

## Model for Superconductivity in Ferromagnetic ZrZn<sub>2</sub>

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We propose that superconductivity in the ferromagnetic state of ZrZn<sub>2</sub> is stabilized by an exchange-type interaction between the magnetic moments of triplet-state Cooper pairs and the ferromagnetic magnetization density. This explains why superconductivity occurs in the ferromagnetic state only, and why it persists deep into the ferromagnetic state. The model of this article also yields a particular order parameter symmetry, which is a prediction that can be checked experimentally.

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Recently, superconducting states have been found to coexist with ferromagnetism in the materials UGe<sub>2</sub> [1–3], ZrZn<sub>2</sub> [4], and URhGe [5]. The initial discovery in UGe<sub>2</sub> was motivated by the idea that parallel-spin (and hence spin-triplet-state) Cooper pairs would be favored in a metallic state close to the border of ferromagnetism. The proximity of a ferromagnetic state would give rise to relatively strong ferromagnetic fluctuations which would promote spin-triplet pairing.

A sketch of the phase diagram as measured in Ref. [4] for ZrZn<sub>2</sub> is shown in Fig. 1. As noted by the authors of Ref. [4], one of the most intriguing and perhaps surprising features of superconductivity in ZrZn<sub>2</sub> (as well as that occurring in UGe<sub>2</sub>) is that it occurs only in the ferromagnetic state. The reason for the surprise is that previous theoretical work had not anticipated that superconductivity could occur in the ferromagnetic phase, unless at the very least it was also stable in the paramagnetic phase. The possibility that superconductivity might appear only in the ferromagnetic phase does not seem to have been considered before the recent experimental discoveries. For example, a very early article [6] had noted that the presence of the large internal magnetic induction in a ferromagnet would suppress superconductivity. Also, another early theoretical article [7], which demonstrated how spin fluctuations can give rise to *p*-wave superconductivity, found that the superconductivity occurs in both the ferromagnetic and paramagnetic phases close to the ferromagnetic quantum critical point (see Fig. 2). Other examples which find superconductivity on the paramagnetic side of a ferromagnetic quantum critical point include Refs. [8–11]. Very recently it has been argued [12] that the critical temperature for spin-triplet *p*-wave superconductivity mediated by spin fluctuations is generically much higher in the Heisenberg ferromagnetic phase than in the paramagnetic phase, due to the coupling of the magnons to the longitudinal spin susceptibility, and this result is qualitatively in agreement with the superconducting phase diagram for UGe<sub>2</sub> (see Fig. 2). Another line of argument [13] is that the pairing symmetry realized in UGe<sub>2</sub> must be a nonunitary spin-triplet pairing similar to that realized [14] in the *A*<sub>1</sub> phase of superfluid <sup>3</sup>He because such states are free from the Pauli limit and

can survive in a huge internal magnetic field. In addition, the superconducting order-parameter symmetry in the ferromagnetic phase of UGe<sub>2</sub> has been studied [15] in terms of the magnetic point group symmetry of the ferromagnetic phase. The ideas introduced below have some overlap with these latter [13–15] ideas. Finally, we note an article that has shown theoretically that coexisting superconductivity and ferromagnetism can occur for the case where the same band electrons produce both phenomena [16].

This article describes a phenomenological model that gives a good description of superconductivity in ferromagnetic ZrZn<sub>2</sub> (although not in ferromagnetic UGe<sub>2</sub>). In particular, the model gives a natural explanation of the fact that superconductivity occurs in the ferromagnetic but not in the paramagnetic phase. The basic idea is that in the superconducting state the Cooper pairs can have magnetic moments—see Ref. [17]. In the presence of a ferromagnetic magnetization density in the sample the magnetic moments of the Cooper pairs can interact with this ferromagnetic magnetization density via an interaction having

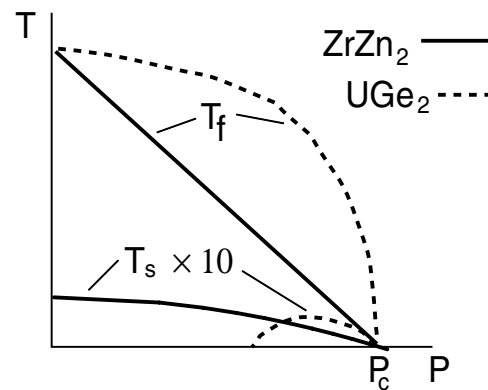


FIG. 1. Phase diagram showing the ferromagnetic ( $T_f$ ) and superconducting ( $T_s$ ) transition temperatures in ZrZn<sub>2</sub> as functions of pressure, as derived from the model of this article and as determined by experiment [4]. For clarity, the temperature scale for the superconducting phase transition has been multiplied by a factor of approximately 10 relative to that for the ferromagnetic phase transition as in Ref. [4]. Note that the qualitative behaviors of both  $T_f$  and  $T_s$  for UGe<sub>2</sub> (sketch of data from Ref. [1]) are quite different from those for ZrZn<sub>2</sub>.

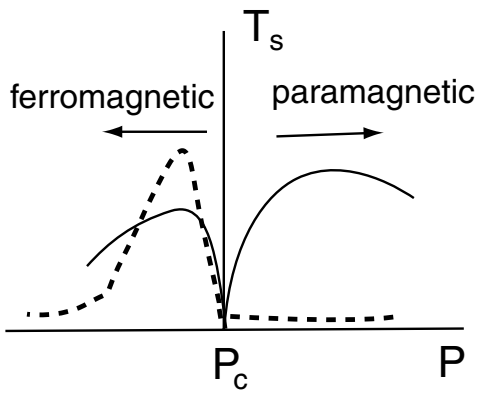


FIG. 2. Schematic reproduction of the results of Ref. [7] (solid line) and Ref. [12] (dashed line) showing theoretical calculations of the  $p$ -wave superconducting transition temperature versus pressure  $P$ . (Here  $P$  represents any parameter characterizing the distance from the quantum critical point.) The results of Ref. [7] and others (see text) were responsible for the idea that superconductivity in a ferromagnetic state would also be accompanied by superconductivity in the neighboring paramagnetic state. The very recent result of Ref. [12] is qualitatively similar to the phase diagram determined for  $\text{UGe}_2$  (which has a small pocket of superconductivity close to  $P_c$ ) but not to that for  $\text{ZrZn}_2$  (where superconductivity occurs at all  $P$  between  $P = 0$  and  $P = P_c$ ).

the form of an exchange interaction. The Cooper pair magnetization density chooses a direction that makes this “exchange” energy negative, and this is the mechanism that makes the superconducting state more stable in the ferromagnetic state than in the paramagnetic state. As will be shown below, in order to give rise to superconductivity in the ferromagnetic state but not in the paramagnetic state, the exchange coupling just described must be greater than a certain critical value.

The ferromagnetic state will be modeled using the Landau free energy [18]

$$F_f = \alpha'_f [T - T_f(P)]M^2 + \frac{1}{2} \beta_f M^4. \quad (1)$$

Here the ferromagnetic transition temperature  $T_f$  is assumed to depend on the pressure  $P$ . Expanding  $T_f(P)$  in a Taylor series about the point  $P_c$  at which it goes to zero, and keeping only the first nonvanishing term, yields  $T_f(P) = T'_f(P_c - P)$ . This linear dependence of  $T_f$  on  $P$  agrees well with the experimentally measured pressure dependence for  $\text{ZrZn}_2$  [4], shown in Fig. 1. From Eq. (1) one finds  $M = (\alpha'_f/\beta_f)^{1/2} [T_f(P) - T]^{1/2}$ .

For cubic ferromagnets (such as  $\text{ZrZn}_2$ ) the only two possibilities for the easy direction of the ferromagnetic magnetization density are the [100] or [111] direction [18]. Although in the absence of ferromagnetism, the C15 Laves phase structure of  $\text{ZrZn}_2$  has cubic  $\mathbf{O}_h$  ( $m\bar{3}m$ ) point group symmetry, the point group symmetry in the presence of ferromagnetism is reduced to the magnetic point group  $\mathbf{D}_{4h}(\mathbf{C}_{4h})$  ( $4/m\bar{m}'m'$ ) symmetry for the ferromagnetic magnetization density in the [100] direction, or  $\mathbf{D}_{3d}(\mathbf{C}_{3i})$  ( $\bar{3}m'$ ) for the ferromagnetic magnetization density in the

[111] direction. Since all of the irreducible representations of  $\mathbf{C}_{4h}$  and  $\mathbf{C}_{3i}$  are one dimensional, it is expected that the transition to superconductivity in the presence of ferromagnetism can be described by a one-component order parameter.

It is of interest to investigate how this one-component order parameter describing superconductivity in the presence of ferromagnetism might be related to order parameters appropriate to the description of superconductivity in cubic  $\text{ZrZn}_2$  in the absence of ferromagnetism. An advantage of treating the paramagnetic, nonsuperconducting state as the reference state is that an explicit dependence of the parameters describing the superconductivity on  $M$  is obtained (see below). Because of the large value of the exchange field compared to the superconducting critical temperature, all spin-singlet states of Cooper pairs are excluded. Thus, assuming spin-triplet pairing, consider the representation  $F_{1u}$  of the group  $\mathbf{O}_h$  for which the order parameter is the three-component quantity  $\boldsymbol{\psi} = (\psi_x, \psi_y, \psi_z)$  whose components transform under rotations like those of a three-dimensional polar vector [19] (the  $F_{2u}$  representation gives the same model). We use a strong spin-orbit coupling scheme, in which rotations transform both spin and orbital degrees of freedom. Also, the time-reversed state corresponding to  $\boldsymbol{\psi}$  is  $\boldsymbol{\psi}^R = (\psi_x^*, \psi_y^*, \psi_z^*)$ . Now define the vector product

$$\mathbf{S} = i\boldsymbol{\psi}^* \times \boldsymbol{\psi}. \quad (2)$$

Because this quantity transforms like a magnetization density under the operations of  $\mathbf{O}_h$  and time reversal, it will be interpreted (to within a constant factor) as a magnetization density associated with the Cooper pairs. It should be noted that, at the phenomenological level of this article, in the strong spin-orbit coupling scheme, the spin and orbital magnetization density of Cooper pairs cannot be distinguished.

Now consider the following terms of an expansion of the Ginzburg-Landau (GL) free energy in powers of the components of the order parameters  $\mathbf{M}$  and  $\boldsymbol{\psi}$

$$F_{S,0} = \alpha \boldsymbol{\psi}^* \cdot \boldsymbol{\psi} - 4\pi \mathbf{J} \mathbf{M} \cdot \mathbf{S}. \quad (3)$$

Only the terms quadratic in the superconducting order parameter and consistent with the cubic symmetry and time-reversal invariance have been included here, since these are all that are necessary (together with the gradient terms) to find the upper critical field for superconductivity. Furthermore, terms up to linear order in  $\mathbf{M}$  have been included. Note that the last term in this equation has the form of an exchange interaction between the ferromagnetic magnetization density and the Cooper-pair magnetization density. If the exchange parameter  $J$  is positive, the formation of a superconducting state in which the Cooper-pair magnetization density is parallel to the ferromagnetic magnetization density is favored. Also, if the ferromagnetic magnetization density  $\mathbf{M}$  is rotated (by an applied magnetic field) this exchange mechanism for stabilizing the

superconductivity is still applicable, and the orientation of the Cooper-pair magnetization density  $\mathbf{S}$  will follow that of the ferromagnetism. (If  $J < 0$ , an equivalent model is obtained in which a Cooper-pair magnetization density antiparallel to the ferromagnetic magnetization density is favored.) The free energy of Eq. (3) is reminiscent of that employed in the description of the  $A_1$  phase of  $^3\text{He}$  [14].

Now call the direction of the nonzero ferromagnetic magnetization density the  $z$  direction (which, as noted above, can be either a [100] or a [111] direction for a cubic ferromagnetic). In addition to the exchange field coupled with the spin of electrons, the magnetization creates an internal magnetic induction which interacts with the electron charge. Thus, the superconductor should be in the mixed state even in the absence of an external magnetic field, and, in order to calculate the transition temperature, one has to take into account the gradient terms in the GL free energy, in addition to the uniform terms given by Eq. (3):

$$F_S = F_{S,0} + K_1(D_i\psi_j)^*(D_i\psi_j) + K_2[(D_i\psi_i)^*(D_j\psi_j) + (D_i\psi_j)^*(D_j\psi_i)] + K_3(D_i\psi_i)^*(D_i\psi_i). \quad (4)$$

Here  $\alpha = \alpha'(T - T_0)$ , and  $T_0$  is the superconducting transition temperature in the absence of the exchange interaction of Cooper pairs with the ferromagnetic magnetization (i.e., at  $J = 0$ ), which is assumed to be positive. The gradient part contains terms which are invariant under rotations from the cubic group [20], with  $D_i = -i\hbar(\partial/\partial x_i) + (2|e|/c)A_i$ , and  $\text{curl}\mathbf{A} = \mathbf{B}$ . The magnetic induction is given by  $\mathbf{B} = \mathbf{H}_{\text{ext}} + 4\pi\mathbf{M}$ , where  $\mathbf{H}_{\text{ext}}$  is the external magnetic field directed along  $z$ , and the magnetization density is  $\mathbf{M} = \mathbf{M}_0 + (\mu - 1)\mathbf{H}_{\text{ext}}/4\pi$ . The long cylinder geometry, with the  $z$  axis along the axis of the cylinder, has been assumed.

Using a variational approach [21] to minimize the free energy (4), we calculate the superconducting critical temperature as a function of the magnetization density and external field, which takes the simple form

$$T_c(M) = T_0 + \frac{4\pi(J - J_c)}{\alpha'} M \quad (5)$$

at  $H_{\text{ext}} = 0$ . The quantity  $J_c$  describes the suppression of the critical temperature due to orbital effects. It takes different values for  $\mathbf{M} \parallel [100]$ :  $J_c = (|e|/\hbar c)(2K_1 + 2K_2 + K_3)$ , and for  $\mathbf{M} \parallel [111]$ :  $J_c = (|e|/\hbar c)(2K_1 + 2K_2 + 2K_3/3)$ . Another result of our calculation is that the only component of the order parameter which is nonzero at  $T = T_c(M) - 0$  is  $\psi_- = (\psi_x - i\psi_y)/\sqrt{2}$  [or  $\psi_+ = (\psi_x + i\psi_y)/\sqrt{2}$  for  $J < 0$ ]. It is this quantity that describes the formation of a superconducting state with its Cooper-pair magnetization density parallel to the ferromagnetic magnetization density. Finally, note from Eq. (5) that, in order for  $T_c$  to be enhanced in the ferromagnetic phase relative to its value  $T_0$  in the paramagnetic phase, the exchange parameter  $J$  must be greater

than  $J_c$ . In the weak-coupling theory,  $J$  is proportional to  $N'(\epsilon_F)$ , the derivative of the single-particle density of states (DOS) at the Fermi level [17]. The smallness of this quantity in  $^3\text{He}$  explains the narrow region of existence of the  $A_1$  phase. In the case of  $\text{ZrZn}_2$ , however, where the DOS is extremely sharply peaked near the Fermi energy [22],  $N'(\epsilon_F)$  could be very large, but estimating  $J$  in terms of  $N'(\epsilon_F)$  is probably too simplistic.

In order to confirm  $\psi_-$  as a possible order parameter describing the formation of superconductivity in the ferromagnetic state, it should be checked that it transforms as a basis vector of some irreducible representation of the magnetic symmetry group of the ferromagnet [15]. Suppose that the ferromagnetic magnetization density is along the [100] direction. Then the magnetic symmetry group is  $\mathbf{D}_{4h}(\mathbf{C}_{4h}) = \mathbf{C}_{4h} + (RC_{2x})\mathbf{C}_{4h}$ . (Here  $R$  is the time-reversal transformation.) In this case,  $\psi_-$  transforms like one of the complex irreducible representations ( $^1E$  or  $^2E$ ) of  $\mathbf{C}_{4h}$ . Furthermore, although there is no time reversal operation in this magnetic group, the operator  $RC_{2x}$  has the effect of replacing  $\psi_-$  by its complex conjugate. Hence  $\psi_-$  is a possible order parameter. A similar analysis can be performed if the ferromagnetic magnetization density is along the [111] direction, when the magnetic point group is  $\mathbf{D}_{3d}(\mathbf{C}_{3i}) = \mathbf{C}_{3i} + (RC_{2x})\mathbf{C}_{3i}$ . Here too the order parameter transforms like one of the complex representations ( $^1E$  or  $^2E$ ) of the relevant point group ( $\mathbf{C}_{3i}$ ). It should be noted that this predicted symmetry of the superconducting state can be verified by experimental measurement (e.g., see [23]).

The pressure dependence of the critical temperature  $T_s$  of the transition to the superconducting state can be found from Eq. (5) to be given by the solution of

$$T_s = T_0 + T^{*1/2}[T_f(P) - T_s]^{1/2}, \quad (6)$$

where

$$T^* = \left(\frac{\alpha'}{\beta_f}\right)\left(\frac{4\pi}{\alpha'}\right)^2 (J - J_c)^2. \quad (7)$$

By assumption, the exchange enhancement results in a superconducting transition temperature  $T_s$  much greater than the superconducting transition temperature  $T_0$  in the paramagnetic state. Furthermore, except for  $P$  very close to  $P_c$ ,  $T_s \ll T_f(P)$ . Under these conditions the pressure dependence of  $T_s$  is given by the formula

$$T_s(P) = T_s(0)(1 - P/P_c)^{1/2}. \quad (8)$$

When  $P$  gets very close to  $P_c$  and  $T_f(P)$  becomes very small this equation is no longer valid. In this extreme circumstance, if one takes  $T_0 = 0$  and  $T_f(P) \ll T^*$ , one finds

$$T_s(P) = T_f(P)[1 - T_f(P)/T^* + \dots], \quad (9)$$

which shows that, for  $P$  very close to  $P_c$  and  $T_0 = 0$ ,  $T_s(P)$  approaches  $T_f(P)$ , and is never greater than  $T_f(P)$ .

Equation (8), together with the equation for the ferromagnetic transition temperature

$$T_f(P) = T_f(0)(1 - P/P_c) \quad (10)$$

arrived at above, have been used to plot the phase diagram of Fig. 1, which shows a remarkable similarity to the experimentally determined [4] phase diagram for  $ZrZn_2$ .

Finally, at a given pressure, we find a temperature dependence of the upper critical field of

$$H_{c2}(T, P) = H_{c2}(0, P)[1 - T/T_s(P)]. \quad (11)$$

This is in reasonable agreement with the experimental result (see Fig. 3 of Ref. [4]), which, however, has somewhat more curvature than the linear temperature dependence shown here. The lack of curvature in the result of Eq. (11) results from the linear dependence of  $M_z$  on  $H_{ext}$  in our relation  $M_z = M_{z0} + (\mu - 1)H_{ext}/(4\pi)$ .

We conclude that the proposed mechanism of stabilizing superconductivity in a ferromagnet (by an exchange type of interaction between the magnetization density of the Cooper pairs and the ferromagnetic magnetization density) gives an excellent qualitative description of the phase diagram determined experimentally for  $ZrZn_2$ . In particular, it explains in a natural way the fact that the superconductivity occurs in the ferromagnetic phase, but not in the paramagnetic phase. For this mechanism to work, the exchange interaction parameter must have a magnitude larger than a certain critical value. A further experimental test of our model would be the determination of the order parameter symmetry. (A prediction of our model is that the order parameter transforms like one of the complex representations of the relevant point group.)

It should be mentioned that the spin-fluctuation mechanism studied in Ref. [12] can provide an alternative explanation of growing  $T_s$  in the ferromagnetic state, given that the magnetization in  $ZrZn_2$  does not reach saturation. To what extent the fluctuation effects discussed in Ref. [12] are essential compared to the mean field interactions studied in this article, is in our view still an open question, and their relative contributions can be different in different materials. For example, it seems that the phase diagram of  $UGe_2$  (see Fig. 1) can be satisfactorily explained by the spin-fluctuation theory, and the apparent absence of contributions from the exchange interaction of our work could be explained by the magnitude of the exchange parameter being less than its critical value.

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