Magnetic properties of exchange-enhanced Pauli paramagnetic metals $AeCo_2P_2$ ($Ae = Sr$, Ba)

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Abstract. We have synthesized single crystals of $AeCo_2P_2$ ($Ae = Sr$, Ba) and polycrystalline powder sample of Sr$_{1-x}$Ba$_x$Co$_2P_2$, and measured their magnetic properties. SrCo$_2P_2$ shows an itinerant-electron metamagnetic transition at $H_c = 600$ kOe and its temperature dependent magnetic susceptibility shows characteristic two anomalies at $T_{\text{max}1} = 25$ and $T_{\text{max}2} = 115$ K, suggesting it is in the vicinity of a ferromagnetic quantum critical point. While, BaCo$_2P_2$ does not show the metamagnetic transition with the applied field up to 600 kOe, and its magnetic susceptibility shows only one anomaly corresponding to $T_{\text{max}1}$ at 33 K. In addition, the Weiss temperature of Sr$_{1-x}$Ba$_x$Co$_2P_2$, decreases to negative as $x$ increases. These results indicate the system recede from the quantum critical point by the Ba substitution.

1. Introduction

Since the discovery of the iron pnictide superconductor LaFeAsO$_{1-x}$F$_x$ [1], layered transition metal pnictides and chalcogenides have been extensively studied. These iron based superconductivities are classified by the structure as 1111-type with ZrCuSiAs type structure [1], 122-type with ThCr$_2$Si$_2$ type structure [2], 111-type with anti-PbFCl structure [3], and so on, and they are based on transition metal layers in which the transition metals are coordinated by pnictogens and chalcogens.

The same structural compounds have been discovered in cobalt systems, e.g., $ACo_2X_2$ ($A = $ Alkali metals, Alkaline earth metals, and rare earth metals; $X = P$, As, S, Se) [4, 5, 6, 7, 8, 9, 10, 11, 12], LaCo$PnO$ ($Pn = P$ and As) [13, 14], and Sr$_2$SeO$_3CoPn$ [15, 16]. In contrast to the iron system with antiferromagnetic interaction, these cobalt compounds have ferromagnetic interaction in their Co$Pn$ layer, thus, they have been investigated as candidates of quasi-two dimensional itinerant-electron ferromagnets. For example, two dimensional ferromagnetic behavior in LaCo$PnO$ ($Pn = P$ and As) is observed by magnetization and NMR measurements [13, 14], and highly magnetic anisotropic behavior is observed in single crystals of $ACo_2Se_2$ [11]. Furthermore, an itinerant-electron metamagnetic transition is discovered in SrCo$_2P_2$, suggesting it is in the vicinity of ferromagnetic quantum critical point [17]. In the Ca substituted system Sr$_{1-x}$Ca$_x$Co$_2P_2$, the metamagnetic transition field decreases as $x$ increases to 0.5, and the
antiferromagnetic ground state appears in the region of $x > 0.6$ [17]. In this system, magnetic properties are closely related to two types of crystal structure. One is the collapsed tetragonal (cT) structure with making interlayer P-P bond, and the other is the uncollapsed tetragonal (ucT) one. Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ ($0 \leq x \leq 0.5$) with the ucT structure does not show any magnetic orderings and Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ ($0.6 \leq x \leq 1$) with cT structure shows antiferromagnetic ordering [17, 18]. In this paper, taking up the magnetic properties of Sr$_{1-x}$Ba$_x$Co$_2$P$_2$ as a counterpart of Sr$_{1-x}$Ca$_x$Co$_2$P$_2$, we synthesized single crystals of AeCo$_2$P$_2$ (Ae = Sr, Ba) and polycrystalline samples of Sr$_{1-x}$Ba$_x$Co$_2$P$_2$ with the ucT structure, and measured their magnetic susceptibility and high magnetization process. We will show that temperature dependent susceptibility and magnetization curves of BaCo$_2$P$_2$ show an anomaly which is not the itinerant-electron metamagnetic transition, and that magnetic interactions of Sr$_{1-x}$Ba$_x$Co$_2$P$_2$ decreases by the Ba substitution.

2. Experimental method

Single crystalline and polycrystalline samples of Sr$_{1-x}$Ba$_x$Co$_2$P$_2$ were prepared from Sr(2N), Ba(2N), Co(3N) and P(red, 5N). The single crystals with $x = 0$ and 1 were obtained by a tin flux method [6]. Excess tin was removed by a dilute hydrochloric acid in the case of SrCo$_2$P$_2$. Because BaCo$_2$P$_2$ is easily soluble in dilute acids, excess tin was removed by centrifugation after heating to 673 K. Polycrystalline samples were synthesized as shown in Ref [17]. These samples were characterized by powder x-ray diffraction (XRD) using Cu Kα radiation. Polycrystalline samples and single crystals were placed on a glass plate and measured in Bragg-Brentano geometry.

The temperature dependent magnetizations of Sr$_{1-x}$Ba$_x$Co$_2$P$_2$ were measured by a Quantum Design MPMS-XL system at the Research Center for Low Temperature and Materials Sciences, Kyoto University. Magnetization curves beyond 700 kOe were measured by using an induction method with a multilayer pulsed magnet at the ultrahigh magnetic field laboratory of the Institute for Solid State Physics, the University of Tokyo.

![Figure 1. X-ray diffraction patterns of a single crystal, polycrystalline sample, and a simulated profile of BaCo$_2$P$_2$. The Miller indices of each peak are represented in the figure. The inset shows a photograph of a single crystal of BaCo$_2$P$_2$.](image-url)
3. Results and discussions

Single crystals and polycrystalline sample of SrCo$_2$P$_2$ were obtained as described in previous work [4] and characterized by using XRD patterns. In the case of BaCo$_2$P$_2$, plate-like tetragonal crystals were obtained. The inset of Fig. 1 shows the photograph of a typical crystal of BaCo$_2$P$_2$. Figure 1 shows XRD patterns of a single crystal and a polycrystalline sample of BaCo$_2$P$_2$. All diffraction peaks are attributed to the ThCr$_2$Si$_2$ type structure with space group of $I4/mmm$. XRD patterns of BaCo$_2$P$_2$ were refined by the Rietveld method, using a computer program RIETAN-FP [19]. The lattice constants $a = 3.8040(2)$ Å and $c = 12.4186(5)$ Å are larger than those of SrCo$_2$P$_2$. The simulated pattern and Miller indices are shown in Fig. 1. The XRD pattern of the single crystal shows large 0 0 / Bragg peaks, and their positions are quite consistent with the lattice parameter $c$, suggesting successful synthesis of single crystals of BaCo$_2$P$_2$.

![Figure 2](image_url). Lattice parameters and magnetic properties of Sr$_{1-x}$Ae$_x$Co$_2$P$_2$ ($Ae = Ca$, Ba). ●: $a$, ■: $c$. △: Weiss temperature. ▽: Néel temperature. The shaded region represents collapsed tetragonal (cT) region and the other does uncollapsed tetragonal (ucT) region. AF stands for the antiferromagnetic state.

Lattice parameters of Sr$_{1-x}$Ba$_x$Co$_2$P$_2$ ($x = 0$, 0.5) were determined from a refinement of the diffraction patterns by using the Le Bail method, using RIETAN-FP. These lattice parameters are shown in Fig. 2 with those of Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ in Ref.[17]. As the ionic radius of alkaline earth cation $Ae^{2+}$ decreases in the order of $Ba^{2+} > Sr^{2+} > Ca^{2+}$, the lattice parameter $c$ corresponding to the inter-CoP-plane distance monotonically decreases. For the substituted system, the lattice parameter $a$ is almost unchanged, and $c$ decreases as the average radius of Sr$^{2+}$ and the substituted Ba$^{2+}$ or Ca$^{2+}$ decreases in the ucT region. In this region, the inter-CoP-plane distance is deemed to be controlled by the cation substitutions and BaCo$_2$P$_2$ expects to have the weakest interlayer interaction in this system. The structural change from the ucT to cT structure occurs at the Ca content $x = 0.5$ with making of interlayer P-P bonds. Therefore, $a$ increases rapidly and $c$ decreases around $x = 0.5$, and magnetic ordering occurs in the cT region.

Figure 3 shows the temperature dependence of magnetic susceptibility $\chi(T)$ and its reciprocal of $AeCo_2P_2$ ($Ae = Sr$, Ba). As shown in Fig. 3(a), $\chi(T)$ of SrCo$_2$P$_2$ shows double maxima at 25 and 115 K and Curie-Weiss-like temperature dependence. The susceptibility with $H \parallel a$ is larger than that with $H \parallel c$, suggesting the easy axis is the $c$ direction. The Weiss temperature $\theta_{CW}$ and the effective Bohr magneton number $p_{\text{eff}}$ are $-95.2$ K and $1.59$ for $H \parallel a$, and $-90.0$ K and $153$
For $H \parallel c$ from Curie-Weiss fit at between 200 to 300 K. In the case of itinerant magnetism with ferromagnetic interaction, the Curie-Weiss like temperature dependence originates in the temperature dependence of the amplitude of the local spin fluctuation, and the Weiss temperature is an indicator of the distance from the quantum critical point [20, 21, 22]. When the system approaches to the quantum critical point, the negative Weiss temperature increases to 0.

Figure 3(b) shows $\chi(T)$ of the polycrystalline powder sample and the single crystal of BaCo$_2$P$_2$. For both field directions, $\chi(T)$ of single crystal shows maximum at 33 K and Curie-Weiss-like temperature dependence at high temperature region. An upturn at low temperature seems to be ascribed to a magnetic impurity. For the powder sample, $\chi(T)$ shows larger upturn at low temperature and therefore does not show the maximum behavior. Thus, to estimate the intrinsic magnetic susceptibility, we calculated susceptibility as $\chi(T) = \Delta M(T)/\Delta H$, where $\Delta M(T)$ is difference between magnetization at 60 and 70 kOe, $\Delta H = 70 - 60$ kOe. It is revealed that the calculated susceptibility also shows the maximum behavior, suggesting this maximum behavior is intrinsic in BaCo$_2$P$_2$. From Curie-Weiss fit at between 200 to 300 K, $\theta_{\text{CW}}$ and $p_{\text{eff}}$ are $-300$ K and 1.67 for $H \parallel a$, and $-400$ K and 1.81 for $H \parallel c$. The Weiss temperature is smaller than that of SrCo$_2$P$_2$, suggesting the system has weaker ferromagnetic interaction and recede from the quantum critical point.

Figure 4 shows $\chi(T)$ and magnetization process at 4.2 K for Sr$_{1-x}$Ba$_x$Co$_2$P$_2$. The maximum behavior was not observed at $x = 0.1, 0.5$ because of probably upturn at low temperature.
Figure 4. Magnetic properties of Sr$_{1-x}$Ba$_x$Co$_2$P$_2$. (a) Temperature dependence of the magnetic susceptibility and its reciprocal. (b) The magnetization $M$ and the differential magnetization $dM/dH$ curves measured at 4.2 K in pulsed high magnetic fields up to 700 kOe.

region. All compounds show Curie-Weiss like temperature dependence. As shown in the bottle panel of Fig. 2, $\theta_{CW}$ decreases continuously as $x$ increases. Combined with the fact that the lattice parameter $c$ increases with increasing $x$, the decrease of the magnetic interaction can be explained by the development of two dimensionality in the layered structure.

The magnetization curve of SrCo$_2$P$_2$ shows two anomalies at 240 and 600 kOe. The high-field anomaly corresponds to the itinerant-electron metamagnetic transition, which is the transition from the Pauli paramagnetic to itinerant ferromagnetic phases. On the other hand, the metamagnetic transition was not observed up to 600 kOe in Ba substituted system. For the result that the metamagnetic transition field decreases with the Ca substitution [17], it is natural to that the metamagnetic transition field increases beyond 600 kOe in the Ba substituted system. The low-field anomaly appears in all compounds of Sr$_{1-x}$Ba$_x$Co$_2$P$_2$, and it shows a little $x$ dependence in comparison to metamagnetic transition field of Sr$_{1-x}$Ca$_x$Co$_2$P$_2$ [17], suggesting this anomaly is related to the lattice parameter $a$ rather than $c$. In addition, this anomaly seems to be related to the small maximum behavior at low-temperature in $\chi(T)$. In this connection, the maximum behavior was not observed when P replaced by As [8, 23, 24, 10]. Thus, the maximum behavior and the low-field anomaly are peculiar behavior of the cobalt phosphide and would originate in their characteristic shape of the electric band structure near the Fermi level.

In this system, the mainly magnetic interaction causing the metamagnetic transition depends on the interlayer distance (proportional to $c$), and the low-field anomaly seems to depend on the intralayer Co distance (proportional to $a$) rather than the interlayer distance.
4. Conclusion
We have synthesized single crystals of $\text{AeCo}_2\text{P}_2$ ($\text{Ae} = \text{Sr, Ba}$) and polycrystalline samples of the solid solution system $\text{Sr}_{1-x}\text{Ba}_x\text{Co}_2\text{P}_2$, and investigated their magnetic properties. Magnetization curve of all compounds show a small anomaly at approximately 200 kOe. The anomaly has a little $x$ dependence in comparison to metamagnetic transition and seems to originate in the characteristic shape of the electric band structure near the Fermi level, depending on the intralayer structure rather than the interlayer structure. While, Ba substituted compounds do not show the metamagnetic transition below 600 kOe and their Weiss temperature systematically decreases with increasing $x$. These results indicate the system moves away from the quantum critical point with increase of the interlayer distance by Ba substitution.

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