

## Longitudinal Spin Fluctuations and Superconductivity in Ferromagnetic $\text{ZrZn}_2$ from *Ab Initio* Calculations

G. Santi,<sup>1</sup> S. B. Dugdale,<sup>1,2</sup> and T. Jarlborg<sup>2</sup>

<sup>1</sup>*H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*

<sup>2</sup>*Département de Physique de la Matière Condensée, Université de Genève,*

*24 Quai Ernest Ansermet, CH-1211 Genève 4, Switzerland*

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The recent discovery of superconductivity coexisting with weak itinerant ferromagnetism in the  $d$ -electron intermetallic compound  $\text{ZrZn}_2$  strongly suggests spin-fluctuation mediated superconductivity. *Ab initio* electronic structure calculations of the Fermi surface and generalized susceptibilities are performed to investigate the viability of longitudinal spin-fluctuation-induced spin-triplet superconductivity in the ferromagnetic state. The critical temperature is estimated to be of the order of 1 K. Additionally, it is shown that in spite of a strong electron-phonon coupling ( $\lambda_{\text{ph}} = 0.7$ ), conventional  $s$ -wave superconductivity is inhibited by the presence of strong spin fluctuations.

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The generalization of the Bardeen-Cooper-Schrieffer (BCS) theory to electron-electron interactions by Kohn and Luttinger [1] paved the way for speculation about the possibility of non- $s$ -wave, or “unconventional,” superconductivity. Following the suggestion that a magnetically mediated interaction plays an important role in the superfluidity of liquid  $^3\text{He}$  [2], the search began for superconductivity in nearly magnetic metals where strong spin fluctuations might provide the pairing mechanism [3,4]. Recent experiments on  $\text{Sr}_2\text{RuO}_4$  [5] have made it a strong candidate for exhibiting spin-triplet, possibly  $p$ -wave, superconductivity. For a spin-singlet Cooper pair, where the electrons have antiparallel spins, the presence of ferromagnetic spin fluctuations will be antagonistic towards the development of such a superconducting state. However, the recent reports of the coexistence of ferromagnetism with superconductivity in  $\text{UGe}_2$  [6] and  $\text{ZrZn}_2$  [7] suggest a spin-triplet Cooper pairing, probably driven by spin fluctuations. Moreover, in  $\text{ZrZn}_2$ , the disappearance of superconductivity at the same point as magnetism, and the sensitivity of its occurrence to sample purity [7,8] are perhaps the strongest indications yet that the superconductivity is intimately connected with the magnetism in this material.

Unlike other “magnetic” superconductors (e.g., borocarbides,  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ ,  $\text{CePd}_2\text{Si}_2$ , and  $\text{CeIn}_3$  [9]) where the magnetism and superconductivity occur in different parts of the unit cell, or in hcp Fe under pressure [10] (where the superconductivity occurs in the nonmagnetic phase), in both  $\text{UGe}_2$  and  $\text{ZrZn}_2$  it is the same itinerant electrons that are thought to form the Cooper pairs as well as produce ferromagnetism. Moreover, whereas some questions regarding the itinerancy of  $5f$  electrons and the roles of the strong magnetocrystalline anisotropy and quasi-two-dimensional electronic structure can be raised with respect to  $\text{UGe}_2$ ,  $\text{ZrZn}_2$  is a three-dimensional intermetallic compound free of such effects. Discovered in the 1950s [11], it was initially of interest because of the pres-

ence of weak ferromagnetism, in spite of the fact that neither constituent was ferromagnetic. It has the C15 cubic Laves crystal structure, with a lattice constant of 7.393 Å (13.97 a.u.) [7]. The possibility of there being triplet pairing in high-purity C15 compounds like  $\text{TiBe}_2$  and  $\text{ZrZn}_2$  was first suggested by Fay and Appel [4]. In this Letter we investigate the viability of their suggestion in the case of  $\text{ZrZn}_2$  from the perspective of *ab initio* calculations.

First, we have calculated the electronic structure of  $\text{ZrZn}_2$  using the linear muffin-tin orbital method within the local spin density approximation (LSDA) [12]. Self-consistency was attained using 505  $k$  points within the irreducible wedge of the face-centered cubic Brillouin zone (BZ). The basis included  $s$ ,  $p$ ,  $d$ , and  $f$  states for all atoms. Our results agree with previous calculations [13]. The Fermi surface (FS), comprising four sheets, is shown in Fig. 1. Both nonmagnetic (NM) and ferromagnetic (FM) calculations were performed at a series of different lattice parameters, and the magnetic moment was found to disappear near 13.47 a.u., where the calculated pressure is 45 kbar. This is just below the total energy minimum, indicating a calculated equilibrium lattice constant of 13.6 a.u., in excellent agreement with a recent full-potential linear augmented-plane-wave calculation [14]. This underestimation ( $\sim 2.5\%$ ) is typical of the local density approximation, particularly when including  $f$  states. Experiments confirm that the system is near the ferromagnetic instability, since the critical pressure for the disappearance of magnetism has been reported in the range 8.5–22 kbar [7,15].

Polarized neutron studies of the magnetization density [16] have shown that there is a significant spin density along the Zr-Zr bond directions. Our calculation also shows this delocalization, but typically with 85% of the total moment on the Zr. The dominance of Zr is also reflected in the density of states (DOS) at  $E_F$ , of which 80% is of Zr- $d$  character. Mattocks and Dixon [17] inferred an exchange splitting of 4.5 mRy (in a field of 8 T) from their de Haas–van Alphen data for orbits on the  $\Gamma$ -centered

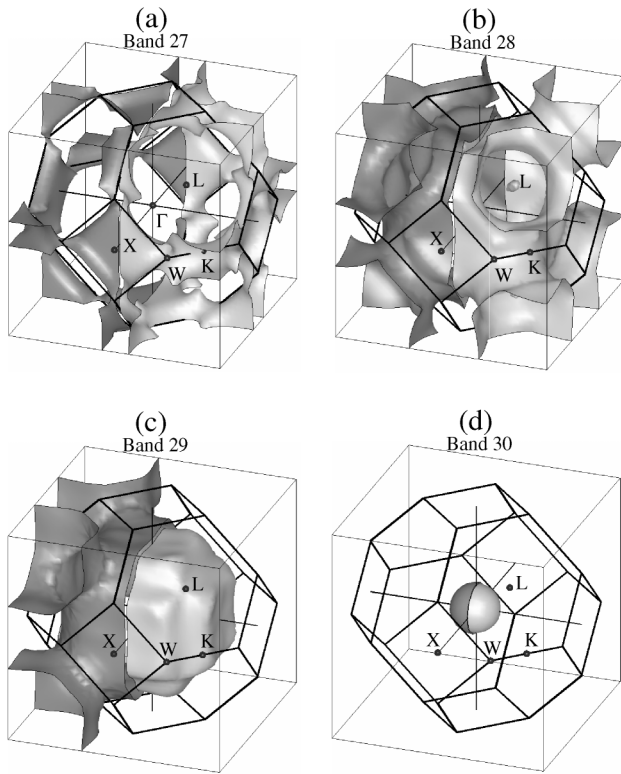


FIG. 1. The spin-polarized Fermi surface for  $a = 13.6$  a.u., from bands 27–30 (a)–(d). The majority spin ( $\uparrow$ ) sheets are shown on the left-hand side and the minority spin ( $\downarrow$ ) on the right.

spheroid (band 30). This compares favorably with the value obtained from the current calculation at the equilibrium lattice constant (see Table I).

Second, we have studied the FS and its nesting properties. As seen in Fig. 1, it is rich in details. Four bands (27–30) cross the Fermi level. We used the relaxed lattice parameter given by LSDA ( $a = 13.6$  a.u.) corresponding to a total moment of  $0.17\mu_B/\text{Zr}$ . All these sheets show a strong Zr- $d$  character, although bands 27 and 30 exhibit a significant hybridization with Zn- $p$  (25% and 30%, respectively). Furthermore, the DOS at  $E_F$  is dominated by the contribution from band 29 (50%) and band 28 (32%), whereas band 30 contributes less than 1%. The effect of the spin splitting is most noticeable in the change in the

topology of the band 29 sheet, where the neck near the  $L$  point, present for majority spin electrons ( $\uparrow$ ), disappears for minority ones ( $\downarrow$ ). From Fig. 1, we expect strong intra- and interband nesting features, especially along the  $\langle 100 \rangle$  direction. In order to understand how the nesting will actually affect the response of the electrons in this system, we have calculated the bare-band generalized static susceptibility,

$$\chi_0^{\sigma\sigma'}(\mathbf{q}, 0) = \sum_{nn'\mathbf{k}} \frac{f_{\sigma n\mathbf{k}}(1 - f_{\sigma'n'\mathbf{k}+\mathbf{q}})}{E_{\sigma'n'\mathbf{k}+\mathbf{q}} - E_{\sigma n\mathbf{k}} + i\delta}, \quad (1)$$

where  $n$  denotes the band index,  $\sigma$  the spin, and  $f_{\sigma n\mathbf{k}}$  the Fermi-Dirac function. This sum was calculated on a mesh of more than  $5 \times 10^5$   $k$  points in the cube (shown in Fig. 1) using a tetrahedron interpolation technique similar to that of Rath and Freeman [18]. These calculations were performed for both NM and FM cases along  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  in  $\mathbf{q}$  space, at the LSDA equilibrium lattice constant. All these are peaked at  $q = 0$  and (rather surprisingly, given the FS topology) show very little structure at  $q > 0$ . This was expected for the NM case because of the ferromagnetism of  $\text{ZrZn}_2$ , but the absence of large  $q > 0$  peaks in the FM case shows that this compound does not favor antiferromagnetic (AF) spin waves as confirmed by our frozen spin-wave calculations. In fact, most significant  $q > 0$  peaks in  $\langle 100 \rangle$  are due to the transverse  $\chi_0^{\uparrow\downarrow}(q)$ . These mainly originate from band 29 intraband contributions near the corner of the cuboidal FS sheet (i.e., near the  $L$  point) and naturally disappear in the NM case. The concentration of the DOS at  $E_F$  near the BZ border (points  $X$ ,  $K$ , and  $L$ ) where band 29 flattens considerably is responsible for the dominance of these peaks. In other words, this means that while nesting is present elsewhere, it is inhibited by the low DOS. These relatively small features in  $\text{Re}\chi_0(q_{100})$  could, however, be much more prominent in  $\text{Im}\chi_0(q_{100})$  as is the case for Cr [19]. Furthermore, the possible van Hove singularity in band 29 near the Fermi level (note that the NM FS is topologically very similar to the minority spin one in Fig. 1) could potentially lead to electronic topological transitions [14].

We now turn to the question of longitudinal spin-fluctuation-driven superconductivity in  $\text{ZrZn}_2$  as proposed by Fay and Appel [4]. On the FM side of the transition, when the band structure is different for the two spins, we

TABLE I. Calculated parameters (per formula unit) for various lattice constants,  $a$ . Shown are the magnetic moment  $\mu$ , the exchange splitting  $\xi$ , the Stoner factor  $S$ , the density of states at the Fermi level for the nonmagnetic (NM) calculations as well as for the ferromagnetic (FM) ones in parentheses ( $\uparrow / \downarrow$ ), Debye temperature (set to 370 K at  $a = 13.573$  a.u.) used to calculate the electron-phonon coupling,  $\lambda_{\text{ph}}$ , in both the NM and FM cases, and the specific heat coefficient renormalized by the electron-phonon interaction,  $\gamma$ .

$a$	$\mu$	$\xi$	$S$	DOS ( $E_F$ )	$\theta_D$	$\lambda_{\text{ph}}$	$\lambda_{\text{ph}}$	$\gamma$
a.u.	$\mu_B$	mRy		$\text{Ry}^{-1}$	K	(NM)	(FM)	$\frac{\text{mJ}}{\text{mol}\cdot\text{K}^2}$
13.970	0.48	19.5	2.9	68 (18/27)	265	1.42	0.90	28.6
13.573	0.10	5.0	8.3	54 (31/25)	370	0.71	0.72	16.1
13.437	0.00	0.0	9.0	52 (26/26)	420	0.56	...	13.8

calculate the longitudinal coupling constant,  $\lambda_{sf}^L$ , from the generalized susceptibilities. In the FM region, within the random phase approximation, the pairing potential can be written as [4]

$$V^{\sigma\sigma}(\mathbf{q}) = \frac{I^2(\mathbf{q})\chi_{0\mathbf{q}}^{-\sigma,-\sigma}}{1 - I^2(\mathbf{q})\chi_{0\mathbf{q}}^{-\sigma,-\sigma}\chi_{0\mathbf{q}}^{\sigma\sigma}}. \quad (2)$$

In the approximation of a spherical FS (not unreasonable, given the dominant influence of band 29 and its FS topology), the longitudinal coupling parameter is given by [4]

$$\lambda_{sf,l}^{L\sigma} = N_{\sigma}(E_F) \int_0^{2k_{F\sigma}} dq \frac{qV^{\sigma\sigma}(q)}{2k_{F\sigma}^2} P_l \left(1 - \frac{q^2}{2k_{F\sigma}^2}\right), \quad (3)$$

where  $P_l$  is the Legendre polynomial. As in the original BCS theory, this model neglects retardation effects. However, they generally have very little influence on the main features of superconductivity (e.g., symmetry of the gap, order of magnitude of  $T_c$ ), which concern us here. The objective is now to estimate the  $s$  and  $p$  components of  $\lambda_{sf}$  from our band structure calculation. The exchange integral,  $I$ , is obtained through the calculation of the Stoner enhancement,  $S$ , defined as the *increase* of the exchange splitting of the Zr potential divided by the energy of the applied magnetic field. An alternative and more general approach would be to use a linear response technique to get the dressed susceptibility [19]. The corresponding Stoner factor  $\bar{S} = 1 - 1/S$  is simply related to  $I$  through  $I = \bar{S}/N$ , where  $N$  is the DOS at  $E_F$ . We have calculated  $S(q)$  for the FM case (see Table I) and for two AF spin waves ( $q = 0$  and  $q = 2\pi/a$ ). We find that  $S$  is quickly suppressed [ $S(q = 2\pi/a) \leq 1.5$ ] for AF spin waves. This shows that ZrZn<sub>2</sub> does not support AF fluctuations (which is consistent with the absence of significant peaks for  $q > 0$  in our calculated generalized susceptibilities) and that the  $q$  dependence of  $I$  cannot be neglected. From  $S(q)$ , we model  $I(q) = I_0/(1 + b^2q^2)$  [4,20] with  $I_0 = 0.04$  Ry and  $b^2 = 0.33 (a/2\pi)^2$ . Since the contribution to  $\lambda_{sf}$  from each spin-wave mode is  $\frac{1}{2}S(q)\bar{S}(q)^2$  [21], we get, as our first estimate,  $\lambda_{sf} = 1.2$  by averaging over these three modes. We make the further approximation  $\chi_0^{\sigma\sigma}(q) = N_{\sigma}(E_F) \forall q$ , and calculate the longitudinal  $\lambda_{sf,l}^{L\sigma}$  in the  $s$  ( $l = 0$ ) and  $p$  ( $l = 1$ ) channels from Eqs. (2) and (3), taking a  $k_{F\sigma} \approx 0.6 2\pi/a$ , appropriate to the band 29 sheet. For the relaxed FM case in which  $\bar{S} = 1.12$ ,  $\lambda_{sf}^L$  is negligible in the  $p$  channel. However, moving closer to the FM transition, i.e., for  $\bar{S} = 1.01$ , we get  $\lambda_{sf,0}^{L\sigma} = 1.9, 2.0$  (for  $\sigma = \uparrow, \downarrow$ ) in the  $s$  channel and  $\lambda_{sf,1}^{L\sigma} = 0.81, 0.76$  (for  $\sigma = \uparrow, \downarrow$ ) in the  $p$  channel. This shift is justifiable given that  $S$  is extremely sensitive close to the transition. As noted by Fay and Appel, the  $s$  component is much larger than the  $p$  one, and both diverge when  $\bar{S} \rightarrow 1$ . These values are consistent with our previous estimate.

The electron-phonon interaction cannot be ignored and can even be expected to be rather large owing to the oc-

currence of conventional superconductivity in both Zr and Zn, and the large DOS at  $E_F$ . This suggests that the electron-phonon coupling could be sufficient to overcome the pair-breaking effects due to spin fluctuations. The electron-phonon coupling constant,  $\lambda_{ph}$ , can be expressed as  $\lambda_{ph} = \sum_i \frac{\eta_i}{M_i \langle \omega_i^2 \rangle}$ , where the sum runs over all atoms,  $i$ , with masses,  $M_i$ , and phonon frequencies,  $\omega_i$ , while the numerator,  $\eta_i = N_i(E_F) \langle (\nabla V_i)^2 \rangle$ , is the Hopfield parameter that describes the electronic contribution [22]. Here  $\eta$  was calculated in the rigid muffin-tin approximation [22], i.e., retaining only dipolar terms and neglecting electronic screening of the ionic displacements. The values for  $\langle \omega_i^2 \rangle$  are taken as one-half of the Debye frequency of the atom  $i$ . Furthermore, we assume that the volume dependence of  $\langle \omega_i^2 \rangle$  follows  $\sqrt{aB}$ , where  $B$  is the (calculated) bulk modulus and  $a$  the lattice parameter, which is reasonable as long as all small- $q$  phonons behave identically with pressure [23]. As shown in Table I,  $\lambda_{ph}$  is of the order of 0.7 near the calculated equilibrium volume and twice as large at the experimental lattice constant. Ignoring completely the destructive effects of spin fluctuations, and using  $\mu^* = 0.13$  in the McMillan formula [24], these correspond to respectable  $T_c$ 's of about 8 and 21 K, at the respective lattice constants. The decrease of  $\lambda_{ph}$  in the FM state can be attributed to the smaller total DOS at  $E_F$ , and its pressure dependence can be ascribed almost entirely to the behavior of the Debye frequency. In the vicinity of the ferromagnetic transition, this  $\lambda_{ph}$  is nevertheless insufficient to overcome the dominance of the spin fluctuations as indicated by the large  $S$  enhancements near the critical pressure (see Table I). A possibility exists for phonon-mediated superconductivity at larger pressures, i.e., well outside of the magnetic region when the Stoner factor would be further decreased to completely suppress spin fluctuations. However, our calculations at  $a = 13.17$  a.u. (equivalent to 160 kbar) indicate that  $\lambda_{ph}$  drops to 0.4 while  $S$  is still 4.1 (giving a  $\lambda_{sf}$  of the order of 0.4), which combine to make the conditions unfavorable for phonon-mediated superconductivity. Note that the persistence of such a large Stoner enhancement over this range of pressures shows again the importance of the spin fluctuations and that the large values for  $S$  in the FM region can be related to the observed absence of saturation of the magnetic moment [7] and the weak ferromagnetism. Since the magnetic moment, Stoner enhancement, and spin fluctuations are associated with the Zr sublattice, phonon-mediated superconductivity might be envisaged to take place within the Zn sublattice, but such an explanation can be ruled out because the Zn contribution to  $\eta_i$  is negligible.

Having presented evidence against the possibility of electron-phonon driven superconductivity, we now try to estimate  $T_c$  from the longitudinal spin fluctuations. The typical spin-fluctuation cutoff frequency,  $\omega_{sf}$ , can be estimated from the Stoner factor by  $\omega_{sf} = 1/(4NS)$  [20], giving about 90 K at the relaxed lattice parameter. Using the

Allen-Dynes formula, we arrive at a simplified expression for the superconducting transition temperature:

$$k_B T_c = \frac{\hbar \omega_{sf}}{1.2} \exp\left(-\frac{1 + \lambda_{ph} + \lambda_{sf,0}^{L,T}}{\lambda_{sf,1}^L}\right). \quad (4)$$

Note that the rather strong electron-phonon interaction  $\lambda_{ph}$  contributes to the mass renormalization (numerator) and is detrimental to superconductivity in this case. Furthermore, the  $s$ -wave  $\lambda_{sf,0}^{L,T}$  contains both the longitudinal (L) and transverse (T) contributions. From the large measured electronic specific heat coefficient  $\gamma_{exp} = 47 \text{ mJ mol}^{-1} \text{ K}^{-2}$  [7], and our calculated values for  $\lambda_{sf,0}^{L,T}$  and  $\lambda_{ph}$ , we infer a transverse contribution  $\lambda_{sf,0}^T$  of about 0.8. Using the values for the case  $\bar{S} = 1.01$ , we get a  $T_c^\sigma = 1.0, 0.8 \text{ K}$  for  $\sigma = \uparrow, \downarrow$ , respectively. These estimates are very approximate, but they confirm, in our opinion, the viability of triplet  $p$ -wave superconductivity in  $\text{ZrZn}_2$ .

In conclusion, we have shown that calculations based on our electronic structure results strongly support the idea that the recently observed superconductivity in  $\text{ZrZn}_2$  [7] is indeed a result of triplet pairing, as suggested by Fay and Appel [4]. This would lead to  $p$ -wave superconductivity, and since impurity scattering acts as a pair breaker for pairing in the  $l \neq 0$  channels, the high purity of samples is crucial. However, the experimental absence of superconductivity in the paramagnetic phase just above the critical pressure [7] is still unanswered by this theory which predicts an even larger  $T_c$  in the NM region. The answer may lie in the peaks of the transverse susceptibility,  $\chi_0^{\uparrow\downarrow}(q_{100})$ , which could provide an attractive coupling that would naturally disappear outside of the FM phase. Finally, it might be worthwhile revisiting the properties of C15 compound  $\text{TiBe}_2$  under pressure since its electronic structure is very similar to that of  $\text{ZrZn}_2$  and conventional superconductivity would be more favored owing to the lighter masses of its constituents.

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