

ZrZn₂: Geometrical enhancement of the local density of states and quantum design of magnetic instabilities

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The recent discovery of coexisting ferromagnetism and superconductivity in ZrZn₂, and the fact that they are simultaneously suppressed on applying pressure [Pfleiderer *et al.*, *Nature* **412**, 58 (2001)] suggest the possibility of a pairing mechanism which is mediated by exchange interactions and connected with the proximity to a magnetic quantum critical point. On the basis of first principles, full potential electronic structure calculations, we study the conditions that, for ZrZn₂, determine the proximity to this magnetic instability. More specifically, we discuss the role played by the geometrical arrangement of the lattice, the hybridization effects, and the presence of disorder, as well as the application of external pressure. These circumstances influence the width of the relevant Zr *d* bands whose narrowing, due to the reduction of the *effective* number of neighbors or to an increase of the cell volume, causes an *enhancement* of the density of states at the Fermi level. Finally, we highlight some general features that may aid the design of other materials close to magnetic instabilities.

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The very recent discovery of the coexistence of ferromagnetism and superconductivity (SC) in ZrZn₂ (Ref. 1) and UGe₂ (Ref. 2) suggests that the current ideas on SC need to be critically reconsidered. Interestingly, ZrZn₂ is a relatively “simple” metal, in the sense that there are no complications arising from *f* electrons³ or oxide planes. This circumstance implies that its electronic properties can be studied in detail within a density-functional theory⁴ framework which is expected to be reliable for such systems.

As known for many years, ZrZn₂ is a weak itinerant ferromagnet,⁵ with a Curie temperature $T_{FM}=28.5$ K, despite the fact that both pure Zr and Zn are not magnetic. Both pure elements also exhibit superconducting transitions with $T_C=0.6$ and 0.85 K, respectively.⁶ Many speculations on the properties of this compound have been stimulated by the discovery⁷ that, at some critical pressure, $P_C \approx 8$ Kbar, it becomes paramagnetic (PM), suggesting that it is very close to a magnetic quantum critical point (MQCP). Notwithstanding the argument of Berk and Schrieffer⁸ about the suppression of the phonon-induced *s*-wave SC by ferromagnetic (FM) spin fluctuations, many authors⁹ argued that, in the vicinity of the MQCP on the PM side (high pressures), *p*-wave SC could be induced by paramagnons. Later on, Fay and Appel¹⁰ suggested the possibility of also having *p*-wave SC for $P < P_C$, *inside* the FM region of the phase diagram. A different scenario, recently proposed by Blagoev *et al.*,¹¹ predicted *s*-wave SC for $P < P_C$ and *p*-wave SC for $P > P_C$.

Recent experiments¹ suggested that the kind of SC observed in ZrZn₂ is related to the presence of ferromagnetism, since both ferromagnetism and SC are simultaneously suppressed as the pressure reaches P_C . This phenomenon could be compatible either with the picture of Ref. 10 or with that of Ref. 11, both of which assumed magnetic excitation-mediated coupling in the proximity of the MQCP. In order to decide between alternative explanations, it is highly desirable to be able to *engineer* materials close to a MQCP and to control the vicinity by changing some variable such as the

external pressure or the concentration of some impurities. In this paper, on the basis of first-principles, full-potential, electronic structure calculations for both ZrZn₂ and related systems, we highlight a rather general feature which may aid this endeavor.

In particular we examine the ZrZn₂ lattice geometry, and follow some important consequences for the physical properties. We find that the density of states (DOS) at Fermi energy $n(E_F)$ is *enhanced*, in a sense to be specified below, by the lattice *geometry*. A high $n(E_F)$ is a crucial attribute for a material to be close to a MQCP, as shown, for example, the Stoner factor (a measure of proximity to a ferromagnetic phase transition) is given by

$$S_0 = [1 - In(E_F)]^{-1}, \quad (1)$$

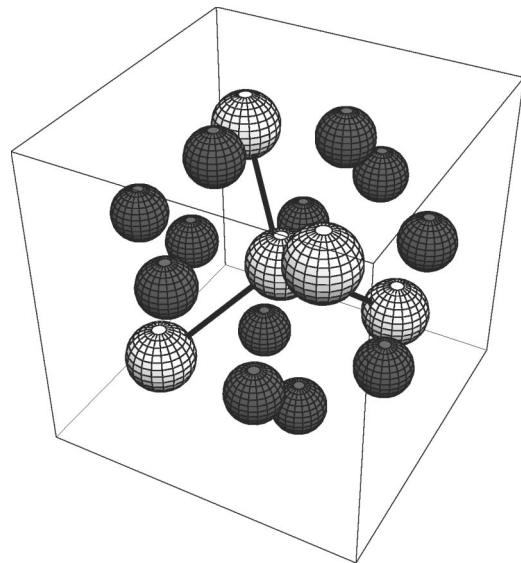


FIG. 1. The local environment of a Zr atom in the C15 cubic Laves structure. Zr atoms: large spheres; Zn: small dark spheres.

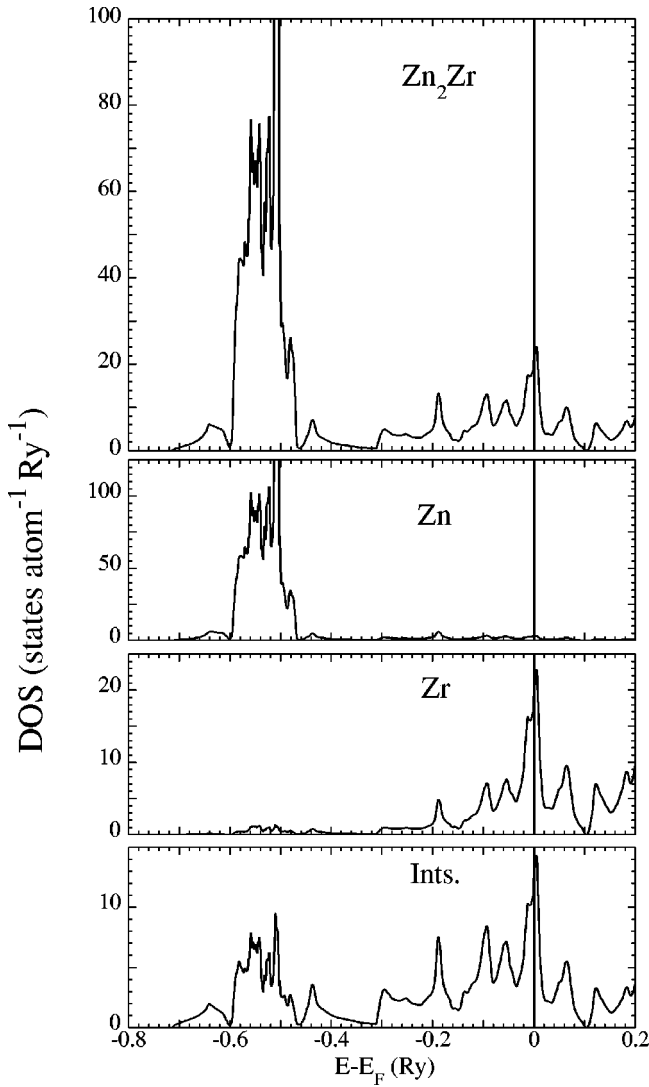


FIG. 2. DOS of PM ZrZn_2 (top panel) at the relaxed lattice constant, $a=13.58$ a.u. The labels Zn and Zr refer to the corresponding muffin-tin spheres. The lower panel shows the interstitial DOS divided by the number of atoms in the unit cell.

where I is the exchange integral. Of course, a large $n(E_F)$ is also important in generating a sizeable electron-phonon coupling,

$$\lambda = \frac{n(E_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle}. \quad (2)$$

where $\langle I^2 \rangle$ is the electronic stiffness parameter of Gaspari and Gyorffy,¹² M the ionic mass, and $\langle \omega^2 \rangle$ some mean value of the phonon frequency. In the above equations we have deliberately used definitions from the simplest available electronic theories for magnetism and SC, just to stress the relevant role played in these phenomena by $n(E_F)$.

ZrZn_2 crystallizes into a cubic C15 superlattice.¹³ In this structure, Zr atoms occupy the positions of a diamond lattice, while the Zn atoms form a network of interconnected tetrahedra. Since the major contributions to $n(E_F)$, as we shall see, come from Zr, the local environment of Zr atoms (Fig.

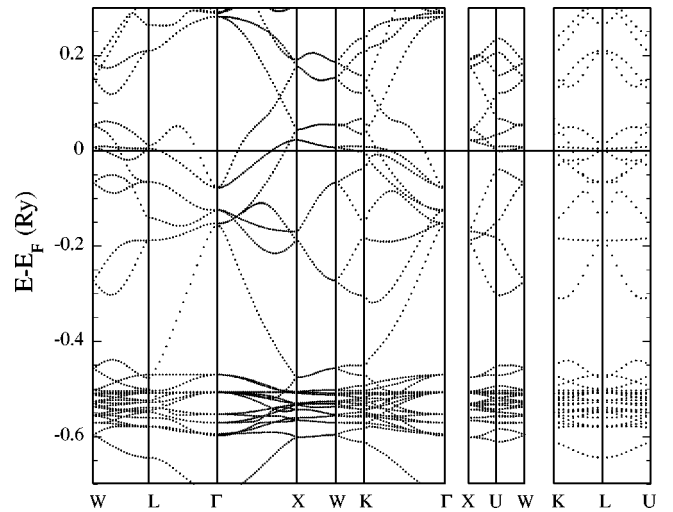


FIG. 3. Band structure of PM ZrZn_2 along relevant symmetry directions.

1) is particularly important for our concerns. Each Zr is surrounded by 12 Zn neighbors and four Zr neighbors, at distances that in terms of the lattice constant a are $d_{\text{ZrZn}} = (\sqrt{11}/8)a$ and $d_{\text{ZrZr}} = (\sqrt{3}/4)a$, respectively. In other words, the distance between two Zr atoms is only 4% larger than the nearest-neighbor (NN) distance d_{ZrZn} . This circumstance leads to an appreciable overlap of the wave functions of two neighboring Zr atoms.¹⁴

We have calculated the band structure of ZrZn_2 in the PM state using the full potential linearized augmented plane waves method¹⁵ within the local-density approximation. The calculated equilibrium lattice constant (13.58 a.u.) is about 3% smaller than the experimental one [13.98 a.u. (Ref. 1)]. Importantly, our full-potential results provide a reference for more approximate, existing band-structure calculations,^{14,16} all based on the linearized muffin-tin orbital method and the atomic sphere approximation. These simpler band-structure

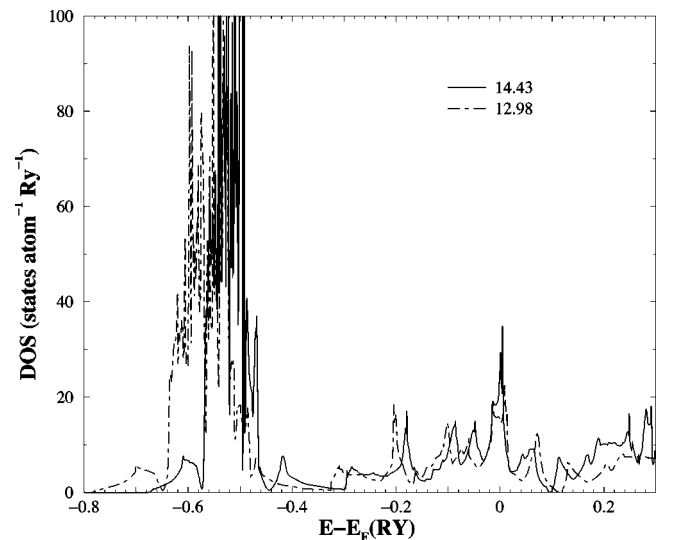


FIG. 4. DOS of PM ZrZn_2 for the values of a indicated by the labels.

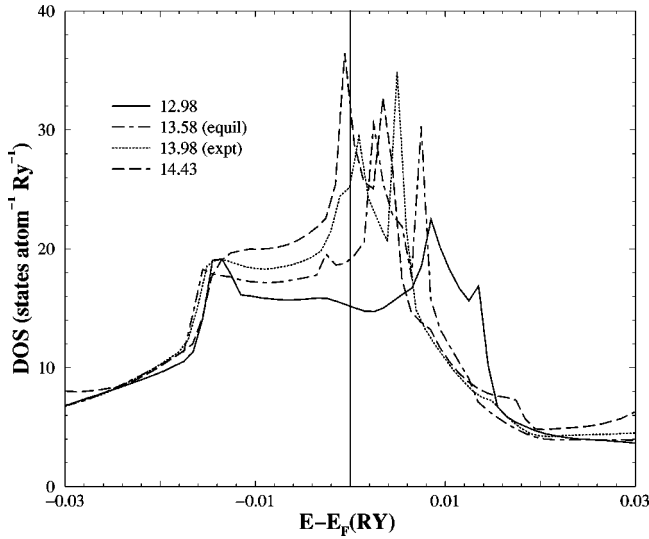


FIG. 5. DOS of PM ZrZn_2 about E_F for the values of a indicated by the labels.

calculations form a starting point for studies of electron-phonon coupling and spin fluctuations in this material.

The DOS (Fig. 2) classifies this compound as a *split band* system: the electronic states are distributed into largely separate energy regions. The Zr d resonances are close to E_F , while those of Zn occur well below. The band structure, plotted in Fig. 3, reveals very narrow d bands, and suggests that these would be appreciably broadened out by a reduction of the interatomic distances. A similar broadening could also be caused by decrease of the quasiparticle lifetimes due to impurities or defects. This view is supported by Fig. 4, where we see how the increase of the bandwidth for smaller values of a results in a dramatic drop of the DOS peaks heights. For the system at hand, the drop of $n(E_F)$ is also affected by electronic topological transitions¹⁷ (ETT's) occurring when the Fermi level crosses the various DOS peaks, as shown in Fig. 5.

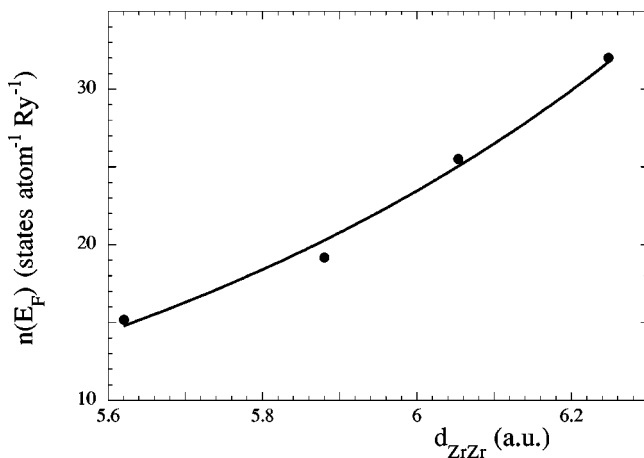


FIG. 6. $n(E_F)$ vs d_{ZrZr} in ZrZn_2 . The circles correspond to the calculated values, and the line is an exponential fit. We find $B = 1.2$ (see the text), in good agreement with the values reported in Ref. 18.

The variation vs. a of the local DOS in Zr muffin-tin spheres at the Fermi level, $n_{\text{Zr}}(E_F)$, is displayed in Fig. 6. These trends can be easily fitted using a simple tight-binding (TB) model:¹⁸ $n_{\text{Zr}}(E_F)$ is inversely proportional to the bandwidth which is proportional to the hopping parameters. These scale exponentially with the relevant distances, say as e^{-Br} with $B > 0$. Accordingly, with Eq. (1), the behavior of $n_{\text{Zr}}(E_F)$ is consistent with the experimental findings^{1,7} that a compression can suppress the magnetic ordering by crossing, at $P = P_C$, the MQCP ($S_0^{-1} = 0$). On the other hand, consistent with Ref. 1, the MQCP could be reached at lower pressures in impure samples, due to the lifetimes effects mentioned above.

Pure Zr forms a hcp crystal structure. Although very well known, the standard explanation as to why it is not ferromagnetic contains some valuable pointers. $n_{\text{Zr}}(E_F) = 4.11$ is about four times smaller than in ZrZn_2 . Such a large factor cannot be simply attributed to the atomic distances involved (see Fig. 6). For pure (hcp) Zr we find $d_{\text{ZrZr}} = 5.900$ a.u., very close to both d_{ZrZr} and d_{ZrZn} in ZrZn_2 . Neither can this factor be caused entirely by ETT's. Such a decrease can be explained only by assuming that, as a consequence of the very weak hybridization with Zn, Zr atoms “see” only their four Zr neighbors, while in pure Zr the number of NN's, f , is 12. This could account for the reduction of the local DOS by factor 3. Using the above TB model, we can draw a relationship

$$n_{\text{Zr}}(E_F) \sim A e^{B d_{\text{ZrZr}} / f_{\text{eff}}}, \quad (3)$$

where f_{eff} is some effective number of NN's. Of course, Eq. (3) should not be taken too literally since ETT's and differences between the shapes of the DOS's in different lattices (e.g., the pseudogap between bonding and antibonding states in hcp lattices) also have some influence.

In order to add substance to our picture of ZrZn_2 in which the Zn atoms play essentially the role of empty spheres placed between Zr atoms to reduce f_{eff} , we have calculated

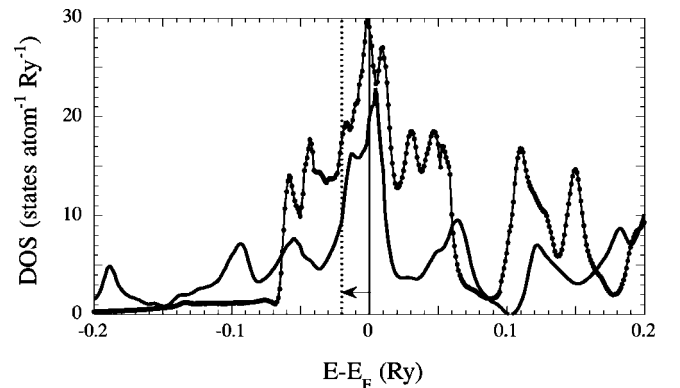


FIG. 7. The density of states of pure Zr in the diamond lattice (dots) compared with the density of states of ZrZn_2 (plain line), at the relaxed lattice constant of ZrZn_2 . All the DOS's refer to Zr muffin-tin spheres only. The arrow indicates the direction in which the Fermi level is expected to move due to charge transfer from Zr to Zn. The dashed line marks an upper bound estimate of the above Fermi-level shift.

the band structure of Zr in the hypothetical diamond lattice phase that would result from the substitution of Zn atoms in the ZrZn_2 lattice with empty spaces. The comparison of the corresponding DOS (Fig. 7) shows up some minor differences, mostly due to the weak hybridization with Zn and with the charge transfer to Zn atoms in the ZrZn_2 system.

In summary: we have pointed out how the addition of Zn to an ideal Zr diamond lattice changes the local DOS on Zr atoms very little. We surmise that this is an example of a rather common occurrence. One can consider a hypothetical geometrical lattice structure formed by adding empty spaces in some metal. The narrowed relevant bands could give rise to exotic, magnetic, or superconducting properties (as shown here for Zr in the diamond lattice, that, of course, cannot be realized in practice). Those same properties could then be obtained by filling the empty spaces with atoms which give rise to little (or zero) DOS at the Fermi level (as Zn), and

which have little hybridization with the metal we want to modify. Indeed, there is an increasing number of materials with striking superconducting or magnetic properties whose electronic structures in the vicinity of E_F are consistent with the sort of analysis we carried out here for ZrZn_2 . For example, there are thin $4d$ and $5d$ metal films,¹⁹ where the reduction of f_{eff} at the surface allows magnetically ordered states to be stable. Another example might be the alkali fullerides,²⁰ where C_{60} molecules could provide the “vacuum” making alkali metals superconducting. Other possible examples are MgB_2 ,²¹ UGe_2 ,² MnSi ,^{10,22} layered cuprate²³ and ruthenate superconductors,²⁴ and A15 compounds.²⁵

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