# Superconducting states in the tetrahedral compound PrOs<sub>4</sub>Sb<sub>12</sub>

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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  $PrOs_4Sb_{12}$  is best described by the three-dimensional representations of the point group  $T_h$ .

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## I. INTRODUCTION

The discovery of superconductivity in the heavy fermion compound  $PrOs_4Sb_{12}$  (Refs. 1 and 2) has spawned a flurry of experimental<sup>3-19</sup> and theoretical<sup>9,20-24,27</sup> activity.  $PrOs_4Sb_{12}$  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  $T_{c1}$  = 1.85 K; an additional phase transition is observed as anomalies in the specific heat<sup>6</sup> and magnetization<sup>12</sup> at  $T_{c2}$  = 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 fourfold (*A* phase) to twofold (*B* phase) at  $T_{c2}$ .<sup>8</sup> Even more intriguing is the observation of broken time-reversal symmetry in the superconducting (SC) state.<sup>15</sup> By all indications,  $PrOs_4Sb_{12}$  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 of  $PrOs_4Sb_{12}$ . 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.<sup>28</sup> 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<sup>29</sup> 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  $PrOs_4Sb_{12}$  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<sup>21</sup> in order to account for the change in symmetry observed in the thermal conductivity experiment.<sup>8</sup> 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  $(s+id_{z^2-x^2})$ -wave combination was proposed. Different (s+g)-wave basis functions were proposed by Maki *et* 

*al.* for both states.<sup>22</sup> An *f*-wave pairing state with weak spinorbit coupling was proposed by Ichioka *et al.* to describe a state with point nodes on all three axes.<sup>23</sup> Finally, Miyake *et al.* considered a microscopic model based on quadrupolar fluctuations and nesting in the Fermi surface, and argued in favor of  $(p_x+ip_y)$ -wave pairing.<sup>24</sup>

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<sub>4</sub>Sb<sub>12</sub> has lower  $T_h$  symmetry (space group  $Im\bar{3}$ ,  $T_h^5$ ).<sup>25,26</sup> (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 such combinations depend in general 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.<sup>30,31</sup>

The first attempt to accomplish such a classification was made by Gufan.<sup>32</sup> In Sec. II of this paper, we use a different approach and reproduce most results of Ref. 32 for  $T_h$  symmetry.<sup>33</sup> 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. Section V is devoted to matching the experimental data with the states found theoretically. Section 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),<sup>28</sup> who listed all SC

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 columm. 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 square brackets [hkl] are used to indicate a specific crystallographic direction and its opposite, while angle brakets  $\langle hkl \rangle$  denote all equivalent directions. The word "same" is used when rigorous nodes coincide with approximate nodes. In the fifth column, (1) indicates that only  $\Delta_{-}(\mathbf{k})$  has nodes, while (2) indicates that both gaps in the triplet state have nodes.

State	Symmetry		Approximate nodes	Rigorous nodes		Approximate nodes	Rigorous nodes
(1)	$T \times \mathcal{K}$	$A_g$	none	none	$A_u$	none	none
(1, 0)	$T(D_2)$		8 points $\langle 111 \rangle$	same		8 points $\langle 111 \rangle (1)$	same
$(\phi_1, \phi_2)$	$D_2  imes \mathcal{K}$	$E_g$	8 points $\langle 111 \rangle$	none	$E_u$	none	none
$(\eta_1, \eta_2)$	$D_2$	-	8 points $\langle 111 \rangle$	none		none	none
(1, 0, 0)	$D_2(C_2) \times \mathcal{K}$		2 lines $k_y=0, k_z=0$	same		2 points [100](2)	same
(1, 1, 1)	$C_3 \times \mathcal{K}$		6 points $\langle 001 \rangle$	none		none	none
$(1, \varepsilon, \varepsilon^2)$	$C_3(E)$		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		none	none
$( \eta_1 ,  \eta_2 , 0)$	$C_2(E) \times \mathcal{K}$	$T_g$	1 line $k_z = 0$ , 2 points [001]	same	$T_{u}$	none	none
$(\eta_1,\eta_2,0)$	$C_2(E)$	-	1 line $k_z = 0$ , 2 points [001]	same		none	none
$(\left \eta_{1}\right , i\left \eta_{2}\right , \left \eta_{3}\right )$	$C'_2(E)$		6 points $\langle 001 \rangle$	none		none	none
$( \eta_1 ,  \eta_2 ,  \eta_3 )$	$\mathcal{K}$		6 points $\langle 001 \rangle$	none		none	none
$(\eta_1,\eta_2,\eta_3)$	Ε		6 points $\langle 001 \rangle$	none		none	none

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 wave function 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 representations that are complex conjugate, and a three-dimensional representation T.<sup>34</sup>

The SC gap function is a 2×2 matrix in pseudospin space given by  $\hat{\Delta}(\mathbf{k}) = i\hat{\sigma}_y \psi(\mathbf{k})$  for singlet pairing and by  $\hat{\Delta}(\mathbf{k}) = i[\mathbf{d}(\mathbf{k})\hat{\sigma}]\hat{\sigma}_y$  for triplet pairing, where  $\hat{\sigma} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$  are Pauli matrices,  $\psi(\mathbf{k})$  is an even scalar function, and  $\mathbf{d}(\mathbf{k})$  is an odd pseudovector function. The gap in the quasiparticle energy spectrum in the singlet SC state is given by  $\Delta(\mathbf{k}) = |\psi(\mathbf{k})|$ , while in the triplet state the spectrum can be nondegenerate with two gaps  $\Delta_{\pm}(\mathbf{k}) = [|\mathbf{d}(\mathbf{k})|^2 \pm |\mathbf{d}(\mathbf{k}) \times \mathbf{d}^*(\mathbf{k})|]^{1/2}$ . The functions  $\psi(\mathbf{k})$  and  $\mathbf{d}(\mathbf{k})$  are expressed in terms of the components of the order parameter  $\eta_i$  as

$$\psi(\mathbf{k}) = \sum_{i} \eta_{i} \psi_{i}(\mathbf{k}), \quad \mathbf{d}(\mathbf{k}) = \sum_{i} \eta_{i} \mathbf{d}_{i}(\mathbf{k}).$$
(1)

Here  $\psi_i(\mathbf{k})$  and  $\mathbf{d}_i(\mathbf{k})$  are the basis functions for the even (spin-singlet case) and odd (spin-triplet case) irreducible representations of the point group, respectively.<sup>30</sup>

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 timereversal, and analyze 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.<sup>35</sup> In practice, terms are restricted to those needed to describe the normal to superconducting phase transition,<sup>28,36</sup> while states resulting from additional phase transitions within the SC state are found by other methods. The VG approach can be applied to  $T_h$  crystals. However, here we use an even simpler approach, based on the fact that  $T_h$  is a subgroup of  $O_h$ . Beginning with the results for the symmetry groups of SC classes obtained by VG for  $O_h$  symmetry, we then *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, which lists all possible SC states for both even and odd parity when 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.<sup>37</sup> 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.<sup>28,38</sup> The secondary order parameters are proportional to the third power of the primary order parameter.<sup>38</sup> 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  $T \rightarrow 0$ . 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  $T \times \mathcal{K}$ . In the lowest order in **k**, the basis function for the singlet channel  $\psi(\mathbf{k})$  is constant on the Fermi surface and for the triplet channel  $\mathbf{d}(\mathbf{k}) \sim k_x \hat{\mathbf{x}} + k_y \hat{\mathbf{y}} + k_z \hat{\mathbf{z}}$ . Here and below, "~" means "transforms like" so that all our results remain valid for higher-order basis functions.

# **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. 28,

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

where  $\varepsilon = \exp(2\pi i/3)$ . Following the usual prescription of the phenomenological theory of phase transitions, we transfer the transformation properties of the basis functions to the transformation properties of  $(\eta_1, \eta_2)$ .<sup>41</sup> The functions (2) do not change under the twofold rotations which reverse the sign of two of the three components of  $\mathbf{k} = (k_x, k_y, k_z)$  and  $(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}})$  simultaneously. The threefold rotation around the [111] axis amounts to the cyclic permutations of  $(k_x, k_y, k_z)$ and  $(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}})$ . Further,<sup>30</sup>

$$\mathcal{K}\psi(\mathbf{k}) = \psi^{*}(-\mathbf{k}) = \eta_{1}^{*}\psi_{1}^{*}(\mathbf{k}) + \eta_{2}^{*}\psi_{2}^{*}(\mathbf{k}) = \eta_{2}^{*}\psi_{1}(\mathbf{k}) + \eta_{1}^{*}\psi_{2}(\mathbf{k}),$$
(3)

where we use Eqs. (1) and  $\psi_1^* = \psi_2$ . A similar result is obtained for the triplet order parameter since  $\mathcal{K}\mathbf{d}(\mathbf{k}) = -\mathbf{d}^*(-\mathbf{k}) = \mathbf{d}^*(\mathbf{k})$ .<sup>30</sup> Therefore, with this complex choice of the basis functions, the order parameter has the following transformation properties:<sup>39</sup>

$$C_2(\eta_1, \eta_2) = (\eta_1, \eta_2),$$
  
 $C_3^{111}(\eta_1, \eta_2) = (\varepsilon \eta_1, \varepsilon^2 \eta_2),$ 

$$\mathcal{K}(\eta_1, \eta_2) = (\eta_2^*, \eta_1^*),$$
$$U(\theta)(\eta_1, \eta_2) = e^{i\theta}(\eta_1, \eta_2), \tag{4}$$

where  $C_2$  stands for any of the twofold rotations in  $T_h$ ,  $C_3^{111}$ , 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  $T_h$  arises 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<sup>28</sup>

$$O(D_2) = \{D_2, 2C_4^x \mathcal{K}, 2C_4^y U(2\pi/3)\mathcal{K}, 2C_4^z U(4\pi/3)\mathcal{K}, \\ 2C_2^{yz} \mathcal{K}, 2C_2^{xz} U(2\pi/3)\mathcal{K}, 2C_2^{xy} U(4\pi/3)\mathcal{K}, \\ 4C_3 U(4\pi/3), 4C_3^2 U(2\pi/3)\},$$
(5)

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

$$T(D_2) = \{D_2, 4U(4\pi/3)C_3, 4U(2\pi/3)C_3^2\}.$$
 (6)

Considering the symmetry groups of the states (1,1) and (1,-1) in  $O_h$ , which are  $D_4 \times \mathcal{K}$  and  $D_4(D_2) \times \mathcal{K}$ , respectively,<sup>28</sup> where

$$D_4(D_2) \times \mathcal{K} = \{ D_2, 2C_4^x U(\pi), 2C_2^{yz} U(\pi) \} \times \mathcal{K}, \qquad (7)$$

we notice that they both reduce to the same symmetry  $D_2 \times \mathcal{K}$  in  $T_h$ . Moreover, it follows from Eqs. (4) 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 may also be verified from the following Landau model, which describes the  $E_{e,u}$  representation of  $T_h$ :

$$F = \alpha(|\eta_1|^2 + |\eta_2|^2) + \beta_1(|\eta_1|^4 + |\eta_2|^4) + 2\beta_2|\eta_1|^2|\eta_2|^2 + \gamma_1(\eta_1^3\eta_2^{*3} + \eta_2^3\eta_1^{*3}) + \gamma_2i(\eta_1^3\eta_2^{*3} - \eta_2^3\eta_1^{*3}),$$
(8)

where  $\alpha$ ,  $\beta_1$ ,  $\beta_2$ ,  $\gamma_1$ , and  $\gamma_2$  are phenomenological parameters. One can easily verify that all terms in Eq. (8) are invariants of transformations (4). 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 in the quasiparticle spectrum of the  $(\phi_1, \phi_2)$  state in the singlet channel is<sup>42</sup>

$$\Delta(\mathbf{k}) \sim |\cos(\phi/2)k_x^2 + \cos(\phi/2 + 2\pi/3)k_y^2 + \cos(\phi/2 + 4\pi/3)k_z^2|,$$
(9)

and in the triplet channel,



FIG. 1. Second-order phase transitions among states of the  $E_g$  and  $E_u$  representations of  $T_h$ .

$$\Delta_{+}(\mathbf{k}) = \Delta_{-}(\mathbf{k}) \sim [\cos(\phi/2)^{2}k_{x}^{2} + \cos(\phi/2 + 2\pi/3)^{2}k_{y}^{2} + \cos(\phi/2 + 4\pi/3)^{2}k_{z}^{2}]^{1/2}.$$
 (10)

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 (9).

In  $O_h$ , the states (1,0), (1,1), and (1,-1) are connected to the normal state by a second-order phase transition.<sup>28</sup> Since up to fourth-order terms the model (8) 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  $D_2 \times \mathcal{K}$ . As is seen from Eqs. (4), it has no constraints on either the magnitudes or phases, therefore we denote this state ( $\eta_1, \eta_2$ ). In principle, the phase transitions to this state can be described together with normal-to-(1,0) and normal-to-( $\phi_1, \phi_2$ ) within the same model. This would require the Landau potential to be expanded up to a very high order. The model (8) would not be sufficient. However, as far as the order of the phase transitions is concerned, we can use the following simplified approach.<sup>40</sup>

The phase transition  $(1,0) \rightarrow (\eta_1, \eta_2)$  is characterized by the appearance of nonvanishing  $\eta_2$ , which therefore can be considered as an effective order parameter of the phase transition.  $\eta_2$  spans a representation of group  $T(D_2)$ , which is defined as follows [see Eqs. (4) and (6)]:  $C_2 \eta_2 = \eta_2$ ,  $U(4\pi/3)C_3 \eta_2 = \varepsilon \eta_2$ , and  $U(2\pi/3)C_3^2 \eta_2 = \varepsilon^2 \eta_2$ . The group  $T(D_2)$  should be complimented by either inversion *I* in the singlet case or  $IU(\pi)$  in the triplet case.<sup>28</sup> We assume that this additional symmetry is not broken in  $(1,0) \rightarrow (\eta_1, \eta_2)$ transition, i.e.,  $\eta_1$  and  $\eta_2$  have the same parity. Therefore, there exists no operation in the symmetry group of the (1,0)state which changes the sign of  $\eta_2$ . The effective Landau potential is therefore

$$F_{\text{eff}}[(1,0) \to (\eta_1, \eta_2)] = \tilde{\alpha} |\eta_2|^2 + \tilde{\gamma}_1(\eta_2^3 + \eta_2^{*3}) + i \tilde{\gamma}_2(\eta_2^3 - \eta_2^{*3}) + \tilde{\beta} |\eta_2|^4,$$
(11)

where  $\tilde{\alpha}$ ,  $\tilde{\gamma}_1$ ,  $\tilde{\gamma}_2$ , and  $\beta$  are real coefficients. The presence of third-order terms in Eq. (11) indicates that the phase transition  $(1,0) \rightarrow (\eta_1, \eta_2)$  cannot be second-order.<sup>40,41</sup>

On the other hand, a second-order transition  $(\phi_1, \phi_2) \rightarrow (\eta_1, \eta_2)$  is possible (see Fig. 1). This transition is described by an effective order parameter  $\delta \equiv |\eta_1| - |\eta_2|$ , which

changes sign under time reversal, hence odd-order terms are prohibited. The effective Landau potential in this case is

$$F_{\text{eff}}[(\phi_1, \phi_2) \to (\eta_1, \eta_2)] = \alpha' \,\delta^2 + \beta' \,\delta^4, \qquad (12)$$

where  $\alpha'$  and  $\beta'$  are real coefficients.

There are no other states described by the *E* representation alone, because the basis functions (2) 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 $T_{g,u}$

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

$$\psi_1 \sim k_y k_z, \quad \psi_2 \sim k_x k_z, \quad \psi_3 \sim k_x k_y, \tag{13}$$

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

$$\mathbf{d}_{1} \sim ak_{y}\hat{\mathbf{z}} + bk_{z}\hat{\mathbf{y}},$$
$$\mathbf{d}_{2} \sim ak_{z}\hat{\mathbf{x}} + bk_{x}\hat{\mathbf{z}},$$
$$\mathbf{d}_{3} \sim ak_{x}\hat{\mathbf{y}} + bk_{y}\hat{\mathbf{x}}.$$
(14)

Here *a* and *b* are arbitrary numbers, in contrast to  $O_h$ , which fixes b=-a in the  $T_{1u}$  representation and b=a in the  $T_{2u}$  representation. It follows that the order parameter transforms as

$$C_{2}^{z}(\eta_{1},\eta_{2},\eta_{3}) = (-\eta_{1},-\eta_{2},\eta_{3}),$$

$$C_{3}^{111}(\eta_{1},\eta_{2},\eta_{3}) = (\eta_{2},\eta_{3},\eta_{1}),$$

$$\mathcal{K}(\eta_{1},\eta_{2},\eta_{3}) = (\eta_{1}^{*},\eta_{2}^{*},\eta_{3}^{*}),$$

$$U(\theta)(\eta_{1},\eta_{2},\eta_{3}) = e^{i\theta}(\eta_{1},\eta_{2},\eta_{3}).$$
(15)

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

$$D_{4}(C_{4}) \times \mathcal{K} = \{E, C_{2}^{x}, 2C_{4}^{x}, 4U(\pi)C_{2}^{\perp x}\} \times \mathcal{K},$$

$$D_{4}(E) = \{E, U(\pi)C_{2}^{x}, 2U(\pm \pi/2)C_{4}^{x}, C_{2}^{x}\mathcal{K},$$

$$U(\pi)C_{2}^{y}\mathcal{K}, 2U(\pm \pi/2)C_{2}^{xy}\mathcal{K}\},$$

$$D_{3}(C_{3}) \times \mathcal{K} = \{E, 2C_{3}, 3U(\pi)C_{2}^{xy}\} \times \mathcal{K},$$

$$D_{3}(E) = \{E, U(4\pi/3)C_{3}, U(2\pi/3)C_{3}^{2}, C_{2}^{yz}\mathcal{K}, \qquad (16)$$

$$U(2\pi/3)C_{2}^{xz}\mathcal{K}, U(4\pi/3)C_{2}^{xy}\mathcal{K}\},$$

respectively.<sup>28</sup> Here *E* is the identity element. Reducing these groups, we find the following classes for  $T_h$ :



FIG. 2. Second-order phase transitions among states of the  $T_g$  and  $T_u$  representations of  $T_h$ .

$$D_{2}(C_{2}) \times \mathcal{K} = \{E, C_{2}^{x}, U(\pi)C_{2}^{y}, U(\pi)C_{2}^{z}\} \times \mathcal{K},$$

$$D_{2}(E) = \{E, U(\pi)C_{2}^{z}, C_{2}^{x}\mathcal{K}, U(\pi)C_{2}^{y}\mathcal{K}\},$$

$$C_{3} \times \mathcal{K} = \{E, C_{3}, C_{3}^{2}\} \times \mathcal{K},$$

$$C_{3}(E) = \{E, U(4\pi/3)C_{3}, U(2\pi/3)C_{3}^{2}\}.$$
(17)

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,

$$\begin{aligned} &|\eta_{1}|^{6} + |\eta_{2}|^{6} + |\eta_{3}|^{6}, \quad |\eta_{1}|^{2} |\eta_{2}|^{2} |\eta_{3}|^{2}, \\ &(|\eta_{1}|^{2} + |\eta_{2}|^{2} + |\eta_{3}|^{2})(\eta_{1}^{2} \eta_{2}^{*2} + \eta_{2}^{2} \eta_{3}^{*2} + \eta_{3}^{2} \eta_{1}^{*2} + \text{c.c.}), \\ &(|\eta_{1}|^{4} |\eta_{2}|^{2} + |\eta_{2}|^{4} |\eta_{3}|^{2} + |\eta_{3}|^{4} |\eta_{1}|^{2}) \\ &\pm (|\eta_{1}|^{2} |\eta_{2}|^{4} + |\eta_{2}|^{2} |\eta_{3}|^{4} + |\eta_{3}|^{2} |\eta_{1}|^{4}), \end{aligned}$$
$$(\eta_{1}^{4} \eta_{2}^{*2} + \eta_{2}^{4} \eta_{3}^{*2} + \eta_{3}^{4} \eta_{1}^{*2}) \pm (\eta_{2}^{4} \eta_{1}^{*2} + \eta_{3}^{4} \eta_{2}^{*2} + \eta_{1}^{4} \eta_{3}^{*2}) + \text{c.c.} \end{aligned}$$
(18)

The negative signs in the last two invariants in (18) occur in  $T_h$  but not in  $O_h$ .

Considering all possible subgroups of the groups in Eqs. (17), we find five more SC states as listed in Table I, where

$$C_{2}(E) = \{E, U_{1}(\pi)C_{2}^{z}\},\$$

$$C_{2}'(E) = \{E, U_{1}(\pi)C_{2}^{y}\mathcal{K}\}.$$
(19)

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. (11) and (12). The diagram of all second-order phase transitions described by the three-dimensional representations of  $T_h$  is given in Fig. 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.

Primary	Secondary
(1)	none
(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)
$( \eta_1 , i \eta_2 , 0)$	none
$( \eta_1 ,  \eta_2 , 0)$	none
$(\eta_1,\eta_2,0)$	none
$( \eta_1 , i \eta_2 ,  \eta_3 )$	(1), $(\phi_1, \phi_2)$
$( \eta_1 ,  \eta_2 ,  \eta_3 )$	(1), $(\phi_1, \phi_2)$
$(\eta_1,\eta_2,\eta_3)$	(1), $(\eta_1, \eta_2)$

Thus we find that the absence of fourfold rotation symmetry in PrOs<sub>4</sub>Sb<sub>12</sub> 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. (9) 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.<sup>28,36</sup> The situation is different for the states ( $\phi_1, \phi_2$ ) and ( $|\eta_1|, i|\eta_2|, 0$ ) in  $T_h$ , 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 secondary 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. In the rest of this section, we denote the primary order parameters as  $\eta_j = |\eta_j| e^{i\phi_j}$  and the secondary order parameters as  $\xi_j$  $= |\xi_j| e^{i\phi_j}$ .

### A. 2D primary with 1D secondary

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

$$(\eta_{1}\eta_{2}^{*2}\xi + \eta_{1}^{2}\eta_{2}^{*}\xi^{*}) + (\eta_{1}^{*2}\eta_{2}\xi + \eta_{1}^{*}\eta_{2}^{2}\xi^{*}),$$

$$i[(\eta_{1}\eta_{2}^{*2}\xi + \eta_{1}^{2}\eta_{2}^{*}\xi^{*}) - (\eta_{1}^{*2}\eta_{2}\xi + \eta_{1}^{*}\eta_{2}^{2}\xi^{*})],$$

$$\eta_{1}^{*}\eta_{2}^{*}\xi^{2} + \eta_{1}\eta_{2}\xi^{*2}, \quad (|\eta_{1}|^{2} + |\eta_{2}|^{2})|\xi|^{2}. \quad (20)$$

In the state (1,0), 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 in 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

$$(\eta_{1}\eta_{2}^{*}\eta_{3}^{*} + \eta_{1}^{*}\eta_{2}\eta_{3}^{*} + \eta_{1}^{*}\eta_{2}^{*}\eta_{3})\xi + \text{c.c.},$$

$$(\eta_{1}^{*2} + \eta_{2}^{*2} + \eta_{3}^{*2})\xi^{2} + \text{c.c.},$$

$$(|\eta_{1}|^{2} + |\eta_{2}|^{2} + |\eta_{3}|^{2})|\xi|^{2}.$$
(21)

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  $(|\eta_1|,|\eta_2|,|\eta_3|)$ ], one obtains  $\theta=\phi_1$ . However, in the state  $(|\eta_1|,i|\eta_2|,|\eta_3|)$  we find  $\theta=\phi_1\pm\pi/2$ .

#### C. 3D primary and 2D secondary

The coupling terms are

$$(\eta_{1}^{*}\eta_{2}\eta_{3} + \varepsilon \eta_{1}\eta_{2}^{*}\eta_{3} + \varepsilon^{2}\eta_{1}\eta_{2}\eta_{3}^{*})\xi_{1}^{*} + (\eta_{1}\eta_{2}^{*}\eta_{3}^{*} + \varepsilon \eta_{1}^{*}\eta_{2}\eta_{3}^{*} + \varepsilon^{2}\eta_{1}^{*}\eta_{2}^{*}\eta_{3})\xi_{2} + \text{c.c.},$$

$$i[(\eta_{1}^{*}\eta_{2}\eta_{3} + \varepsilon \eta_{1}\eta_{2}^{*}\eta_{3} + \varepsilon^{2}\eta_{1}\eta_{2}\eta_{3}^{*})\xi_{1}^{*} - (\eta_{1}\eta_{2}^{*}\eta_{3}^{*} + \varepsilon \eta_{1}^{*}\eta_{2}\eta_{3}^{*} + \varepsilon^{2}\eta_{1}^{*}\eta_{2}^{*}\eta_{3})\xi_{2} - \text{c.c.}],$$

$$(\eta_{1}^{*2} + \eta_{2}^{*2} + \eta_{3}^{*2})\xi_{1}^{*}\xi_{2}^{*} + \text{c.c.},$$

$$(|\eta_{1}|^{2} + \varepsilon |\eta_{2}|^{2} + \varepsilon^{2}|\eta_{3}|^{2})\xi_{1}\xi_{2}^{*} + \text{c.c.},$$

$$(|\eta_{1}|^{2} + |\eta_{2}|^{2} + |\eta_{3}|^{2})(|\xi_{1}|^{2} + |\xi_{2}|^{2}).$$

$$(22)$$

For this type of mixing, we only consider the  $(1, \varepsilon, \varepsilon^2)$  state of the primary order parameter, since in the other 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  $6 |\eta_1|^3 |\xi_2| \cos(\theta_2 - \phi_1)$  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.<sup>43,44</sup> Such a measurement has not yet been reported for  $PrOs_4Sb_{12}$ . Thus, here we consider all representations for the normal-to-*A* phase transition.

The elastic energy for  $T_h$  is the same as for  $O_h$ ,

$$F_{el} = \frac{C_{11}^0}{2} (e_1^2 + e_2^2 + e_3^2) + C_{12}^0 (e_1 e_2 + e_2 e_3 + e_1 e_3) + \frac{C_{44}^0}{2} (e_4^2 + e_5^2 + e_6^2), \qquad (23)$$

where  $e_{1,...,6}$  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 normalto-SC transition and discontinuities of the elastic moduli are shown in Table III.

## 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:

$$F_{\eta e} = \rho |\eta|^2 (e_1 + e_2 + e_3). \tag{24}$$

The dilatational strain  $e_1+e_2+e_3$  appears as a secondary order parameter, and the only elastic constant which is discontinuous is  $C_{11}$ .

#### B. 2D order parameter

The coupling terms are

$$F_{\eta e} = \rho_1(|\eta_1|^2 + |\eta_2|^2)(e_1 + e_2 + e_3) + \rho_2[\eta_1\eta_2^*(e_1 + \varepsilon e_2 + \varepsilon^2 e_3) + \text{c.c.}] + i\rho_3[\eta_1\eta_2^*(e_1 + \varepsilon e_2 + \varepsilon^2 e_3) - \text{c.c.}].$$
(25)

The third term is absent in  $O_h$ . The free energy of the OP is given by Eq. (8), which describes the second-order phase transitions between the normal state and the superconducting states (1,0) and  $(\phi_1, \phi_2)$ .

Deviatoric 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

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. (8). For the 1D and 3D order parameter, they correspond to the following terms:<sup>30</sup>  $\beta |\eta|^4$  and  $\beta_1(|\eta_1|^2 + |\eta_2|^2 + |\eta_3|^2)^2 + \beta_2 |\eta_1^2 + \eta_2^2 + \eta_3^2|^2 + \beta_3(|\eta_1|^2 |\eta_2|^2 + |\eta_2|^2 + |\eta_3|^2)$ , respectively. The domain average values for the elastic moduli  $C_{ij}$  are calculated as  $C_{11}^{av} = (C_{11} + C_{22} + C_{33})/3$ ,  $C_{12}^{av} = (C_{12} + C_{23} + C_{13})/3$ . The superscript 0 denotes the values in the normal state.

Transition: Normal to	Strains which appear as secondary order parameters	Elastic moduli in the SC state
(1)	$e_1 + e_2 + e_3 = \frac{-3\rho  \eta ^2}{C_{11}^0 + 2C_{12}^0}$	$C_{11} = C_{22} = C_{33} = C_{11}^0 - \frac{\rho^2}{2\beta}$
		$C_{11} - C_{12}, C_{44}$ continuous
(1,0)	$e_1 + e_2 + e_3 = \frac{-3\rho_1  \eta ^2}{C_{11}^0 + 2C_{12}^0}$	$C_{11} = C_{22} = C_{33} = C_{11}^0 - \frac{\rho_1^2}{2\beta_1}$
		$C_{11} - C_{12}, C_{44}$ continuous
$(\phi_1,\phi_2)$	$e_1 + e_2 + e_3 = \frac{-6\rho_1  \eta_1 ^2}{C_{11}^0 + 2C_{12}^0}$	$C_{11}^{\rm av} = C_{11}^0 - \frac{2\rho_1^2 + \rho_2^2 + \rho_3^2}{2\beta_1 + \beta_2}$
	$2e_1 - e_2 - e_3 = \frac{-6 \eta_1 ^2(\rho_2 \cos \phi - \rho_3 \sin \phi)}{C_{11}^0 - C_{12}^0}$	$C_{12}^{\text{av}} = C_{12}^{0} - \frac{4\rho_1^2 - \rho_2^2 - \rho_3^2}{2(2\beta_1 + \beta_2)}$
	$e_2 - e_3 = \frac{2\sqrt{3}  \eta_1 ^2 (\rho_2 \sin \phi + \rho_3 \cos \phi)}{C_{11}^0 - C_{12}^0}$	$C_{44}$ continuous
(1,0,0)	$e_1 + e_2 + e_3 = \frac{-3\rho_1  \eta_1 ^2}{C_{11}^0 + 2C_{12}^0}$	$C_{11}^{\text{av}} = C_{11}^{0} - \frac{3\rho_1^2 + 24\rho_2^2 + 8\rho_3^2}{6(\beta_1 + \beta_2)}$
	$2e_1 - e_2 - e_3 = \frac{-12\rho_2  \eta_1 ^2}{C_{11}^0 - C_{12}^0}$	$C_{12}^{\text{av}} = C_{12}^0 - \frac{3\rho_1^2 - 12\rho_2^2 - 4\rho_3^2}{6(\beta_1 + \beta_2)}$
	$e_2 - e_3 = \frac{4\rho_3  \eta_1 ^2}{C_{11}^0 - C_{12}^0}$	$C_{44}$ continuous
(1,1,1)	$e_1 + e_2 + e_3 = \frac{-9\rho_1 \eta_1 ^2}{C_{11}^0 + 2C_{12}^0}$	$C_{11} = C_{22} = C_{33} = C_{11}^0 - \frac{3\rho_1^2}{2(3\beta_1 + 3\beta_2 + \beta_3)}$
	$e_{4,5,6} = -\frac{2\rho_4 \eta_1 ^2}{C_{44}^0}$	$C_{11} - C_{12}$ continuous
		$C_{44} = C_{44}^0 - \frac{2\rho_4^2}{3(3\beta_1 + 3\beta_2 + \beta_3)}$
$(1,\varepsilon,\varepsilon^2)$	$e_1 + e_2 + e_3 = \frac{-9\rho_1  \eta_1 ^2}{C_{11}^0 + 2C_{12}^0}$	$C_{11} = C_{22} = C_{33} = C_{11}^0 - \frac{3\rho_1^2}{2(3\beta_1 + \beta_3)}$
	$e_{4,5,6} = \frac{\rho_4  \eta_1 ^2}{C_{1,5}^0}$	$C_{11} - C_{12}$ continuous
	~ <sub>44</sub>	$C_{44} \!=\! C_{44}^0 \!-\! rac{ ho_4^2}{6(3eta_1\!+\!eta_3)}$

Transition: Normal to	Strains which appear as secondary order parameters	Elastic moduli in the SC state
$( \eta_1 ,i \eta_2 ,0)$	$e_1 + e_2 + e_3 = \frac{-3\rho_1(\eta_1^2 + \eta_2^2)}{C_{11}^0 + 2C_{12}^0}$	$C_{11}^{\text{av}} = C_{11}^{0} - \frac{3\rho_1^2(4\beta_2 - \beta_3) + 4(3\rho_2^2 + \rho_3^2)(6\beta_1 + 2\beta_2 + \beta_3)}{6(4\beta_2 - \beta_3)(4\beta_1 + \beta_3)}$
	$e_1 + e_2 - 2e_3 = \frac{-6\rho_2( \eta_1 ^2 +  \eta_2 ^2) + 6\rho_3( \eta_1 ^2 -  \eta_2 ^2)}{C_{11}^0 - C_{12}^0}$	$C_{12}^{\mathrm{av}} = C_{12}^{0} - \frac{3\rho_{1}^{2}(4\beta_{2} - \beta_{3}) - 2(3\rho_{2}^{2} + \rho_{3}^{2})(6\beta_{1} + 2\beta_{2} + \beta_{3})}{6(4\beta_{2} - \beta_{3})(4\beta_{1} + \beta_{3})}$
	$e_1 - e_2 = \frac{-6\rho_2( \eta_1 ^2 -  \eta_2 ^2) - 2\rho_3( \eta_1 ^2 +  \eta_2 ^2)}{C_{11}^0 - C_{12}^0}$	$C_{44}$ continuous

$$F_{\eta e} = \rho_{1}(|\eta_{1}|^{2} + |\eta_{2}|^{2} + |\eta_{3}|^{2})(e_{1} + e_{2} + e_{3}) + \rho_{2}[3(|\eta_{2}|^{2} - |\eta_{3}|^{2})(e_{2} - e_{3}) + (2|\eta_{1}|^{2} - |\eta_{2}|^{2} - |\eta_{3}|^{2}) \times (2e_{1} - e_{2} - e_{3})] + \rho_{3}[(|\eta_{2}|^{2} - |\eta_{3}|^{2})(2e_{1} - e_{2} - e_{3}) - (2|\eta_{1}|^{2} - |\eta_{2}|^{2} - |\eta_{3}|^{2})(e_{2} - e_{3})] + \rho_{4}[(\eta_{2}^{*}\eta_{3} + \eta_{2}\eta_{3}^{*})e_{4} + (\eta_{3}^{*}\eta_{1} + \eta_{3}\eta_{1}^{*})e_{5} + (\eta_{1}^{*}\eta_{2} + \eta_{1}\eta_{2}^{*})e_{6}].$$
(26)

The third term appears in  $T_h$  but not  $O_h$ . Shear strains  $e_{4,5,6}$ , but not deviatoric strains, are present when all three components of the OP have the same magnitude. Deviatoric 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 PrOs<sub>4</sub>Sb<sub>12</sub> are far from resolved. Anomalies at  $T_{c2}$  have been observed in many experiments.<sup>4,6–8,12,13,15,18,19</sup> Specific-heat measurements by Vollmer *et al.*<sup>6</sup> found a jump at  $T_{c2}$ , indicative of a second-order phase transition. On the other hand, Aoki et al.<sup>4,15</sup> 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.<sup>8</sup> The double transition was also observed in magnetization measurements as a peak effect in M(H).<sup>12,13</sup> One of these measurements found strong anisotropies,<sup>12</sup> possibly indicative of a change in symmetry; the other did not.13 Finally, recent penetration depth measurements have been interpreted not as a phase transition, but rather as a crossover due to two-band superconductivity.<sup>19</sup>

The temperature range in which the *A* phase exists is very narrow, thus with two exceptions<sup>8,13</sup> 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.<sup>2,3,5,8,16</sup> However, the presence of point nodes in the *B* phase is clearly indicated by a power-law temperature dependence of the specific heat,<sup>2</sup> the thermal conductivity measurement,<sup>8</sup> and the penetration depth.<sup>18</sup> Nuclear quadrupolar resonance experiments<sup>3</sup> can be interpreted as either fully gapped or nodes. Tunneling spectroscopy<sup>16</sup> finds no nodes at all in the *B* phase, but this measurement was per-

formed at very low temperatures, perhaps consistent with rigorous nodes rather than approximate nodes. Finally,  $\mu$ SR (Ref. 5) indicates that the *B* phase is fully gapped.

Only a couple of experiments have specifically dealt with the symmetry of the gap function.<sup>8,18</sup> 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.<sup>8</sup> However, in this measurement, there is no clear explanation for why the twofold 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.<sup>18</sup> No studies of the nodal structure along the [111] direction have been reported so far. An extremely important finding is due to another  $\mu$ SR measurement, which showed that time-reversal symmetry is broken in the *B* phase.<sup>15</sup>

In determining which of the states listed in Table I best describes  $PrOs_4Sb_{12}$ , 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 the  $T_g$  and  $T_u$  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).<sup>28</sup> Such nodes may be pronounced dips in  $T_h$  if the Fermi surface has the approximate  $O_h$  symmetry, as found in Ref. 9. Therefore, the two most likely possibilities for the sequence of SC phase transitions in PrOs<sub>4</sub>Sb<sub>12</sub> are

normal 
$$\rightarrow (|\eta_1|, i|\eta_2|, 0) \rightarrow (|\eta_1|, i|\eta_2|, |\eta_3|)$$

in the singlet channel and

normal 
$$\rightarrow (1,0,0) \rightarrow (|\eta_1|,i|\eta_2|,0)$$

in the triplet channel.

We note that both scenarios proposed here are actually inconsistent with the four-node-to-two-node change in the gap found in Ref. 8. In order to describe that experiment, one tempting possibility would be to associate the *A* phase with the state (1,1,1) in the singlet channel, while the *B* state with (1,0,0) or  $(|\eta_1|,i|\eta_2|,0)$  (with approximate  $O_h$  symmetry as discussed above) in the triplet channel. Then, however, the *A*-*B* transition could only be first-order. We also note that other experiments have not reproduced the results of Ref. 8 for the *B* phase: the penetration depth measurements found six point nodes in the gap,<sup>18</sup> and the *A*-*B* transition line lies in a higher magnetic field.<sup>12</sup>

If future experiments fail to be consistently described within the framework described in this paper, 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  $PrOs_4Sb_{12}$ , 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 summarize, 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  $PrOs_4Sb_{12}$  is best described by the three-dimensional representations of the point group  $T_h$ . Considering experimental results, we propose the two most likely scenarios for the SC phase-transition sequence found in  $PrOs_4Sb_{12}$ , one in the singlet and another in the triplet channel.

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