Kondo effect and quantum critical point in Mn$_{1-x}$Co$_x$Si

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Abstract.
We report magnetic, transport and neutron diffraction studies of the solid solution Mn$_{1-x}$Co$_x$Si. For the Mn rich compounds, a sharp decrease of the Curie temperature is observed upon cobalt doping and neutron elastic scattering shows that the helimagnetic order of MnSi persists up to $x = 0.06$ with a shortening of the helix period. For higher Co concentrations ($0.06 < x < 0.90$), the Weiss temperature changes sign and the system enters an antiferromagnetic state upon cooling ($T_N = 9K$ for $x = 0.50$). In this doping range, the antiferromagnetic coupling leads to a Kondo effect marked by a minimum in the resistivity. This scenario is supported by the scaling of the magnetoresistance with a $T_K \approx 6.5K$, close to the change in curvature of the resistivity and in agreement with the Weiss temperature from magnetic susceptibility. The sign change of the Weiss temperature and the transition from a helimagnetic to an antiferromagnetic ground state, with increasing the Co doping, point toward the existence of a quantum critical point at the composition Mn$_{0.94}$Co$_{0.06}$Si.

1. Introduction
Transition metal monosilicides MSi with the B20 cubic structure are the object of intense studies due to their interesting and various ground states. Indeed, when increasing the number of electrons in the d shell of the transition metal ion, one goes from CrSi, a the Pauli paramagnet [1, 2], MnSi, an itinerant helimagnetic metal for $T < 30$ K [3], FeSi, a paramagnetic Kondo insulator [4], and CoSi, a diamagnetic metal [2, 5, 6]. The number of d electrons as well as the structural features do not explain the magnetic phase diagram. The solid solution Fe$_x$Co$_{(1-x)}$Si exhibits itinerant helimagnetic metallic behavior like MnSi for $0.4 < x < 0.9$ ($T_c = 60$ K for $x = 0.6$) although the two end-compounds FeSi and CoSi have no magnetic ordering [7–10]. The study of the magnetic properties of slightly doped Mn$_{1-x}$Co$_x$Si has shown that the helimagnetic structure is conserved up to $x = 0.04$ in Mn$_{1-x}$Co$_x$Si [11]. Motoya et al. already measured the magnetization over the whole range of compositions of Mn$_{1-x}$Co$_x$Si [12] but they never observed any ordering at low temperature above the critical concentration at which the ferromagnetism is suppressed. A recent work on FeSi doped with Mn has revealed that unscreened Kondo effect was at the origin of non Fermi liquid behaviors [13]. They showed that the Weiss temperature changes sign when 20% of Mn is replaced by iron in MnSi. Despite the clear evidences of antiferromagnetic coupling, no ordering was reported.

In this article, transport and magnetic properties of the solid solution Mn$_{1-x}$Co$_x$Si are presented. The unusual transport and magnetotransport behaviors are discussed in the frame...
of a spin $\frac{1}{2}$ Kondo problem. The vanishing of helimagnetism and the indication of a zero temperature magnetic transition was directly observed using neutron diffraction.

2. Experimental

All samples were synthesized using a home made arc furnace with a water cooled copper crucible, starting from 4N purity transition metals and 6N silicon chunks. An annealing of 48 hours at 900°C in high vacuum (about $5.10^{-7}$ mbars) is necessary to improve the crystalline order and the homogeneity of the solid solutions. For magnetoresistance (MR) and neutron diffraction measurements, single crystals were grown by Czochralski pulling from a levitating melt under 3 bars of argon.

X-ray powder diffraction (XRD) was performed in a Philips PW1820 diffractometer using the $K_\alpha$ radiation of a Cu tube ($\lambda = 1.5406$ Å). The XRD spectra were analyzed with a full pattern profile refinement method using the Fullprof program suite[14]. Magnetic susceptibility, magnetization and MR were measured in a squid magnetometer and the Neel temperature was determined as the point were zero-field cooled and field cooled curves overlap.

3. Results and discussion

The magnetic phase diagram presented in figure 1 a) shows for the first time that another magnetic ordering exists at intermediate doping, in addition to the region I of slightly doped MnSi and the region III of Fe$_{1-x}$Co$_x$Si. The "B20" Mn$_{1-x}$Co$_x$Si transition metal silicide exhibits a second dome with antiferromagnetic ordering (region II in Fig 1 a)).

![Figure 1.](image-url)

Figure 1. a) magnetic transition temperatures of different monosilicides solid solutions. yellow dot is the position of a possible quantum critical point. b) $\Theta_{\text{Weiss}}$, $T_N$, $T_C$ of Fe$_{1-x}$Mn$_x$Si [13] and Mn$_{1-x}$Co$_x$Si as a function of doping. Temperature dependence of the upturn of the resistivity (squares) compared to the magnetic ordering temperature (triangles).

In this rich magnetic phase diagram of monosilicides most of the studies focus on MnSi or the Fe$_{1-x}$Co$_x$Si solid solution because of their exotic helimagnetic (Region I in Fig.1 a)) or half-metallic (region III in Fig.1 a)) phases and their relatively high Curie temperatures. Recently,
by doping MnSi with iron, Manyala et al. showed that the Weiss temperature was switched from positive \((x < 0.2)\) to negative values and then to zero when approaching the insulating FeSi [13]. Nevertheless, they surprisingly did not observe any magnetic ordering when the temperature is lowered.

For \(\text{Mn}_{1-x}\text{Co}_x\text{Si}\), in the composition range of the antiferromagnetic ground state, the resistivity curves exhibit non monotonous temperature dependence with a minimum at a temperature about 4 times higher than that of magnetic ordering (Fig.1 b)).

Despite the sharp decrease of the \(T_c\) (region I in Fig.1 a)), the signature of the magnetic ordering on the resistivity (Fig.2 a-b)) is very similar to what is observed when MnSi is exposed to hydrostatic pressure [15]. Neutron diffraction reveals magnetic satellites below \(T_C\) (Fig.2 d)) along the [111] direction indicating that the helimagnetic order is preserved, with an helix period that decreases with increasing cobalt content [11]. This shortening of the helix, also observed when pressure is applied on MnSi [16], leads the system to a more “antiferromagnetic order” and, as will be discussed further, to a quantum critical point (yellow dot on Fig.1 a)). These two measurements show that for small doping, substitution of Mn with smaller radius ion (Co) in the MnSi structure is a relevant way to mimic hydrostatic pressure by a chemical route. Moreover, a negative magnetoresistance with a peak at \(T_c\) was measured, similarly to previous reports on MnSi [17] (Fig.2 c)).

As shown above, for higher cobalt concentration, the resistivity exhibits a non-monotonic temperature dependence (Fig.2 e)) with an upturn far above the antiferromagnetic ordering transition \((T_{\text{up-turn}} \simeq 4 \times T_N)\). This “metal-insulator” transition is presumably attributed to the onset of Kondo effect resulting from the antiferromagnetic coupling. The absolute value of the magnetoresistance is very small (less than 1%) and presents two distinct behaviors (Fig.2 f)). At high temperature, the positive magnetoresistance can be attributed to either standard Kohler contribution or quantum interference effects, as pointed out by Manyala et al. in \(\text{Fe}_{1-x}\text{Co}_x\text{Si}\) [8]. At low temperature, the magnetoresistance is negative, as it is usually the case in Kondo systems. The value of the Kondo temperature \(T_K = 14 K\) obtained from the curvature inversion

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**Figure 2.** Temperature dependence of a)-b) the resistivity \(\rho(T)\) c) relative magnetoresistance \(\Delta \rho/\rho_0\) for \(\text{Mn}_{0.05}\text{Co}_{0.05}\text{Si}\). Magnetic fields are given in the figure. d) Neutron diffraction pattern at 1.8 K showing the magnetic satellites of the helimagnetic structure along the [111] direction. Temperature dependence of e) the resistivity \(\rho\) f) relative magnetoresistance \(\Delta \rho/\rho_0\) for \(\text{Mn}_{0.5}\text{Co}_{0.5}\text{Si}\). Magnetic fields are given in the figure. The cross on plots e) corresponds to the inversion of the curvature at \(T_K = 14 K\).
of the temperature dependance of the resistivity has the same order of magnitude with the Kondo temperature derived from Curie-Weiss fit \( T_K \simeq \frac{\Theta_{\text{Weiss}}}{\sqrt{2}} = 6 \text{ K} \)[18].

4. Conclusion
In this work, we have investigated magnetic properties of Mn\(_{1-x}\)Co\(_x\)Si that exhibit two different magnetic ground states upon doping. For low cobalt dopings, helimagnetic order is found with an helix that shortens leading to a quantum critical point for \( x = 0.06 \) where the system switches from a ferromagnetic to an antiferromagnetic ground state. In this state, antiferromagnetic coupling induces Kondo effect.

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