Magnetic phases in $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ studied by $\mu^+\text{SR}$

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Abstract

In order to elucidate the dependence of the magnetic ground state on the Ca content ($x$) in $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ ($0 \leq x \leq 1$, ThCr$_2$Si$_2$-type structure), we have performed muon spin rotation and relaxation ($\mu^+\text{SR}$) experiments on $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ powder samples mainly in a zero applied field. The end member compound, $\text{SrCo}_2\text{P}_2$, is found to be paramagnetic down to 19 mK. As $x$ increases, such a paramagnetic ground state is observed down to 1.8 K until $x = 0.45$. Then, as $x$ increases further, a short-range antiferromagnetic (AF) ordered phase appears at low temperatures for $0.48 \leq x \leq 0.75$, and finally, a long-range AF ordered phase is stabilized for $x > 0.75$. The internal magnetic field of the other end member compound, $\text{CaCo}_2\text{P}_2$, is well consistent with that of the $A$-type AF order state, which was proposed from neutron scattering experiments. The phase diagram determined with $\mu^+\text{SR}$ is different from that proposed by macroscopic measurements. For an isostructural compound, $\text{LaCo}_2\text{P}_2$, static magnetic order is found to be formed below $\sim 130$ K.

Keywords: muon spin rotation and relaxation, cobalt phosphide, antiferromagnet, phase diagram

1 Introduction

Although iron pnictides with the ThCr$_2$Si$_2$-type (122) structure, e.g. $\text{CaFe}_2\text{As}_2$ and $\text{BaFe}_2\text{As}_2$, show unconventional superconductivity under pressure and/or with substitution for Ba by K...
Figure 1: The variation of magnetic phases with $x$ for $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ determined with $\mu^+\text{SR}$ [8]. PM is a paramagnetic phase, SRO is a phase with wide field distribution probably due to short-range AF order, LRO is a long-range $A$-type AF ordered phase. Copyright 2015 American Physical Society.

[1, 2, 3], the related compounds $\text{AM}_2\text{P}_2$ with $\text{A} = \text{Ca, Sr, or Ba, and M} = \text{Fe, Co, or Ni}$ exhibit, instead, interesting properties with associated structural changes. For the present target system, $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$, the crystal structure changes from an uncollapsed tetragonal (ucT) phase for $x = 0$ to a collapsed tetragonal (cT) phase for $x = 1$ [4]. Based on macroscopic measurements [4], 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 ferromagnetic (FM)-like ground state within which the magnetic ordering temperature is highest for $x \sim 0.9$. For the sample with $x \geq 0.9$, an AF ground state reappears [5]. Similar behavior was also reported for $\text{Ca(Fe}_{1-x}\text{Co}_x)_2\text{P}_2$ [6], $\text{Ca(Ni}_{1-x}\text{Co}_x)_2\text{P}_2$ [6], and $\text{SrCo}_2(\text{Ge}_{1-x}\text{P}_x)_2$ [7].

However, according to our muon spin rotation and relaxation ($\mu^+\text{SR}$) experiment on $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ [8] (Fig. 1), a paramagnetic ground state is stable in the $x$ range between 0 and 0.45 down to the lowest temperature measured. Then, as $x$ increases from 0.45, a short-range antiferromagnetic (AF) ordered phase appears at low temperatures for $0.48 \leq x \leq 0.75$, and finally, a long-range AF ordered phase is stabilized for $x > 0.75$. The discrepancy between the phase diagram obtained by macroscopic measurements and that by $\mu^+\text{SR}$ is due to the unique spatial and time resolution of $\mu^+\text{SR}$ [9, 10, 11, 12, 13].

Since the phase diagram of $\text{Sr}_{1-x}\text{Ca}_x\text{Co}_2\text{P}_2$ was already described in detail [8], here, we report the detailed $\mu^+\text{SR}$ result on $\text{SrCo}_2\text{P}_2$, $\text{CaCo}_2\text{P}_2$ and an isostructural compound $\text{LaCo}_2\text{P}_2$.

2 Experimental

Polycrystalline samples of $\text{SrCo}_2\text{P}_2$, $\text{CaCo}_2\text{P}_2$, and $\text{LaCo}_2\text{P}_2$ were prepared from elemental P, Sr, Ca, La, and Co using a two step reaction. For the first step, SrP, CaP, LaP, and Co$_2$P were synthesized by a solid state reaction between Sr (Ca, La, Co) and P in an evacuated quartz tube at 800°C (700°C for $\text{Co}_2\text{P}$). In the second step, $\text{SrCo}_2\text{P}_2$, $\text{CaCo}_2\text{P}_2$, and $\text{LaCo}_2\text{P}_2$ were synthesized by a solid state reaction between SrP, CaP, LaP, and Co$_2$P at 1000°C for 20 hours in an Ar atmosphere. After grinding, the obtained powder was annealed two times at 1000°C for 40 hours in an Ar atmosphere [14].

High quality single-crystal platelets of $\text{SrCo}_2\text{P}_2$ were grown by a flux technique using ele-
mental Sr, Co, and P as starting materials. Sn was used as the flux. The mixture of Sr, Co, P, and Sn were sealed in a quartz tube in an Ar atmosphere with 0.3 atm, and heated at 900°C for 72 hours, and then cooled down to 600°C with a rate of 3°C/h. The typical dimension of the crystal is 3 × 3 × 0.5 mm³.

According to powder x-ray diffraction (XRD) analyses, all the samples were almost single phase of tetragonal symmetry with space group $I4/mmm$. The $\mu$SR spectra were measured at surface muon beam lines using the LAMPF spectrometer on M15 and M20 of TRIUMF in Canada and Dolly and LTF spectrometers of PSI in Switzerland. On LAMPF and Dolly, approximately 500 mg of powder sample was placed in an envelope with 1 × 1 cm² area, made of 0.05 mm thick Al-coated Mylar tape in order to minimize the background signal from the envelope. The envelope was attached to a low-background sample holder in a liquid-He flow-type cryostat for measurements in the $T$ range between 1.8 and 150 K. At LTF, about 100 mg of platelets was attached onto a silver plate with an Apiezon-N grease, and the silver cell was set into a dilution refrigerator (DR) down to $T = 19$ mK. The experimental techniques are described in more detail elsewhere [9, 10].

3 Results and Discussion

3.1 SrCo$_2$P$_2$

Figure 2(a) shows the zero field (ZF-) $\mu$SR spectra for the SrCo$_2$P$_2$ crystals recorded at $T = 19$ mK, 4 K and 10 K. The ZF-spectrum exhibits a clear Kubo-Toyabe type relaxation at 10 K, indicating a paramagnetic nature of SrCo$_2$P$_2$. However, a small minimum appears around $t = 1$ μs at 4 K and 19 mK, while the shape and position of the minimum does not depend on temperature at $T \leq 4$ K. Such behavior was also observed for a powder sample. In order to understand the nature of such minima, $\mu$SR spectra were also recorded under ZF and in two longitudinal fields (LF = 25 and 100 Oe). (Here, a longitudinal field means the field parallel to the initial muon spin polarization.) Figure 2(b) shows the ZF- and two LF-$\mu$SR spectra for the SrCo$_2$P$_2$ crystals obtained at 100 mK. The relaxation in the ZF-spectrum is clearly suppressed by LF, i.e. a decoupling behavior due to LF. The ZF- and LF-spectra
were well fitted by a combination of two static Kubo-Toyabe functions \(G(\Delta, t, H_{LF})\) and a time-independent background signal from muons stopping in the silver plate.

\[
A_0 P(t) = A_{KT1} G(\Delta_1, t, H_{LF}) + A_{KT2} G(\Delta_2, t, H_{LF}) + A_{BG}.
\]  

(1)

Here \(A_i\) are the asymmetries and \(\Delta_i\) are the field distribution width at the muon sites. The fit for the ZF- and two LF-spectra using common \(A_{KT1}, A_{KT2}, A_{BG}, \Delta_1,\) and \(\Delta_2\) provided that \(A_{KT1} = 0.0144 \pm 0.0011, A_{KT2} = 0.0364 \pm 0.0017, A_{BG} = 0.1910 \pm 0.0018, \Delta_1 = (2.33 \pm 0.09) \times 10^6 \text{ sec}^{-1},\) and \(\Delta_2 = (0.337 \pm 0.014) \times 10^6 \text{ sec}^{-1}\). This means that there are two different muon sites in the SrCo\(_2\)P\(_2\) lattice, and the muons at the two sites sense a small random internal magnetic field. Therefore, SrCo\(_2\)P\(_2\) is found to be a paramagnet even at 19 mK, being consistent with the recent study on a single crystal down to 1.5 K [15]. In addition, a relatively large \(A_{BG}\) compared with \(A_{KT1}\) and \(A_{KT2}\) is due to a small sample size.

DFT calculations with generalized gradient approximation (GGA) [16] predicted the presence of two muon sites in the lattice (Fig. 3 and Table 1). The ratio between \(\Delta_s\) for the two sites is 6.9(= 2.33/0.377) from the experiment, vs. 2.0(= 0.4860/0.2425) from the calculations. Note that only nuclear magnetic moments were taken into account for the calculations. Since \(\Delta_2\) ranges between the two predicted values, the muons at one site, probably at the \(\mu_2\) site, clearly see a nuclear magnetic field. However, \(\Delta_1 (= 2.33 \times 10^6 \text{ sec}^{-1} \sim 27 \text{ Oe})\) is rather large compared with the predicted values. This implies that the muons at the \(\mu_1\) site sense not only a nuclear magnetic field but also randomly distributed localized magnetic moments of Co, which appear below 10 K. The magnitude of such localized moment is estimated as 0.014 \(\mu_B\). Note that \(A_{KT1}/(A_{KT1} + A_{KT2}) = 0.28\), corresponding to that 28 % muons in the SrCo\(_2\)P\(_2\) sample see the internal magnetic field due to the Co moments. Therefore, such behavior is not induced by magnetic impurities but an intrinsic nature of SrCo\(_2\)P\(_2\) and is likely to suggest the appearance of short-range correlation below 10 K. This is because ZF- and LF-spectra for the ordered phase is not explained by a static Kubo-Toyabe function [8].
Table 1: Possible muon sites ($\mu_n$) and the field distribution width in SrCo$_2$P$_2$ and CaCo$_2$P$_2$ predicted by DFT calculations with GGA and dipole field calculations. The optimized structural parameters (and experimental values [5, 17]) are $a = 3.792$ (3.760) Å, $c = 11.793$ (11.602) Å, and $z = 0.3511$ (0.3525) for SrCo$_2$P$_2$, and $a = 3.843$ (3.85) Å, $c = 9.603$ (9.55) Å, and $z = 0.3714$ (0.3722) for CaCo$_2$P$_2$. Here, the atomic positions of Sr/Ca, Co, and P are (0,0,0), (0,1/2,1/4), and (0,0,$z$), respectively. $\Delta$ is calculated based only on nuclear magnetic moments and 1 Oe corresponds to $0.08516 \times 10^6$ s$^{-1}$. $E$ represents the potential energy. There are 4 equivalent positions in the unit cell for the 4e sites, 2 equivalent positions for the 2b sites, and 32 equivalent positions for the 32o sites. One of them for each site is shown in Fig. 3.

<table>
<thead>
<tr>
<th>compound</th>
<th>site</th>
<th>$(x, y, z)$</th>
<th>$E$</th>
<th>$\Delta$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCo$_2$P$_2$</td>
<td>4e ($\mu_1$)</td>
<td>(0.0000,0.0000,0.1954)</td>
<td>-13.93</td>
<td>5.707</td>
<td>0.4860</td>
</tr>
<tr>
<td></td>
<td>2b ($\mu_2$)</td>
<td>(0.0000,0.0000,0.5000)</td>
<td>-14.10</td>
<td>2.848</td>
<td>0.2425</td>
</tr>
<tr>
<td>CaCo$_2$P$_2$</td>
<td>4e ($\mu_1$)</td>
<td>(0.0000,0.0000,0.1991)</td>
<td>-14.10</td>
<td>5.912</td>
<td>0.5035</td>
</tr>
<tr>
<td></td>
<td>32o ($\mu_2$)</td>
<td>(0.5099,0.0253,0.0717)</td>
<td>-14.23</td>
<td>4.944</td>
<td>0.4210</td>
</tr>
</tbody>
</table>

Figure 4: (a) the ZF-$\mu^+$SR spectra for CaCo$_2$P$_2$ obtained at 2, 60, and 90 K. Each spectrum is shifted upward by 0.05 for clarity of display. (b) the temperature dependence of the muon spin precession frequencies ($f_{AF_i}$) in CaCo$_2$P$_2$. Solid lines in (a) represent the best fit using Eq. (2).

3.2 CaCo$_2$P$_2$

Neutron diffraction studies [5] revealed that CaCo$_2$P$_2$ is an antiferromagnetic metal with $T_N \sim 85$ K, below which the Co moments ($\mu_{Co}$) are aligned ferromagnetically in the $c$-plane, but antiferromagnetically along the $c$-axis below $T_N$, i.e. the $A$-type AF order with $q=(0,0,1)$. The ZF-$\mu^+$SR spectrum for CaCo$_2$P$_2$ exhibits a clear oscillation due to the formation of static AF order below $T_N$. Since there are two oscillatory signals with different muon spin precession frequencies, the ZF spectrum was fitted by

$$ A_0 P_{ZF}(t) = \sum_{i=1}^{2} A_{AF_i} \cos(2\pi f_{AF_i} t + \phi_i) \exp(-\lambda_{AF_i} t) + A_{tail} \exp(-\lambda_{tail} t) + A_{BG} G(\Delta_{BG}, t), \quad (2) $$

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Figure 5: (a) the ZF-\(\mu^+\)SR spectra for LaCo\(_2\)P\(_2\) obtained at 5, 120, and 160 K. (b) the temperature dependence of the muon spin precession frequency \(f_{\text{FM}}\) in LaCo\(_2\)P\(_2\). Solid lines in (a) represent the best fit using Eq. (3).

where \(A_i\) are the asymmetries and \(A_{\text{tail}} = \frac{1}{2} \sum A_{\text{AF}i}\), \(\lambda_i\) are exponential relaxation rates, and \(2\pi f_i (\equiv \omega_i)\) are the muon Larmor frequencies of the three signals. \(G\) is a static Kubo-Toyabe function \[18\], \(G = \frac{1}{3} + \frac{2}{3} (1 - \Delta^2 t^2) \exp(-\frac{1}{2} \Delta^2 t^2)\), and \(\Delta\) (in this case \(\Delta_{\text{BG}}\)) is proportional to the field distribution width at the muon site. The \(A_{\text{tail}}\) signal corresponds to the ZF "1/3 tail" due to the field component parallel to the initial muon spin polarization. Finally, the \(A_{\text{BG}}\) signal corresponds to a static nuclear field component due to a nonmagnetic impurity phase with about 13 vol\%, most likely CaP. In fact, \(\Delta_{\text{BG}} = 0.358(8) \times 10^6\) s\(^{-1}\) (implying a distribution of local fields with a width of \(\sim 4.2\) Oe) at 2 K and was almost \(T\) independent until \(T_N\).

Both \(f_{\text{AF}1}(T)\) and \(f_{\text{AF}2}(T)\) curves show an order parameter like \(T\) dependence and drop to zero at \(T_N\) [see Fig. 4(b)], indicating the presence of two magnetically different muon sites in the lattice, as predicted by DFT calculations [Fig. 3(b) and Table 1]. If we compare the internal magnetic field estimated by dipole field calculations at the two muon sites with the experimental results, we obtain that \(\mu_{\text{Co}} = 0.41(1)\) \(\mu_B\) at 2 K, which is roughly comparable to the past neutron work \((0.32\) \(\mu_B\) \[5\]). Such small \(\mu_{\text{Co}}\) compared with the effective magnetic moment of Co \((\mu_{\text{eff}} \sim 1.7\) \(\mu_B\) \[4\]) supports an itinerant electron nature of CaCo\(_2\)P\(_2\).

### 3.3 LaCo\(_2\)P\(_2\)

LaCo\(_2\)P\(_2\) is known as a ferromagnetic metal with \(T_C = 132\) K \[19\]. Figure 5(a) shows the variation of the ZF-\(\mu^+\)SR spectrum with temperature. Since the spectrum below \(T_C\) exhibits a clear oscillation due to the formation of a static magnetic field, the spectrum was fitted by a combination of an exponentially damped cosine oscillation for the static internal magnetic field and an exponentially damped non-oscillatory signal for a "1/3" tail for a powder sample:

\[
A_0 P_{\text{ZF}}(t) = A_{\text{FM}} \exp(-\lambda_{\text{FM}} t) \cos(2\pi f_{\text{FM}} t + \phi_{\text{FM}}) + A_{\text{tail}} \exp(-\lambda_{\text{tail}} t),
\]

where \(A_i\) are the asymmetries, \(\lambda_i\) are the exponential relaxation rates, \(f_{\text{FM}}\) is the muon spin precession frequency, and \(\phi_{\text{FM}}\) is the initial phase.

Figure 5(b) shows the temperature dependence of \(f_{\text{FM}}\) for LaCo\(_2\)P\(_2\). The \(f_{\text{FM}}(T)\) curve exhibits an order parameter-like temperature dependence, as expected. However, for unmagnetized ferromagnetic materials in zero applied field, the internal magnetic field at a muon site
$(H_\mu)$ is represented by [20, 21, 22];

$$H_\mu = H_{\text{dip}} + H_{\text{L}} + H_{\text{hf}},$$

(4)

where $H_{\text{dip}}$ is the dipolar field, $H_{\text{L}}$ is the Lorentz field, and $H_{\text{hf}}$ is the hyperfine field. Furthermore, $H_{\text{L}}$ and $H_{\text{hf}}$ are connected to the saturated magnetization ($M_s$) and the local spin density at the muon sites ($\rho_{\text{spin}}$), as follows;

$$H_{\text{L}} = \frac{4\pi}{3} \times M_s,$$

$$H_{\text{hf}} = \frac{8\pi}{3} \times \rho_{\text{spin}}(r_\mu).$$

(5)

Since $M_s = 0.391 \mu_B$/Co along the $a$-axis at 5 K [19], $H_{\text{L}}$ is calculated as $(190, 0, 0) \text{ Oe}$ [22].

If we assume that the implanted muons locate at the $\mu_1$ site, as in the case for SrCo$_2$P$_2$, and that the Co moments align along the $a$-axis, as proposed by neutron diffraction measurements, then $H_{\text{dip}} = 1884 \text{ Oe}/\mu_B$ along the $a$-axis. Since the ordered moment was reported as $\mu_{\text{ord}} = 0.47(5) \mu_B$, $H_{\text{dip}} = (885, 0, 0) \text{ Oe}$ and $H_{\text{hf}} = (-610, 0, 0) \text{ Oe}$. Thus, $H_{\text{hf}}$ is found to be almost comparable to $H_{\text{dip}}$, as in the case of other ferromagnetic materials [22, 23, 24].

4 Summary

The magnetic phase diagram of the solid solution system between SrCo$_2$P$_2$ and CaCo$_2$P$_2$ was studied with $\mu^+\text{SR}$ using mainly powder samples. The end compound, SrCo$_2$P$_2$, was found to be an enhanced paramagnetic metal [25] down to 19 mK, although small random localized magnetic moments, which probably suggests the presence of short-range correlation, appear below 10 K. The other end compound, CaCo$_2$P$_2$, enters into an $A$-type antiferromagnetic ordered phase below $\sim 85$ K. The isostructural compound, LaCo$_2$P$_2$, was found to undergo a magnetic transition below $\sim 130$ K. Using the past neutron data, the hyperfine field was also estimated.

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