Effect of spin fluctuations in the thermodynamic and transport properties of itinerant ferromagnet CoS_2.

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Through a detailed study of the specific heat, resistivity and susceptibility under pressure in polycrystalline and single-crystal CoS_2, we demonstrate that the thermodynamic and transport properties of this system are governed by spin density fluctuations. We give the correct (P, T) coordinates of its tricritical point, and discuss the origin of the first-order magnetic phase transition in this system. Our results highlight the importance of having clean single crystals in order to extract definitive conclusions about the intrinsic properties of itinerant weak ferromagnets.

The successful description of low temperature electronic properties of paramagnetic (PM) metals in terms of the Landau Fermi-Liquid (FL) model relies on the existence of fermionic quasiparticles, which stay long-lived provided their interactions remain short-ranged and repulsive. A strong exchange interaction among the quasiparticles can split the original PM Fermi surface into spin up/down bands, leading to a ferromagnetic (FM) instability in which the FL description is still valid. In the intermediate situation, *i.e.* the itinerant weak ferromagnet, the thermodynamic and transport properties are governed by coupled long wavelength spin density fluctuations.[1] A quantitative treatment of the amplitude of the spin-density fluctuations and its temperature dependence is possible, and predicts key experimental observations like the Curie-Weiss susceptibility above T_C, or the enhanced paramagnetic moment, μ_{eff}, with respect to the ordered moment, μ_s (the so called Rhodes-Wohlfarth ratio μ_{eff}/μ_s).[1,2] On the other hand, the long-wavelength character of the spin-fluctuations brings in long-range spin

correlations that may well suppress the FL-like quasiparticle excitations in the itinerant weak ferromagnet, leading to a resistivity, magnetic susceptibility, and specific heat of the form $\Delta\rho \sim T^{5/3}$, $\Delta\chi^{-1} \sim T^{4/3}$, and $\Delta C/T \sim \ln T$ respectively, in 3D. Some of these characteristics were observed in Ni_xPd_{1-x} alloys in a narrow range of composition close to the FM limit,[3] and in weak ferromagnet $ZrZn_2$,[4] while other systems, like MnSi or $Sr_{1-x}Ca_xRuO_3$ show a more dramatic breakdown of the FL state under pressure. [5,6,7]

The cubic pyrite CoS_2 is a 3D FM metal whose T_C=122 K can be tuned to 0 K by application of a moderate pressure (p_c ~ 60 kb).[8] We have measured a Rhodes-Wohlfarth ratio for this material μ_{eff}/μ_s ~ 3,[9] which places it in a situation that approaches the weakly ferromagnetic limit.[1] On the other hand, different authors[8,10] suggested the proximity of this material to a tricritical point, which from the thermal evolution of the magnetization under pressure was placed at ~4 kb and ~117 K.[11] So, CoS_2 could be an ideal system to check the predictions of the spin-fluctuation theory, and to look for a smooth deviation of the FL model as the quantum phase transition towards the paramagnetic state is approached.

Here we present high-field resistivity, specific heat and high-pressure magnetization results that demonstrate that spin-fluctuations dominate the thermodynamic and transport properties of CoS_2. We have found fundamental differences in the properties of the single crystal with respect to the polycrystalline samples, in which extrinsic effects can lead to a completely erroneous interpretation of the results.

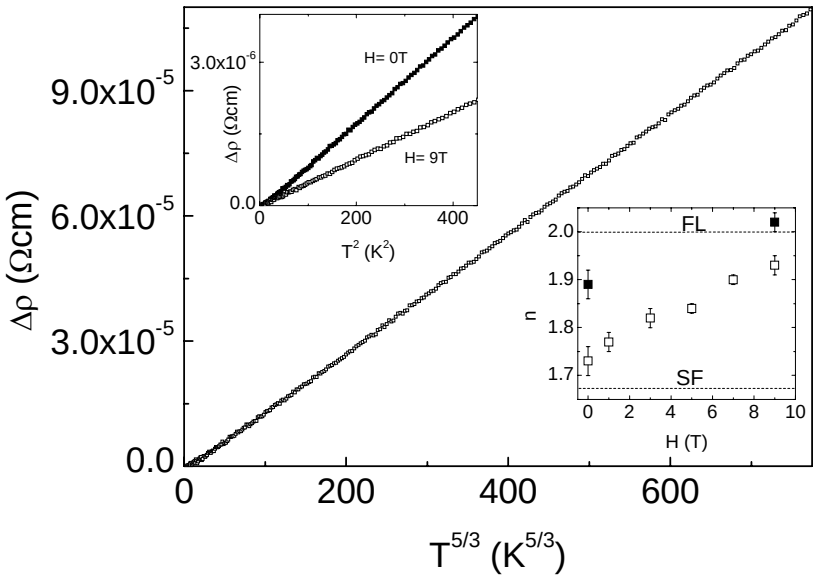

Figure 1: Resistivity vs. temperature for a polycrystalline sample of CoS_2 at zero magnetic field, according to the prediction of the spin fluctuation theory for an itinerant weak ferromagnet. Upper inset: Evolution of the resistivity (at H=0 T and at H=9 T) according to the Fermi-Liquid model in a single crystal of CoS_2. In both polycrystalline and single crystals the low temperature magnetoresistance is about 18% in 9T. Lower inset: Magnetic field dependence of the temperature exponent of the resistivity ($\Delta\rho \sim AT^n$) in a polycrystal (open symbols) and a single crystal (closed symbols). The horizontal lines mark the expected values of spin-fluctuation (SF) and Fermi-Liquid (FL) models.

Large single crystals (3×3×3 mm) were synthesized from elemental Co and S in a flux of $CoBr_2$ with a molar ratio Co:S:$CoBr_2$=1:3:2. The mixture was sealed into a quartz ampoule and kept at 750ºC for 8 days, prior to cooling to 400ºC at a rate of 4º/hr and quenched in ice-water. Residual resistivities of single crystals ranged between 5 to 7 μΩcm, with a ratio ρ_{300K}/ρ_{2K} ~ 16. Polycrystalline CoS_2 was synthesized by conventional solid state reaction in evacuated silica tubes. Sulfur stoichiometry was determined by thermo-gravimetrical analysis. In some cases the as-synthesized sample is non-stoichiometric (typically $CoS_{2.2}$) and an additional thermal process is needed to reach the desired S/Co=2.00 ratio. The residual resistivity of dense pellets of polycrystalline material was always between 40 to 50 μΩcm comparable to the best results in polycrystalline samples.[10] All the results discussed below are independent of the particular residual resistivity and checked to be reproducible and sample independent.

Magnetization up to 10 kbar was measured in a commercial Be-Cu Cell from Easylab, using Sn as an internal manometer.

In Fig. 1 we show a summary of the results of electronic transport. The low temperature fitting of the resistivity to $\Delta\rho \sim AT^n$ gives completely different results for the polycrystal and the single crystal. In the polycrystalline sample, $\Delta\rho \sim T^n$ gives a straight line for n~1.72, only slightly larger (~4%) than predicted by the spin fluctuation theory for a 3D itinerant weak ferromagnet. A careful inspection of the log-log plot shows that below ~4 K, the exponent starts increasing somewhat pointing to the recovery of the FL phase at low temperatures, but measurements below 1.8 K should corroborate this point. In any case, the fitting to the $T^{5/3}$ law is satisfactory from 4 K up to ~40 K, demonstrating the

persistence of the contribution of spin fluctuations to the resistivity. Application of a magnetic field increases the resistivity exponent continuously towards the FL limit (lower inset to Fig.1) at the time that reduces the value of the coefficient of the T^n term in the resistivity about 45% in 9 T (not shown). So, in principle the results are perfectly consistent with a low temperature state in which the transport properties are governed by long-wavelength spin fluctuations; suppression of the amplitude of the spin fluctuations by a magnetic field recovers the FL state continuously.

However, in single crystal CoS_2 the zero field resistivity exponent n~1.9 increases to n~2.02 at 9T, down to 1.8 K. The slight deviation from the predictions of FL theory at zero field are too weak to be taken as conclusive. So, we instead suggest that the apparent agreement between the resistivity of polycrystalline CoS_2 and the predictions of SF theory is due to magnetic scattering at the intergrain boundary in a metallic ferromagnet with a high degree of magnetic polarization.

On the other hand, the value of the A-coefficient of the resistivity is ~8.7×10^{-3} $\mu\Omega cmK^{-2}$, is similar to other moderately correlated metals like Sr_2RuO_4, $La_{1.7}Sr_{0.3}CuO_4$, Rb_3C_{60}, etc.[12] Application of H=9T reduces A by 44%, revealing the role played by spin-fluctuations in the large scattering rate of the quasiparticles.

Consistent with this result, the effect of exchange-enhanced spin fluctuations is also reflected in a very large value of the electronic specific heat, which is very sensitive to the application of a magnetic field. The results are shown in Fig. 2.

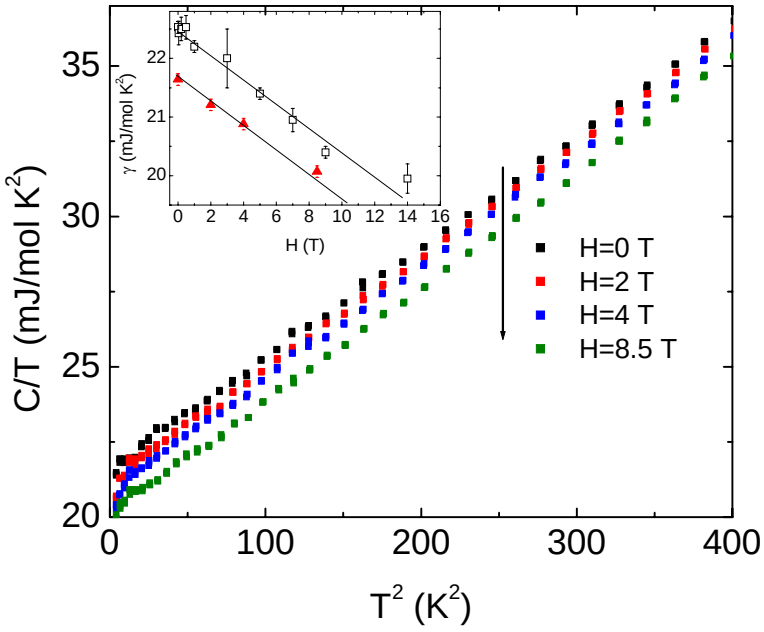

Figure 2: Low temperature specific heat at different magnetic fields for a single crystal of CoS_2. Inset: Evolution of γ with the magnetic field in single crystals (solid triangles) and polycrystalline CoS_2 (open squares). Lines are guides to the eye to show that the rate of reduction is similar in both cases.

The plot C/T vs T^2 at different fields gives a set of parallel straight lines; linear fitting between 3 K and 20 K results in a field independent Debye temperature θ_D=352(2) K and a zero field value of the electronic specific heat coefficient γ = 21.6 (2) mJ/molK^2. This value is anomalously large, and is highly field dependent, being suppresed by ~14% in 9T (see the inset to Fig. 2). The resulting Kadowaki-Woods ratio for CoS_2 is ~2.0(2) a_0, where a_0= 10 $\mu\Omega$cm mol^2 K^2/J^2 is the universal value found in heavy-fermions.

We have calculated γ ab initio, based on the density functional theory (DFT) with the WIEN2k software[13,14]. This uses a full-potential, all-electron scheme implemented via the APW+lo method[15]. The value obtained within the GGA approximation[16] for γ = 2.4 mJ/molK^2 is smaller than the experimental value by a factor 10. Our calculations do not include the spin fluctuation that could be key for such a large value of the parameter γ. Introducing strong correlation effects by using the LDA+U approach[17] does not improve the picture, reducing further the value obtained for γ (γ = 1.5 mJ/molK^2 for U~6 eV). The experimental value is then compatible with an enhancement of the quasiparticle effective mass m*/m ~11(2) by coupling to magnetic excitations, and shows that the same effect is probably responsible for the increase in A and γ.

On the other hand, our data does not show the ΔC/T~lnT upturn. Experiments at lower temperatures should confirm this point.

Now we will discuss the results of high-pressure magnetization at different fields and temperatures. In order to confirm the presence of a tricritical point in the (T,H) phase diagram of CoS_2 we have performed an analysis of the magnetic phase transition based on Landau´s formalism.[18] For an isotropic ferromagnet, χ can be derived from the expansion of the free energy in even terms of M:

$$H = aM + bM^3 + cM^5 + \ldots \qquad (1)$$

where the Pauli susceptibility, χ_0, and the effective exchange field, λ, enter the equation in a = (χ_0 - λ). Then, if the presence of a high-pressure first-order transition is confirmed in CoS_2, the system will go through a tricritical point characterized by b=0 in eq. (1).

Experimentally, the sign of b and hence the nature of the magnetic phase transition can be obtained from the slope of the H/M vs M^2 isotherms, slightly above T_C. This is shown in the inset to Fig. 3. The slope of the curves, at the same equivalent temperature of 1.02 T_C, decreases with pressure. Fitting to equation (1) shows that the transition is already first-order (b<0) at p>0.2(1) kb. This is an important correction to the critical pressure, previously estimated in ~4.5 kbar.[11]

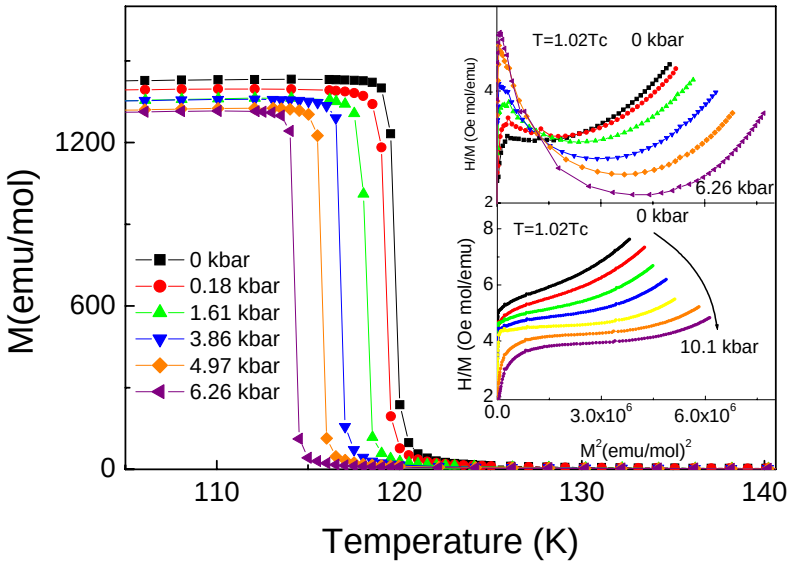

Figure 3: Pressure dependence of the magnetization in a single crystal of CoS_2. Pressure dependence of the H/M vs M^2 isotherm (T=1.02 T_C) for different pressures in a single crystal (upper inset) and a polycristalline sample (lower inset).

It is well known that quenched disorder suppressed first-order magnetic phase transitions, giving them an apparent look of continuous behavior.[19] To check whether previous misplacement of the tricritical point could be an effect of the disorder inherent to grain boundaries, we have repeated the high-pressure magnetic experiments in a polycrystalline sample. Although the pressure dependence of T_C is similar to the single crystal ($d\ln T_C/dP = 6.1(4)\ 10^{-3}$ kb^{-1}, assuming linearity), the drop of magnetization at the critical temperature is not so abrupt, and more important, fitting of the H/M vs M^2 isotherms shows a crossover to b<0 at p~4.5 (5) kbar (see the lower inset to Fig. 3) in agreement with previous reports. So, our results demonstrate that the magnetic phase transition in CoS_2 is already first-order (or at least the critical pressure is below 0.2

kbar). Previous results are clearly influenced by the presence of disorder due to the polycrystalline nature of the sample probed.

On the other hand, increasing temperature reduces the bulk FM moment of the system through the excitation of thermal fluctuations which determine the temperature dependence of the magnetization. This process can be treated by considering the effect of a random exchange field in equation (1), as shown by Lonzarich[2]

$$H = (a+3b\ \bar{m}^2)M + bM^3 + \ldots \qquad (2)$$

where $\bar{m}^2$ refers to the variance of the fluctuations. A derivation of the temperature dependence of $\bar{m}^2$ results in $\Delta\chi^{-1}\sim T^{4/3}$, for the case relevant here.[2] From equation (2) also follows that it is the existence of an anharmonic term ($b\neq 0$) that introduces the temperature dependence.

The low pressure susceptibility fits very nicely this prediction, following an approximate variation $\Delta\chi^{-1}\sim T^{4/3}$ in a wide temperature range above T_C (Fig. 5). However, increasing pressure results in a faster variation of $\Delta\chi^{-1}$. This result is reproduced in both kind of samples, polycrystalline and single crystals.

From the above discussion it is clear that if $b=0$, then higher order terms must be considered in the expansion ($\ldots+cM^5$), and

$$A=a+3b\ \bar{m}^2+5c(\ \bar{m}^2)^2 \text{ and } \Delta b=b+10c\ \bar{m}^2 \qquad (3)$$

leading to a more rapidly varying susceptibility, $\Delta\chi^{-1}\sim(T^{4/3})^2$. On the other hand, on crossing to the first-order side of the tricritical point $b<0$, and higher order terms must be retained to keep the stability of the function. Hence the rate of variation of the inverse paramagnetic susceptibility should increase at higher pressures, as observed. This result provides a very accurate confirmation of spin fluctuation theory, and completes a consistent picture with the transport and specific heat measurements.

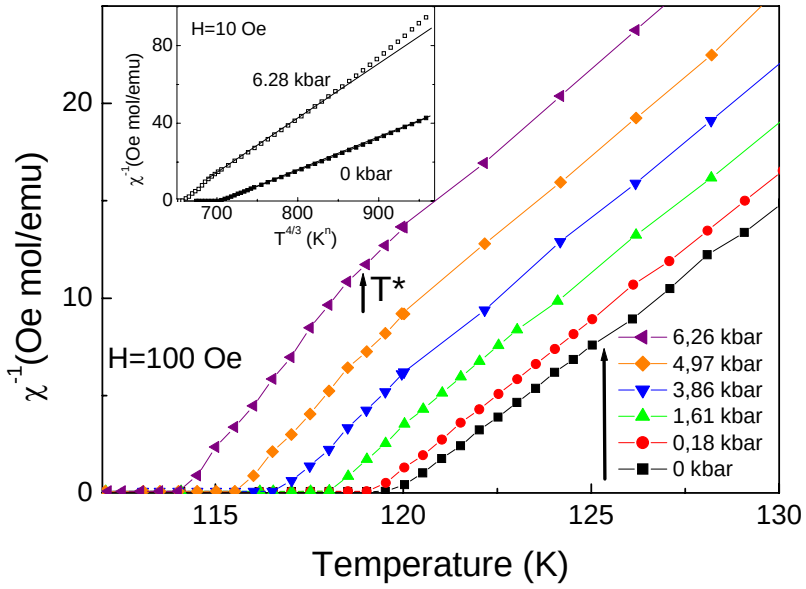

Figure 4: Inverse paramagnetic susceptibility at different pressures, in the vicinity of T_C. The arrow marks the rapid downturn of the susceptibility below T* at high pressures. The apparent linear dependence of the inverse susceptibility above T* is due to the small temperature interval plotted. Inset: Inverse paramagnetic susceptibility at two different pressures, according to the expected $\Delta\chi^{-1}\sim T^{4/3}$ from the spin fluctuation theory. Increasing pressure results in a faster variation of the susceptibility. The straight lines are guides to the eye.

On the other hand, the low field susceptibility in the vicinity of T_C shows a change in the slope of the inverse susceptibility in the interval $T_C < T < T^*$ (Fig. 4) becoming more evident at high pressures. The effect is completely erased by a relatively small magnetic field (H >1 kOe). On the other hand, the cooling and heating metastability limits derived from the fittings of the H/M vs M^2 curves around T_C to equation (1), results in a predicted maximum hysteresis of ~0.1 K.[18] Consistent with this result, we have not observed thermal hysteresis in the M(T) curves.

A situation like that points to a rather weak first-order transition in CoS_2, in which the energy barrier separating the ordered and disordered states is strongly suppressed. In this scenario a thermodynamically favorable coexistence of the ordered and disordered phases becomes more plausible around T_C, like in the case of a spinodal phase segregation,[18] and the faster than expected evolution of the inverse susceptibility could be reflecting the existence of local magnetic order in the temperature interval $T_C < T <$

T*. This is further supported by a rapidly increasing T_C with field, at a rate $d\ln T_C/dH = 3.3(2)\times10^{-3}$ kOe^{-1}. Also consistent with our hypothesis is the report by Goto *et al.*[11] of a metamagnetic transition in a narrow range of temperature above the first-order magnetic phase transition.

On the basis of our results, the features of phase diagram of CoS_2 should be reconsidered at the light of the similarities shown with compounds like MnSi, and $ZrZn_2$, dominated by long-wavelength spin fluctuations. The existence of a pressure induced tricritical point in these materials must not be accidental, but rooted in a common effect. Long-wavelength correlations are known to introduce a negative M^4 term in the expansion of the free energy (the equivalent to b in equation (1)), and hence the magnetic first-order phase transition should be generic to itinerant weak ferromagnets.[20] In the same line, spontaneous magnetic phase separation has been found to be common to many of these systems, as shown by Uemura *et al.*[7] The previous report of $\Delta\rho\sim T^{3/2}$ right beyond the quantum phase transition in CoS_2,[8] along with our report of a possible phase separation, could point to a common origin of both effects.

In summary, the behavior of the resistivity, specific heat and magnetic susceptibility of CoS_2 is dominated by exchange-enhanced spin density fluctuations. Coupling of the quasiparticles to magnetic excitations makes this material a moderate-strongly correlated Fermi liquid. We have confirmed and relocated the position of the tricritical point in the phase diagram of this material. The change in the order of the nature of the magnetic phase transition allows a very accurate determination of the predictions of the spin-fluctuation theory, in a system which is very simple from a chemical and structural point of view. Our results also demonstrate that having clean single crystals is crucial in order to extract valid conclusions about the intrinsic thermodynamic properties of itinerant weak ferromagnets.

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