Magnetic phase diagram of $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$

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Abstract. In order to study the phase diagram from a microscopic viewpoint, we have measured $\mu$TF- and ZF-$\mu$SR spectra for the $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ powder samples with $x = 0, 0.2, 0.4, 0.5, 0.6, 0.8$, and $1$. Due to a characteristic time window and spatial resolution of $\mu$SR, the obtained phase diagram was found to be rather different from that determined by magnetization measurements. That is, as $x$ increases from 0, a Pauli-paramagnetic phase is observed even at the lowest $T$ measured (1.8 K) until $x = 0.4$, then, a spin-glass like phase appears at $0.5 \leq x \leq 0.6$, and then, a phase with wide field distribution probably due to incommensurate AF order is detected for $x = 0.8$, and finally, a commensurate $A$-type AF ordered phase (for $x = 1$) is stabilized below $T_N \sim 80$ K. Such change is most likely reasonable and connected to the shrink of the $c$-axis length with $x$, which naturally enhances the magnetic interaction between the two adjacent Co planes.

1. Introduction

The appearance of unconventional superconductivity in iron pnictides with the ThCr$_2$Si$_2$-type (122) structure, i.e. $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ reconfirmed the competition between antiferromagnetism and superconductivity [1, 2]. Similar to the K-doping effect, the magnetic state of $\text{CaFe}_2\text{As}_2$ varies with pressure from antiferromagnetic (AF) to superconducting, and finally to nonmagnetic [3], while its structure changes from an “uncollapsed tetragonal” (ucT) phase, an orthorhombic phase, and a “collapsed tetragonal” (cT) phase [4]. Here, in the collapsed phase, the ratio of stacking to in-plane lattice parameters ($c/a$) is significantly smaller than that expected from simple atomic size considerations [5].

In contrast to $\text{CaFe}_2\text{As}_2$ and $\text{BaFe}_2\text{As}_2$, the related compounds, $\text{AM}_2\text{P}_2$ with $A = \text{Ca, Sr, and Ba}$, and $M = \text{Fe, Co, and Ni}$ do not show unconventional superconductivity, but exhibit an interesting magnetic transition with the structural change. For the present target system, $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$, the crystal structure changes from ucT for $x = 0$ to cT for $x = 1$ [6]. According to the electronic and magnetic phase diagram determined from the macroscopic
measurements [6], the system evolves from a nonmagnetic metallic ground state to an AF metallic
ground state through a crossover composition regime at $x \sim 0.5$. Then, in the $x$ range between
0.8 and 0.9, the system manifests a FM-like ground state within which the magnetic ordering
temperature is highest at $x \sim 0.9$. For the sample with $x \geq 0.9$, an AF ground state reappears
[7]. A similar behavior was also reported for $\text{Ca(Fe}_{1-x}\text{Co}_x\text{P}_2$ [8], $\text{Ca(Ni}_{1-x}\text{Co}_x\text{P}_2$ [8], and $\text{SrCo}_2(\text{Ge}_{1-x}\text{P}_x)\text{P}_2$ [9].

Note that $\chi$ measurements usually give us a significant insight into the ground state
of magnetically ordered solids. However, such measurements are sometimes not suitable,
particularly for the materials exhibiting order with a broad field distribution, i.e. when short-
range order, random, nearly-random order, or incommensurate order appears in a material, due
to the absence of periodic structure and/or the presence of rapid fluctuations. We have therefore
performed a $\mu$SR experiment on $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ in order to investigate the variation of the
magnetic nature with the Ca content ($x$).

2. Experimental

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** The change in the lattice constants and magnetic properties of $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$
with $x$ determined by XRD analyses and $\chi$ measurements [11].

**Figure 2.** $T$ dependence of $\chi$ for $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ with $x \geq 0.2$ [11].

Polycrystalline samples of $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ with $x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$ were
prepared from elemental P, Sr, Ca, and Co using two step reaction. For the first step, SrP,
CaP, and Co$_2$P were synthesized by a solid state reaction between Sr (Ca, Co) and P in an
evacuated quartz tube at 800°C (700°C for Co$_2$P). Then, for the second step, Sr$_{1-x}$Ca$_x$Co$_2$P$_2$
were synthesized by a solid state reaction between SrP, CaP and Co$_2$P at 1000°C for 20 hours
in an Ar atmosphere. After grinding, the obtained powder was fired two times at 1000°C for 40
hours in an Ar atmosphere [10, 11].

According to powder x-ray diffraction (XRD) analyses, all the samples were single phase
of tetragonal symmetry with space group $I4/mmm$. Also, as $x$ increases from 0, the $c$-axis
length monotonically decreases with $x$ until $\sim 0.5$, then rapidly decreases until 0.9, and finally,
levels off to a constant value above $x = 0.9$. This behavior is consistent with the literature [6]. Susceptibility ($\chi$) measurements suggested the presence of magnetic transition above $\sim 60$ K for the samples with $x \geq 0.6$.

The $\mu^+$SR spectra were measured at surface muon beam lines using the LAMPF spectrometer of M20/TRIUMF in Canada. An approximately 500 mg powder sample was placed in an envelope with $1 \times 1$ cm$^2$ area, made with Al-coated Mylar tape with 0.05 mm thickness in order to minimize the signal from the envelope. Then, the envelope was attached to a low-back ground sample holder in a liquid-He flow-type cryostat for measurements in the $T$ range between 1.8 and 150 K.

3. Results and discussion

Figure 3 shows the ZF-$\mu^+$SR spectrum for Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ with $x = 0.5$, 0.6, 0.8, and 1 at the lowest $T$ measured. The ZF-spectrum for CaCo$_2$P$_2$ exhibits a clear oscillation due to the formation of static AF order below $T_N \sim 80$ K, as reported by neutron diffraction measurements [7]. However, according to the detailed analysis, it was found that the ZF-spectrum consists of two muon-spin precession signals with different frequencies [$f_{AF1} = 34.6(1)$ MHz and $f_{AF2} = 9.5(3)$ MHz at 2 K]. As $T$ increases from 2 K, the two signals disappeared at $T_N$. This suggests that there are two magnetically different muon sites in the CaCo$_2$P$_2$ lattice.

Although a clear oscillation is also observed in the ZF-spectrum for Sr$_{0.6}$Ca$_{0.4}$Co$_2$P$_2$, the initial phase ($\phi$) was found to delay by $12 - 60^\circ$, when we attempted to fit the oscillatory signal by an exponential relaxing cosine function: $A_0 P_{ZF}(t) = A_{AF} \cos(2\pi f_{AF} t + \phi)$. This implies the wide distribution of an internal field at the muon site(s). The most probable reason is that the magnetic order is incommensurate (IC) to the lattice [12]. This is because, due to the mismatch of the period between the muon site(s) and magnetic order, IC order always provides an oscillatory signal with wide field distribution in the ZF-$\mu^+$SR spectrum. But, the

![Figure 3](image3.png)

**Figure 3.** The ZF-$\mu^+$SR spectra at 2 K for the Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ sample with $x = 0, 0.2, 0.4, \text{and} 0.5$.

![Figure 4](image4.png)

**Figure 4.** The ZF- and LF-$\mu^+$SR spectra at 2 K for the Sr$_{0.6}$Ca$_{0.4}$Co$_2$P$_2$ sample. The applied LF was 5 and 10 Oe. Solid lines represent the fit result using a static Gaussian Kubo-Toyabe function. By fitting both ZF- and LF-spectra using a common field distribution width ($\Delta$), we can obtain reliable $\Delta$. 
other explanation is also available, as in the case for Ag$_2$NiO$_2$ [13] and LiCrO$_2$ [14]. Therefore, neutron diffraction measurements is required for further clarifying the magnetic nature of the $x = 0.8$ sample.

For Sr$_{0.5}$Ca$_{0.5}$Co$_2$P$_2$, the ZF-spectrum shows a static Kubo-Toyabe-type relaxation. Since the field distribution width ($\Delta$) was estimated as $12 \times 10^6$ s$^{-1}$ ($\sim 141$ Oe), such KT behavior is naturally caused by disordered Co moments. Furthermore, weak transverse field $\mu^+\text{SR}$ measurements revealed the appearance of a large internal magnetic field below $\sim 50$ K. Therefore, the ground state of Sr$_{0.5}$Ca$_{0.5}$Co$_2$P$_2$ is most likely a spin-glass like state, although it is more preferable to measure AC-$\chi$ to confirm the spin-glass state. The situation for Sr$_{0.4}$Ca$_{0.6}$Co$_2$P$_2$ was the same to that for Sr$_{0.5}$Ca$_{0.5}$Co$_2$P$_2$.

On the other hand, for the samples with $x \leq 0.4$, the ZF-spectrum exhibits an almost static KT behavior even at 2 K (Fig. 4), but $\Delta = 0.22 \times 10^6$ s$^{-1}$ ($\sim 2.6$ Oe). This is a typical value for nuclear magnetic fields at the muon site(s), and for this case, the origin is mainly due to the nuclear magnetic moments of $^{59}\text{Co}$ and $^{31}\text{P}$. Hence, the ground state for Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ with $x \leq 0.4$ is assigned to be a Pauli-paramagnet.

Based on these results, the magnetic phase diagram for Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ was determined (Fig. 5). That is, thanks to a unique power of $\mu^+\text{SR}$, the phase with $x \sim 0.8$ was found to be not an FM phase [6] but an incommensurate (IC) AF phase. Then, next to the IC-AF phase, a spin-glass (SG) like phase appears in the $x$ range between $\sim 0.7$ and $\sim 0.4$. The samples with $x \leq 0.4$ was found to be nonmagnetic down to 2 K. However, since the phase boundaries between C and IC, between IC and SG, and SG and PM are still not clarified, we need additional measurements on several Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ samples.

![Figure 5. The tentative phase diagram for Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ determined by $\mu^+\text{SR}$, where PM is a paramagnetic phase, SG is a spin-glass like phase, IC-AF is a phase with wide field distribution probably due to incommensurate AF order, and C-AF is a commensurate AF phase.](image)

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