The Magnetic Phase Transition of $CoS_{2-x}Se_x$

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The nature of the magnetic phase transition of the itinerant ferromagnet CoS_2 has been studied. We have measured high-pressure X-ray diffraction and magnetization, at different temperatures and fields. Our results are discussed on the basis of a thermodynamic model applicable to itinerant ferromagnets with strong spin fluctuations.

Index Terms—**Pyrite, CoS_2, first-order magnetic phase transition, high pressure.**

I. Introduction

STRONGLY correlated transition-metal compounds have attracted considerable attention since they show interesting physical properties such as temperature and magnetic field induced metal-insulator transition, colossal magnetorresistence, and different forms of superconductivity. [1] Among them, pyrite-type 3d transition-metal disulfides (MS_2; $M = $ Fe, Co and Ni) exhibit a variety of electrical and magnetic properties [2].

For example, CoS_2 is an itinerant ferromagnet whose T_c is reduced with pressure, the magnetic transition becoming first order. It has been reported [3], [4] that when the sulfur atoms are partially replaced by selenium, $CoS_{2-x}Se_x$, the Curie temperature (T_c) decreases in spite of the volume increase; a first-order phase transition has also been suggested for a moderate amount of Se ($\sim 10-20\%$). These results indicate that Se is not just increasing the volume of the unit cell, but it is playing a more decisive role (still to be clarified) in the physical properties of the material.

In this work we present experimental results of magnetization under pressure at different magnetic fields and temperatures, to monitor the change in the nature of the magnetic phase transition. From a phenomenological Landau analysis [5], [6] of the phase transition and, contrary to previous suggestions, we found that the transition is first order (or nearly first order) in CoS_2, but becomes second order after Se doping. We discus the implications of our founding on the basis of the spin-fluctuation theory [8].

II. Experimental Results and Discussion

All of the experimental results presented correspond to polycrystalline samples synthesized by conventional solid state reaction in evacuated quartz tubes. All of the samples analyzed are single phase with a stoichiometric S content, as checked by thermo-gravimetrical analysis. In some cases, the as-synthesized sample was nonstoichiometric (Fig. 1) and we applied an additional thermal treatment to reach the desired composition, $CoS_{2.00}$.

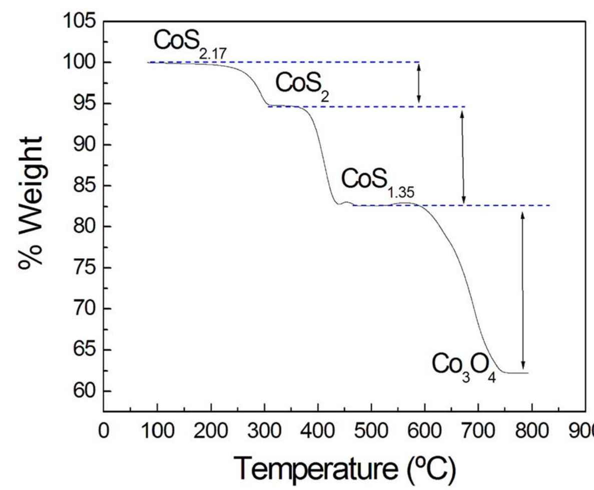

Fig. 1. Thermo-gravimetrical analysis, showing the different steps of the decomposition of CoS_x in flowing oxygen.

The magnetic measurements were done in a magnetometer (SQUID) and magnetization at high pressure (hydrostatic pressure) was measured up to 10 kbar with a commercial Be-Cu Cell from Easylab, using Sn as an internal manometer. Powder-diffraction spectra were collected at room temperature at series of different static pressures at the Daresbury Synchrotron Radiation Source (SRS). Each pattern was collected for about 10 min. A diamond anvil cell was used to generate high pressure. A small ruby mixed with the sample was used to monitor the internal pressure through its fluorescence. A mixture of ethanol-methanol was used as the pressure transmitting medium.

In Fig. 2, we show a detail of the evolution of the (002) peak of the X-ray diffraction pattern with pressure. Lattice parameters at each pressure were obtained from Rietveld refinement of the powder patterns, and the dependence of the unit cell volume with pressure is shown in Fig. 3, along with the fitting to the Birch-Murnaghan equation

$$P = \frac{3}{2}K_0\left[\left(\frac{V_o}{V}\right)^{\frac{7}{3}} - \left(\frac{V_o}{V}\right)^{\frac{5}{3}}\right] \times \left\{1 - \frac{3}{4}\left(4 - \frac{dK_0}{dV}\right)\left[\left(\frac{V_o}{V}\right)^{\frac{2}{3}} - 1\right] + \cdots\right\} \quad (1)$$

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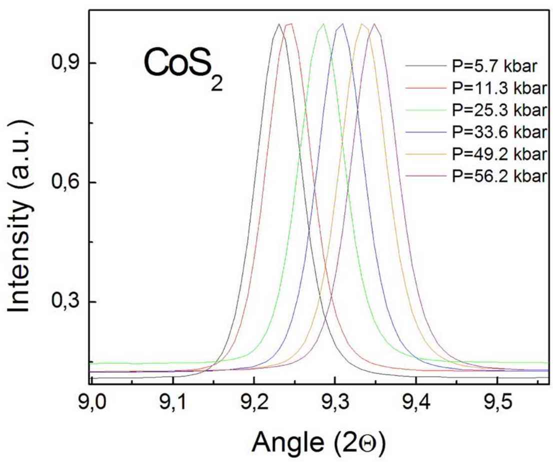

Fig. 2. Detail of the displacement of the (002) peak of the X-ray diffraction pattern as a function of pressure.

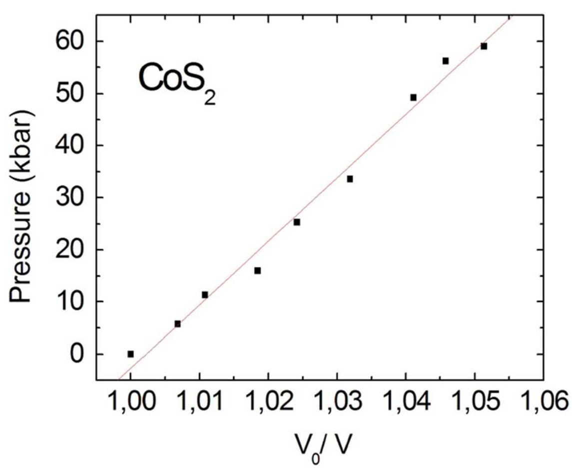

Fig. 3. Fitting of the experimental $\mathrm{P(V/V_0)}$ data to the Birch-Murnaghan equation.

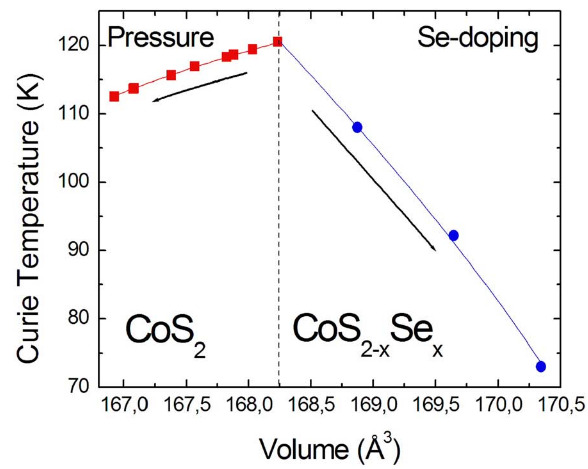

Fig. 4. Volume dependence of $\mathrm{T_c}$ under hydrostatic pressure for CoS_2 (squares) and for $CoS_{2-x}Se_x$ (circles), x= 0, 0.5, 0.10, 0.15.

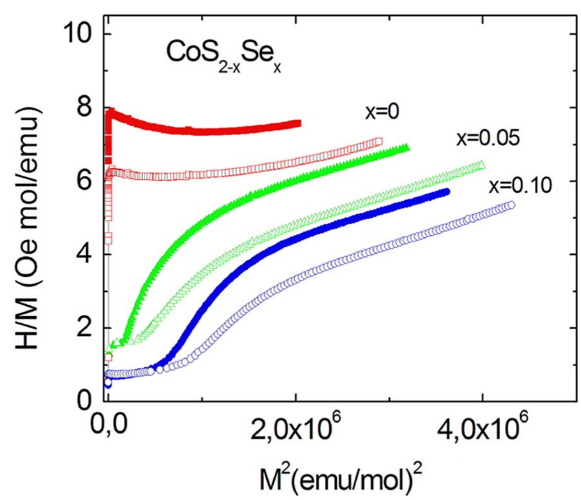

Fig. 5. Isothermal H/M versus M^2 curves for different samples of the series $CoS_{2-x}Se_x$. Solid symbols correspond to 1.03 $\mathrm{T_c}$ and open symbols to 1.04 $\mathrm{T_c}$.

where $\mathrm{K_0}$ represents the bulk modulus. The experimental value from this fitting is $\mathrm{K_0} = 115(5)$ GPa.

Se is bigger than S, what is reflected in the linear volume increase with x in $CoS_{2-x}Se_x$ (not shown). On the other hand, Se doping reduces $\mathrm{T_c}$ at a faster rate than pressure does (Fig. 4).

Some authors suggested that CoS_2 undergoes a second-order magnetic transition which becomes first-order after moderate Se doping ~10–20% [3], [4]. In order to verify this result, we have studied the nature of the magnetic phase transition as a function of Se doping. The equation of state of a ferromagnetic system close to $\mathrm{T_C}$ can be derived from a series expansion of the Free energy as a function of the magnetization [5], [6]. Hence, the inverse isothermal susceptibility is given by

$$\chi^{-1} = \frac{H}{M} = A + BM^2 + \cdots. \qquad (2)$$

A first-order phase transition is characterized by a secondary minimum at $\mathrm{M} \neq 0$ in the free energy. This is reflected in a $\mathrm{B} < 0$ of (2). Hence, an inspection of the slope of the H/M versus M^2 isotherms just above $\mathrm{T_c}$ could give us an indication of the nature of the magnetic phase transition: positive for second order, and negative for first order.

H/M versus M^2 isotherms are shown in Fig. 5 for several compositions. We observed that CoS_2 shows a weak first-order magnetic phase transition or is close to the tricritical point because B of the (2) expansion is slightly negative or almost zero. Doping with Se results in a reduced $\mathrm{T_c}$ and an increasingly positive slope. The reduction of $\mathrm{T_c}$ upon Se doping is probably reflecting a larger degree of hybridization between the Co:3d and the Se:4p with respect to S:3p.

So, on the basis of this result and looking at Fig. 3, it seems that we should reduce the volume of CoS_2 to go toward a first-order transition. To explore this hypothesis, we have done magnetic measurements of the isothermal M(H) with pressure. The effect of pressure on CoS_2 is clearly observed in the magnetization measurements: the magnetization is reduced and the Curie Temperature decreases (see Fig. 6).

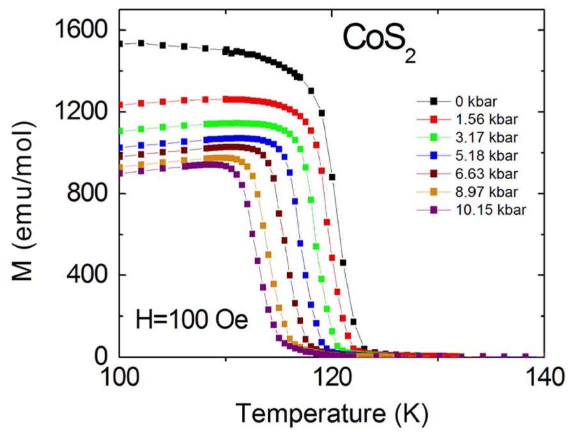

Fig. 6. Pressure dependence of M(T) in CoS_2.

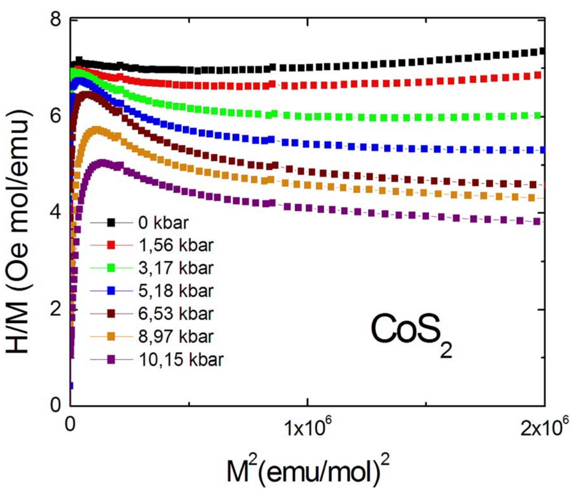

Fig. 7. Pressure dependence of the H/M versus M^2 isotherms at 1.03Tc. The transition becomes clearly first order above ~ 5 kbar.

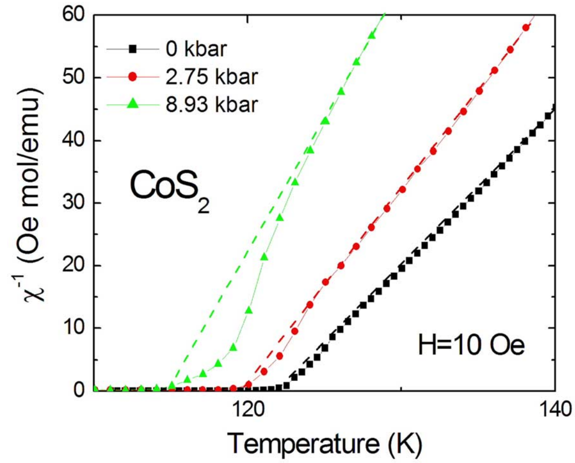

Fig. 8. Inverse susceptibility around Tc of CoS_2 at different pressures. Note the progressive deviation of χ^{-1} (T) right above Tc from linearity, as pressure increases.

Our experimental results show that when pressure increases the transition becomes clearly first order in nature, as it is reflected in a growing-with-pressure negative slope of the H/M versus M^2 curves (Fig. 7).

In order to understand what is the origin of the first-order magnetic phase transition, we measured the low field χ^{-1} for different pressures (Fig. 8) around $\mathrm{T_c}$.

Many aspects of these curves are in conflict with what is expected. First of all, the χ of an itinerant paramagnet should be temperature independent, unless the system is close to a critical point that enhances electronic correlations. Second, the slope of the curve increases gradually with pressure. And third, there is a strong deviation of χ^{-1} (T) from the high-T linear behavior at high pressure. Given that the suppression of $\mathrm{T_c}$ by pressure occurs at ~ 60 K [8], it does not seem that the system is close enough to this quantum critical point. Whether the proximity to the tricritical point [$\mathrm{B}=0$ in (2)] is causing this effect deserves further investigation.

On the other hand, the deviation of χ^{-1} (T) close to $\mathrm{T_c}$ at high pressure indicates a growing magnetic moment, probably related to the appearance of short-range local-order related to the decrease of volume.

In summary, our results demonstrate that CoS_2 is very close to a magnetic tricritical point, which can be crossed with pressure. The origin of the first-order magnetic transition is tentatively attributed to the emergence of local moments at high-pressures due to a magneto-volume effect.

Acknowledgment

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