Conduction-electron spin resonance and spin-density fluctuations of $CoS_{2-x}Se_x$ ($x \leqslant 0.1$)

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I report the observation of conduction electron spin resonance (CESR) in the paramagnetic phase of weak itinerant ferromagnet (WIFM) CoS_2. The observation of a narrow Lorentzian line above T_C is interpreted as a signature of long-wavelength exchange-enhanced spin-density fluctuations, whose amplitude increases up to $T^* \approx 2\ T_C$. I propose that this temperature marks a characteristic energy scale below which strong exchange interactions between spin fluctuations determine the spin lifetime. This study shows that the characteristic parameters of CESR are very sensitive to electronic correlations and can be very useful in the study of the spin interactions and relaxation in itinerant electron systems in the intermediate coupling regime.

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CoS_2 is one of the classic examples of weak itinerant ferromagnet (WIFM),[1,2] according to Moriya's spin fluctuation theory.[3] In these systems the thermodynamic and transport properties are completely determined by the temperature dependence of the amplitude of the local spin density $\langle S_L{}^2\rangle$.[4–6] An interesting effect is the Curie-Weiss temperature dependence of the paramagnetic susceptibility in spite of the absence of local moments, which has been reported in other itinerant systems in the intermediate-strong coupling regime like Na_xCoO_2,[7] LaCoO(As,P),[8] etc. Another consequence is the first-order ferromagnetic-to-paramagnetic phase transition at T_C observed in $CoS_{2-x}Se_x$.[6,9]

On the other hand CoS_2 and its alloys (Fe, Se, etc.) were intensively studied during the last few years because of the possibility of presenting a large-spin polarization, which makes them candidates as sources of spin-polarized electrons above liquid nitrogen.[10–15]

Here we report the existence of an observable conduction electron-spin resonance (CESR) at X-band in metallic $CoS_{2-x}Se_x$ ($x \leqslant 0.1$) in a wide temperature range up to $T^* \approx 2\ T_C$. We demonstrate that the strong exchange interaction between the spin fluctuations suppresses the spin-lattice relaxation, increasing $T_1{}^{-1}$ enough so as to make CESR observable in this itinerant system. The linewidth (intensity) increases (decreases) very fast from T_C up to T^*, where it first distorts and then becomes unobservable. We suggest that T^* represents a characteristic energy scale marked by the strong exchange interactions between long wavelength spin fluctuations.

Millimeter-sized single crystals of CoS_2 were synthesized in a flux of Co, S, and $CoBr_2$ (molar ratio Co:S:$CoBr_2$ 1:3:2 to a total weight of 25 g), as reported in Ref. 6. Polycrystalline samples of $CoS_{2-x}Se_x$ ($0 \leqslant x \leqslant 0.1$) were synthesized by conventional solid state reaction in evacuated silica ampoules at temperatures between 550 °C and 750 °C. All samples are single phase and have the correct stoichiometry, as determined by thermogravimetric analysis (TGA) and elemental analysis.

The temperature dependence of the magnetization and resistivity for CoS_2 is shown in Fig. 1. The saturation moment below T_C is $\mu_s = 0.8\ \mu_B$ (see the inset to Fig. 1). Above T_C, the susceptibility follows a Curie-Weiss dependence (Fig. 2) with $\mu_{eff} = 2\ \mu_B$ in spite of the good metallic conductivity. The Curie temperature has been previously shown to decrease fast with pressure, going through a quantum phase transition at $p_c \approx 6$ GPa.[16] We have collected room-temperature powder-diffraction spectra at different pressures (not shown).[17] Fitting the experimental parameters of the equation of state to the Birch-Murnaghan equation[18] gives a bulk modulus $K_0 = 115(5)$ GPa. The positive and large $\partial T_C/\partial V$ confirms the Stoner-Wolfarth criterion for itinerant electron magnetism in CoS_2.

The electron spin resonance (ESR) lines are shown in the inset to Fig. 2 for various representative temperatures above T_C.

Below T_C the lines distort and increase its width with lowering temperature (ΔH goes through a minimum at $\approx 1.1\ T_C$). In this Brief Report we will discuss the results above this minimum, i.e., the paramagnetic resonance. The crystals have been finely crushed and dispersed in ESR-quality quartz powder. In these conditions a Lorentzian line is observed from T_C to $\approx 2\ T_C$ ($= T^*$). In this interval the absolute magnetic susceptibility obtained by integration of the ESR line and comparison with a reference (we have used both Gd_2BaCuO_5 and $La_{2/3}Ca_{1/3}MnO_3$)[19] matches the magnetic susceptibility from dc experiments (Fig. 2). This demonstrates that the same set of spins contributing to the dc signal is also the origin of the electronic paramagnetic resonance, discarding the possibility of a resonant impurity as the source of the ESR line. From this result and the good metallic conductivity we have ascribed this line to a CESR.

The results for $\Delta H = 1/(\gamma T_1)$ are shown in Fig. 3 ($T_1{}^{-1} = T_2{}^{-1}$ in a metal[20]). ΔH increases linearly up to T^*, where it first distorts and then disappears.

According to Elliot[21] the spin and momentum relaxation time are directly related through the spin-orbit coupling. This interaction is directly reflected in the displacement of the CESR signal away from the free-electron value ($g = 2.0023$),

$$T_1^{-1} = \Delta g^2/\tau, \tag{1}$$

$\Delta g = \lambda/\Delta E$, where λ is the spin-orbit interaction energy, ΔE is the energy difference between the split levels, and τ is the momentum relaxation time that can be obtained from resistivity measurements[22]

$$\tau = \frac{m^*}{ne^2\rho(T)}. \tag{2}$$

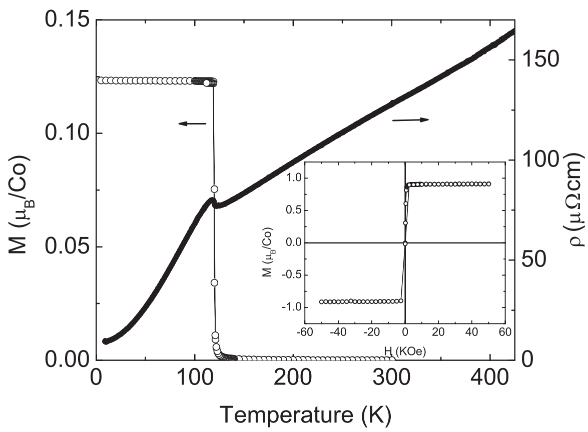

FIG. 1. Temperature dependence of the magnetization (H = 100 Oe; zero-field and field-cooled curves are shown) and resistivity of a CoS_2 single crystal. Inset: Hysteresis M(H) loop at 5 K.

Note that combining Eqs. (1) and (2) predict a linear relationship between ΔH and ρ. As both magnitudes are linear in T above T_C (see Figs. 1 and 3), this observation further confirms conduction electrons as the origin of the resonance.

Taking $n \approx 2.4 \times 10^{22}$ cm^{-3} from Ref. 23, $m^* \approx$ 10 m_e (from the comparison of the calculated and experimental electronic specific heat),[6] and the experimental resistivity $\rho(T) \approx 90(20)$ $\mu\Omega$ cm in the temperature range of the ESR measurements, we have obtained $\tau \approx 10^{-14}$ s. This corresponds to ΔH ≈ 30 kGauss, which is an order of magnitude larger than observed experimentally.[24]

Therefore, there must be an additional interaction providing the extra narrowing to make the line observable; the most plausible hypothesis points to the exchange coupling between the spin fluctuations. Given that the magnitude to the exchange field can be approximated by the value of the magnetization, a linear relationship must occur between $T_1{}^{-1}$ and M,

$$\Delta H = \Delta H^{\circ}(1 + \beta\, H/M), \qquad (3)$$

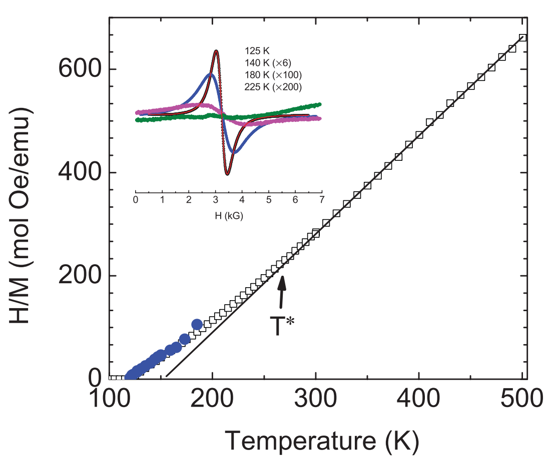

FIG. 2. (Color online) Temperature dependence of the inverse susceptibility of single crystal CoS_2 above T_C, H = 100 Oe (open squares). Closed dots represent the absolute magnetic susceptibility obtained from the integration of the ESR signal (see text). Inset: ESR curves at different temperatures. The lines have been multiplied by the factor indicated to fit them into the same scale. The ESR curve at 125 K is fitted to a Lorentzian function (solid line).

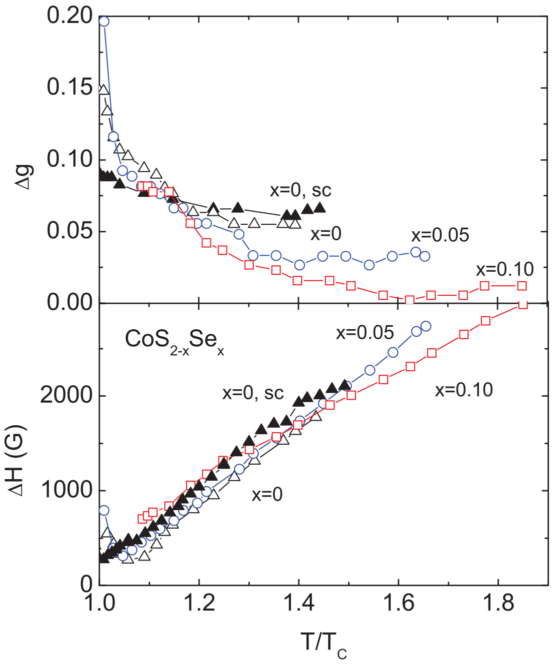

FIG. 3. (Color online) Temperature dependence of the g-shift (top) and ΔH (bottom) for $CoS_{2-x}Se_x$, normalized to the corresponding Curie temperature. The g-factor and ΔH are, within the error, not affected by the sample resistivity from comparison of single crystal and powder samples.

where β is a multiplicative factor and ΔH° is the expected linewidth in the absence of the exchange interaction.[25] The results are shown in Fig. 4. Both ΔH and H/M show the same temperature dependence in the paramagnetic metallic range. The agreement with the prediction of Eq. (3) confirms that a moderate-strong exchange coupling enhances the spin lifetime in metallic CoS_2.

On the other hand the slight decrease of the slope of $T_1{}^{-1}$(T) produced by Se doping (Fig. 3, bottom) indicates a progressive reduction of the exchange-correlation energy in Se-doped samples. Also the decrease of the g-shift [Fig. 3(a)] points to a faster increase of ΔE than λ after Se doping. These two effects show the extreme sensitivity of CESR to subtle band-structure

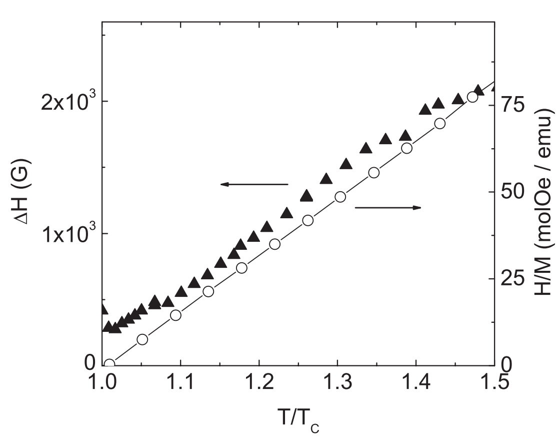

FIG. 4. Comparison of the temperature dependence of ΔH and H/M following the prediction of Eq. (3).

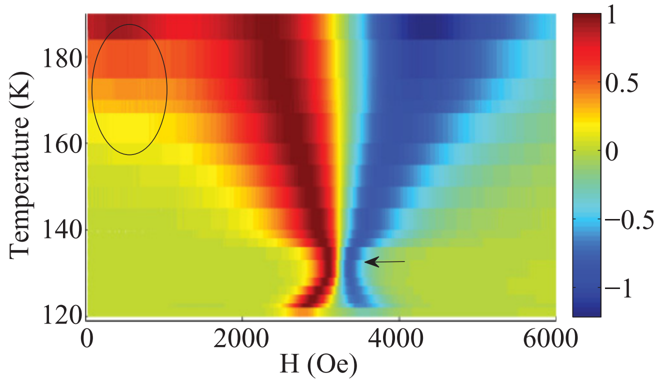

FIG. 5. (Color online) Temperature dependence of the CESR lines in polycrystalline CoS_2 presented in the T vs H plane. The lines are normalized to its maximum intensity to observe the appearance of low-field absorption at high temperatures. The minimum linewidth, marked with an arrow, is observed at $\approx 1.1\ T_C$. The elipse shows the development of a low-field absorption at high temperature.

effects that could be useful to study other itinerant systems in the intermediate coupling regime.

On approaching $T^* \approx 2\ T_C$ the line distorts, presenting a strong absorption at low fields, and above T^* it becomes too broad to be observable. This change is clearer in polycrystalline samples (Fig. 5).

The disappearance of the CESR line at T^* coincides with the change of slope previously observed in the temperature dependence of $\chi^{-1}(T)$.[5] This puzzling behavior of $\chi(T)$ was originally taken as evidence of the saturation of $\langle S_L{}^2\rangle$, reaching a Curie-Weiss (CW) regime in which the systems behave as if local-moments were induced by temperature.[5] $\chi^{-1}(T)$ in weak itinerant magnets and nearly ferromagnetic metals is proportional to the mean square of the local amplitude of spin fluctuations $\langle S_L{}^2\rangle$. In the paramagnetic regime $\langle S_L{}^2\rangle \propto T$, resulting in a Curie-Weiss–like $\chi(T)$ with a slope determined by the stiffness against a change in the amplitude of the spin fluctuations. If the spin stiffness is small $\langle S_L{}^2\rangle$ increases very fast until saturation at T^*; the maximum amplitude of the spin density is fixed by the band structure and the occupation. Then above T^* the spin fluctuations behave as local moments (temperature-induced local moments).[3,5]

From our results it is more likely that T^* represents a characteristic energy scale marked by the strong exchange interaction between long-wavelength spin fluctuations. This effect can justify a departure of χ^{-1} from the high temperature linear behavior as well as the observance of the CESR.

In any case the same effect (linear increase of ΔH and disappearance of the line above $\approx 2\ T_C$) was observed in MnSi,[26] pointing to a common origin and probably to the existence of the same effect in other WIFMs or nearly magnetic paramagnets.

To summarize we have shown that there is an important difference between the momentum and spin-relaxation time in the paramagnetic phase of the WIFM CoS_2 due to the strong exchange interaction between long-wavelength spin fluctuations. This occurs in a wide temperature interval above T_C up to a temperature that marks the transition to an uncorrelated paramagnon regime. The observation of CESR in other itinerant systems, like heavy fermions,[27,28] MgB_2,[29] etc., along with its extreme sensitivity to subtle variations in the band structure and spin-orbit interaction, raises the interest to extend these studies to other itinerant electron systems in the moderate correlation regime, such as nearly ferromagnetic metals (Na_xCoO_2), Ln^{3+}(Fe,Co)OAs, etc.

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