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

M. Otero-Leal,[1] F. Rivadulla,[2,*] M. García-Hernández,[3] A. Piñeiro,[1,3] V. Pardo,[1,3] D. Baldomir,[1,3] and J. Rivas[1]
[1]*Departamento de Física Aplicada y Química-Física, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain*
[2]*Departamento de Química-Física, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain*
[3]*Instituto de Investigaciones Tecnológicas, Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain*
[4]*Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, Cantoblanco, Madrid 28049, Spain*
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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.

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The successful description of low-temperature electronic properties of paramagnetic (PM) metals in terms of the Landau-Fermi-liquid 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 or spin-down bands, leading to a ferromagnetic (FM) instability in which the Fermi-liquid (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 such as 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 (SFs) 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 three dimensions. 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, such as MnSi, Ni_3Al, or $Sr_{1-x}Ca_xRuO_3$, show a more dramatic breakdown of the FL state under pressure.[5–8]

The cubic pyrite CoS_2 is a three-dimensional (3D) FM metal whose $T_C=122$ K can be tuned to 0 K by application of a moderate pressure ($p_c \sim 60$ kbar).[9] We have measured a Rhodes-Wohlfarth ratio for this material, $\mu_{\text{eff}}/\mu_s \sim 3$,[10] which places it in a situation that approaches the weakly ferromagnetic limit.[1] On the other hand, different authors[9,11] suggested the proximity of this material to a tricritical point, which from the thermal evolution of the magnetization under pressure was placed at ~4 kbar and ~117 K.[12] 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 toward 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.

Large single crystals ($3\times3\times3$ mm^3) 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, kept at 750 °C for 8 days, prior to cooling to 400 °C at a rate of 4°/h, and quenched in ice water. Residual resistivities of single crystals ranged between 5 and 7 $\mu\Omega$ cm, with a ratio $\rho_{300\text{ K}}/\rho_{2\text{ K}} \sim 16$. Polycrystalline CoS_2 was synthesized by conventional solid-state reaction in evacuated silica tubes. Rietveld refinement of x-ray diffraction showed a cubic single phase, with cubic lattice parameter $a=5.530(3)$ Å for both types of samples. Sulfur stoichiometry was determined by thermogravimetrical analysis. In some cases the as-synthesized sample is nonstoichiometric (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 and 50 $\mu\Omega$ cm comparable to the best results in polycrystalline samples.[11] 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 $n \sim 1.72$, 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

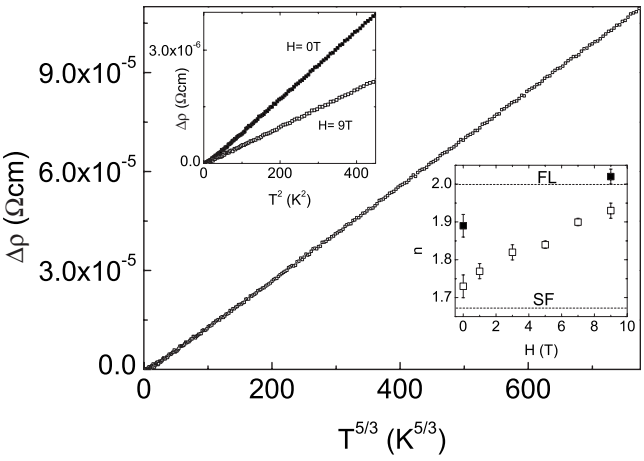

FIG. 1. Resistivity vs temperature for a polycrystalline sample of CoS_2 at zero magnetic field, according to the prediction of the spin-fluctuation theory for an itinerant weak ferromagnet. Upper inset: evolution of the resistivity (at $H=0$ T and at $H=9$ T) according to the Fermi-liquid model in a single crystal of CoS_2. In both polycrystalline and single crystals the low-temperature magnetoresistance is about 18% at 9 T. 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 SF and FL models.

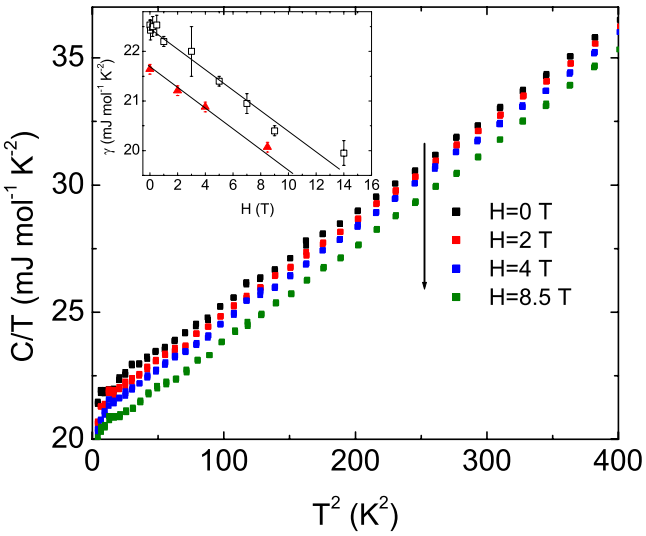

FIG. 2. (Color online) Low–temperature specific heat at different magnetic fields for a single crystal of CoS_2. Inset: evolution of γ with the magnetic field in single crystals (solid triangles) and polycrystalline CoS_2 (open squares).

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 toward the FL limit (lower inset of Fig. 1) at the time that reduces the value of the A coefficient of the T^n term in the resistivity about 45% at 9 T (not shown). 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 $n \sim 1.9$ increases to $n \sim 2.02$ at 9 T down to 1.8 K. The slight deviation from the predictions of FL theory at zero field is too weak to be taken as conclusive. 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.

The value of the A coefficient of the resistivity for the single crystal is $\sim 8.7 \times 10^{-3}$ $\mu\Omega$ cm K^{-2} (and is reduced by 44% in 9 T) and is similar to other moderately correlated metals such as Sr_2RuO_4, $La_{1.7}Sr_{0.3}CuO_4$, Rb_3C_{60}, etc.[13] 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.

The plot C/T vs T^2 at different fields gives a set of parallel straight lines; linear fitting between 3 and 20 K results in a field independent Debye temperature $\theta_D = 352(2)$ K and a zero-field value of the electronic specific-heat coefficient $\gamma = 21.6(2)$ mJ/mol K^2. This value is anomalously large and is highly field dependent, being suppressed by ~14% in 9 T (see the inset of Fig. 2). The resulting Kadowaki-Woods ratio for CoS_2 is $\sim 2.0(2)a_0$, 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.[14] This uses a full-potential all-electron scheme implemented via the augmented plane-wave (APW)+LO method.[15] The value obtained within the generalized gradient approximation (GGA) (Ref. 16) for $\gamma = 2.4$ mJ/mol K^2 is smaller than the experimental value by a factor of 10. Our calculations do not include the spin fluctuations that could be key for such a large value of the parameter γ. Introducing strong correlation effects by using the local-density approximation (LDA)+U approach[17] does not improve the picture, reducing further the value obtained for γ ($\gamma = 1.5$ mJ/mol K^2 for $U \sim 6$ eV). The experimental value is then compatible with an enhancement of the quasiparticle effective mass $m^*/m \sim 11(2)$ 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 do not show the expected $\Delta C/T \sim \ln T$ upturn according to spin-fluctuation theory. Experiments at lower temperatures should confirm this point.

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,

$$H = aM + bM^3 + cM^5 + \cdots, \quad (1)$$

where the Pauli susceptibility, χ_0, and the effective exchange field, λ, enter the equation in $a = \chi_0 - \lambda$. 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

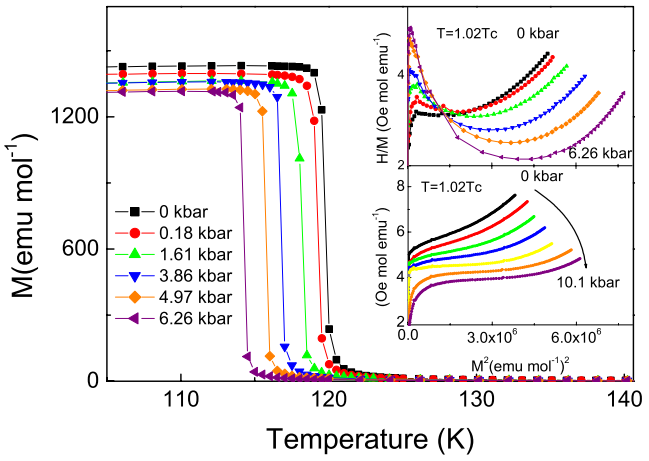

FIG. 3. (Color online) Pressure dependence of the magnetization in a single crystal of CoS_2. Pressure dependence of the H/M vs M^2 isotherm ($T=1.02\,T_C$) for different pressures in a single crystal (upper inset) and a polycrystalline sample (lower inset).

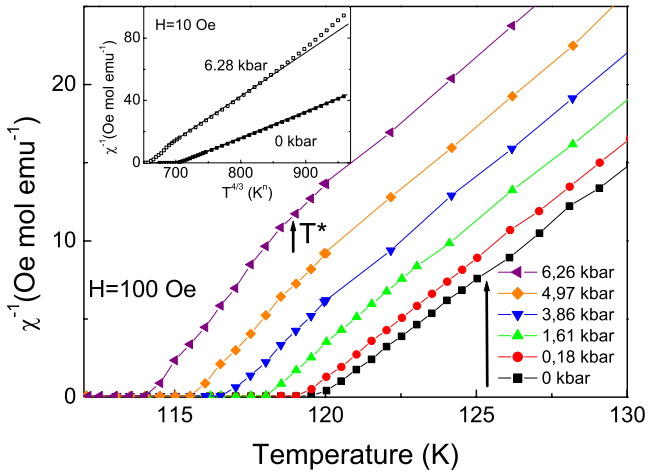

FIG. 4. (Color online) Inverse paramagnetic susceptibility at different pressures in the vicinity of T_C. The arrow marks the rapid downturn of the susceptibility below T^* at high pressures. The apparent linear dependence of the inverse susceptibility above T^* is due to the small temperature interval 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 in the susceptibility. The straight lines are guides for the eyes.

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 of Fig. 3. The slope of the curves, at the same equivalent temperature of $1.02\,T_C$, decreases with pressure. Fitting to Eq. (1) shows that the transition is already first order ($b<0$) at $p>0.2(1)$ kbar. This is an important correction to the critical pressure, previously estimated in ~4.5 kbar.[12]

It is well known that quenched disorder suppresses 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 ($d\ln T_C/dP=6.1(4)\times10^{-3}$ kbar^{-1}), 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 $p\sim4.5(5)$ kbar (see the lower inset of 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) and that previous results are clearly influenced by the polycrystalline nature of the samples.

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 Eq. (1), as shown by Lonzarich,[2]

$$H=(a+3b\bar{m}^2)M+bM^3+\cdots, \tag{2}$$

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 Eq. (2) also follows that it is the existence of an anharmonic term ($b\neq0$) 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. 4). Increasing pressure results in a faster variation in $\Delta\chi^{-1}$. This result is reproduced in both kinds 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 $(\cdots+cM^5)$, and

$$A=a+3b\bar{m}^2+5c(\bar{m}^2)^2,\quad \Delta b=b+10c\bar{m}^2, \tag{3}$$

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 $b<0$, higher order terms must be retained to keep the stability of the function. Hence the rate of variation in the inverse paramagnetic susceptibility should increase at higher pressures, as observed. Although these results fit nicely the predictions of spin-fluctuation theory, this behavior could also be influenced by the proximity to the finite-temperature phase transition and in particular by the tricritical point. This is a very important point and should be further investigated in CoS_2 and other weak itinerant ferromagnets.

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).

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 $d \ln T_C / dH = 3.3(2) \times 10^{-3}$ kOe^{-1}. Also consistent with our hypothesis is the report by Goto *et al.*[12] 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 the phase diagram of CoS_2 should be reconsidered in light of the similarities shown with compounds such as 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 Eq. (1)], and hence the magnetic first-order phase transition should be generic to itinerant weak ferromagnets.[20] However, in other systems such as Ni_3Al this tricritical point has not been reported yet. On the other hand, spontaneous magnetic phase separation has been found to be common to many of these systems, as shown by Uemura *et al.*[7] Our report of a possible phase separation beyond the tricritical point 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. Our results also demonstrate that having clean single crystals is crucial in order to extract valid conclusions about the intrinsic transport and thermodynamic properties of itinerant weak ferromagnets.

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*f.rivadulla@usc.es

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