superconducting states in the tetrahedral compound PrOs$_4$Sb$_{12}$

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We find possible superconducting states for tetrahedral ($T_h$) symmetry crystals with strong spin-orbit coupling using Landau theory. Additional symmetry breaking within the superconducting state is considered. We discuss nodes of the gap functions for the different states, secondary superconducting order parameters and coupling to the elastic strain. By comparing our results to experiments, we find that superconductivity in PrOs$_4$Sb$_{12}$ is best described by the three-dimensional representations of point group $T_h$.

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I. INTRODUCTION

The discovery of superconductivity in the heavy fermion compound PrOs$_4$Sb$_{12}$ has spawned a flurry of experimental[1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19] and theoretical[20,21,22,23,24,25] activity. PrOs$_4$Sb$_{12}$ is the first Pr-based heavy fermion superconductor and the first among the family of rare-earth filled skutterudite compounds. The onset of superconductivity occurs at $T_c = 1.85$ K; an additional phase transition is observed as an anomaly in the specific heat[20] and magnetisation[21] at $T_c = 1.75$ K. Thermal conductivity measurements in a rotating magnetic field revealed the presence of nodes and a lowering of the symmetry of the gap function from four-fold (A-phase) to two-fold (B-phase) at $T_c$. Even more intriguing is the observation of broken time-reversal symmetry in the superconducting (SC) state[21]. By all indications, PrOs$_4$Sb$_{12}$ is a new kind of unconventional superconductor.

A central issue in the study of unconventional superconductivity is the symmetry of the SC order parameter. The phenomenological Landau theory approach is particularly useful when little is known about the mechanism of superconductivity at a microscopic level, and is ideal for describing multiple phase transitions as is the case for PrOs$_4$Sb$_{12}$. The starting point is knowledge of the crystal symmetry group, according to whose representations order parameters are classified. The outcome of this approach is detailed knowledge of all possible phase diagrams and symmetry properties of the SC state, including nodes of the gap function[26]. Phenomenological theory can also predict the order of the phase transition. While the normal-to-SC phase transition is expected to be second order since third-order terms in the Landau potential expansion are prohibited because of gauge symmetry, this is not generally the case for phase transitions within the SC state.

Several theoretical models of the SC order parameter in PrOs$_4$Sb$_{12}$ have been proposed in order to account for the experimental data. Goryo suggested different combinations of s- and d-wave gap functions for the A- and B-phases[22] in order to account for the change in symmetry observed in the thermal conductivity experiment[23]. The A-phase was assumed to have an anisotropic s-wave gap function that has six minima along the [100], [010], and [001] directions. In the B-phase, an $s + id_{x^2-y^2}$-wave combination was proposed. Different $s + g$-wave basis functions were proposed by Maki et al. for both states[23]. An f-wave pairing state with weak spin-orbit coupling was proposed by Ichioka et al. to describe a state with point nodes on all three axes[24]. Finally, Miyake et al. considered a microscopic model based on quadrupolar fluctuations and nesting in the Fermi surface, and argued in favour of $p_x + ip_y$-wave pairing[25].

While the models mentioned above may describe particular experiments, they can only be considered as empirical. There are at least two fundamental shortcomings: (i) the models are in fact based on the assumption that the point group crystal symmetry is $O_h$. PrOs$_4$Sb$_{12}$ has lower $T_h$ symmetry (space group $I4_3$, $T_h$); (ii) there is no physical reason why the system should choose one particular combination of the basis functions of the irreducible representation of the symmetry group over the others. Strictly speaking, the theory allows all basis functions to contribute to the gap function. Moreover, the coefficients in the such combinations in general depend on the external conditions (temperature, magnetic field, etc.). Only such a general state is thermodynamically stable and occupies a finite region of the phase diagram.

In this paper we use the Landau theory approach to classify SC phases for tetrahedral ($T_h$) crystals, including those which may be reached by additional symmetry breaking within the SC state. We use the strong spin-orbit coupling limit in which the spin rotation symmetry is broken[26,29].

The first attempt to accomplish such a classification was made by Gufan[30]. In Sec. II of this paper we use a different approach and reproduce most results of Ref. 30 for $T_h$ symmetry. In addition, we discuss the basis functions of the irreducible representations, the gap function nodes and the orders of the phase transitions between different SC states. In Sec. III we consider secondary SC order parameters which influence the nodes of the gap functions. In Sec. IV the coupling between the SC order parameters and elastic strain is discussed. Sec. V is devoted to matching the experimental data with the states...
found theoretically. Sec. VI summarizes the paper.

II. CLASSIFICATION OF SUPERCONDUCTING STATES

A procedure for constructing SC classes and finding the gap nodes with strong spin-orbit coupling was originally proposed by Volovik and Gor’kov (VG) who listed all SC states which can be reached from the normal state by a second order phase transition for \( O_h \), \( D_{4h} \) and \( D_{6h} \) crystals. One begins by classifying possible order parameters according to the representations of the crystal point group. In systems with inversion symmetry, all representations have a definite parity. Those with even parity must be matched with singlet pairing of the spin states for the pair wavefunction to be antisymmetric; likewise odd parity representations are matched with triplet spin states. For each parity, the group \( T_h \) has a one dimensional representation \( A \), a two dimensional representation \( E \), which is reducible to two one-dimensional representations that are complex conjugate, and a three dimensional representation \( T \).

The SC gap function is a \( 2 \times 2 \) matrix in pseudospin space given by \( \Delta(k) = i \sigma \psi(k) \) for singlet pairing and by \( \Delta(k) = i(d(k)\sigma) \sigma \psi \) for triplet pairing, where \( \sigma = (\hat{x}, \hat{y}, \hat{z}) \) are Pauli matrices. \( \psi(k) \) is an even scalar function and \( d(k) \) is an odd pseudovector function. \( \psi(k) \) and \( d(k) \) are expressed in terms of the components of the order parameter \( \eta_i \) as \( \psi(k) = \sum_i \eta_i \psi_i(k) \) and \( d(k) = \sum_i \eta_i d_i(k) \). Here \( \psi_i(k) \) and \( d_i(k) \) are the basis functions for the even (spin-singlet case) and odd (spin-triplet case) irreducible representations of the point group, respectively.

The method of finding the SC states implemented by VG is to construct a Landau energy functional of \( \eta_i \) for each order parameter that is invariant under \( G \times U \times K \), where \( G \) is the point group, \( U \) is gauge symmetry and \( K \) is time-reversal, and analyse its extrema. In order to account for all possible phase diagrams, a very large number of terms must be included and the analysis of such a cumbersome model is tedious at best. In practice, terms are restricted to those needed to describe the normal to superconducting phase transition, while states resulting from additional phase transitions within the SC state must be found by other methods. The VG approach can be applied \( T_h \) crystals. However, here we use even an easier method. We use the fact that \( T_h \) is a subgroup of \( O_h \). Therefore we start with the results for the symmetry groups of SC classes obtained by VG for \( O_h \) symmetry and reduce them by removing the symmetry elements that are absent in the normal state of \( T_h \) symmetry.

We consider additional symmetry breaking within the SC state by constructing effective Landau functionals of effective order parameters, which describe the phase transitions between SC states with a group-subgroup relation. This procedure is straightforward, since the symmetry group of a SC state is discrete (the continuous gauge symmetry is already broken). In the following, we consider the two dimensional representation in detail, while only the results are given for the three dimensional representation.

Our results are summarized in Table I. It lists all possible SC states for both even parity and odd parity which are possible if only a single irreducible representation is present. We define the relations between the components of the order parameters, the symmetry of the SC state, and the structure of nodes in the gap function. We make the distinction between accidental, approximate and rigorous nodes. Accidental nodes occur in empirical models when a particular form of the gap function is chosen a priori, such as that proposed in Ref. 22. Such nodes cannot be stable because even small contributions of functions with the same symmetry remove them immediately. Accidental nodes are unphysical and so we disregard them. Approximate nodes are a property of all possible basis functions which can be constructed for a given representation. These nodes may be removed when admixtures of other representations, which couple to the SC state as secondary order parameters, are taken into account, thus leaving only rigorous nodes required by the symmetry of the SC state. The secondary order parameters are proportional to the third power of the primary order parameter. Hence, the experiments that probe the symmetry of the gap function close to \( T_c \) may find the approximate nodes, while only the rigorous nodes remain when \( T \to 0 \). A more detailed discussion of the secondary order parameters is given in Sec. III.

A. 1D representation \( A_g,u \)

The analysis of the one-dimensional representations \( A_g \) and \( A_u \) is straightforward. Only gauge symmetry is broken and there are no nodes. The symmetry of the SC state is \( T \times K \). In the lowest order in \( k \), the basis function for the singlet channel \( \psi(k) \) is constant on the Fermi surface and for the triplet channel \( d(k) \sim k_x \hat{x} + k_y \hat{y} + k_z \hat{z} \).

B. 2D representation \( E_g,u \)

We choose the basis functions of the two-dimensional representations \( E_g \) and \( E_u \) in complex form as in Ref. 20:

\[
\psi_1 \sim k_x^2 + \varepsilon k_y^2 + \varepsilon^2 k_z^2, \quad \psi_2 \sim k_x^2 + \varepsilon^2 k_y^2 + \varepsilon k_z^2; \\
\mathbf{d}_1 \sim k_x \hat{x} + \varepsilon k_y \hat{y} + \varepsilon^2 k_z \hat{z}, \quad \mathbf{d}_2 \sim k_x \hat{x} + \varepsilon k_y \hat{y} + \varepsilon k_z \hat{z}
\]

where \( \varepsilon = \exp(2\pi i/3) \). With this choice of the basis functions, the order parameter has the following trans-
TABLE I: SC states described by one irreducible representation of the point group $T_h$. The relative magnitudes and phases of the components of the order parameter are defined in the first column. The symmetry groups of the SC states are listed in the second column. Approximate and rigorous nodes of the gap function for even parity are listed in the third and fourth columns, similarly for odd parity in the fifth and sixth columns. The word ‘same’ is used when rigorous nodes coincide with approximate nodes. The numbers in parentheses in the fifth column indicate whether one or both gaps have nodes.

| State          | Symmetry | Approximate nodes | Rigorous nodes | Approximate nodes | Rigorous nodes |
|----------------|----------|-------------------|----------------|-------------------|----------------|
| $(1, 0)$       | $T(D_2)$ | 8 points $(111)$   | same           | 8 points $(111)$  | (1)           |
| $(\phi_1, \phi_2)$ | $D_4 \times K$ | 8 points $(111)$ | none           | $E_u$            | none           |
| $(\eta_1, \eta_2)$ | $D_2$    | 8 points $(111)$   | none           | $E_u$            | none           |
| $(1, 0, 0)$    | $D_2(C_2) \times K$ | 2 lines $k_y = 0, k_z = 0$ | same          | 2 points $(100)(2)$ | same          |
| $(1, 1, 1)$    | $C_3 \times K$ | 6 points $(001)$  | none           | none              | none           |
| $(1, i, \epsilon^2)$ | $C_3(E)$ | 6 points $(001)$, 2 points $(111)$ | 2 points $[111]$ | 2 points $[111](1)$ | same          |
| $(\eta_1, i|\eta_2|, 0)$ | $D_2(E)$ | 1 line $k_z = 0, 2$ points $(001)$ | same          | $T_u$            | none           |
| $(\eta_1, \eta_2, 0)$ | $C_2(E)$ | 1 line $k_z = 0, 2$ points $(001)$ | same          | $T_u$            | none           |
| $(\eta_1, i|\eta_2|, \eta_3)$ | $C_2'(E)$ | 6 points $(001)$  | none           | none              | none           |
| $(\eta_1, |\eta_2|, \eta_3)$ | $K$     | 6 points $(001)$   | none           | none              | none           |
| $(\eta_1, \eta_2, \eta_3)$ | $E$     | 6 points $(001)$   | none           | none              | none           |

where $C_2$ stands for any of the twofold rotations in $T_h$, and $C_3$ is a $2\pi/3$ rotation about the [111] direction, and $U(\theta)$ is a gauge transformation.

In Table I, three states are listed for the two-dimensional representations of $T_h$. These differ from the $O_h$ states $(1,0)$, $(1,1)$ and $(1,-1)$. As shown below, the extra freedom in the phase and magnitude of the last two states of $T_h$ arise from terms in the free energy which are allowed under $T_h$ but not $O_h$.

The SC state $(1,0)$ in $O_h$ corresponds to the group $D_2$ as

$$O(D_2) = \{ D_2, 2C_4^0 K, 2C_4^0 U(2\pi/3)K, 2C_4^0 U(4\pi/3)K, 2C_4^0 K, 2C_4^{xyz} U(2\pi/3)K, 2C_4^{xyz} U(4\pi/3)K, 4C_4 U(\pi/3), 4C_4 U(2\pi/3) \}.$$  \hspace{1cm} (3)

where $D_2$ is the group of two-fold rotations about the [100], [010], and [001] axes. In $T_h$, the remaining symmetry elements are

$$T(D_2) = \{ D_2, 4U(\pi/3)C_3, 4U(2\pi/3)C_3^2 \}.$$  \hspace{1cm} (4)

Considering the symmetry groups of the states $(1,1)$ and $(1,-1)$ in $O_h$, which are $D_4 \times K$ and $D_4(D_2) \times K$ respectively, we notice that they both reduce to the same symmetry $D_2 \times K$ in $T_h$. Moreover, it follows from (2) that this symmetry does not fix the relation between the phases $\phi_1$ and $\phi_2$ of the OP components $\eta_1,2 = \eta_1,2 \exp(i\phi_1,2)$, but the magnitudes are equal $|\eta_1| = |\eta_2|$. Therefore, we denote this state as $(\phi_1, \phi_2)$. This also may be verified from the following Landau model which describes the $E_u$ representation of $T_h$:

$$F = \alpha(|\eta_1|^2 + |\eta_2|^2) + \beta_1(|\eta_1|^4 + |\eta_2|^4) + 2\beta_2|\eta_1|^2|\eta_2|^2 + \gamma_1|\eta_1^3\eta_2^3 + \eta_2^3\eta_1^3| + \gamma_2|\eta_1^3|\eta_2^3 - \eta_2^3|\eta_1^3|,$$  \hspace{1cm} (6)

where $\alpha, \beta_1, \beta_2, \gamma_1$, and $\gamma_2$ are phenomenological parameters. The last two terms reduce to $2\gamma_1|\eta_1|^3|\eta_2|^3\cos(3\phi) + 2\gamma_2|\eta_1|^3|\eta_2|^3\sin(3\phi)$, where $\phi \equiv \phi_1 - \phi_2$. Thus the equilibrium value of $\phi$ depends on the (generally temperature dependent) ratio $\gamma_1/\gamma_2$. In contrast, in $O_h$ symmetry the $\gamma_2$ term is prohibited, hence $\phi$ is fixed to be either 0 [for $(1,1)$ state] or $\pi$ [for $(1,-1)$ state].

The gap function of the $(\phi_1, \phi_2)$ state in the singlet channel is

$$\Delta(k) \sim \cos(\phi/2)k_x^2 + \cos(\phi/2 + 2\pi/3)k_y^2$$  \hspace{1cm} (7)

and in the triplet channel,

$$\Delta(k) \sim \cos^2(\phi/2)k_x^2 + \cos^2(\phi/2 + 2\pi/3)k_y^2$$  \hspace{1cm} (8)

We would like to stress that the state $d_{x^2-y^2}$ and its equivalents, obtained by permutations of $x, y$, and $z$, are not stable in $T_h$. Instead, they are replaced by the more general state $(\phi_1, \phi_2)$ with the gap function $\Delta(k)$.
FIG. 1: Second order phase transitions among states of the $E_g$ and $E_u$ representations of $T_h$.

Normal state

\[ (1, 0) \quad (\phi_1, \phi_2) \quad (\eta_1, \eta_2) \]

In $O_h$, the states $(1, 0)$, $(1, 1)$, and $(1, -1)$ are connected to the normal state by a second order phase transition. Since up to fourth order terms, the model coincides with that of $O_h$, we conclude that the states $(1, 0)$ and $(\phi_1, \phi_2)$ can be reached from the normal state in $T_h$ by a second order phase transition.

There is a third state which can be described by the $E$ representation in $T_h$. Its symmetry group is $D_2$ (time reversal is broken), which is a common subgroup of both $T(D_2)$ and $D_2 \times K$. As is seen from the factor group $T(D_2)/D_2$ is isomorphic to the cyclic group $C_3$ and thus third order terms are allowed in the effective free energy describing the $(1, 0) \rightarrow (\eta_1, \eta_2)$ transition. This implies that it cannot be second order. The effective free energy is a functional of the effective order parameter $\eta_2$,

\[
F_{eff}(1, 0) \rightarrow (\eta_1, \eta_2) = \tilde{\alpha}|\eta_2|^2 + \tilde{\gamma}_1(\eta_2^4 + \eta_2^6) + i \tilde{\gamma}_2(\eta_2^6 - \eta_2^4) + \beta|\eta_2|^4 \tag{9}
\]

On the other hand, a second order transition $(\phi_1, \phi_2) \rightarrow (\eta_1, \eta_2)$ is possible. This transition is described by an effective order parameter $\delta \equiv |\eta_1| - |\eta_2|$. Third order terms are prohibited in the effective free energy because of time reversal symmetry,

\[
F_{eff}(\phi_1, \phi_2) \rightarrow (\eta_1, \eta_2) = \alpha'|\delta|^2 + \beta'|\delta|^4 \tag{10}
\]

There are no other states described by the $E$ representation alone, because the basis functions are invariant with respect to all symmetry operations of $D_2$ group and there are no other symmetry groups containing $D_2$.

C. 3D representation $T_{h,u}$

The lowest order basis functions for the $T_g$ representation of $T_h$ are ‘d-wave’ (i.e. second order in $k$),

\[
\psi_1 \sim k_y k_z, \quad \psi_2 \sim k_z k_z, \quad \psi_3 \sim k_x k_y, \quad \psi_4 \sim k_y k_x
\]

while for the $T_u$ representation the lowest order basis functions are ‘p-wave’, and there are two independent sets of them,

\[
d_1 \sim ak_y\hat{z} + bk_z\hat{y}, \quad d_2 \sim ak_z\hat{x} + bk_y\hat{z}, \quad d_3 \sim ak_x\hat{y} + bk_y\hat{x}
\]

Here $a$ and $b$ are arbitrary numbers, in contrast to $O_h$, which fixes $b = -a$ in $T_{hu}$ representation and $b = a$ in $T_{du}$ representation. It follows that the order parameter transforms as

\[
C_2^g(\eta_1, \eta_2, \eta_3) = (-\eta_1, -\eta_2, \eta_3), \quad C_3^{11}(\eta_1, \eta_2, \eta_3) = (\eta_2, \eta_3, \eta_1), \quad K(\eta_1, \eta_2, \eta_3) = (\eta_1^2, \eta_2^2, \eta_3^2), \quad U(\theta)(\eta_1, \eta_2, \eta_3) = e^{i\theta}(\eta_1, \eta_2, \eta_3). \tag{13}
\]

To find the SC states of the three dimensional representation, we again use the $O_h$ states as a starting point.

For $O_h$, there are four states accessible by a second order phase transition from the normal state: $(1, 0, 0)$, $(1, i, 0)$, $(1, 1, 1)$ and $(1, \varepsilon, \varepsilon^2)$, with symmetries

\[
D_4(C_4) \times K = \{ E, C_4^x, 2C_4^x, 4U(\pi)(C_4^z) \} \times K, \quad D_4(E) = \{ E, U(\pi)C_4^x, 2U(\pm \pi)C_4^z K, U(\pi)C_4^x K, U(\pm \pi)C_4^z K, \}
\]

\[
D_3(3C) \times K = \{ E, 2C_3, 3U(\pi)C_2^{x,y} \} \times K, \quad D_3(E) = \{ E, U(4\pi/3)C_3, U(2\pi/3)C_3, C_2^{x,y} K, U(2\pi/3)C_2^{x,y} K, U(4\pi/3)C_2^{x,y} K \} \tag{14}
\]

respectively. Here $E$ is the identity element. Reducing these groups, we find the following classes for $T_h$:

\[
D_2(C_2) \times K = \{ E, C_2^x, U(\pi)(C_2^y) \} \times K, \quad D_2(E) = \{ E, U(\pi)C_2^x, C_2^x K, U(\pi)C_2^y K \}
\]

\[
C_3 \times K = \{ E, C_3, C_2^z \} \times K, \quad C_3(E) = \{ E, U(4\pi/3)C_3, U(2\pi/3)C_3 \} \tag{15}
\]

We notice that the $D_2(E)$ symmetry actually does not require $|\eta_1| = |\eta_2|$. Hence, the state $(1, i, 0)$ is not stable in $T_h$. Instead, it is replaced by the state $(|\eta_1|, i |\eta_2|, 0)$. A direct second order normal-to-$|\eta_1|, i |\eta_2|, 0)$ transition is possible in $T_h$. These findings are also evident in the form of the Landau potential for the 3D order parameter. In order to display the $T_h$ (but not $O_h$) symmetry, a Landau model for $T_g$ and $T_u$ must include at least sixth order terms, as in the case of $E_g$ and $E_u$. These sixth order terms are composed of five linearly independent invariants:

\[
|\eta_1|^6 + |\eta_2|^6 + |\eta_3|^6, \quad |\eta_1|^2|\eta_2|^2|\eta_3|^2, \quad (|\eta_1|^2 + |\eta_2|^2 + |\eta_3|^2)(\eta_1^2\eta_2^2 + \eta_2^2\eta_3^2 + \eta_3^2\eta_1^2 + c.c.), \quad (|\eta_1|^4|\eta_2|^2 + |\eta_2|^4|\eta_1|^2 + |\eta_1|^4|\eta_2|^2) \pm (|\eta_1|^2|\eta_2|^4 + |\eta_2|^2|\eta_1|^4 + |\eta_1|^2|\eta_2|^4), \quad (\eta_1^4\eta_2^2 + \eta_2^4\eta_3^2 + \eta_3^4\eta_1^2) \pm (\eta_1^2\eta_2^4 + \eta_2^2\eta_3^4 + \eta_3^2\eta_1^4) + c.c. \tag{16}
\]

The negative signs in the last two invariants in (10) occur in $T_h$ but not in $O_h$. 
FIG. 2: Second order phase transitions among states of the \( T_2 \) and \( T_4 \) representations of \( T_b \).

Normal state

\[
(1, 0, 0) \quad (1, 1, 1) \quad (1, \varepsilon, \varepsilon^2) \\
(\eta_1, \eta_2, 0) \quad (\eta_1, i\eta_2, 0) \quad (\eta_1, \eta_2, \eta_3)
\]

Consisting all possible subgroups of the groups in [13], we find five more SC states as listed in Table I where

\[
\begin{align*}
C_2(E) &= \{ E, U_1(\pi)C_2^* \}, \\
C_2'(E) &= \{ E, U_1(\pi)C_2'^*K \}.
\end{align*}
\]

We have examined the transitions within the SC state by considering effective free energies which describe them, similar to those described for the 2D order parameter, Eqs. (9), (10). The diagram of all second order phase transitions described by the three-dimensional representations of \( T_b \) is given in Fig. 2.

Thus we find that the absence of four-fold rotation symmetry in \( \text{PrOs}_4\text{Sb}_{12} \) essentially changes the structure of possible SC states. The states \((1, 1)\) and \((1, -1)\) are not stable, because the value of \( \phi \) in Eq. (6) is not fixed. Similarly, the state \((1, i, 0)\) is absent in the three-dimensional representations. Additionally, all SC states which may be connected to the normal state in \( O_h \), \( D_{4h} \) or \( D_{6h} \) symmetry by a second order phase transition are one-parameter in the sense that all components of the order parameter are proportional to one quantity, its absolute value \( |\eta| \). The situation is different for the states \((\phi_1, \phi_2)\) and \( (|\eta_1|, |i\eta_2|, 0) \) in \( T_b \), for which two independent quantities describe the SC state.

III. SECONDARY SC ORDER PARAMETERS

In general, the primary order parameter is accompanied by secondary order parameters which do not change the symmetry of the SC state. The influence of secondary order parameters on the gap nodes was discussed in Sec. I. Since secondary order parameters do not change the overall symmetry of the superconducting state, they are most easily found by identifying supergroups of the states listed in the second column of Table I which correspond to another superconducting state. Table II lists them.

In order to calculate how the second order parameters appear in the ordered phases, we need invariants of the types \( \eta^3 \xi \) and \( \eta^2 \xi^2 \), where \( \eta \) is the primary order parameter and \( \xi \) is the secondary order parameter. From the first type of invariant, it is clear that \( \xi \) and \( \eta \) must have the same parity. There are three scenarios to consider: i) The 2D primary order parameter with 1D secondary OP ii) 3D primary with 1D secondary and iii) 3D primary with 2D secondary.

A. 2D primary with 1D secondary

The coupling terms of the two order parameters in the Landau potential are

\[
(\eta_1^2 \eta_2^2 + \eta_1^2 \eta_2^2 + \eta_1^2 \eta_2^2 \eta_3) \xi + c.c,
(n_1^2 + n_2^2 + n_3^2) \xi^2 + c.c,
(|\eta_1|^2 + |\eta_2|^2 + |\eta_3|^2) |\xi|^2
\]

In the state \((1, 0, 0)\), the first two terms vanish, hence \( \xi = 0 \). In the state \((\phi_1, \phi_2)\), the first two terms are finite and \( |\xi| \propto |\eta|^3 \). Minimization with respect to \( \theta \) yields \( \theta = \frac{1}{2} (\phi_1 + \phi_2) \). This relation between the phases of the OP’s ensures that time reversal symmetry is preserved. There is no such relation between the phases when the primary order parameter state is \((\eta_1, \eta_2)\). This reflects the fact that time reversal symmetry is broken.

B. 3D primary and 1D secondary

The coupling terms are

\[
(\eta_1^2 \eta_2^2 \eta_3 + \eta_1^2 \eta_2^2 \eta_3 + \eta_1^2 \eta_2^2 \eta_3) |\xi|^2 + c.c,
\]

It follows that if any of the components of the 3D order parameter is zero then the potential has a minimum at \( \xi = 0 \). This is also the case for the state \((1, \varepsilon, \varepsilon^2)\). In the states in which \( \phi_1 = \phi_2 = \phi_3 \) [i.e. \((1, 1, 1)\) and \((|\eta_1|, |i\eta_2|, |\eta_3|)\)], one obtains \( \theta = \phi_1 \). However, in the state \((|\eta_1|, |i\eta_2|, |\eta_3|)\) we find \( \theta = \phi_1 \pm \frac{\pi}{2} \).

C. 3D primary and 2D secondary

The coupling terms are

\[
(\eta_1^2 n_2 n_3 + \varepsilon n_1 n_2 n_3 + \varepsilon^2 n_1 n_2 n_3) |\xi|^2 + c.c,
\]

For this type of mixing we only consider the \((1, \varepsilon, \varepsilon^2)\) state of the primary order parameter, since in the other
components of the strain tensor and certain anomalies in symmetry in addition to gauge. If the crystallographic class appears as a secondary effect. Note that to-SC transition and discontinuities of the elastic moduli respectively. Thus, the state \((0,\theta_1, \eta)\) where 

\[ \rho \eta^2 (e_1 + e_2 + e_3) \]  

(22)

The dilatation al strain \(e_1 + e_2 + e_3\) appears as a secondary order parameter, and the only elastic constant which is discontinuous is \(C_{11}\).

| Primary | Secondary |
|---------|-----------|
| \((1,0)\) | none |
| \((\phi_1, \phi_2)\) | (1) |
| \((\eta_1, \eta_2)\) | (1) |
| \((1,0,0)\) | none |
| \((1,1,1)\) | (1) |
| \((1,\varepsilon, \varepsilon^2)\) | (1,0) |
| \((|\eta_1|, |\eta_2|, 0)\) | none |
| \((|\eta_1|, |\eta_2|, 0)\) | none |
| \((\eta_1, \eta_2, 0)\) | none |
| \((|\eta_1|, |\eta_2|, |\eta_3|)\) | \((1), (\phi_1, \phi_2)\) |
| \((|\eta_1|, |\eta_2|, |\eta_3|)\) | \((1), (\phi_1, \phi_2)\) |
| \((\eta_1, \eta_2, \eta_3)\) | \((1), (\eta_1, \eta_2)\) |

TABLE II: Secondary SC order parameters. The primary SC order parameters are listed in the first column and all secondary SC order parameters are listed in the second column.

states where \(E_{g,u}\) is present as a secondary order parameter, \(A_{g,u}\) is also present, and it surely removes all nodes. The first two invariants in the \((1,\varepsilon, \varepsilon^2)\) state reduce to \(6|\eta_1|^2 \xi_2 \cos(\theta_2 - \phi_1)\) and \(6|\eta_1|^3 \xi_2 \sin(\theta_2 - \phi_1)\) respectively. Thus, the state \((0,1)\), which is equivalent to \((1,0)\), appears as a secondary effect. Note that \(\theta_2 - \phi_1\) is not fixed, which is expected since the state breaks time reversal symmetry.

IV. STRAINS AND ELASTIC MODULI

Unconventional SC states normally break spatial symmetry in addition to gauge. If the crystallographic class changes, one can expect the development of new components of the strain tensor and certain anomalies in the elastic moduli which can be measured by ultrasound propagation. Such a measurement has not yet been reported for PrOs4Sb12. Thus, here we consider all representations for the normal-to-A phase transition.

The elastic energy for \(T_h\) is the same as for \(O_h\),

\[
F_{el} = \frac{C_{60}}{2}(e_1^2 + e_2^2 + e_3^2) + C_{14}^2(e_1 e_2 + e_2 e_3 + e_1 e_3) + \frac{C_{44}}{2}(e_1^2 + e_2^2 + e_3^2),
\]

(21)

where \(e_1, e_2, \ldots, e_6\) are the components of the strain. Generally, if the strain is a secondary order parameter it couples to the primary order parameter as \(\eta^2 e\), which leads to a development of the secondary order parameter as \(e \sim \eta^2\).

The development of the strains following each normal-to-SC transition and discontinuities of the elastic moduli are shown in Table II.

A. 1D order parameter

There is no difference between \(O_h\) and \(T_h\) in this case. The coupling of the strain to the SC order parameter is described by the following term in the Landau potential

\[
F_{\eta e} = \rho |\eta|^2 (e_1 + e_2 + e_3)
\]

(22)

B. 2D order parameter

The coupling terms are

\[
F_{\eta e} = \rho_1 (|\eta_1|^2 + |\eta_2|^2)(e_1 + e_2 + e_3) + \rho_2 (|\eta_1|^2 + |\eta_2|^2)(e_1 + e_2 + e_3 + c.c.) + i\rho_3 (|\eta_1|^2 + |\eta_2|^2)(e_1 + e_2 + e_3 - c.c.].
\]

(23)

The third term is absent in \(O_h\). The free energy of the OP is given by Eq. (16), which describes the second order phase transitions between the normal state and the superconducting states \((1,0)\) and \((\phi_1, \phi_2)\).

Diatomic strains \(e_2 - e_3\) and \(2e_1 - e_2 - e_3\) appear in the transition to \((\phi_1, \phi_2)\). Therefore, it is necessary to average the elastic moduli in all three directions to take into account domains.

C. 3D order parameter

The coupling terms are

\[
F_{\eta e} = \rho_1 (|\eta_1|^2 + |\eta_2|^2 + |\eta_3|^2)(e_1 + e_2 + e_3) + \rho_2 (|\eta_1|^2 + |\eta_2|^2)(e_1 - e_2 - e_3) + (2|\eta_1|^2 - |\eta_2|^2 - |\eta_3|^2)(e_1 - e_2 - e_3) + \rho_3 (|\eta_2|^2 - |\eta_3|^2)(e_2 - e_3) - (2|\eta_1|^2 - |\eta_2|^2 - |\eta_3|^2)(e_2 - e_3) + 4(|\eta_2|^2 + \eta_2 \eta_3) e_4 + (\eta_3 \eta_1 + \eta_3 \eta_1) e_5 + (\eta_1 \eta_2 + \eta_1 \eta_2) e_6.
\]

(24)

The third term appears in \(T_h\) but not \(O_h\). Shear strains \(e_{4,5,6}\), but not diatomic strains, are present when all three components of the OP have the same magnitude. Diatomic strains appear when any of the magnitudes differ.

V. DISCUSSION

Experimentally, the symmetry of the SC states and the nature of the phase transition between them in PrOs4Sb12 is far from resolved. Anomalies at \(T_c2\) have been observed in many experiments. Specific heat measurements by Volume et al. found a
TABLE III: Strains and discontinuities in the elastic moduli following normal-to-SC phase transitions in $T_h$ crystals. The SC states are listed in the first column. Strains which appear as secondary order parameters and discontinuities of the elastic moduli are listed in the second and third columns respectively, as functions of the primary order parameter and the phenomenological constants. The fourth-order coefficients $\beta_i$ in the Landau potential for the 2D order parameter are defined in Eq. (10). For the 1D and 3D order parameter they correspond to the following terms $\tilde{\beta}_{ij} \eta^i \eta^j$ and $\beta_i (|\eta|^2 + |\eta|^2 + |\eta|^2 + |\eta|^2 + |\eta|^2 + |\eta|^2 + \beta_i (|\eta|^2 |\eta|^2 + |\eta|^2 |\eta|^2 + |\eta|^2 |\eta|^2 + |\eta|^2 |\eta|^2)$, respectively. The domain average values for the elastic moduli $C_{ij}$ are calculated as $C_{ij}^N = (C_{11} + C_{22} + C_{33})/3$. The superscript 0 denotes the values in the normal state.

| Transition: | Strains which appear as secondary order parameters | Elastic moduli in the SC state |
|------------|---------------------------------|-------------------------------|
| Normal to  | $e_1 + e_2 + e_3 = -\frac{4\eta_1 |\eta|^2}{C_{11} + 2C_{12}}$ | $C_{11} = C_{22} = C_{33} = C_{11}^0 - \frac{2\eta_1}{\eta_2}$ |

| (1)        | $e_1 + e_2 + e_3 = -\frac{4\eta_1 |\eta|^2}{C_{11} + 2C_{12}}$ | $C_{11} = C_{22} = C_{33} = C_{11}^0 - \frac{2\eta_1}{\eta_2}$ |

| (1, 0)     | $e_1 + e_2 + e_3 = -\frac{4\eta_1 |\eta|^2}{C_{11} + 2C_{12}}$ | $C_{11} = C_{22} = C_{33} = C_{11}^0 - \frac{2\eta_1}{\eta_2}$ |

| ($\phi_1, \phi_2$) | $e_1 + e_2 + e_3 = -\frac{4\eta_1 |\eta|^2}{C_{11} + 2C_{12}}$ | $C_{11}^N = C_{11}^0 - \frac{2\eta_1 + 2\eta_2 + 3\eta_3}{2(\eta_1 + \eta_2)}$ |

| (1, 0, 0)   | $e_1 + e_2 + e_3 = -\frac{4\eta_1 |\eta|^2}{C_{11} + 2C_{12}}$ | $C_{11}^N = C_{11}^0 - \frac{2\eta_1 + 2\eta_2 + 3\eta_3}{2(\eta_1 + \eta_2)}$ |

| (1, 1, 1)   | $e_1 + e_2 + e_3 = -\frac{4\eta_1 |\eta|^2}{C_{11} + 2C_{12}}$ | $C_{11}^N = C_{11}^0 - \frac{2\eta_1 + 2\eta_2 + 3\eta_3}{2(\eta_1 + \eta_2)}$ |

| (1, $\varepsilon$, $\varepsilon^2$) | $e_1 + e_2 + e_3 = -\frac{4\eta_1 |\eta|^2}{C_{11} + 2C_{12}}$ | $C_{11}^N = C_{11}^0 - \frac{2\eta_1 + 2\eta_2 + 3\eta_3}{2(\eta_1 + \eta_2)}$ |

| ($|\eta_1|, i|\eta_2|$, 0) | $e_1 + e_2 + e_3 = -\frac{4\eta_1 |\eta|^2}{C_{11} + 2C_{12}}$ | $C_{11}^N = C_{11}^0 - \frac{2\eta_1 + 2\eta_2 + 3\eta_3}{2(\eta_1 + \eta_2)}$ |

jump at $T_{c2}$, indicative of a second-order phase transition. On the other hand, Aoki et al. found a kink, resulting in a steeper temperature dependence below $T_{c2}$, which seems to correspond to a first-order phase transition. The most dramatic observation is the change in symmetry at the A-B phase transition seen in thermal conductivity measurements. The double transition was also observed in magnetisation measurements as a peak effect in $M(H)$.

The temperature range in which the A-phase exists is very narrow, thus with two exceptions the reported experiments probe the properties of the gap in the B-phase. Experiments consistently rule out the existence of line nodes in the B-phase. However, the presence of point nodes in the B-phase is clearly indicated by a power law temperature dependence of the specific heat, the thermal conductivity measurement and the penetration depth. Nuclear quadrupolar resonance experiments can be interpreted as either fully gapped or nodes. Very low temperature tunneling spectroscopy finds no nodes at all in the B-phase, perhaps consistent with rigorous nodes, rather than approximate nodes. Finally, $\mu$SR indicates that the B-phase is fully gapped.

Only a couple of experiments have specifically dealt with the symmetry of the gap function. In the thermal conductivity experiment, point nodes were found in the [010] direction in the B-phase and in both the [100] and [010] directions in the A-phase. However, in this measurement, there is no clear explanation for why the two-fold symmetry is actually observed as such, rather than averaged out into domains. The penetration depth has a power law temperature dependence corresponding to point nodes along all three principal crystallographic axes. No studies of the nodal structure along the [111]
direction have been reported so far. An extremely important finding is due to another μSR measurement, which showed that time reversal symmetry is broken in the B-phase.\(^6\)

In determining which of the states listed in Table I best describes PrOs\(_4\)Sb\(_{12}\) we make the following assumptions: i) the B-phase breaks time reversal symmetry; ii) there are point nodes in the B-phase located in the [100] and/or equivalent directions, and there are no line nodes in the B-phase; iii) the A-B phase transition is second order; iv) both phases are described by the same order parameter. The first two assumptions are based on fairly conservative interpretations of the experimental data available to date. We use the last two assumptions to narrow the choices of possible states. Their validity is subject to further experimental study.

We exclude the A and E representations because of ii). In \(T_h\) and \(T_d\) representations, the first four states listed in Table I are connected to the normal state by a second-order phase transition (see Fig. 2), but among them only \((1, 0, 0)\) and \((|\eta_1|, i|\eta_2|, 0)\) may be followed by another second order phase transition involving the same order parameter. Therefore, these are the only two possibilities for the A-phase. If the A-phase is \((|\eta_1|, i|\eta_2|, 0)\), then the B-phase is either \((|\eta_1|, \eta_2, 0)\) or \((|\eta_1|, i|\eta_2|, |\eta_3|)\). The former is excluded because it has line nodes in the singlet channel and no nodes at all in the triplet channel. The latter possibility must be singlet because it has no nodes at all in the triplet channel. If the A-phase is \((1, 0, 0)\), then the B-phase is the \((|\eta_1|, i|\eta_2|, 0)\) state. Because there are no line nodes in the B-phase, the pairing is therefore triplet. Strictly speaking, \((|\eta_1|, i|\eta_2|, 0)\) has no nodes at all under \(T_h\) symmetry. However, nodes appear in the corresponding \(O_h\) state \((1, i, 0)\). Such nodes may be pronounced dips in \(T_h\) if the Fermi surface has the approximate \(O_h\) symmetry as found in Ref. 5. Therefore, the two most likely possibilities for the sequence of SC phase transitions in PrOs\(_4\)Sb\(_{12}\) are

\[
\text{normal} \rightarrow \left( |\eta_1|, i|\eta_2|, 0 \right) \rightarrow \left( |\eta_1|, i|\eta_2|, |\eta_3| \right)
\]

in the singlet channel and

\[
\text{normal} \rightarrow \left( 1, 0, 0 \right) \rightarrow \left( |\eta_1|, i|\eta_2|, 0 \right)
\]

in the triplet channel.

If future experiments fail to be consistently described within the framework described in this article, then it is likely that the assumption that the order parameters of both transitions belong to the same representation will merit closer examination. It is possible that the B-phase may be due to the appearance of an order parameter that belongs to a different representation than that of the A-phase. This possibility is somewhat unsatisfactory in situations when the phase transitions occur very close together, as in PrOs\(_4\)Sb\(_{12}\), because it suggests a rather fine tuning of the phenomenological parameters. Second-order phase transitions between any states which are related as group-subgroups are allowed, provided third order terms of the effective order parameter are absent in the free energy. The order parameter of the B-phase may be a superconducting order parameter that belongs to a different representation than that of the A-phase, or it could even be something completely different, such as a structural order parameter, or a state with broken translational symmetry.

VI. SUMMARY

To summarise, we find group-theoretically the SC states which can be realized in crystals with \(T_h\) symmetry. Additional symmetry breaking within the SC state is considered. Heavy fermion superconductivity in PrOs\(_4\)Sb\(_{12}\) is best described by the three-dimensional representations of \(T_h\) point group. Considering experimental results, we propose the two most likely scenarios for the SC phase transition sequence found in PrOs\(_4\)Sb\(_{12}\), one in the singlet and another in the triplet channel.

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