Microscopic theories for cubic and tetrahedral superconductors: application to PrOs$_4$Sb$_{12}$

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We examine weak-coupling theory for unconventional superconducting states of cubic or tetrahedral symmetry for arbitrary order parameters and Fermi surfaces and identify the stable states in zero applied field. We further examine the possibility of having multiple superconducting transitions arising from the weak breaking of a higher symmetry group to cubic or tetrahedral symmetry. Specifically, we consider two higher symmetry groups. The first is a weak crystal field theory in which the spin-singlet Cooper pairs have an approximate spherical symmetry. The second is a weak spin orbit coupling theory for which spin-triplet Cooper pairs have a cubic orbital symmetry and an approximate spherical spin rotational symmetry. In hexagonal UPt$_3$, these theories easily give rise to multiple transitions. However, we find that for cubic materials, there is only one case in which two superconducting transitions occur within weak coupling theory. This sequence of transitions does not agree with the observed properties of PrOs$_4$Sb$_{12}$. Consequently, we find that to explain two transitions in PrOs$_4$Sb$_{12}$ using approximate higher symmetry groups requires a strong coupling theory. In view of this, we finally consider a weak coupling theory for which two singlet representations have accidentally nearly degenerate transition temperatures (not due to any approximate symmetries). We provide an example of such a theory that agrees with the observed properties of PrOs$_4$Sb$_{12}$.

I. INTRODUCTION

It has been observed that a wide variety of heavy fermion superconductors appear to undergo multiple phase transitions within the superconducting state. These materials include UPt$_3$, U$_{1-x}$Th$_x$Be$_{13}$ and PrOs$_4$Sb$_{12}$. The fact that multiple transitions are being observed in such a significant fraction of the total number of heavy fermion superconductors discovered is presumably providing a valuable insight into the nature of the superconducting state. Among the heavy fermion superconductors showing multiple phase transitions, UPt$_3$ has been most extensively studied. It has a hexagonal point group symmetry and shows two transitions with a small (about 10%) splitting of the superconducting transition temperature. Three main approaches have been used to theoretically model the phase diagram of UPt$_3$ and it would be of interest to see if any of these approaches apply to the other materials. The first approach uses a weak symmetry breaking field (SBF) to break the hexagonal symmetry. This field lifts the degeneracy of a multi-component order parameter leading to two transitions. The origin of this symmetry breaking field has been questioned and other proposals have emerged. Zhitomirsky and Ueda have postulated a weak crystal field model in which spin-singlet Cooper pairs experience an approximate spherical symmetry which is weakly broken to hexagonal symmetry. Along similar lines, Machida and co-workers have postulated a weak spin orbit coupling for spin-triplet Cooper pairs. The third approach uses a phenomenological model which considers two different irreducible representations of the hexagonal point group that accidentally have nearly the same $T_c$. In all these cases, it is possible to develop microscopic theories based on weak coupling theory that give rise to the two transitions and such theories have been useful in developing a qualitative understanding of this superconductor.

Among the materials with cubic or tetrahedral point group symmetry: U$_{1-x}$Th$_x$Be$_{13}$ and PrOs$_4$Sb$_{12}$ have shown multiple superconducting transitions. Both these materials have been the subject of phenomenological studies. U$_{1-x}$Th$_x$Be$_{13}$ has been studied using a phenomenological approach by Sigrist and Rice while PrOs$_4$Sb$_{12}$ has been examined phenomenologically by Goryø et al., Ichioka et al., Matsunaga et al., and more recently by Sergienko and Curnoe. There have been a variety of microscopic proposals for the superconducting states in PrOs$_4$Sb$_{12}$. It is interesting to note that none of these microscopic theory attempts to provide an origin for the two transitions for cubic or tetrahedral materials. Existing microscopic theories predict the properties of the A phase but are forced to make ad-hoc assumptions about the origin of the transition in the B phase. This is in sharp contrast to the case of UPt$_3$ where microscopic justification for the second transition exist based on weak coupling theories.

In the hope of identifying a common origin to multiple transitions for heavy fermion superconductors, we apply the conceptual frameworks developed for hexagonal UPt$_3$ to cubic and tetrahedral superconductors. One goal is to examine under what circumstances weak coupling BCS provides a microscopic description of the two transitions. We expect that BCS theory will capture a large contribution to the condensation energy of these heavy fermion superconductors and therefore provides a reasonable basis for such studies. This is partially justified by the agreement between the observed size of the specific heat jumps at $T_c$ and that predicted by weak coupling theories. In neither U$_{1-x}$Th$_x$Be$_{13}$...
nor PrOs$_4$Sb$_{12}$ has any weak symmetry breaking fields been identified. Therefore, we begin by exploring possible higher symmetry groups that are weakly broken. We consider two higher symmetries groups. The first is motivated by weak crystal field theory of Zhitomirsky and Ueda for UPt$_3$. In this theory, the spin-singlet superconducting state has an approximate spherical symmetry $SO(3)$ which is weakly broken to cubic or tetrahedral symmetry. We next consider the possibility of weak spin-orbit coupling so that the spin-triplet superconductor has an approximate $O \times SO(3)$ symmetry. We find that weak coupling theory for only the latter of these two higher symmetries allow for one possible scenario for two transitions. The sequence of transitions found this way does not agree with experimental data for PrOs$_4$Sb$_{12}$. We further show that the weak crystal field theory does allow for two transitions when strong coupling corrections are included. However, the condensation energy associated with the strong coupling corrections must be comparable to that of weak coupling theory to account for experimental results on the specific heat. These results indicate that a weak coupling theory does not provide an adequate description of the superconducting state within the context of weakly broken higher symmetry groups.

Given the failure of weak coupling theory for PrOs$_4$Sb$_{12}$ in the above context, we finally ask if it is possible for weak coupling theory to provide a description of the two transitions that agrees with the experimental results. We find that it is possible for such an approach to succeed and give one example of when it does. However, without the constraints imposed by higher symmetries, a general analysis of resulting weak coupling theories is not possible and requires a detailed knowledge of the quasi particles within the material.

The paper is organized as follows. We initially provide an overview of experimental results for PrOs$_4$Sb$_{12}$ and U$_{1-x}$Th$_x$Be$_{13}$. Then we provide an analysis that results in all the possible high temperature superconducting phases allowed within weak coupling theory for cubic and tetrahedral superconductors. Finally, we examine the origin of the second transition within the frameworks discussed above.

II. EXPERIMENTAL PROPERTIES OF THE SUPERCONDUCTORS PROS$_{12}$ AND U$_{1-x}$TH$_x$BE$_{13}$

The heavy fermion superconductor PrOs$_4$Sb$_{12}$ is the first among the rare-earth filled skutterudite compounds showing a superconducting behavior. It undergoes a normal to superconducting transition with $T_{c1} = 1.85$ K (the high temperature phase is known as the A phase) followed by another transition at $T_{c2} = 1.75$ K from the A phase to the B phase. This second transition shows up as a pronounced anomaly in the specific heat and magnetization measurements. Note that the specific heat measurements by Measson et al. have raised questions about the intrinsic nature of the double superconducting transition. Various experiments have reported a similar field dependence of the $H_{c2}$ curve for both the transition temperatures. Though the symmetry and type of nodes of the gap structure in the A phase remains inconclusive, experiments suggest the presence of two point nodes in the B phase. This has been observed by the power law temperature dependence in specific heat, thermal conductivity and penetration depth measurements. A possible third phase transition ($T_{c3}$) has been observed as an enhancement of the lower critical field $H_{c1}(T)$ below $T \approx 0.6$ K. Interestingly this anomaly has not been detected by specific heat measurements at low temperatures. Experiments have also observed local broken time reversal symmetry in the superconducting phase through $\mu$SR measurements.

One experimental result on PrOs$_4$Sb$_{12}$ which has not received much theoretical attention yet provides a strong constraint is the low field measurement of the vortex lattice geometry. The key result is that the vortex lattice is not hexagonal near $H_{c1}$ for the field along the $c$ axis. As the authors of have pointed out, this is a strong constraint because this lattice structure results from a London free energy whose form depends upon the symmetry of the superconducting state. The London free energy can be expanded in powers of the reciprocal lattice vector $q$ of the vortex lattice. The form of the free energy is

$$F = \frac{\hbar^2}{8\pi} \sum_q [1 + \lambda^2 \sum_{i,j} (1 + m_{ij}q_i^2 - m_{ij}q_i q_j)] \quad (1)$$

here $\lambda$ is the penetration depth and $m$ is the normalized London effective mass tensor whose components in weak coupling theory for a singlet superconductor is given by $m_{ij}^{-1} \propto v_f | \Delta(k) |^2 >_{FS}$ with $v_f$ being the $i$th component of Fermi velocity and $| \Delta(k) |$ representing the gap magnitude. We are justified in keeping $q$ terms up to second order near $H_{c1}$ because in this region $q$ has a small magnitude being approximately given by $q \approx \sqrt{\frac{H}{\Omega}}$. If we consider that the gap to be invariant under a three fold rotation we find that the components of the effective mass tensor are given by

$$m_{xx} = m_{yy} = m_{zz}, m_{xy} = m_{yz} = m_{xz} = 0$$
This situation would result in a hexagonal vortex lattice near $H_{c1}$. No other symmetry element of the tetrahedral point group implies a hexagonal vortex lattice. Since the observed vortex lattice is not hexagonal near $H_{c1}$, we conclude that superconducting state does not contain a three fold symmetry axis.

The alloy $U_{1-x}Th_xBe_{13}$ which has cubic point group symmetry shows two second order superconducting transition for concentration of thorium exceeding $x = 0.018$ in specific heat measurements. A pronounced peak has been observed in the ultrasonic attenuation for longitudinal sound propagated along a [100] direction at $T = T_{c2}$.

Significant anomalies have been observed in $H_{c2}(T)$ at $T = T_{c2}$ and the zero field $\mu$SR line width shows a marked increase as $T$ decreases below $T_{c2}$ in samples with $x \approx 0.033$. Finally Lambert et al. found differences in the pressure dependence of $T_c$ for $x < 0.018$ and $x > 0.018$.

### III. THEORY OF THE HIGH TEMPERATURE SUPERCONDUCTING PHASE

For all the theories we consider, the initial transition into the superconducting state is characterized by either cubic or tetrahedral symmetry. Therefore, this transition is described by a single order parameter symmetry. Here, we provide a general analysis of the possible superconducting states that weak-coupling theory allows for this phase. A similar analysis of this problem has appeared recently by Kuznetsova and Barzykin. However, we find that weak coupling theory provides even stronger constraints than found in this work. As a consequence, some of the phases found by these authors are ruled out.

The cubic group $O_h$ has ten irreducible representations (irreps) that are listed in Table I. The tetrahedral group has one three dimensional irrep and three one dimensional irreps, two of which are complex conjugate and combine to form a single irrep when time reversal symmetry is present. In this Section we study the superconducting phases of materials with cubic and tetrahedral point group symmetry whose basis functions transform as a multiplet by the point group representation.

The superconducting gap is given by $\Delta(k) = |\psi(k)\sigma_0 + d(k) \cdot \sigma| i\sigma_y$ where $\psi(k) = \psi(-k)$ is the even-parity spin-singlet component, $d(k) = -d(-k)$ is the odd-parity spin-triplet component, and $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ represent the Pauli spin matrices. Among the various irreps of the point group symmetry there is one, say $\Gamma$, which gives the highest transition temperature. The superconducting state can be written as a linear combination of the basis functions of this representation $\Delta(\Gamma, m; k)$

$$\Delta(k) = \sum_m \eta(\Gamma, m) \Delta(\Gamma, m; k)$$

Here $\eta(\Gamma, m)$ are in general complex and act as the order parameter. For a single representation the fourth order free energy for the superconducting state can be written as an expansion in $\eta(\Gamma, m)$

$$F_4(T, \eta) = F_0(T) + \alpha \sum_m |\eta(\Gamma, m)|^2 + f_4|\eta(\Gamma, m)|^4$$

with $\alpha = \alpha_0 [T/T_c(\Gamma) - 1]$, and the fourth order energy contains all terms which are invariant under $G \times R \times U(1)$. The normal state of the system is represented by the free energy $F_0(T)$. Here $G$ is the crystal point group symmetry, $R$ and $U(1)$ are the time reversal and gauge symmetry groups respectively. The fourth order terms in the Ginzburg Landau theory are characterized by several coefficients $\beta_i$ which are arbitrary in a general theory but are constrained in the weak coupling limit.

| Representation | Representative basis function($f$) | Representation | Representative basis function($f$) |
|---------------|----------------------------------|---------------|----------------------------------|
| $A_{1u}$      | $k_x^2 + k_y^2 + k_z^2$         | $A_{1u}$      | $\hat{x}k_x + \hat{y}k_y + \hat{z}k_z$ |
| $A_{2g}$      | $(k_x^2 - k_y^2)(k_y^2 - k_z^2)(k_z^2 - k_x^2)$ | $A_{2u}$      | $\hat{x}k_x(k_x^2 - k_y^2) + \hat{y}k_y(k_y^2 - k_z^2) + \hat{z}k_z(k_z^2 - k_x^2)$ |
| $E_u$         | $2k_x^2 - k_y^2 - k_z^2, k_z^2 - k_y^2$ | $E_u$         | $2\hat{z}k_z - \hat{x}k_x - \hat{y}k_y$ |
| $T_{1u}$      | $k_yk_z(k_y^2 - k_z^2), k_zk_x(k_z^2 - k_x^2), k_xk_y(k_x^2 - k_y^2)$ | $T_{1u}$      | $\hat{y}k_z + \hat{z}k_y, \hat{z}k_x - \hat{x}k_z, \hat{x}k_y - \hat{y}k_x$ |
| $T_{2u}$      | $k_yk_z, k_zk_x, k_xk_y$        | $T_{2u}$      | $\hat{y}k_z + \hat{z}k_y, \hat{z}k_x + \hat{x}k_z, \hat{x}k_y + \hat{y}k_z$ |

**TABLE I:** The irrep and corresponding representative basis functions for even and odd parity states of cubic symmetry.
For the spin triplet systems the fourth order free energy within weak-coupling theory can be evaluated from the average

$$\langle |d(k)|^4 + |q(k)|^2 \rangle$$

with \( q = id(k) \times d(k)^* \). The \( q \) vector is zero for unitary states and takes finite values for non unitary states. Since \(|q|^2\) gives a positive fourth order contribution to the free energy for non unitary states it is unusual for these states to be preferred stable states within a weak coupling theory. For the spin-triplet representations, sixth order terms in the free energy are required to remove a residual degeneracy and completely specify the solution. The sixth order free energy is given by

$$\frac{1}{3} \langle |d(k)|^6 + 3|q(k)|^2|d(k)|^2 \rangle .$$

For spin singlet systems the fourth order free energy will be given by

$$\langle |\psi(k)|^4 \rangle .$$

We now analyze the possible superconducting ground states for cubic symmetry within the weak coupling limit.

A. Two Dimensional Representation

The cubic group contains one two dimensional representation for even parity states with the gap function

$$\psi(k) = \eta_1 f_{1E_u}(k) + \eta_2 f_{2E_u}(k)$$

where \( f_{1E_u}(k) \) and \( f_{2E_u}(k) \) form a basis for the \( E_u \) irrep. For the odd parity states the representative basis functions \( f_{1E_u} \) and \( f_{2E_u} \) are given in Table I and the gap function is given by

$$d(k) = \eta_1 f_{1E_u}(k) + \eta_2 f_{2E_u}(k)$$

The general free energy can be expressed as an expansion in the order parameter \( \eta_1 \) and \( \eta_2 \) as

$$F = \alpha_0 \left[ 1 - \frac{T}{T_c} \right] \left( |\eta_1|^2 + |\eta_2|^2 \right) + \frac{7\zeta(3)}{16(\pi T_c)^2} N_0 \Delta^4 |\beta_1 (|\eta_1|^2 + |\eta_2|^2) + \beta_2 (\eta_1^* \eta_2 - \eta_2^* \eta_1)|^2$$

(2)

Where \( \alpha_0 = 1 \) in the weak coupling limit. The weak coupling values of the fourth order coefficient for the even parity states are

$$\beta_1 = 3 \beta_2 = < f_{1E_u}^4(k) >$$

with the bracket meaning the average over the Fermi surface. All averages in the current and future discussion are in a normalized form such that \(< f^2(k) > = 1 \) where \( f(k) \) represents the basis function. If we minimize this free energy we find that since \( \beta_1 > 0 \), the phase \( \omega^2(1, i) \) will minimize the free energy. This is true for arbitrary Fermi surfaces and gap basis functions. This phase belongs to the superconducting class \( O(D_2)_{\text{spin}} \) and has point nodes along the cube diagonals. The gauge factor \( \omega^2 \) has been multiplied to keep the notation consistent with Ref. 36.

For the odd parity irreps the weak coupling values for the fourth order coefficients are

$$\beta_1 = 3 < f_x^2(k) >, \beta_2 = < f_y^2(k) >$$

where \( x = f_x^2(k) > / < f_x^2(k) > \), and \( f_x(k), f_y(k), f_z(k) \) form an arbitrary basis of \( T_{1u} \) symmetry and have the same rotation properties as the vector \( k \). If we minimize this free energy within the weak coupling limit, the non magnetic phase \( \nu = (1, 0) \) belonging to the superconducting class \( D_4 \otimes R \) is found to be stable for \( x < 7 \) (note that a residual continuous degeneracy remains for which any real combination of the two components minimizes the fourth order free energy, this is lifted by sixth-order terms). For \( x > 7 \) the magnetic phase \( \nu = \omega^2(1, i) \) is stable. Again the gauge factor \( \omega^2 \) has been multiplied to keep the notation consistent with Ref. 36. This phase belongs to the \( O(D_2) \) superconducting class and contains point nodes along the cube diagonals. It is interesting to find a non unitary phase that is stabilized within weak coupling theory in zero applied field. The second non-magnetic phase \( \nu = (0, 1) \) appears to be prohibited in a weak coupling theory by the sixth order term in the free energy

$$-\gamma_3 |\eta_1|^2 |\eta_2|^2 - |\eta_1| |\eta_2|^2$$
where $\gamma_3$ is given by the weak coupling value

$\gamma_3 = \frac{1}{54} < f_x^6(k) + 2f_y^2(k)f_y^2(k) - 3f_z^4(k)f_y^2(k) >$

we numerically find $\gamma_3 > 0$ for a variety of basis functions and Fermi surface structures, but we could not prove this analytically.

Tetrahedral symmetry does not change the structure of the $\omega^2(1,i)$, but does introduce an additional sixth order term in the free energy that modifies the $\nu$ we numerically find explain the observed properties are the $(1,i,0)$, consider that there is single superconducting transition and ask if any of the above stable phases can explain the $\nu = (1,i,0)$ phase. This term is

$$\frac{\sqrt{3}}{72} < f_x^2(k)f_y^2(k) > \left( |3(\eta_1\eta_2 + \eta_2\eta_1)|(|\eta_1|^4 + |\eta_2|^4 - 3|\eta_1|^2|\eta_2|^2) - (\eta_1^3\eta_2^3 + \eta_1^3\eta_2^3) \right)$$

as a result the stable $\Lambda$ phase ground state is given by $(\phi_1, \phi_2)$, where both $\phi_1$ and $\phi_2$ are real (note that there is no continuous degeneracy in this phase).$

B. Three Dimensional Representation

The Free energy for the three dimensional representation can be written as

$$F = \alpha_0 \left[ 1 - \frac{T}{T_c} (|p_1|^2 + |p_2|^2 + |p_3|^2) + \frac{7\zeta(3)}{16(\pi T_c)^2} N_0 \Delta^4 |\beta_1 (|p_1|^2 + |p_2|^2 + |p_3|^2) + \beta_2 (p_1^2 + p_2^2 + p_3^2) (p_1^2 + p_2^2 + p_3^2) + \beta_3 (|p_1|^4 + |p_2|^4 + |p_3|^4) | \right]$$

(3)

The weak coupling values of the coefficients are

$$\beta_1 = 2\beta_2 = 2 < f_{1T_2g}(k)f_{2T_2g}(k) >, \beta_3 = < f_{1T_2g}(k) > - 3 < f_{1T_2g}(k)f_{2T_2g}(k) >$$

The functions $f_{1T_2g}(k), f_{2T_2g}(k), f_{3T_2g}(k)$ form a basis for the $T_{2g}$ irrep. If we define the parameter space in terms of one free parameter

$$\tilde{x} = \frac{< f_{1T_2g}(k) >}{< f_{2T_2g}(k)f_{2T_2g}(k) >}$$

we find that for $\tilde{x} < 3$, the state $(1,i,0)$ is the ground state. This state belongs to the class $D_4(E)$ and contains line nodes in the $z = 0$ plane. For $\tilde{x} > 3$, the phase $(1,\omega,\omega^2)$ is stable high temperature phase. This state belongs to the class $D_4(E)$ and contains point nodes. The boundary $\tilde{x} = 3$ corresponds to a spherical Fermi surface. The weak coupling values provide a tighter restriction on the allowed phases than found by Kuznetsova et al. and result in only magnetic states being the stable weak coupling phases. In particular, it should be noted that $\tilde{x} > 1$ for any choice of basis functions, and this constraint rules out any non-magnetic phases.

For the odd parity states the weak coupling values are given by

$$\beta_1 = x + 3, \beta_2 = -\frac{(x+1)}{2}, \beta_3 = \frac{x-3}{2}$$

where again $x = < f_{1T_2g}(k) > / < f_{2T_2g}(k)f_{2T_2g}(k) >$.

We find that the state $(1,1,1)$ is stable for $x > 3$ whereas $(1,0,0)$ is stable for $x < 3$ for both $T_{1u}$ and $T_{2u}$ irreps. The boundary $x = 3$ corresponds to the spherical Fermi surface.

All the possible solutions for the high temperature phase within the weak coupling limit are listed in table [I] For the tetrahedral symmetry the analysis will be similar to the cubic at the fourth order as tetrahedral and cubic group have the same invariants. The difference in the tetrahedral and cubic invariants at the sixth order results in the state $(|\eta_1|, i|\eta_2|, 0)$ belonging to $D_2(E)$ symmetry group giving the ground state for the tetrahedral symmetry rather than the $(1,i,0)$ state belonging to the $D_4(E)$ symmetry group giving the ground state for cubic symmetry.$^{27}$

In view of the controversy between the extrinsic versus intrinsic nature of the transition in PrO$_4$Sb$_{12}$, we briefly consider that there is single superconducting transition and ask if any of the above stable phases can explain the experimental properties observed at low temperatures. In particular, the ground states listed in table [I] which may explain the observed properties are the $(1,0)$ state of $E_u$, $(1,i,0)$ for $T_{2g}$, and the $(1,0,0)$ state of $T_{1u}$ and $T_{2u}$.
These states have a gap structure with point nodes or are highly anisotropic. In addition, each of these states break tetrahedral symmetry which would result in a distorted vortex lattice structure. Note that the observation of an increased muon relaxation rate in the superconducting phases does not imply that time reversal symmetry is globally broken, but only locally broken. We take this to imply that the order parameter must be multi-component but that ordered phase need not break time reversal symmetry globally.

| Representation | State | Nodes | Symmetry Class |
|----------------|-------|-------|----------------|
| $E_g$          | $\frac{1}{\sqrt{4}}(1,i)$ | $P$   | $O(D_2)$       |
| $E_u$          | $(1,0)$ | $-$   | $D_4 \otimes R$ |
| $E_u$          | $\frac{1}{\sqrt{6}}(1,i)$ | $P$   | $O(D_2)$       |
| $T_{2g}$       | $\frac{1}{\sqrt{2}}(1,i,0)$ | $L$   | $D_3(E)$       |
| $T_{2g}$       | $\frac{1}{\sqrt{2}}(1,\omega,\omega^2)$ | $P$   | $D_3(E)$       |
| $T_{2u}$       | $\frac{1}{\sqrt{2}}(1,1,1)$ | $P$   | $D_3(D_2) \otimes R$ |
| $T_{2u}$       | $(1,0,0)$ | $P$   | $D_3(D_2) \otimes R$ |
| $T_{1u}$       | $\frac{1}{\sqrt{2}}(1,1,1)$ | $P$   | $D_3(C_3) \otimes R$ |
| $T_{1u}$       | $(1,0,0)$ | $P$   | $D_3(C_4) \otimes R$ |

*TABLE II: Stable high temperature phases in the weak coupling limit. The corresponding representative basis functions are listed in table I. Here $\omega = \exp[2\pi i/3]$. 

These states have a gap structure with point nodes or are highly anisotropic. In addition, each of these states break tetrahedral symmetry which would result in a distorted vortex lattice structure. Note that the observation of an increased muon relaxation rate in the superconducting phases does not imply that time reversal symmetry is globally broken, but only locally broken. We take this to imply that the order parameter must be multi-component but that ordered phase need not break time reversal symmetry globally.

**IV. WEAKLY BROKEN $SO(3)$ THEORY FOR SPIN SINGLET STATES**

We now turn to the role that higher symmetries may play in giving rise to two superconducting phase transitions. In this section, we consider the weak crystal field theory for which there is an approximate $SO(3)$ for spin-singlet superconductors. Such an approach was proposed to explain the phase diagram of UPt$_3$ by Zhitomirsky, and Ueda.

We find the possible superconducting transitions for a state in which the spin singlet Cooper pairs are in the $E_g \oplus T_{2g}$ of the cubic group. The free energy for the $l = 2$ irrep of $SO(3)$ has been found by Mermin and Staex, incorporating the weak crystal field gives

$$f = \alpha_1(|\eta_1|^2 + |\eta_2|^2) + \alpha_2(|p_1|^2 + |p_2|^2 + |p_3|^2) + \beta_1|TrB|^2 + \beta_2(TrB^*B)^2 + \beta_3Tr(B^2B^*)^2$$

(4)

here $B$ is a $3 \times 3$ traceless symmetric complex matrix given by the $l = 2$ order parameter $\psi(k) = \sum_{\mu\nu} B_{\mu\nu} k_\mu k_\nu$. Note that since the symmetry breaking is weak, spherical symmetry is broken by the second order term only. The weak coupling limit corresponds to the special case $\beta_2 = 2\beta_1$, $\beta_3 = 0$. The magnitude of $\beta_3$ is only due to strong coupling effects and is of order $T_c/E_F$. The general form of the gap is

$$\psi(k) = \frac{\eta_1}{\sqrt{6}}(2k_x^2 - k_x^2 - k_y^2) + \frac{\eta_2}{\sqrt{2}}(k_x^2 - k_y^2) + \sqrt{2}p_1k_xk_y + \sqrt{2}p_2k_yk_z + \sqrt{2}p_3k_zk_x$$

here $\eta = (\eta_1, \eta_2)$ transform like the $E_g$ representation and $P = (p_1, p_2, p_3)$ transform like the $T_{2g}$ representation of the cubic group. The components of matrix $B$ can be written as

$$B_{xx} = \frac{\eta_1}{\sqrt{3}} + \eta_2, B_{yy} = \frac{\eta_1}{\sqrt{3}} - \eta_2, B_{zz} = \frac{2\eta_1}{\sqrt{3}}, B_{xy} = p_1, B_{yz} = p_2, B_{zx} = p_3$$

We now look for the various transitions into the B phase which can result in further stable superconducting transitions. The form of this theory is simple enough to enable us to perform a general analysis beyond the weak coupling limit. We will therefore look for all possible transitions from all possible stable A phase solutions listed in Table II. From the values of the fourth order energies in Table III, we find that for $\beta_2 > 0$, $\beta_3 > 0$ the states $P = (1,i,0)$ and $P = (1,\omega,\omega^2)$ will tend to stabilize deep in the B phase when the second order coefficients can be ignored whereas for $\beta_2 > 0$, $\beta_3 < 0$ the state $\eta = \omega^2(1,i)$ tends to stabilize. Within the weak coupling theory these states do not give any stable second
This transition gives a specific heat jump ratio of the order $\beta_1 + \beta_2 + \beta_3/2$. It is also interesting to note that this transition corresponds to a change in penetration depth of order $\beta_2 + \beta_3/3$.

The specific heat jump ratio between the transition at the B phase to the transition at the A phase is

$$P = \frac{\eta}{\sqrt{2}}(1, i, 0)$$

which is negligible close to the weak coupling limit. It is also interesting to note that this transition corresponds to a change in penetration depth of order $\beta_3$ which can be a significant change to observe in an experiment. A similar explanation may hold for the $T_{c3}$ in PrOs$_4$Sb$_{12}$ observed in penetration depth measurements below $T=0.6K$ but not yet observed in specific heat measurements.

**TABLE III:** The fourth order free energies ($F_4$) for possible A phase representation ($\Gamma$) for spherical symmetry. Here $\eta = (\eta_1, \eta_2)$, $P = (p_1, p_2, p_3)$ transform as irreps of $E_g$ and $T_{2g}$ respectively of cubic symmetry. Here $\omega = \exp[2\pi i/3]$.

| $\Gamma$ | $F_4$ |
|---------|-------|
| $\eta = (1, 0), P = 0$ | $\beta_1 + \beta_2 + \beta_3/2$ |
| $\eta = \frac{\omega}{\sqrt{2}}(1, i), P = 0$ | $\beta_2 + \beta_3/3$ |
| $\eta = 0, P = \frac{\omega}{\sqrt{2}}(1, i, 0)$ | $\beta_2 + \beta_3/4$ |
| $\eta = 0, P = (1, 0, 0)$ | $\beta_1 + \beta_2 + \beta_3/2$ |
| $\eta = 0, P = \frac{1}{\sqrt{2}}(1, \omega, \omega^2)$ | $\beta_2 + \beta_3/4$ |
| $\eta = 0, P = (1, 1, 1)$ | $\beta_1 + \beta_2 + \beta_3/2$ |

order transitions into the B phase. If we include strong coupling effects ($\beta_3 \neq 0$) we find that there is only one second order transition for $\beta_2 > 0, \beta_3 < 0$ from the state $P = \frac{\omega}{\sqrt{2}}(1, i, 0)$ in the A phase. This transition corresponds to a B phase given by a linear combination of $P = \frac{\omega}{\sqrt{2}}(1, i, 0)$ and $\eta = |\eta| e^{i\pi/4}(1, 0)$ with a transition temperature

$$T_{cB} = T_{cA} + 3(1 + \frac{4\beta_2}{\beta_3} )(T_{cA} - T_<)$$

where $T_<$ is the transition temperature corresponding to pure $\eta = (\eta_1, \eta_2)$ state. This state is highly anisotropic and gives a distorted vortex lattice structure. It is therefore a possible transition sequence for PrOs$_4$Sb$_{12}$. The specific heat jump ratio between the transition at the B phase to the transition at the A phase is

$$\frac{C_B}{C_A} = \frac{T_{cB}}{T_{cA}} \frac{\beta_2^2 (\beta_2 + \beta_3/4)}{144(1 + \beta_2 + \beta_3/2)(\beta_2 + \beta_3/3)^2}$$

This transition gives a specific heat jump ratio of the order $\beta_3^2$ which is negligible close to the weak coupling limit. It is also interesting to note that this transition corresponds to a change in penetration depth of order $\beta_3$ which can be a significant change to observe in an experiment. A similar explanation may hold for the $T_{c3}$ in PrOs$_4$Sb$_{12}$ observed in penetration depth measurements below $T=0.6K$ but not yet observed in specific heat measurements.

**V. WEAKLY BROKEN $O \times SO(3)$ THEORY FOR SPIN-TRIPLET STATES**

We will now analyze the transition for the spin triplet states within a weak coupling theory. We consider the effects of a weak spin orbit coupling and also include the crystal field with cubic symmetry and allow the spin channel to be isotropic. The irreps of the symmetry group are given by the combined group $O_h \times SO(3) \times R$. If we consider a weak spin orbit coupling in our system, the basis functions split up into four different irreps. We write the vector gap equation in terms of these irreps as $d(k) = \Sigma_{\Gamma} d^{\Gamma}(k)$ where the components are given by

\[
\begin{align*}
\text{d}^{A_1+}(k) & = \lambda \frac{1}{\sqrt{3}} [\hat{x} f_x(k) + \hat{y} f_y(k) + \hat{z} f_z(k)], \\
\text{d}^{E_<(k)} & = \nu_1 \frac{1}{\sqrt{2}} [\hat{x} f_x(k) - \hat{y} f_y(k)] + \nu_2 \frac{1}{\sqrt{6}} [-2 \hat{z} f_z(k) + \hat{x} f_x(k) + \hat{y} f_y(k)], \\
\text{d}^{T_1+}(k) & = p_1 \frac{1}{\sqrt{2}} [\hat{y} f_y(k) - \hat{z} f_z(k)] + p_2 \frac{1}{\sqrt{2}} [\hat{x} f_x(k) - \hat{y} f_y(k)] + p_3 \frac{1}{\sqrt{2}} [\hat{z} f_z(k) - \hat{x} f_x(k)], \\
\text{d}^{T_2+}(k) & = q_1 \frac{1}{\sqrt{2}} [\hat{y} f_y(k) + \hat{z} f_z(k)] + q_2 \frac{1}{\sqrt{2}} [\hat{x} f_x(k) + \hat{y} f_y(k)] + q_3 \frac{1}{\sqrt{2}} [\hat{z} f_z(k) + \hat{x} f_x(k)]
\end{align*}
\]

(5)

the components of the vector gap equation can be written in terms of the basis $d(k) = \Sigma_{\eta} \eta_j f_j(k)$, and we will use both bases for convenience.

For a weak spin orbit coupling, we get a free energy of the form

$$F = \alpha_1 |\lambda|^2 + \alpha_2 (|v_1|^2 + |v_2|^2) + \alpha_3 (|p_1|^2 + |p_2|^2 + |p_3|^2) + \alpha_4 (|q_1|^2 + |q_2|^2 + |q_3|^2) + \beta_1 (|\eta_x|^4 + |\eta_y|^4 + |\eta_z|^4)$$
We find that there is only one stable second order transition into the B phase. This instability is from the combination of weak coupling values in units of $W.C$. The weak coupling values are in units of $\beta = \frac{x + 3}{6}$.

$$Q = \frac{1}{\sqrt{2}}(0,1,1) \quad \frac{(3\beta_1 + \beta_2 - \beta_3 - \beta_6)/8 + (\beta_3 + \beta_5 + 5\beta_7)/16}{(x + 3)/6}$$

It may be seen from Table IV that for $x > 3$ the states $P = (1,1,1)$ and $Q = (1,1,1)$ will minimize the fourth order terms whereas for $x < 3$, $\mathbf{v} = (1,0), P = (1,0,0), Q = (1,0,0)$ and equivalent states minimize the fourth order free energy. At $x = 3$ we have a spherical fermi surface.

To understand if phase transitions are possible we compare the states that minimize the second order term with those that minimize the fourth order terms. If these are different, then a transition is possible. However many of these transitions are first order. For example the non unitary state $\mathbf{v} = \omega^2(1, i)$ which is stable in the A phase for $x > 7$ undergoes a first order transition to a mixed state with $\mathbf{v} = \omega^2(1, i)$ and $P = -i(1, \omega, \omega^2)$. We find that there is only one stable second order transition into the B phase. This instability is from $P = p(1,1,1)$ to the combination of $P = q(1,1,1)$, where $p$ and $q$ are the order parameter values. Within the assumption of a small spin orbit coupling we write the general form of the gap for the states $P = (1,1,1)$ and $Q = (1,1,1)$ as

$$\Delta(k) = \cos \theta([\hat{x}f_x(k) + \hat{y}f_y(k)] + [\hat{z}f_z(k) + \hat{x}f_y(k) + \hat{z} + f_y(k)])$$

Here $\theta$ acts as the order parameter. If we assume that the $P = (1,1,1)$ state has the highest transition temperature, there is a transition from a $\theta = 0$ state in A phase for which $\theta$ becomes non zero and grows towards a fully gapped system at $\theta = \pi/4$ (at which the gap has the form $\hat{x}f_x(k) + \hat{y}f_y(k) + \hat{z}f_z(k)$). This gives a second order transition temperature

$$T_{cB} = T_{cA} - \frac{1}{2}(x + 3)(T_{cA} - T_{cZ})$$

and the ratio of jumps in the specific heat at the transition temperatures of the A and the B phases is

$$\frac{c_B}{c_A} = \frac{T_{cB}}{T_{cA}}(x + 3)$$

It should be pointed out that for tetrahedral group there will be an additional bilinear coupling term in the free energy

$$\alpha_m(P^* \cdot Q + P \cdot Q^*)$$
The spherical fermi surface corresponds to the special case of $\eta f$ functions. In this state, the sequence does not satisfy the nodal structure of the gap in the $B$ phase as observed in thermal conductivity experimental observations where the distortions from a hexagonal structure increase at low temperatures would give a vortex lattice structure which becomes hexagonal at the lower temperatures which is contrary to the experimental observations where the distortions from a hexagonal structure increase at low temperatures. In addition, this state does not satisfy the nodal structure of the gap in the $B$ phase as observed in thermal conductivity and magnetization measurements.

### VI. WEAK COUPLING ACCIDENTAL DEGENERACY THEORIES

Here we consider the accidental degeneracy between the $T_{2g}$ and $E_g$ irreps as an example, since as explained at the end of this section there are many theories that have multiple transitions.

In weak coupling theory, we can write the fourth order free energy by evaluating the average

$$
< |\psi(k)|^4 > = < \eta_1 f_{1E_g}(k) + \eta_2 f_{2E_g}(k) + p_1 f_{1T_{2g}}(k) + p_2 f_{2T_{2g}}(k) + p_3 f_{3T_{2g}}(k) |^4 >
$$

In the above expression $\eta = (\eta_1, \eta_2)$ and $P = (p_1, p_2, p_3)$ are the order parameter values and the representative basis functions $f$ are assumed real. The free energy expression is

$$
F = \alpha_1(|\eta_1|^2 + |\eta_2|^2) + \alpha_2(|p_1|^2 + |p_2|^2 + |p_3|^2) + \beta_1[\text{Re}(\eta_1^2 + \eta_2^2) + \frac{1}{3}(\eta_1^* \eta_2^* - \eta_2 \eta_1^*)^2]
$$

$$
+ \beta_2(|p_1|^4 + |p_2|^4 + |p_3|^4)
$$

$$
+ \beta_3[4(|\eta_1|^2|p_1|^2 + |p_2|^2|p_3|^2 + |p_3|^4|p_1|^2) + p_1^2 p_2^2 + p_2^2 p_3^2 + p_3^2 p_1^2 + c.c]
$$

$$
+ \beta_4/2[4(|\eta_1|^2 + |\eta_2|^2)(|p_1|^2 + |p_2|^2 + |p_3|^2) + \text{Re}(\eta_1^2 + \eta_2^2)(p_1^* p_2 + p_2^* p_3 + p_3^* p_1 + c.c)]
$$

$$
- \beta_5/2[4(|\eta_1|^2 - |\eta_2|^2)(2|p_3|^2 - |p_1|^2 - |p_2|^2) - 4\sqrt{3}(\eta_1^* \eta_2 + \eta_1 \eta_2^*)(|p_1|^2 - |p_2|^2) + (\eta_1^2 - \eta_2^2)(2p_3^* - p_2^* - p_1^*) + 2\sqrt{3}\eta_1 \eta_2 (p_1^* - p_2^* + p_3^*) + c.c]}
$$

(8)

Within a weak coupling theory, the normalized coefficients are given by the following cubic averages

$$
\beta_1 = < f_{1E_g}^4(k) >, \beta_2 = < f_{1T_{2g}}^4(k) >, \beta_3 = < f_{2T_{2g}}^4(k) f_{1T_{2g}}^2(k) >, \beta_4 = < [f_{1E_g}^2(k) + f_{2E_g}^2(k)] f_{1T_{2g}}^2(k) >
$$

$$
\beta_5 = < [f_{1E_g}^2(k) - f_{2E_g}^2(k)] f_{1T_{2g}}^4(k) >
$$

The spherical fermi surface corresponds to the special case

$$
\beta_1 = \beta_2 = 3 \beta_3 = \frac{3}{2} \beta_4, \beta_5 = 0
$$

From Table V, we find that for $\beta_5 < 0$ the lowest 3 fourth order energies in increasing order correspond to states $P = (1, i, 0), P = (1, \omega, \omega^2), \eta = (1, i)$. We do not find any second order weak coupling transitions within this range.
For $\beta_5 > 0$ the lowest 3 fourth order energies in increasing order correspond to states $\eta = (1, i)$, $P = (1, \omega, \omega^2)$, $P = (1, i, 0)$. In this case we find only one stable second order transition from the state $P = |r|(1, i, 0)$ in the A phase to a B phase where it mixes to the state $\eta = e^{i\pi/4}(|\eta_1|, |\eta_2|e^{i\pi/2})$ with a transition temperature

$$T_{cB} = T_{cA} - \frac{1}{1 - \frac{2\beta_1 - \sqrt{7}\beta_3}{\beta_2 + \beta_3}}(T_{cA} - T_c)$$

The specific heat jump ratio at the transition temperatures is given by

$$\frac{c_B}{c_A} = \frac{T_{cB}}{T_{cA}} \left( \frac{7(\beta_2 + \beta_3 - 2\beta_4 + \sqrt{7}\beta_5)^2}{12\beta_1(\beta_2 + \beta_3) - 7(2\beta_4 - \sqrt{7}\beta_5)} \right)$$

We find that a specific heat jump ratio that is comparable to observed value for the skutterudite PrOs$_4$Sb$_{12}$ which is about one$^{21}$ can be obtained if the gap functions contain substantial cubic anisotropy. In addition this situation will result in an anisotropic state with two fold degeneracy. This sequence of phase transition would also result in a distorted vortex lattice structure owing to the large anisotropy of this state as shown in Figure 1.

We find that in many cases, the A to B transition is first order. The reason for this is as follows: for two order parameters $\psi$ and $\eta$ the free energy takes the form

$$F = \alpha_1|\psi|^2 + \alpha_2|\eta|^2 + \beta_1|\psi|^4 + \beta_2|\eta|^4 + \beta_{m1}|\psi|^2|\eta|^2 + \beta_{m2}(\psi^2\eta^2 + \eta^2\psi^2)$$

Let $(\psi, \eta) = (|\psi|, |\eta|e^{i\phi})$ and minimize with respect to $\phi$. The the free energy becomes

$$F = \alpha_1|\psi|^2 + \alpha_2|\eta|^2 + \beta_1|\psi|^4 + \beta_2|\eta|^4 + \beta_{m1}|\psi|^2|\eta|^2$$

where $\beta_m = \beta_{m1} - 2\beta_{m2} \approx \psi^2(k)f_\psi^2(k)$, $f_\eta(k)$ are the wave functions $f_\psi(k)$ and $f_\eta(k)$ that have been chosen. However we can get a second order transition by considering a two band theory for which $f_\psi(k)$ is large and $f_\eta(k)$ is small in one band while $f_\eta(k)$ is large and $f_\psi(k)$ is small on the other. Then the condition $\beta_m < 4\beta_1\beta_2$ will be easily satisfied and a second order A$\rightarrow$B phase transition can exist for almost any two different order parameter irreps.

VII. CONCLUSIONS

We have considered microscopic theories of unconventional superconductivity in cubic and tetrahedral superconductors. We have identified the stable weak-coupling unconventional superconducting states that belong to a single irreducible representation and have highlighted which of these can describe the low temperature properties of PrOs$_4$Sb$_{12}$. 

FIG. 1: (color online)Gap structure in the B phase for the $P = |r|(1, i, 0) + \eta = e^{i\pi/4}(|\eta_1|, |\eta_2|e^{i\pi/2})$ phase.
We have further examined theories for two intrinsic superconducting transitions in PrOs$_4$Sb$_{12}$. We have found that a theory for which the two transitions are due to a weakly broken $SO(3)$ symmetry for spin singlet Cooper pairs cannot give rise to two transitions in the weak-coupling limit. However, it is possible for such a theory to produce two transitions that agree with the experimental properties of PrOs$_4$Sb$_{12}$ only when extended to the strong-coupling limit. We further find that for spin-triplet Cooper pairs, weak spin-orbit coupling in the weak-coupling limit does not give rise to two superconducting transitions that agree with the experimental properties of PrOs$_4$Sb$_{12}$. Finally, we consider an example of a weak coupling theory that does not assume an approximate higher symmetry, but is based on the accidental closeness of the transition temperatures for two different representations. This example is able to describe the observed properties of PrOs$_4$Sb$_{12}$.

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