Symmetry of the order parameter in superconducting ZrZn₂

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We apply symmetry considerations to study the possible superconducting order parameters in ferromagnetic $ZrZn_2$. We predict that the presence and the location of the superconducting gap nodes depend on the direction of magnetization M. In particular, if M is directed along the z axis, then the order parameter should always have zeros. We also discuss how to determine the gap symmetry in $ZrZn_2$ using ultrasound attenuation measurements.

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Recently, superconductivity was found in $ZrZn_2$,¹ which is a weak itinerant ferromagnet. The most surprising fact is that the superconductivity occurs only in the ferromagnetic phase. The exchange splitting of Fermi surfaces makes a conventional singlet BCS-like pairing strongly suppressed. A number of theories have been proposed which show how the exchange by spin fluctuations can lead to a triplet Cooper pairing both in paramagnetic and ferromagnetic phases,² or to the enhancement of the superconducting critical temperature T_c on the ferromagnetic side.³ Another feature of the phase diagram is that T_c grows as pressure moves away from the ferromagnetic quantum critical point, which can be explained by the exchange-type interaction of the magnetic moments of the Cooper pairs with the magnetization density.⁴

Symmetry considerations can identify the possible order parameters, even in the absence of a firmly established microscopic mechanism of pairing, which is often the case for unconventional superconductors. The presence of ferromagnetism brings about a number of interesting features in the symmetry analysis. In this paper, we give a detailed analysis of the pairing symmetry in $ZrZn_2$, and discuss its consequences for the superconducting gap structure. Our work has some overlap with recent theoretical studies^{5,6} of the gap symmetry in another ferromagnetic superconductor UGe_2 .⁷ We find that the presence and location of the gap zeros depend on the direction of magnetization. We also discuss in some detail the design of ultrasonic attenuation experiments that can be used for experimental probing the order parameter symmetry.

The symmetry group \mathcal{G} of the system in the normal state is defined as a group of transformations which leave the system Hamiltonian H_0 invariant, i.e., $[G,H_0]=0$ for all elements $G \in \mathcal{G}$. In nonmagnetic superconductors the time-reversal symmetry K is not broken, and $\mathcal{G}=S \times K \times U(1)$, where S is the space group of the crystal and U(1) is the gauge group.⁸ In contrast, in magnetic superconductors the time-reversal symmetry is broken, and $\mathcal{G}=S_M \times U(1)$, where S_M is the magnetic space group which is a group of symmetry operations leaving both the crystal lattice (the microscopic charge density) and the magnetization density M invariant.⁹ For example, if there is a crystal point group rotation R which transforms M to -M, then the combined operation KR will be an element of S_M , because the time reversal restores the original M not affecting the lattice symmetry. In the above expressions, it is assumed that the space group elements act on the orbital and spin coordinates simultaneously, which is the case when the spin-orbit coupling is present. In the absence of spin-orbit coupling, the transformations of the orbital and spin spaces are independent, so that $\mathcal{G}=S_{orb}$ $\times G_{spin} \times U(1)$, where $G_{spin} = SO(2)$ is the group of spin rotations about the direction of M.

The crystal structure of $ZrZn_2$ in the absence of ferromagnetism is described by a face-centered-cubic Bravais lattice, with the Zr atoms forming a diamond structure. For cubic ferromagnets, the only two possibilities for the easy direction of magnetization are a [001] or [111] direction, and these possibilities are analyzed in this paper. Since a relatively small magnetic field (0.05 T at T=1.75 K) is required to line up the magnetic moments along a given direction,¹ it is expected that experiments could be carried out for M parallel to either [001] or [111]. The change in the superconducting gap structure when M is rotated by an external magnetic field is one of the interesting and unusual properties of $ZrZn_2$ that could be investigated experimentally.

If M is along [001], then S_M is generated by (i) lattice translations by the primitive vectors of the fcc lattice, $t_1 = (a/2)(1,1,0)$, $t_2 = (a/2)(0,1,1)$, and $t_3 = (a/2)(1,0,1)$, where a is the lattice constant; (ii) the rotations C_{4z} about the z axis by an angle $\pi/2$ followed by a fractional translation by a vector $\tau = (a/4)(1,1,1)$; (iii) the combined rotations KC_{2x} about the x axis by an angle π accompanied by the time reversal; and (iv) the inversion I. The point symmetry of the crystal is described by the magnetic group $\mathbf{D}_{4h}(\mathbf{C}_{4h})$ $= \mathbf{D}_4(\mathbf{C}_4) \times \mathbf{C}_i$, where $\mathbf{C}_i = \{E, I\}$. The subgroup in parentheses (the unitary subgroup) incorporates all symmetry elements which are not multiplied by the antiunitary and antilinear operation KC_{2x} , i.e., $\mathbf{D}_4(\mathbf{C}_4) = \mathbf{C}_4 + KC_{2x} \times \mathbf{C}_4$.

If *M* is along [111], then S_M is generated by (i) primitive lattice translations, (ii) rotations C_{3xyz} about the [111] direction by an angle $2\pi/3$, (iii) combined rotations KC_{2xy} about the [$\overline{1}10$] direction by an angle π accompanied by the time reversal, and (iv) the inversion *I*. The point symmetry is described by the magnetic group $\mathbf{D}_{3d}(\mathbf{C}_{3i}) = \mathbf{D}_3(\mathbf{C}_3) \times \mathbf{C}_i$, where $\mathbf{D}_3(\mathbf{C}_3) = \mathbf{C}_3 + KC_{2xy} \times \mathbf{C}_3$.

Using the standard notation for the space group operations, which combine rotations R and translations t, $r \rightarrow (R|t)r = Rr + t$, the transformation rules for the spinor wave functions can be written as

$$(R|t)\psi_{\sigma}(r) = [D^{(1/2)}(R)]_{\sigma\sigma'}\psi_{\sigma'}[R^{-1}(r-t)].$$
(1)

Here $\sigma = \uparrow, \downarrow$ is the spin projection on the direction of M, and $D^{(1/2)}(R)$ is the spinor representation of rotations: for a rotation by an angle θ around some axis n, $D^{(1/2)}(R) = U_n^{(s)}(\theta) = \exp[-i(\theta/2)(\boldsymbol{\sigma} \cdot \boldsymbol{n})]$. We will also need the transformation rules under the time reversal operation

$$K\psi_{\sigma}(\mathbf{r}) = (i\sigma_2)_{\sigma\sigma'}\psi^*_{\sigma'}(\mathbf{r}), \qquad (2)$$

and the inversion

$$I\psi_{\sigma}(\mathbf{r}) = \psi_{\sigma}(-\mathbf{r}). \tag{3}$$

In the presence of the exchange field and spin-orbit coupling, the single-particle wavefunctions are linear combinations of the eigenstates of the spin operator s_z : $\langle \mathbf{r} | \psi \rangle$ $= u(\mathbf{r}) |\uparrow\rangle + v(\mathbf{r}) |\downarrow\rangle$. Because the normal-state Hamiltonian H_0 is invariant with respect to the crystal-lattice translations, the eigenfunctions are Bloch waves $\psi_k(\mathbf{r})$ corresponding to wave vectors \mathbf{k} in the Brillouin zone. If the energy spectrum consists of a single band which is doubly degenerate in a zero exchange field due to the Kramers theorem, then diagonalization of the Hamiltonian in the presence of the exchange field results in two nondegenerate energy bands $\boldsymbol{\epsilon}_{\pm}(\mathbf{k})$. The corresponding single-particle wave functions have the form

$$\langle \boldsymbol{r}|\boldsymbol{k},\pm\rangle = u_{\boldsymbol{k}}^{(\pm)}(\boldsymbol{r})|\uparrow\rangle + v_{\boldsymbol{k}}^{(\pm)}(\boldsymbol{r})|\downarrow\rangle.$$
(4)

These states are referred to as pseudospin states. The operations from the group \mathcal{G} conserve the pseudospin in the following sense: $G|\mathbf{k},\pm\rangle = \exp[i\phi_{\pm}(\mathbf{k},G)]|G_{orb}\mathbf{k},\pm\rangle$, with G_{orb} describing the "orbital" part of the symmetry operation, e.g., rotations or reflections, and the undetermined phase factors ϕ_{\pm} coming from the freedom in choosing the overall phases of $|\mathbf{k},\pm\rangle$ at every point of the Brillouin zone. Here we adopt a convention introduced in Ref. 10, according to which the pseudospin states [Eq. (4)] transform similar to the spin eigenstates $|\mathbf{k},\uparrow\rangle$ and $|\mathbf{k},\downarrow\rangle$.

Let us first consider the case $M \parallel [001]$. From Eqs. (1)–(3), the transformation rules for the creation operators of electrons in states (4) are

$$(C_{4z}|\boldsymbol{\tau}):c_{\boldsymbol{k},\pm}^{\dagger} \rightarrow e^{-i(C_{4z}\boldsymbol{k})\cdot\boldsymbol{\tau}}e^{\pm i\pi/4}c_{C_{4z}\boldsymbol{k},\pm}^{\dagger},$$
$$(KC_{2x}|\boldsymbol{0}):\lambda c_{\boldsymbol{k},\pm}^{\dagger} \rightarrow \pm i\lambda^{*}c_{-C_{2x}\boldsymbol{k},\pm}^{\dagger},$$
(5)

$$I:c_{k,\pm}^{\dagger} \rightarrow c_{-k,\pm}^{\dagger}$$

Here λ is an arbitrary *c* number.

The pseudospin states can be used as a basis for constructing the Hamiltonian which takes into account the Cooper pairing between electrons with opposite momenta k and -k. Treating the Cooper interaction in the mean-field approximation we obtain $H=H_0+H_{sc}$, with the noninteracting part

$$H_0 = \sum_{\boldsymbol{k}} \left[\boldsymbol{\epsilon}_+(\boldsymbol{k}) c_{\boldsymbol{k}+}^{\dagger} c_{\boldsymbol{k}+} + \boldsymbol{\epsilon}_-(\boldsymbol{k}) c_{\boldsymbol{k}-}^{\dagger} c_{\boldsymbol{k}-} \right]$$
(6)

describing two separate sheets of the Fermi surface corresponding to different pseudospin indices, and

$$H_{sc} = \sum_{k} \sum_{\alpha,\beta=\pm} \left[\Delta_{\alpha\beta}(k) c^{\dagger}_{k\alpha} c^{\dagger}_{-k,\beta} + \text{H.c.} \right].$$
(7)

Here $\Delta_{++}(k)$ and $\Delta_{--}(k)$ represent the superconducting order parameters at the "+" and "-" sheets of the Fermi surface respectively, and $\Delta_{+-}(k) = -\Delta_{-+}(-k)$ is the order parameter composed of quasiparticles on different sheets. From the Pauli exclusion principle, $\Delta_{++}(k)$ and $\Delta_{--}(k)$ are odd functions of k, but $\Delta_{+-}(k)$ does not have a definite parity. Separating the odd and the even parts, the order parameter matrix can also be cast in a more familiar form $\Delta(k) = (i\sigma\sigma_2)d(k) + (i\sigma_2)\psi(k)$, where d and ψ are the pseudospin-triplet and the pseudospin-singlet components, respectively.⁸ The fact that the Fermi surface of ZrZn₂ consists of several sheets of different topology¹¹ does not change our results.

From Eqs. (5), the band spectra $\epsilon_{\pm}(k)$ are invariant under the operations from the point group \mathbf{D}_{4h} . Also, we obtain the transformation rules for the order parameters under rotations C_{4z} :

$$\Delta_{++}(\mathbf{k}) \rightarrow -i\Delta_{++}(C_{4z}^{-1}\mathbf{k}),$$

$$\Delta_{--}(\mathbf{k}) \rightarrow +i\Delta_{--}(C_{4z}^{-1}\mathbf{k})$$

$$\Delta_{+-}(\mathbf{k}) \rightarrow \Delta_{+-}(C_{4z}^{-1}\mathbf{k})$$
(8)

(note the cancellation of the τ -dependent phase factors on the right-hand side of these equations), and under the combined time reversal and rotations KC_{2x} :

$$\Delta_{++}(k) \to \Delta_{++}^{*}(C_{2x}^{-1}k),$$

$$\Delta_{--}(k) \to \Delta_{--}^{*}(C_{2x}^{-1}k),$$
(9)

$$\Delta_{+-}(k) \to \Delta_{+-}^{*}(-C_{2x}^{-1}k).$$

In the presence of the exchange band splitting E_{ex} , the low-frequency part of the spectrum of excitations (e.g., spin fluctuations) responsible for the interband Cooper pairing is cut out.² Since E_{ex} is by far the largest energy scale in the system: $E_{ex} \approx 5 \text{ mRy} \approx 800 \text{ K}$,¹² the pairing interactions $c_{k+}^{\dagger}c_{-k,-}^{\dagger}c_{k'-c_{-k',+}}$, which are responsible for Δ_{+-} , are negligibly small¹³ (some of the consequences of taking these interactions into account will be discussed below). On the other hand, the interband pairing terms $c_{k+}^{\dagger}c_{-k,+}^{\dagger}c_{k'-c_{-k',-}}$ can induce order parameters of the same symmetry on both sheets of the Fermi surface. We expect the effect of these terms to be small at small spin-orbit coupling, because they are absent at zero spin-orbit coupling due to the spin conservation.

The superconducting order parameter which emerges at T_c transforms according to one of the irreducible representations Γ of the normal state symmetry group \mathcal{G} . It can be represented as the expansion $\Delta_{\Gamma}(\mathbf{k}) = \sum_i \eta_{\Gamma,i} f_i(\mathbf{k})$, where *i* labels the orbital basis functions, and $\eta_{\Gamma,i}$ are the order parameter components which enter, e.g., the Ginzburg-Landau

TABLE I. The character table and the examples of the odd basis functions for the irreducible co-representations of the magnetic point group $\mathbf{D}_4(\mathbf{C}_4)$. The overall phases of the basis functions are chosen so that $KC_{2x}f_{\Gamma}(\mathbf{k}) = f_{\Gamma}(\mathbf{k})$. $\lambda_{1,2}$ are arbitrary real constants.

Г	Ε	C_{4z}	$f_{\Gamma}(\pmb{k})$	
A	1	1	k _z	
В	1	-1	$k_z[\lambda_1(k_y+ik_x)^2+\lambda_2(k_y-ik_x)^2]$	
^{1}E	1	i	$k_y + ik_x$	
^{2}E	1	-i	$k_y - ik_x$	

free energy. In our case, \mathcal{G} contains the antiunitary and antilinear operation KC_{2x} , and, instead of usual representations, one should use corepresentations of the magnetic point group $\mathbf{D}_4(\mathbf{C}_4)$, which can be derived from one-dimensional representations of the unitary subgroup C_4 .¹⁴ The results for odd corepresentations are listed in Table I. Note that the action of the unitary and antiunitary orbital symmetry elements on scalar functions $f(\mathbf{k})$ is defined as $Rf(\mathbf{k}) = f(R^{-1}\mathbf{k})$, and $KRf(\mathbf{k}) = f^*(-R^{-1}\mathbf{k}).$

If the superconductivity appears on the "+" sheet, then the order parameter is $\Delta_{++}(k)$ (in terms of the vector order $d(\mathbf{k}) = d_z(\mathbf{k})\hat{z} + [d_+(\mathbf{k})(\hat{x} - i\hat{y}) + d_-(\mathbf{k})(\hat{x})]$ parameter $(+i\hat{y})$]/2, it corresponds to $d_{-}=d_{x}-id_{y}$). Using Eqs. (8) and Table I, we obtain the following expressions:

$$\Delta_{++,A}(\mathbf{k}) = i \eta_A f_{1_E}(\mathbf{k}),$$

$$\Delta_{++,B}(\mathbf{k}) = i \eta_B f_{2_E}(\mathbf{k}),$$

$$\Delta_{++,1_E}(\mathbf{k}) = i \eta_{1_E} f_B(\mathbf{k}),$$

$$\Delta_{++,2_E}(\mathbf{k}) = i \eta_{2_E} f_A(\mathbf{k}).$$

$$(10)$$

The appearance of different representations on the left and right-hand sides of these expressions can be easily understood if we look at Eqs. (8). The transformed order parameter Δ_{++} has an extra factor -i which comes from the rotation of spin coordinates. In terms of d(k), this factor is the result of the rotation of the basis spin vector $\hat{x} + i\hat{y}$, which transforms according to the ${}^{2}E$ representation. Thus, for instance, the first of Eqs. (10) follows from the fact that $A = {}^{2}E \times {}^{1}E$. So far, we have discussed the transformation properties of order parameters (10) under the rotations from the unitary subgroup C_4 . Because of our choice of the overall phase of the basis functions (see the caption to Table I) and the factors i on the right-hand sides of Eqs. (10), the effect of the antiunitary operation KC_{2x} on η_{Γ} is equivalent to complex conjugation: $KC_{2x}\eta_{\Gamma} = \eta_{\Gamma}^*$.

As seen from Eqs. (10) and Table I, the order parameters Δ_A and Δ_B vanish at the poles of the Fermi surface $k_x = k_y$ =0, while the order parameters Δ_{1_E} and Δ_{2_E} vanish at the equator $k_z = 0$. One can prove that these gap zeros are not artifacts of our choice of the basis functions but are imposed by symmetry. Indeed, one of the elements of the unitary component C_{4h} of the magnetic point group is the basal plane reflection $\sigma_h = C_{2z} \times I$. Therefore,

$$\sigma_h f_{A,B}(\mathbf{k}) = f_{A,B}(k_x, k_y, -k_z) = -f_{A,B}(\mathbf{k}), \qquad (11)$$

so that $f_{A,B}(k_x, k_y, 0) = 0$, and $\Delta_{1_F}(k_x, k_y, 0) = \Delta_{2_F}(k_x, k_y, 0)$ =0. Similarly, under a fourfold rotation around the z axis,

$$C_{4z}f_{1_{E},2_{E}}(\boldsymbol{k}) = f_{1_{E},2_{E}}(k_{y},-k_{x},k_{z}) = \pm if_{1_{E},2_{E}}(\boldsymbol{k})$$

hence $f_{1_{E},2_{E}}(0,0,k_{z})=0$, and $\Delta_{A}(0,0,k_{z})=\Delta_{B}(0,0,k_{z})=0$. It also follows from Eq. (11) that $f_A(\mathbf{k})$ and $f_B(\mathbf{k})$ go to zero at $k_z = \pm \pi/a$, i.e., at the surface of the Brillouin zone, because $(k_x, k_y, \pi/a)$ and $(k_x, k_y, -\pi/a)$ are equivalent points. In order to take into account the crystal periodicity leading to the presence of these additional gap zeros, one has to represent the basis functions as the lattice Fourier series f(k)= $\sum_{n} f_n e^{i \mathbf{k} \cdot \mathbf{R}_n}$, where summation goes over the sites \mathbf{R}_n of the Bravais lattice of the crystal. The expansion appropriate for an odd order parameter has the form

$$f(\boldsymbol{k}) = \sum_{n} c_{n} \sin \boldsymbol{k} \cdot \boldsymbol{R}_{n}, \qquad (12)$$

where \mathbf{R}_n are the sites of a fcc cubic lattice, which cannot be transformed one into another by inversion. In the nearestneighbor approximation, we choose the following set of $\{\mathbf{R}_n\} = a/2\{(101), (\overline{1}01), (011), (0\overline{1}1), (110), (\overline{1}10)\}.$ **R**_n's: Using the representation characters from Table I, we obtain the basis functions which have symmetry-imposed zeros at the surface of the Brillouin zone:

$$f_{A}(\mathbf{k}) = \sin\frac{k_{z}a}{2} \left(\cos\frac{k_{x}a}{2} + \cos\frac{k_{y}a}{2}\right),$$

$$f_{B}(\mathbf{k}) = \sin\frac{k_{z}a}{2} \left(\cos\frac{k_{x}a}{2} - \cos\frac{k_{y}a}{2}\right),$$

$$f_{1_{E}}(\mathbf{k}) = \cos\frac{k_{z}a}{2} \left(\sin\frac{k_{y}a}{2} + i\sin\frac{k_{x}a}{2}\right),$$

$$+ \lambda_{1} \left[e^{i\pi/4}\sin\left(\frac{k_{x}a}{2} + \frac{k_{y}a}{2}\right) - e^{-i\pi/4}\sin\left(\frac{k_{x}a}{2} - \frac{k_{y}a}{2}\right)\right],$$

$$f_{2}(\mathbf{k}) = \cos\frac{k_{z}a}{2} \left(\sin\frac{k_{y}a}{2} - i\sin\frac{k_{x}a}{2}\right).$$

$$+\lambda_2 \left[e^{-i\pi/4} \sin\left(\frac{k_x a}{2} + \frac{k_y a}{2}\right) - e^{i\pi/4} \sin\left(\frac{k_x a}{2} - \frac{k_y a}{2}\right) \right].$$

Here $\lambda_{1,2}$ are arbitrary real constants. The polynomial expressions for the basis functions from Table I are recovered in the limit of a "small" Fermi surface $k \rightarrow 0$ [note that $f_B(k)$] from Table I can be obtained by including the next-nearest neighbors in expansion (12)]. It should be noted that these nearest-neighbor results also give gap zeros not required by symmetry, e.g., $f_B(\mathbf{k}) = 0$ on the plane $k_x = k_y$. These "accidental" zeros will be removed if higher-neighbor terms are

 f_{1}

included, but if nearest-neighbor terms turn out to be dominant, experiment could find indications of these accidental zeros.

The order parameter on the pseudospin-down sheet of the Fermi surface is $\Delta_{--}(k)$ [in terms of d(k), it corresponds to $d_{+}=d_{x}+id_{y}$, and the relevant basis spin vector is $\hat{x}-i\hat{y}$, which transforms according to the ¹*E* representation]. Its *k* dependence is given by the following expressions:

$$\Delta_{--,A}(\mathbf{k}) = i \,\eta_A f_{2_E}(\mathbf{k}),$$

$$\Delta_{--,B}(\mathbf{k}) = i \,\eta_B f_{1_E}(\mathbf{k}),$$

$$\Delta_{--,1_E}(\mathbf{k}) = i \,\eta_{1_E} f_A(\mathbf{k}),$$

$$\Delta_{--,2_E}(\mathbf{k}) = i \,\eta_{2_E} f_B(\mathbf{k}).$$
(13)

If we take into account the interband pairing interaction of the form $c_{k+}^{\dagger}c_{-k,+}^{\dagger}c_{k'-c_{-k',-}}$, then both Δ_{++} and Δ_{--} are nonzero and correspond to the same irreducible corepresentation of the magnetic point group. Comparing Eqs. (10) and (13), we see that, although the orbital symmetries of Δ_{++} and Δ_{--} are different, they have symmetry-imposed gap nodes at the same locations on both sheets of the Fermi surface. For example, if the order parameter corresponds to the A corepresentation, then both $\Delta_{++,A}(\mathbf{k}) \sim f_{1E}(\mathbf{k})$ and $\Delta_{--,A}(\mathbf{k}) \sim f_{2E}(\mathbf{k})$ have point nodes at $k_x = k_y = 0$.

The gap nodes disappear only if the interband pairing interactions $c_{k+}^{\dagger} c_{-k,-}^{\dagger} c_{k'-} c_{-k',+}$ are taken into account. These terms induce a nonzero order parameter Δ_{+-} , whose momentum dependence in the triplet channel, according to Eqs. (8) and Table I, is given by $\Delta_{+-,\Gamma}(k) \sim f_{\Gamma}(k)$, where Γ = $A, B, {}^{1}E$, or ${}^{2}E$. To see explicitly how the structure of the nodes in the different components of the gap function is translated into zeros of the spectrum of Bogoliubov quasiparticle excitations, it is necessary to diagonalize the Hamiltonian of Eqs. (6) and (7). This gives the following condition for the energy E(k) of a quasiparticle to be zero at some k:

$$\epsilon_{+}^{2} \epsilon_{-}^{2} + \epsilon_{+}^{2} |\Delta_{--}|^{2} + \epsilon_{-}^{2} |\Delta_{++}|^{2} + \epsilon_{+} \epsilon_{-} (|\Delta_{+-}|^{2} + |\Delta_{-+}|^{2}) + |\det \Delta|^{2} = 0.$$
(14)

The condition for zeros in the excitation energy on the "+" sheet of the Fermi surface [i.e., at $\epsilon_+(k)=0$] is that $\Delta_{++}(k) = \Delta_{+-}(k) = 0$, while for zeros in the excitation energy on the "-" sheet [i.e., at $\epsilon_-(k)=0$] we must have $\Delta_{--}(k) = \Delta_{+-}(k) = 0$. Thus a nonzero Δ_{+-} will remove the nodes in the spectrum of elementary excitations. For example, $\Delta_{+-,A}(k) \sim f_A(k)$ does not vanish at $k_x = k_y = 0$, so that these point nodes should be filled. However, as discussed above, this effect is expected to be negligibly small.

In the absence of a complete understanding of the microscopic mechanism of the superconductivity in ZrZn₂, one cannot tell which order parameter from lists (10) and (13) corresponds to the highest critical temperature. For example, if the superconductivity is due to the exchange by spin fluctuations, then, at vanishing spin-orbit coupling, the order parameters $\Delta_{++,A}$, $\Delta_{++,B}$, and $\Delta_{++,2E}$ correspond to the

TABLE II. The character table and the examples of the odd basis functions for the irreducible co-representations of the magnetic point group $\mathbf{D}_3(\mathbf{C}_3)$, $\omega = e^{2\pi i/3}$. The overall phases of the basis functions are chosen so that $KC_{2\bar{x}v}f_{\Gamma}(\mathbf{k}) = f_{\Gamma}(\mathbf{k})$.

Г	Е	C_{3xyz}	C_{3xyz}^{-1}	$f_{\Gamma}(\boldsymbol{k})$
A	1	1	1	$k_x + k_y + k_z$
^{1}E	1	ω	ω^*	$e^{-i\pi/3}k_x - k_y + e^{i\pi/3}k_z$
^{2}E	1	ω^*	ω	$e^{i\pi/3}k_x - k_y + e^{-i\pi/3}k_z$

p-wave equal-spin-pairing superconducting states studied in Ref. 2; in these terms, $\Delta_{++,1E}$ corresponds to *f*-wave pairing. In Ref. 4, a simple phenomenological model of the phase diagram of $ZrZn_2$ was proposed. The basic idea was that the underlying order parameter is a vector quantity transforming according to a three-dimensional representation of the cubic group. Then, the exchange-type interaction of the magnetization splits the superconducting critical temperature and lowers the dimensionality of the order parameter from three to one. In this model, the order parameters Δ_{1E} and Δ_{2E} are the possible ones, and the experimental determination of the gap symmetry will thus be helpful in assessing the validity of the model.

A similar analysis can be done if the easy axis for magnetization is [111]. In this case, the band spectra are invariant under the operations from the group \mathbf{D}_{3d} , the relevant magnetic point group is $\mathbf{D}_3(\mathbf{C}_3)$, and transformation rules (8) and (9) for the order parameter are replaced by

$$\Delta_{++}(\mathbf{k}) \rightarrow e^{-2i\pi/3} \Delta_{++}(C_{3xyz}^{-1}\mathbf{k}),$$

$$\Delta_{--}(\mathbf{k}) \rightarrow e^{+2i\pi/3} \Delta_{--}(C_{3xyz}^{-1}\mathbf{k}),$$

$$\Delta_{+-}(\mathbf{k}) \rightarrow \Delta_{+-}(C_{3xyz}^{-1}\mathbf{k})$$

(15)

under rotations C_{3xyz} , and

$$\Delta_{++}(\mathbf{k}) \to \Delta_{++}^{*}(C_{2xy}^{-1}\mathbf{k}),$$

$$\Delta_{--}(\mathbf{k}) \to \Delta_{--}^{*}(C_{2xy}^{-1}\mathbf{k})$$
(16)

$$\Delta_{+-}(\mathbf{k}) \to \Delta_{+-}^{*}(-C_{2xy}^{-1}\mathbf{k}),$$

under the combined operation KC_{2xy} .

Using Table II, we obtain the following k dependences of the order parameter at the pseudospin-up sheet:

$$\Delta_{++,A}(\mathbf{k}) = i \,\eta_A f_{1_E}(\mathbf{k}),$$

$$\Delta_{++,^{1_E}}(\mathbf{k}) = i \,\eta_{1_E} f_{2_E}(\mathbf{k}),$$

$$\Delta_{++,^{2_E}}(\mathbf{k}) = i \,\eta_{2_E} f_A(\mathbf{k}).$$
(17)

As above, the factors *i* here guarantee that the action of KC_{2xy} on η_{Γ} is equivalent to complex conjugation.

A consequence of the above results is that there are no gap nodes for $\Delta_{2_{\overline{E}}}$ whereas Δ_A and $\Delta_{1_{\overline{E}}}$ have point nodes where the line $k_x = k_y = k_z$ cuts the Fermi surface. For completeness, we also give the expressions for the basis functions of the magnetic point group $\mathbf{D}_3(\mathbf{C}_3)$ in terms of the lattice Fourier series in the nearest-neighbor approximation:

$$\begin{split} f_A(\mathbf{k}) &= S_1^+ + S_2^+ + S_3^+ + i\lambda_1(S_1^- + S_2^- + S_3^-), \\ f_{1_E}(\mathbf{k}) &= \omega^* S_1^+ + \omega S_2^+ + S_3^+ + i\lambda_2(\omega^* S_1^- + \omega S_2^- + S_3^-), \\ f_{2_E}(\mathbf{k}) &= \omega S_1^+ + \omega^* S_2^+ + S_3^+ + i\lambda_3(\omega S_1^- + \omega^* S_2^- + S_3^-), \end{split}$$

where $S_1^{\pm} = \sin(k_x a/2 \pm k_y a/2)$, $S_2^{\pm} = \sin(k_y a/2 \pm k_z a/2)$, and $S_3^{\pm} = \sin(k_z a/2 \pm k_x a/2)$, and $\lambda_{1,2,3}$ are arbitrary real constants.

For the order parameter at the "-"-sheet of the Fermi surface:

$$\Delta_{--,A}(\mathbf{k}) = i \,\eta_A f_{2_E}(\mathbf{k}),$$

$$\Delta_{--,^{1_E}}(\mathbf{k}) = i \,\eta_{1_E} f_A(\mathbf{k}),$$

$$\Delta_{--,^{2_E}}(\mathbf{k}) = i \,\eta_{2_E} f_{1_E}(\mathbf{k}).$$
(18)

There are no gap nodes for Δ_{1_E} , but Δ_A and Δ_{2_E} have point nodes at $k_x = k_y = k_z$. If the interband hybridization of the form $c_{k+}^{\dagger}c_{-k,+}^{\dagger}c_{k'-}c_{-k',-}$ is taken into account, the order parameters are nonzero on both sheets of the Fermi surface. From Eqs. (17) and (18), we see that both $\Delta_{++,A}(\mathbf{k}) \sim f_{1_E}(\mathbf{k})$ and $\Delta_{--,A}(\mathbf{k}) \sim f_{2_E}(\mathbf{k})$ vanish on the line $k_x = k_y$ $= k_z$. The gap nodes disappear only in the presence of the interband pairing $c_{k+}^{\dagger}c_{-k,-}^{\dagger}c_{k'-}c_{-k',+}$, which induces the order parameter $\Delta_{+-,\Gamma}(\mathbf{k}) \sim f_{\Gamma}(\mathbf{k})$, where $\Gamma = A$, ${}^{1}E$, or ${}^{2}E$. Again, we expect Δ_{+-} to be negligibly small in the presence of a large exchange field.

The presence of gap nodes would manifest themselves in power-law temperature dependences of the thermodynamic and transport properties.⁸ For example, the electronic specific heat at low temperatures should be $C(T)/T = \gamma_0 + \gamma_1 T$ for the line nodes and $C(T)/T = \gamma_0 + \gamma_1 T^2$ for the point nodes. The temperature-independent contributions on the right-hand side of these equations come from the normal excitations at the unpaired sheet of the Fermi surface. If the magnitudes of both order parameters Δ_+^2 are Δ_-^2 are comparable (we expect this to be the case only if the spin-orbit coupling is strong enough), then γ_0 is absent and a power-law dependence should be observed.

One of the most powerful methods of determining the presence and the location on the Fermi surface of gap nodes in unconventional superconductors has been ultrasonic attenuation.^{15–19} The method is based on finding which sound waves are particulary weakly attenuated by the nodal quasiparticles. Nodal quasiparticles are "inactive" in attenuating a particular sound wave if the electron-phonon interaction for the nodal quasiparticle with the particular sound wave is zero. Symmetry arguments determining the inactive nodes were developed in a previous paper.¹⁹ We refer to that

paper for a detailed treatment of the basic ideas, and here give an extension of the arguments which is necessary for treating magnetic groups.

If a symmetry operation of the crystal (i.e. an element of its magnetic point group) leaves the wave vector k characterizing a given electron state invariant, then the interaction of this electron with certain phonons can be shown to be zero. Consider a phonon of wave vector \boldsymbol{q} and polarization direction e. The interaction of the given electron with the given phonon can be shown to be zero if the symmetry operation causes an odd number of changes of sign of the two quantities iq and e (the factor *i* is important because the time-reversal operation contains complex conjugation). The transformation rules for k, q, and e are as follows: (i) Under the point-group operations R, they transform like polar vectors, i.e., $k \rightarrow R^{-1}k$, etc. (ii) Under the combined operations KR, $k \rightarrow -R^{-1}k$, $e \rightarrow R^{-1}e$, and $q \rightarrow -R^{-1}q$, so that iq $\rightarrow iR^{-1}q$. For example, suppose that the magnetic group contains the symmetry element KC_{2x} . The wave vectors \boldsymbol{k} of electrons lying in the $k_x = 0$ plane are invariant under KC_{2x} . According to the rule just stated, these electrons have zero interaction with transverse phonons having their wave vectors along the x axis because, under the operation KC_{2x} , iq remains invariant, but e changes sign.

As shown above, one should expect the order parameter in $ZrZn_2$ to have nodes if $M \parallel [001]$, when the magnetic point group is $\mathbf{D}_4(\mathbf{C}_4)$. The gap nodes are always active for longitudinal sound waves. If the order parameter has point nodes $[\Delta_A \text{ or } \Delta_B \text{ in Eqs. (10)}]$, then these point nodes are inactive for the transverse waves T100 and T110 polarized either in the basal plane or along [001], and also for the waves T001 polarized either along [100] or [110]. (By definition, a *Thkl* sound wave is a transverse wave having its wave vector qalong the [hkl] direction.) If the order parameter has line nodes in the plane $k_z = 0$ [Δ_{1_E} or Δ_{2_E} in Eqs. (10)], then these line nodes are inactive for the transverse waves T100and T110 polarized along [001], and also for T001 waves polarized either along [100] or [110]. Note that the attenuation of the T100 and T110 waves polarized in the basal plane can be used to distinguish between the equatorial line nodes and the point nodes, because the former are active but the latter are inactive. The presence of unpaired electrons on one of the sheets of the Fermi surface will not cause difficulties in symmetry determination by ultrasonic attenuation, as this will simply make a contribution to the low-temperature temperature-independent background, which is easily distinguished from the temperature-dependent contribution of the gapped sheet (or sheets) of the Fermi surface.

To summarize, we have studied the symmetry of the superconducting order parameter in $ZrZn_2$. If the spin-orbit coupling is weak then superconductivity should appear on only one of the sheets of the Fermi surface. The interband scattering can, in principle, induce nonzero order parameters on other sheets and also fill the gap zeros, but we expect these effects to be small. The symmetry of the order parameter depends on the direction of the easy axis for magnetization. If M || [001], then the magnetic point group is $D_4(C_4)$, and the order parameter goes to zero on the line $k_x = k_y = 0$

for the gap symmetries A and B, or on the planes $k_z=0$, $\pm \pi/a$ for the symmetries 1E and 2E , on both sheets of the Fermi surface. The positions of the gap zeros can be probed by ultrasonic attenuation measurements, and to assist in the design of appropriate experiments we have given a detailed discussion of the zeros of the electron-phonon interaction in ferromagnetic ZrZn₂ which are imposed by the magnetic point symmetry. If $M \parallel [111]$, then the magnetic point group is $\mathbf{D}_3(\mathbf{C}_3)$, and the order parameter has point zeros on the line $k_x = k_y = k_z$ on both sheets of the Fermi surface, for the gap symmetry A, and on one of the sheets, for the symme-

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tries ${}^{1}E$ and ${}^{2}E$. It should be possible to fix the magnetization density M along an arbitrary crystallographic direction by the application of an external magnetic field, and hence to determine the gap structure for $ZrZn_{2}$ for M along both [001] and [111] and to find the changes that occur when M is rotated from [001] to [111].

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