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Spin fluctuations and the magnetic phase diagram of $ZrZn_2$

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The magnetic properties of the weak itinerant ferromagnet $ZrZn_2$ are analyzed using Landau theory based on a comparison of density-functional calculations and experimental data as a function of field and pressure. We find that the magnetic properties are strongly affected by the nearby quantum critical point, even at zero pressure; local-density approximation LDA calculations neglecting quantum critical spin fluctuations overestimate the magnetization by a factor of ≈ 3. Using renormalized Landau theory, we extract pressure dependence of the fluctuation amplitude. It appears that a simple scaling based on the fluctuation-dissipation theorem provides a good description of this pressure dependence.

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The physics of metals near ferromagnetic quantum critical points (QCP's) has attracted renewed interest following several recent discoveries of materials with unusual still poorly understood transport and thermodynamic properties, as well as unusual low-temperature states, particularly superconductivity coexisting with ferromagnetism.[1–3] From a generic, qualitative point of view, the phenomena are understood as being connected with renormalization, scattering, and pairing due to strong fluctuations in the ferromagnetic order parameter (i.e., spin fluctuations) as the critical point is approached. Besides the mentioned superconducting transition, in clean samples of many weak itinerant ferromagnetic metals the magnetic transition near the QCP crosses over from the second order to the weakly first order, although whether this happens in $ZrZn_2$ is not yet established. The physics of this crossover is not clear yet. In any case, quantitative, material specific understanding of these phenomena is still lacking.

$ZrZn_2$ is a prototypical example of a weak itinerant (Stoner) ferromagnet. Very small magnetic moments ($0.12\mu_B$–$0.23\mu_B$) have been reported. These do not saturate even at magnetic fields up to 35 T, indicating softness of the magnetic moment amplitude and suggesting existence of soft longitudinal spin fluctuations. The Curie temperature T_C drops approximately linearly with pressure, starting at ≈ 29 K at $P=0$ and decreasing to ≈ 4 K at $P=16$ kbar,[4] which extrapolates to a QCP at $P=18$–20 kbar. The discovery of superconductivity in the ferromagnetic phase[3] resulted in renewed interest in this compound, including several theoretical studies (Refs. 5–9 and others). The relative structural simplicity of this compound and the availability of high quality experimental data as functions of H, T, and P on clean samples suggest this material as a test case for developing understanding of quantum critical phenomena in ferromagnetic metals. Here we focus on the magnetic properties, in particular, the renormalization of local-density approximation (LDA) results due to fluctuations.

Density-functional theory is in principle an exact ground-state theory. It should, therefore, correctly describe the spin density of magnetic systems. This is usually the case in actual state of the art density-functional calculations. However, common approximations to the exact density-functional theory, such as the LDA, may miss important physics and indeed fail to describe some materials. A well-known example is found in strongly Hubbard correlated systems, where the LDA treats the correlations in an orbitally averaged mean-field way and underestimates the tendency towards magnetism. Overestimates of magnetic tendencies, especially in the LDA, are considerably less common, the exceptions being materials near magnetic QCP's; here the error comes from neglect of low-energy quantum spin fluctuations. Indeed, the LDA is parametrized based on the uniform electron gas at densities typical for atoms and solids. However, the uniform electron gas at these densities is stiff against magnetic degrees of freedom and far from magnetic QCP's. Thus, although the LDA is exact for the uniform electron gas, and therefore does include all fluctuation effects in the uniform electron gas, its description of magnetic ground states in solids and molecules is mean-field-like. This leads to problems such as the incorrect description of singlet states in molecules with magnetic ions as well as errors in solids when spin-fluctuation effects beyond the mean field are important. In solids near a QCP, the result is an overestimate of the magnetic moments and tendency toward magnetism (i.e., misplacement of the position of the critical point) due to neglect of the quantum critical fluctuations.[10,11] Examples include Sc_3In,[12] $ZrZn_2$,[6] and $Sr_3Ru_2O_7$.[13] $Sr_3Ru_2O_7$ displays a novel metamagnetic quantum critical point,[14] while, as mentioned, $ZrZn_2$ shows coexistence of ferromagnetism and superconductivity. The effects of such quantum fluctuations can be described on a phenomenological level using a Ginzburg-Landau theory, in which the magnetic properties defined by the LDA fixed spin moment curve are renormalized by averaging with an assumed (usually Gaussian) function describing the beyond LDA critical fluctuations.[15,16] Although a quantitative theory allowing extraction of this function from first-principles calculations has yet to be established, one can make an estimate based on the LDA fixed spin moment curves as compared with experiment.

LDA calculations of the magnetic properties of $ZrZn_2$ (Refs. 5–7 and 17) are found to be sensitive to shape approximations, possibly because of the very small energy scales involved. In particular, atomic sphere approximations result in smaller magnetizations than those found by more accurate full-potential methods.[5–7] In fact, it was found that full-potential calculations produce a Stoner factor of ≈ 1.16, as opposed to 1.01 in the atomic sphere calculations, indicating a stronger tendency to magnetism in the full-potential calculations.[17]

Our full-potential LDA calculations for $ZrZn_2$ at its experimental volume yield a magnetization of $0.72\mu_B$ per formula unit – 3 to 4 times larger than experiment, reflecting a crucial role for the renormalization of the magnetization due to beyond LDA fluctuations, presumably associated with the QCP.

As mentioned, one can incorporate such fluctuations into LDA calculations by renormalizing the Landau expansion for the free energy with Gaussian spin fluctuations of a given rms amplitude (see Refs. 15,16 and references therein). The latter can be obtained empirically, or estimated from the parameters of the band structure with an ansatz to separate spin fluctuations included in the LDA from those neglected, as discussed in Ref. 16. Here we report renormalized Landau functional calculations where one parameter, the rms amplitude of the beyond LDA fluctuations at $P=0$, is taken as an adjustable parameter, determined by comparison with the experimental $P=0$ magnetization, and use it to describe, without further empirical parameters, the pressure and field dependence of the magnetic properties of $ZrZn_2$.

The LDA calculations were done using the general potential linearized augmented plane-wave (LAPW) method. Local-orbital extensions were included to accurately treat high-lying core states and avoid linearization errors.[18,19] The Hedin-Lundqvist exchange-correlation function was used with von-Barth-Hedin spin scaling.[20,21] The valence and Zr semicore *p* states were treated in a scalar relativistic approximation, while the core states were treated fully relativistically. LAPW sphere radii $R=2.1a_0$ were employed with a dimensionless basis set cutoff $RK_{max}=9$. Brillouin-zone samplings were done using the special **k**-points method, with 182 points in the irreducible 1/48 wedge of the zone. Convergence tests were done, showing that these parameters were adequate. For example, fixed spin moment calculations at the experimental lattice parameter were done using up to 1300 points in the wedge, with very slight changes of less than $0.01\mu_B$ in the magnetization. Calculations at the experimental lattice parameter were also done with a different sphere radius $R=2.45a_0$, again with negligible changes in magnetization.

In order to construct the Landau expansion, we did fixed spin moment calculations, determining the total energy as a function of magnetic moment and volume, using seven lattice parameters from $13.0a_0$ to $13.9a_0$ plus the experimental lattice parameter of $13.9358a_0$.[22] The variation of the energy with volume yields a bulk modulus $B=1.0$ Mbar, which we use to set the pressure scale,[23] since there is no experimental value in the literature to our knowledge. Using this value, the QCP at $P=18$–20 corresponds to a volume compression of 1.7–1.9 %.

We now turn to the magnetic properties in the LDA. As shown in Fig. 1, the magnetization drops slowly from $0.72\mu_B$ at zero pressure ($V=338a_0^3$) to $0.68\mu_B$ at $V=299a_0^3$, $P=161$ kbar (all volumes and magnetizations are given per formula unit). At this pressure the ground state becomes nonmagnetic and the moment suddenly collapses to zero. The ferromagnetic state remains metastable until $V=290a_0^3$, $P=212$ kbar. Thus, the LDA predicts not a QCP, but a first-order transition at a pressure of $P\approx 161$ kbar. Leaving aside the question of the order of the transition, the LDA strongly overestimates the magnetization and has a much higher transition pressure than experiment, implying an overestimate of T_C as well. Additionally, the LDA yields very weak P dependence of the moment up to the transition pressure, while experiment finds moments that decrease considerably with P until at least $P\approx 16$ kbar.[24]

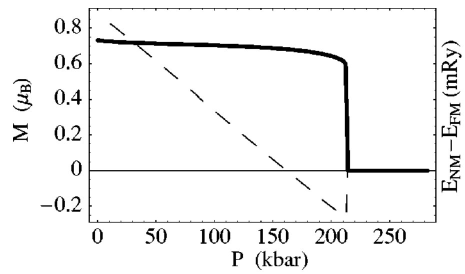

FIG. 1. Unrenormalized LDA magnetic phase diagram: the solid line is the calculated magnetic moment for those pressures where a magnetic solution exists (left axis); the dashed line is the magnetic stabilization energy (right axis, same scale as left axis but units are millirydberg). Note a metamagnetic behavior at $P \gtrsim 161$ kbar: there exists a magnetic solution, although its energy is higher than that of the nonmagnetic state.

To proceed, we use the fluctuation-renormalized Landau theory.[25] A large literature exists on this subject, for instance, the review of Ref. 15. The basis of this theory is that the main omission in LDA calculations is from long-range ferromagnetic spin fluctuations, which are important near a QCP. One writes the Landau expansion of the LDA total energy as

$$E_{LDA}(M)=a_0+\sum_{n\geqslant 1}\frac{1}{2n}a_{2n}M^{2n}, \tag{1}$$

and then introduces additional Gaussian zero-point fluctuations of a rms magnitude ξ for each of the d components of the magnetic moment (for a three-dimensional material $d=3$). After averaging over these, one obtains a fluctuation-corrected functional. The general expression[15,16] reads

$$E_{renormalized}(M)=a_0+\sum_{n\geqslant 1}\frac{1}{2n}\tilde{a}_{2n}M^{2n}, \tag{2}$$

$$\tilde{a}_{2n}=\sum_{i\geqslant 0}C_{n+i-1}^{n-1}a_{2(n+i)}\xi^{2i}\prod_{k=n}^{n+i-1}\left(1+\frac{2k}{d}\right).$$

Two approaches are, in principle, possible at this point: one is to evaluate ξ using the fluctuation-dissipation theorem,

$$\xi^2=\frac{4\hbar}{\Omega}\int d^3q\int\frac{d\omega}{2\pi}\frac{1}{2}\mathrm{Im}\,\chi(\mathbf{q},\omega), \tag{3}$$

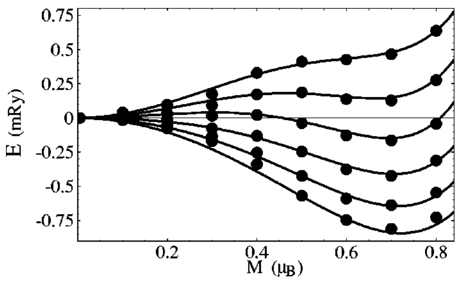

FIG. 2. Fixed spin moment calculations for lattice parameters $13.15a_0$, $13.30a_0$, $13.45a_0$, $13.60a_0$, $13.75a_0$, and $13.90a_0$. Solid lines are the sixth power fits according to Eq. (1).

however, this requires some knowledge of the susceptibility $\chi(\mathbf{q},\omega)$, and a choice for the cutoff in the integration. This choice gives the separation between the fluctuations accounted for in LDA from those missing. In the most pessimistic view it converts one unknown parameter ξ into another, though it should be said that the cutoff may be much less material and pressure dependent than ξ itself. The other approach is to treat ξ as an adjustable parameter. Here we are interested in the magnetic phase diagram of $ZrZn_2$ in a pressure range corresponding to that where magnetism is observed experimentally, so it is possible to adjust ξ to reproduce the magnetic moment at ambient pressure and then use it for the whole pressure range. The fluctuation-dissipation theorem, though not used directly, is used implicitly to construct an ansatz for the P dependence of ξ^2: the lowest-order expansion of the bare susceptibility $\chi_0(\mathbf{q},\omega)$,

$$\chi_0(\mathbf{q},\omega)=N(E_F)-aq^2+ib\omega/q \tag{4}$$

gives rise, near a QCP, to the formula (see, e.g., Refs. 26 and 27)

$$\xi^2=\frac{bv_F^2N(E_F)^2}{2a^2\Omega}[Q^4\ln(1+Q^{-4})+\ln(1+Q^4)],$$

where $Q=q_c\sqrt{a/bv_F}$, q_c is a cutoff in the momentum space, Ω is the Brillouin-zone volume, and v_F and $N(E_F)$ are the Fermi velocity and the density of states, respectively. The expression in the square brackets depends on its argument logarithmically, so the main volume dependence comes from the prefactor. Following the arguments of Ref. 16, this prefactor scales with V as V^{-1} in the effective-mass approximation. Thus, in the first approximation we write $\xi^2(V)=\xi^2(V_0)V_0/V$.

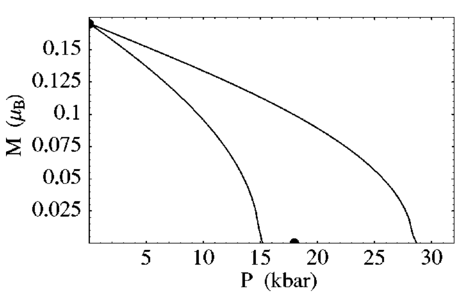

FIG. 3. Magnetization as a function of pressure, calculated from Eq. (2), using either a constant $\xi=0.5\mu_B$ or with ξ^2 scaled as the inverse cell volume (the right curve). Dots show the experimental magnetization at zero pressure and the experimental critical pressure.

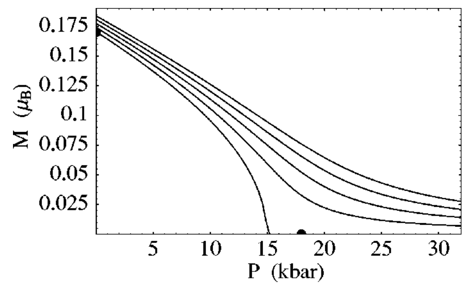

FIG. 4. Magnetization as a function of pressure, calculated with the scaled ξ^2, in an external fields of 0, 1, 2, 3, or 4 T.

In order to ensure stable fits, we have chosen the minimal power in the expansion of (1), $n=6$. Figure 2 shows the quality of the fits, which is quite good. The value of $\xi(V_0)$ that yields the experimental value of the magnetic magnetization $M=0.17$ μ_B is then found to be $\xi(V_0)=0.5\mu_B$. Although the resulting dependence of ξ on V is relatively weak, its effect on the phase diagram is large: In Fig. 3 we show the (zero-temperature) equilibrium magnetization in zero field, as a function of volume. One can see that neglecting the volume dependence of ξ leads to a QCP at $P_c\approx 29$ kbar, while using the above scaling, one gets a nearly exact value $P_c\approx 15$ kbar. We should recall, however, that this is the idealized phase diagram in zero field, while actual measurements are performed in a small, but finite field. Near a QCP even a small field can change magnetization drastically, as Figs. 4 and 5 illustrate. It is interesting to note that the metamagnetism present in the bare LDA calculations disappears when the renormalization is included and as a result a QCP appears. In reality, it may be that symmetry breakings other than uniform ferromagnetism occur near the QCP and change the transition to first order. It would be very interesting to experimentally investigate whether this in fact is the case, and if so how close to the transition it occurs and what the relevant order parameter is.

In summary, we report LDA calculations of the magnetic energy of $ZrZn_2$ under pressure. Our results demonstrate that the LDA substantially overestimates the tendency to magnetism in the whole experimentally studied pressure range. This is an indication of strong quantum spin fluctuations,

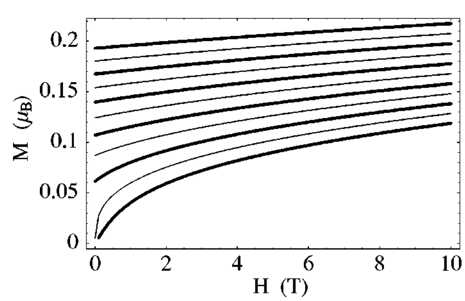

FIG. 5. Magnetization as a function of field; the pressures are from 0 to 20 kbar, spaced by 2 kbar, with alternating light and heavy lines.

associated with the QCP. Using fluctuation-renormalized Landau theory, we find that spin fluctuations with a rms amplitude of $0.5\mu_B$ are needed at $P=0$ to obtain agreement with the experimental magnetization. We further find that using a simple scaling based on the fluctuation-dissipation theorem we are able to describe the phase diagram up to the critical pressure with a good accuracy.

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