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Substitution Effects in the Itinerant Electron Metamagnetic Compound $SrCo_2P_2$

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Abstract

The $ThCr_2Si_2$-type layered compound $SrCo_2P_2$ shows an itinerant-electron metamagnetic transition at high magnetic field. To investigate substitution effects on the itinerant metamagnetic transition, we synthesized $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$ and measured their magnetic properties, including magnetizations under pulsed high magnetic fields. We have revealed a strong x dependence of the metamagnetic transition which is consistent with the band theory describing the physical properties in metals.

Keywords: Itinerant-electron magnet, metamagnetic transition, layered compound

1 Introduction

Many ternary transition-metal compounds AT_2X_2 (A: alkaline earth element, lanthanide, T: transition metal, X: metalloid) with the $ThCr_2Si_2$ type structure have been intensively and extensively studied since Ban and Sikirica reported ThM_2Si_2(M = Cr, Mn, Fe, Co, Ni and Cu) in 1965 [1]. These layered compounds show various interesting physical properties such as heavy-fermion superconductivity as in $CeCu_2Si_2$ [2], mixed valency as in $EuNi_2P_2$ [3], and high-temperature superconductivity in 122-type iron pnictide [4].

Especially, cobalt phosphides ACo_2P_2 (A: alkaline earth element, lanthanide) are attractive as itinerant electron magnets and exhibit a wide variety of magnetism by changing A, e.g., $LaCo_2P_2$ shows ferromagnetism [5, 6] and $CaCo_2P_2$ does A-type antiferromagnetism with the intralayer ferromagnetic and interlayer antiferromagnetic couplings [7, 8].

In ACo_2P_2, the A layers and Co_2P_2 layers consisting of edge-sharing CoP_4 tetrahedrons are stacked alternately along the c-axis (Fig.1). Their structures are classified into two groups with

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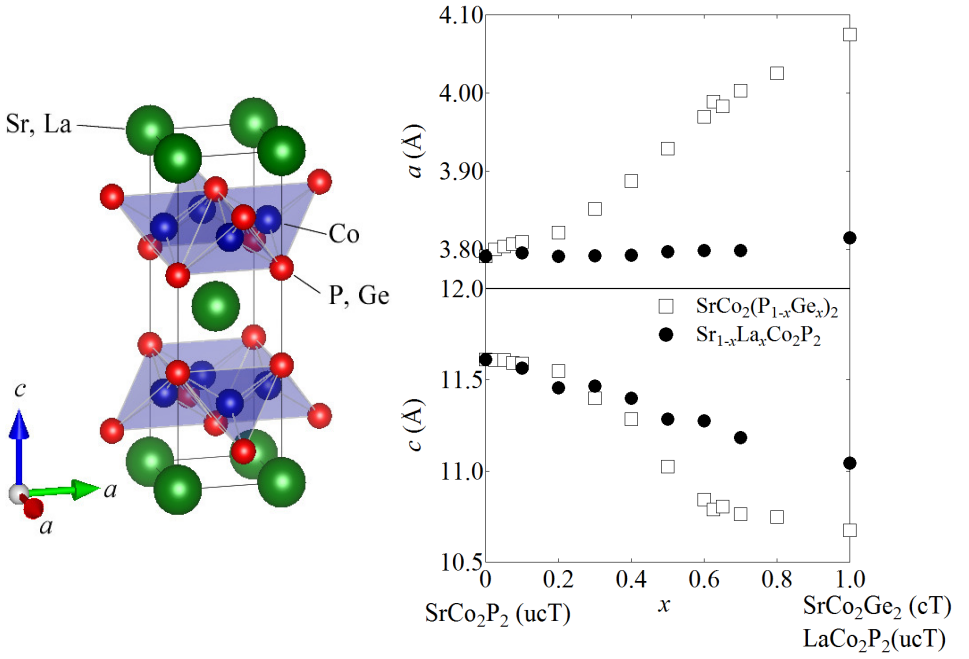

Figure 1: The structure and lattice parameters of $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$. Open squares and closed circles show the lattice parameters of $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$, respectively. All the $Sr_{1-x}La_xCo_2P_2$ compounds have the uncollapsed tetragonal(ucT) structure, while $SrCo_2(P_{1-x}Ge_x)_2$ ($x > 0.6$) has the collapsed tetragonal structure.

the viewpoint of P-P bonds. The first is the collapsed tetragonal structure with P-P bonds between Co_2P_2 layers and the second is the uncollapsed tetragonal one without P-P bonds. From a band calculation, it is predicted whether or not the P-P bonds exist, depending on the ionic radius of A cation [9]. In fact, ACo_2P_2 with small A cations such as A = Ca and Ce has the collapsed tetragonal structure and ACo_2P_2 with large A cations like Sr and La has the uncollapsed tetragonal structure [7, 8].

Among these compounds, $SrCo_2P_2$ is certainly a candidate for nearly ferromagnetic itinerant systems. That is, the magnetic susceptibility of $SrCo_2P_2$ shows Curie-Weiss-like temperature dependence at high temperatures and a broad maximum approximately at 100 K, which suggest that $SrCo_2P_2$ can be considered as an exchange-enhanced Pauli paramagnet with ferromagnetic spin fluctuations [7, 10].

In the $Sr_{1-x}Ca_xCo_2P_2$ system, the uncollapsed tetragonal structure transforms to the collapsed tetragonal one at $x = 0.5$ and then an antiferromagnetic ground state appears for $x > 0.5$ [11]. $Sr_{1-x}Ca_xCo_2P_2$ ($x < 0.5$) compounds are exchange-enhanced Pauli paramagnetic metals, and the temperature dependence of the magnetic susceptibility $\chi(T)$ has a maximum, which is a typical behavior of itinerant-electron metamagnetic compounds [11, 12]. Moreover, the itinerant-electron metamagnetic transition occurs under the high magnetic field [12], suggesting that the system is in the vicinity of a ferromagnetic quantum critical point. This is consistent with the ferromagnetic quantum critical behavior reported in the solid solution system of $SrCo_2(P_{1-x}Ge_x)_2$ [13].

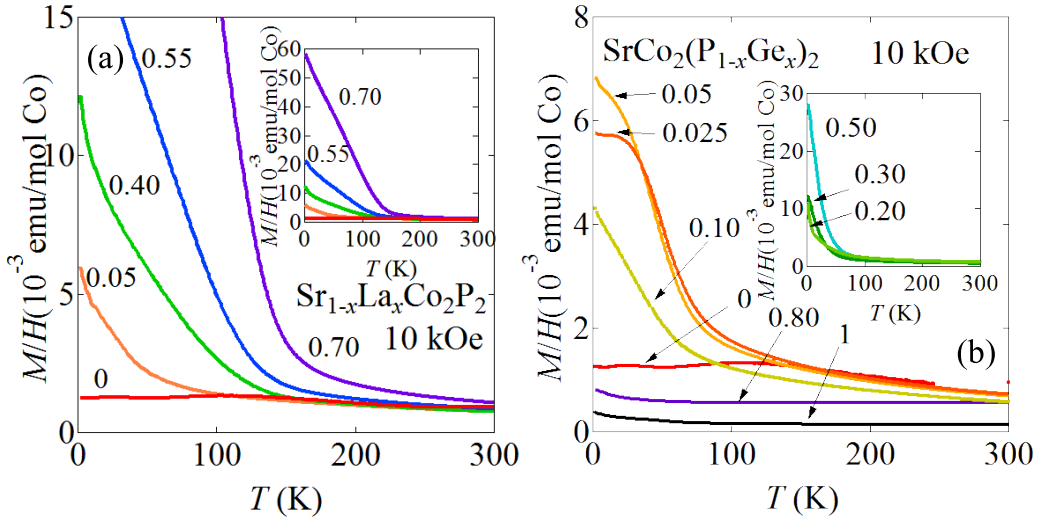

Figure 2: The temperature dependence of magnetization M divided by magnetic field H, M/H, which is equal to magnetic susceptibility in paramagnetic region, at 10 kOe. (a) The temperature dependence of M/H in $Sr_{1-x}La_xCo_2P_2$. (b) The temperature dependence of M/H in $SrCo_2(P_{1-x}Ge_x)_2$.

In this work, we synthesized $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$ and investigated their magnetic properties,including their magnetization under pulsed high magnetic fields. $LaCo_2P_2$ is a ferromagnetic metal with the Curie temperature of 133 K. Thus, ferromagnetic phases also exists in $Sr_{1-x}La_xCo_2P_2$ ($x > 0.5$). By contrast, though $SrCo_2Ge_2$ is a Pauli paramagnet, $SrCo_2(P_{1-x}Ge_x)_2$ has a weak itinerant-electron ferromagnetic phase in the intermediate x region [13]. These substitutions do not only change the ground state but also affect the metamagnetic transition. The metamagnetic transition disappears with only 5% of La substitution and 10% of Ge substitution. We will discuss the origin of the itinerant metamagnetic transition in the context of the band theory.

2 Experiment

Polycrystalline $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$ samples were prepared from elemental Sr(2N), La(3N), Co(3N), P(red, 5N) and Ge(5N), as described in Refs. [11] and [13]. Obtained samples were characterized by x-ray diffraction (XRD) with a Cu-Kα radiation using Bragg-Brentano geometry. The lattice parameters were calculated from XRD patterns by using the computer program RIETAN-FP [14]. The temperature dependent magnetizations of $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$ were measured by a Quantum Design MPMS-XL system at the research Center for Low Temperature and Materials Sciences, Kyoto University. Magnetization curves beyond 600 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.

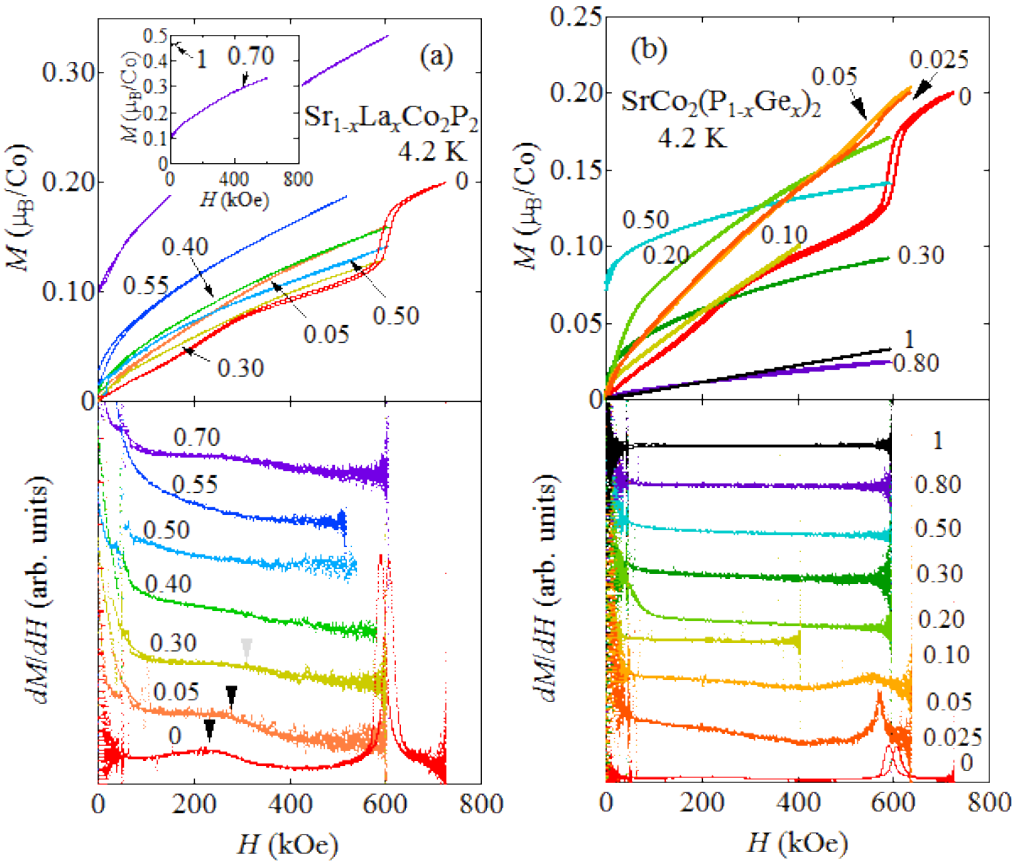

Figure 3: Magnetic properties in high pulsed magnetic fields up to 700 kOe. The magnetization M and the differential magnetization dM/dH curves measured at 4.2 K. (a) and (b) are the graphs of $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$, respectively.

3 Results and Discussion

The lattice parameters a and c of $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$ systems are shown in Fig. 1. In $Sr_{1-x}La_xCo_2P_2$, the lattice parameter a shows very little variation, while c decreases monotonically with increasing x. This result is consistent with both facts that $SrCo_2P_2$ and $LaCo_2P_2$ are the uncollapsed tetragonal (ucT) structure without P-P bonds between neighboring Co_2P_2 tetrahedral layers and that the ionic radius of La^{3+} is smaller than that of Sr^{2+}.

By contrast, a and c change markedly depending on x in $SrCo_2(P_{1-x}Ge_x)_2$, because of the transition from ucT to cT with the formation of P(Ge)-P(Ge) bonds. The slopes of x-dependencies of a and c change at $x = 0.2$ and 0.6, which is almost consistent with Ref. [13]. Based on the P(Ge)-P(Ge) bonds, the regions $x < 0.2$, $0.2 < x < 0.6$, and $x > 0.6$ are classified as ucT, intermediate and cT regions, respectively, in accordance with Ref. [13].

Figure 2 shows the temperature dependence of the magnetization M divided by the magnetic field H in $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$ measured at H =10 kOe. In the paramagnetic region, $M(T)/H$ corresponds to the magnetic susceptibility $\chi(T)$. The temperature dependent

$\chi(T)$ of $SrCo_2P_2$ shows the Curie-Weiss like behavior at high temperatures and has two maxima at $T_{max1} = 25$ and $T_{max2} = 110$ K. In itinerant-electron ferromagnetic compounds, the Curie-Weiss-like temperature dependence of $\chi(T)$ originates in the temperature dependence of spin fluctuations [15, 16]. The maximum of $\chi(T)$ is often observed in itinerant-electron metamagnetic compounds [17, 18] and discussed by using the scheme of spin fluctuations [19, 20]. In our previous report of the $Sr_{1-x}Ca_xCo_2P_2$ system, we presented both the metamagnetic transition field and T_{max2} where $\chi(T)$ shows the maximum decrease as x increases toward 0.5 and revealed that the transition field and T_{max2} are correlated with each other [12].

In the $Sr_{1-x}La_xCo_2P_2$ system, $\chi(T)$ shows the Curie-Weiss-like behavior at high temperatures and the maximum in $M(T)/H$ has disappeared with more than only 5% substitution of La as shown in Fig. 2(a), and then $M(T)/H$ increases as x increases. In $x \geq 0.4$, the ground state is the ferromagnetic one with the spontaneous magnetization determined by using Arrott plots. The spontaneous magnetic moment monotonically increases with increasing x. Our result is different from a phase diagram of $Sr_{1-x}La_xCo_2P_2$ where the Curie temperature decreases monotonically as Sr content increases, reported by Jia and Cava [21]. Thus, we can only speculate about the difference between our and their results because they did not provide any detailed information the way they determined their phase diagram. One possibility are different ways of evaluating the Curie temperature. In our results, $M(T)/H$ curves increase rapidly below a certain temperature even in the paramagnetic region, and this temperature may be regarded as the Curie temperature in Ref [21]. Another possibility is the difference in sample quality.

As shown in Fig. 2(b), $M(T)/H$ in the low temperature region becomes larger with 2.5% substitution of Ge in the $SrCo_2(P_{1-x}Ge_x)_2$ system. The value of susceptibility below 20 K shows non-monotonous dependence on x. The susceptibility increases for small Ge contents $0.025 \leq x \leq 0.05$ and $0.1 < x < 0.5$, but the susceptibility drops at $x = 0.1$. The non-monotonous dependence on x can be related to the characteristic band structure near Fermi level. Indeed, the maximum of $\chi(T)$ at 20 K in $SrCo_2P_2$ indicates a sharp peak of the electron density of state curve near Fermi level. The ground state for $x < 0.2$ is enhanced Pauli paramagnet. In the region of $0.3 < x < 0.65$, the ground state is the weak ferromagnetic metal with a small spontaneous magnetic moment. In the region of $x > 0.65$, the ground state becomes Pauli paramagnetic metal again, and $\chi(T)$ does not show Curie-Weiss like temperature dependence in the region of $x > 0.8$, being consistent with Ref. [13].

The high field magnetization processes of $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$ measured at 4.2 K are shown in Fig. 3. There are two anomalies in the magnetization process of $SrCo_2P_2$. As shown in the differential magnetization dM/dH curve in Fig. 3(a), the magnetization process of $SrCo_2P_2$ shows a high field anomaly with hysteresis and a low field anomaly without hysteresis. The former is an itinerant-electron metamagnetic transition and the latter is a crossover between different paramagnetic states with a larger χ. In $Sr_{1-x}La_xCo_2P_2$ system, the metamagnetic transition with hysteresis is not observed up to 600 kOe. As the La substitution ratio x increases, the small anomaly shifts to the higher field, and the peak in dM/dH curve becomes small.

By contrast, the metamagnetic transition appears in Ge substituted system within the applied field of 600 kOe and the transition field becomes small with increasing x. In addition, the value of the magnetization in the lower field region becomes large and the height of magnetization jump markedly becomes small. In the weak ferromagnetic region with $0.2 < x < 0.5$, the saturation magnetic moment is smaller than that of $SrCo_2P_2$.

We here discuss the effect of La and Ge substitutions on the band structure. The La substitution for Sr leads to electron doping in the Co band. In the case of the Ge substitution

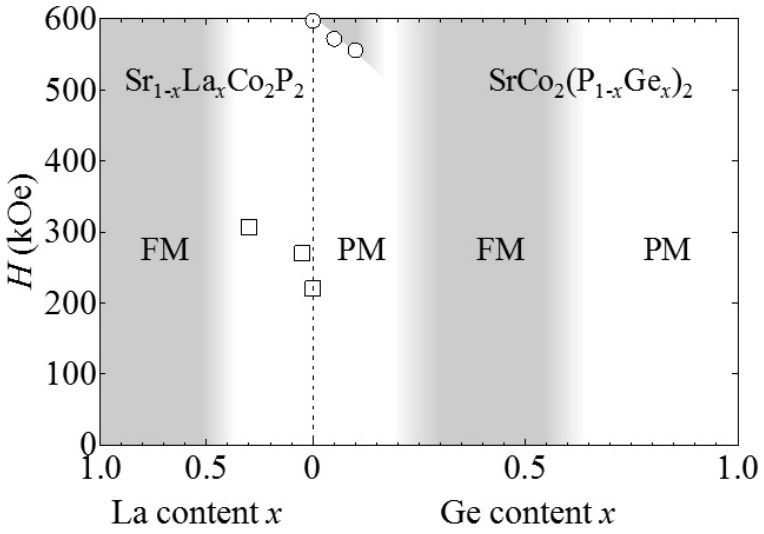

Figure 4: Magnetic phase diagrams of $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$. The shaded region represents ferromagnetic metal (FM) region and the other does Pauli paramagnetic metal (PM) region. Circles and squares are the metamagnetic transition field and the field where the magnetization shows crossover-like anomaly without hysteresis, respectively.

for P, the doping effect is slightly complicated because of the structural transition from ucT to cT phase. In the ucT region, the Ge substitution can lead to hole doping in the Co band in a simple assumption that Ge^{4-} replaces P^{3-}. In the intermediate region between ucT and cT, the formation of P(Ge)-P(Ge) bonds leads not only to electron doping in the Co band but also the intrinsic change of the band structure itself.

Figure 4 shows the magnetic phase diagrams of $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$. The metamagnetic transition field decreases and the lower-field crossover disappears with hole doping by the Ge substitution. On the other hand, the crossover-field increases and the metamagnetic transition field seems to increase above 600 kOe with the electron doping by the La substitution. In the case of the same valence ion substituted $Sr_{1-x}Ca_xCo_2P_2$ system without carrier doing, the metamagnetic transition occurs in the wide region of $x < 0.5$. In addition, their saturation moments above metamagnetic transition fields are approximately the same value of 0.2 μ_B/Co. In contrast, the metamagnetic transition disappears by a small amount of substitution in the present carrier doping systems. The existence of a sharp peak in the electronic density of states near the Fermi level is associated with the doping effect of the metamagnetic transition. Moreover, the saturation moments markedly change, also suggesting that the Fermi level shifts with doping. From the de Haas-van Alphen experiment and the band calculation of $SrCo_2P_2$ in Ref. [22], the Co-3*d* electron dominantly contributes to Fermi surfaces and forms a sharp peak in its electronic density of states. For all the results, we should conclude that the itinerant-electron metamagnetic transition in $SrCo_2P_2$ origins in its characteristic band structure.

4 Conclusion

We synthesized polycrystalline $Sr_{1-x}La_xCo_2P_2$ and $SrCo_2(P_{1-x}Ge_x)_2$ samples and measured their magnetic properties. The metamagnetic transition field decreases and the height of magnetization jump becomes smaller with hole doping by the Ge substitution, while the metamagnetic transition could not be observed under 600 kOe in the La substitution system. The carrier doping by La or Ge substitution affects the itinerant electron metamagnetic transition, in contrast to the isovalent substituted $Sr_{1-x}Ca_xCo_2P_2$ system, suggesting that the itinerant-electron metamagnetic transition originates in a sharp peak of the electronic density of state curve near the Fermi level.

5 Acknowledgments

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