

# NMR study of the layered cobalt oxyphosphide $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$

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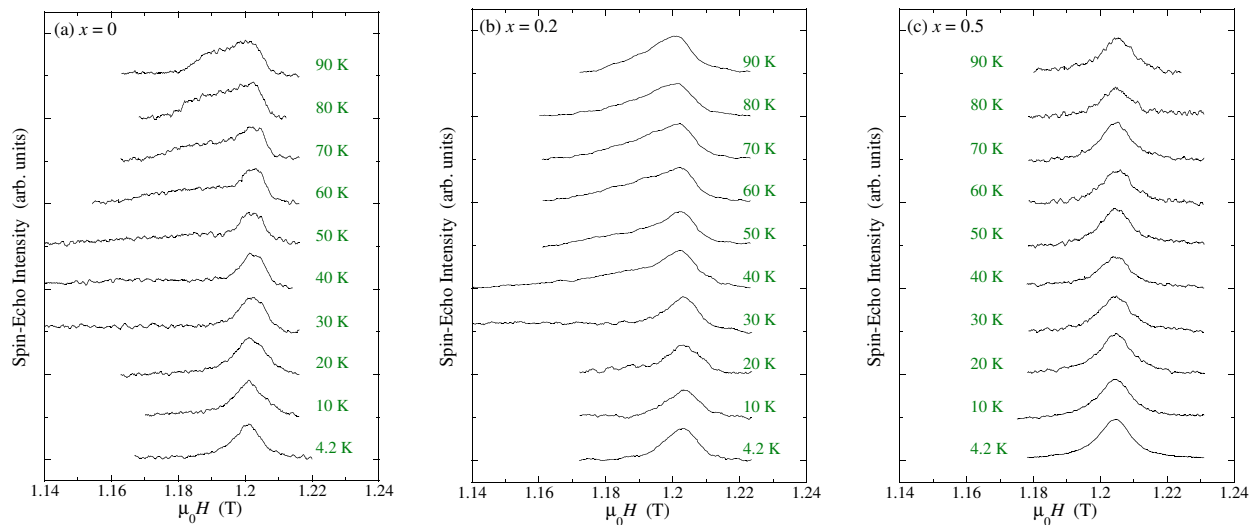
**Abstract.** We report the results of <sup>31</sup>P-nuclear magnetic resonance (NMR) measurements on the layered cobalt oxyphosphide  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  in order to investigate the magnetic properties at low temperatures from a microscopic view point. The <sup>31</sup>P-Knight shifts measured at the resonance peak maximum of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  have positive values and are  $T$ -independent in an entire temperature range, and the absolute value decreases with increasing Fe content. Also, the nuclear spin-lattice relaxation rate  $1/T_1$  is almost proportional to the temperature at low temperatures. The magnitude of  $1/T_1T$  decreases with increasing the Fe content, which suggests the decrease of the density of states around the Fermi level.

## 1. Introduction

Since the discovery of iron-based superconductivity in F-doped  $\text{LaFe}(\text{P,As})\text{O}$ [1, 2], many researchers focus on physical properties on oxypnictides with quasi-two dimensional structure separated by a carrier blocking layer. In the case of Co-substitution in place of Fe,  $\text{LaCoPO}$  and  $\text{LaCoAsO}$  show weak itinerant ferromagnets with Curie temperatures of about 43 K and 66 K, respectively[3]. In these compounds, it has been proposed that spin fluctuations play an important role in the magnetic behavior[3, 4, 5, 6, 7].

Recently, we have successfully synthesized and evaluated the transport properties of a novel cobalt oxypnictide  $\text{Sr}_2\text{ScCoPO}_3$ [8], which crystallizes in an unusual intergrowth structure consisting of a CoP layer and a perovskite related  $\text{K}_2\text{NiF}_4$ -type  $\text{Sr}_4\text{Sc}_2\text{O}_6$  layer. This structure is isomorphic to  $\text{Sr}_2\text{ScFePO}_3$  which exhibits superconductivity below 17 K[9]. The electrical resistivity  $\rho$  of  $\text{Sr}_2\text{ScCoPO}_3$  decreases upon cooling like a metal. However, the superconducting transition is not observed on that of  $\text{Sr}_2\text{ScCoPO}_3$ . Also, we investigate the effect of changing the number of  $3d$  electrons and show the detailed physical properties[10]. The electrical resistivity  $\rho$ 's for  $\text{Sr}_2\text{ScMPO}_3$  ( $M = \text{Ni}$  and  $\text{Co}_{0.5}\text{Fe}_{0.5}$ ) show the metallic behavior similar to that of  $\text{Sr}_2\text{ScCoPO}_3$ . The value of  $\rho$  for  $\text{Sr}_2\text{ScNiPO}_3$ , where the substitution of Ni at an Co site effectively dopes electrons, is smaller than that for  $\text{Sr}_2\text{ScCoPO}_3$ . In contrast, the value of  $\rho$  for  $\text{Sr}_2\text{Sc}(\text{Co}_{0.5}\text{Fe}_{0.5})\text{PO}_3$ , where partially substitution of Fe at an Co site effectively reduces electrons, is larger than that for  $\text{Sr}_2\text{ScCoPO}_3$ . Quite recently, the transport





**Figure 1.** Temperature evolution of  $^{31}\text{P}$ -NMR spectra of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  for (a)  $x = 0$ , (b)  $x = 0.2$ , and (c)  $x = 0.5$  in a temperature range of 4.2 K – 90 K at  $f = 20.760$  MHz.

properties of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  ( $0.04 \leq x \leq 0.8$ ) were reported[11]. The electrical resistivity  $\rho$ 's for  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  decrease with decreasing temperature like a metal, but the superconducting transition is not observed. The value of  $\rho$  increases with increasing the Fe content  $x$ .

In the paper, we will report on the  $^{31}\text{P}$ -nuclear magnetic resonance (NMR) results of  $\text{Sr}_2\text{ScCoPO}_3$  and partially Fe-substituted  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$ , and discuss the microscopic electronic states and the variation of the magnetic properties by changing the number of  $3d$  electrons. It is quite helpful to make use of the NMR method for a study of local electronic properties.

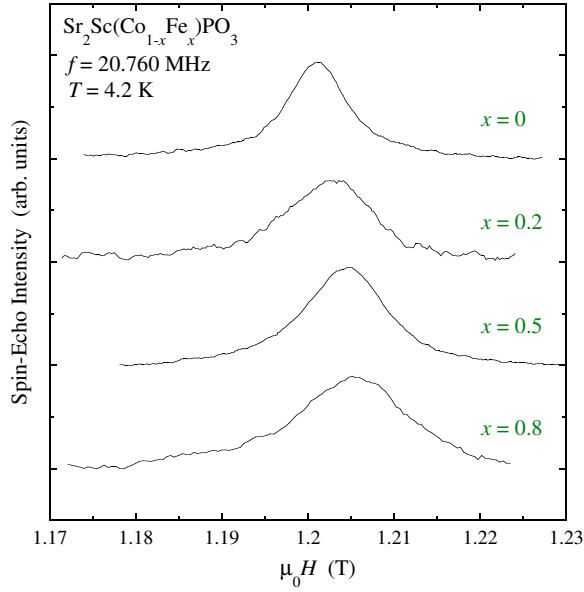
## 2. Experimental

The polycrystalline sample of  $\text{Sr}_2\text{ScCoPO}_3$  was synthesized by a standard solid state reaction method in a quartz tube from of CoP, SrO, Sr and  $\text{Sc}_2\text{O}_3$ . In case of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$ , the starting materials were  $\text{Co}_{1-x}\text{Fe}_x\text{P}$ , SrO, Sr and  $\text{Sc}_2\text{O}_3$ . The precursor  $\text{Co}_{1-x}\text{Fe}_x\text{P}$  was prepared by a solid state reaction of Co,  $\text{Fe}_2\text{P}$  and P. The detailed synthesis condition was described elsewhere[8, 10]. Samples were characterized by powder X-ray diffraction (XRD) at room temperature. The powder XRD patterns of all samples are similar to that of  $\text{Sr}_2\text{ScFePO}_3$ [9], which indicates that all samples are isomorphic to  $\text{Sr}_2\text{ScFePO}_3$ [10, 11]. For the NMR measurements, samples were crushed into powder.  $^{31}\text{P}$ -NMR ( $I = 1/2$ ) measurements were performed in the temperature range of 1.5 K – 200 K in an external magnetic field of 1.2 T using a conventional phase-coherent pulsed spectrometer. NMR spectrum was obtained by sweeping magnetic field. The nuclear spin-lattice relaxation rate  $1/T_1$  was measured by the saturation recovery method.

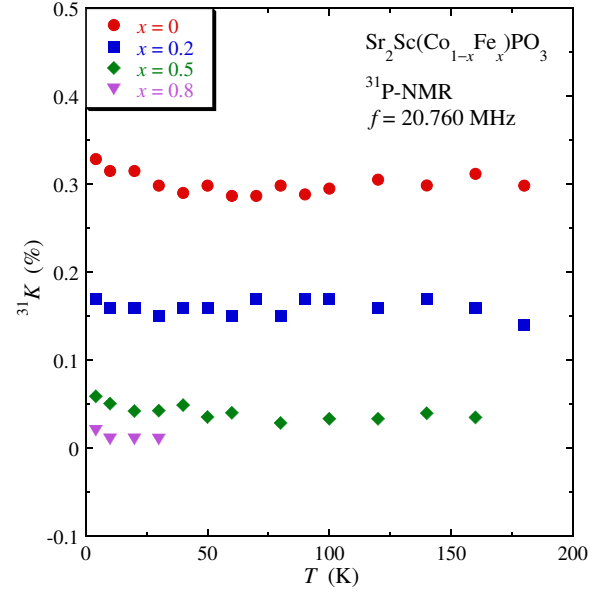
## 3. Results and discussion

### 3.1. NMR spectra

Figure 1 shows the temperature evolution of  $^{31}\text{P}$ -NMR spectra of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  for (a)  $x = 0$ , (b)  $x = 0.2$ , and (c)  $x = 0.5$  in a temperature range of 4.2 K – 90 K at  $f = 20.760$  MHz. For the samples of  $x = 0$  and 0.2, the  $^{31}\text{P}$ -NMR spectrum at high temperatures shows a typical powder pattern due to anisotropic Knight shift for a spin  $I = 1/2$  nucleus experiencing



**Figure 2.**  $^{31}\text{P}$ -NMR spectra of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  for the compounds of  $x = 0, 0.2, 0.5$  and  $0.8$  at  $T = 4.2$  K and  $f = 20.760$  MHz.



**Figure 3.** Temperature dependences of the  $^{31}\text{P}$ -Knight shift of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  for the compounds of  $x = 0, 0.2, 0.5$  and  $0.8$  measured at  $f = 20.760$  MHz.

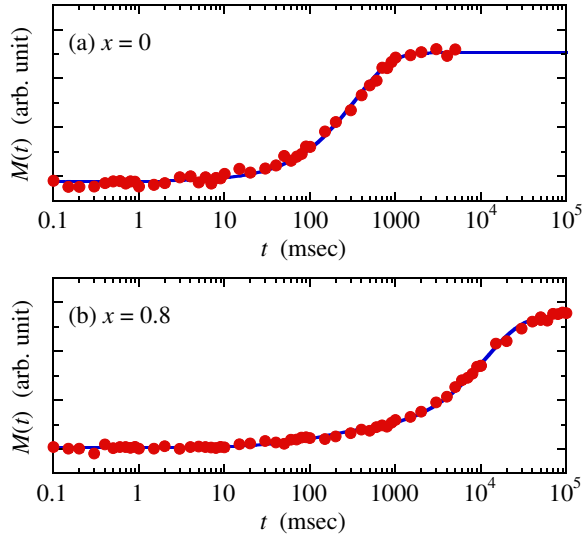
an axially symmetric local magnetic field. The Knight shift components perpendicular  $K_{\perp}$  and parallel  $K_{\parallel}$  to the principal axis are derived from the peak maximum and the shoulder peak in the spectra, respectively. The component  $K_{\parallel}$  shifts markedly upon cooling, and the spectrum becomes broader at low temperatures. In contrast, for the sample of  $x = 0.5$ , the spectrum is symmetric and almost independent of temperature. It suggests that the electronic states are changed by reducing the number of  $3d$  electrons.

Figure 2 shows the  $^{31}\text{P}$ -NMR spectra of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  for the compounds of  $x = 0, 0.2, 0.5$  and  $0.8$  at  $T = 4.2$  K and a frequency of  $f = 20.760$  MHz. At low temperature, the spectrum is symmetric, and the resonance magnetic field  $H_{\text{res}}$  shifts higher field side with increasing the substituted Fe content, where indicates the Knight shift decreases with increasing Fe content. The Knight shift is obtained from the relation  $K = (2\pi f / \gamma_{\text{N}} - H_{\text{res}}) / H_{\text{res}}$ , where  $\gamma_{\text{N}}$  is the gyromagnetic ratio of  $^{31}\text{P}$  ( $^{31}\gamma_{\text{N}} / 2\pi = 17.237$  MHz/T). In general, the Knight shift is proportional to the spin susceptibility,  $K = \frac{A_{\text{hf}}}{N_{\text{A}}\mu_{\text{B}}} \chi_{\text{s}}$ , where  $A_{\text{hf}}$  is the hyperfine coupling constant,  $N_{\text{A}}$  is the Avogadro number and  $\mu_{\text{B}}$  is the Bohr magneton.

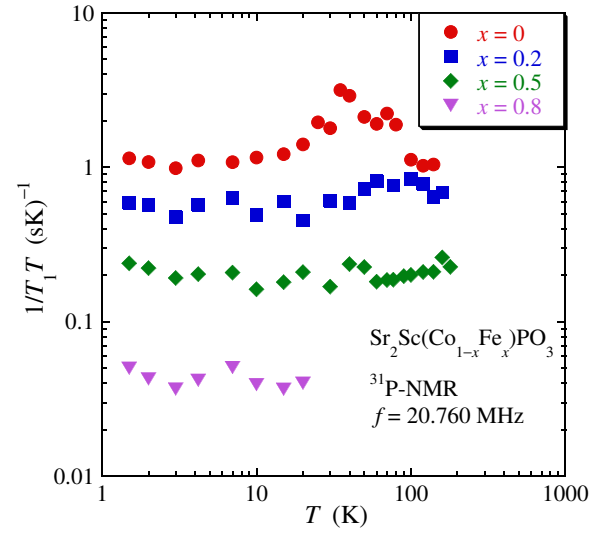
Figure 3 indicates the temperature dependence of the Knight shift of the  $^{31}\text{P}$  nuclei,  $^{31}K$ , of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$ . The Knight shift was determined at the resonance peak maximum, which corresponds to the component  $K_{\perp}$ . The Knight shift is almost  $T$ -independent, which is mainly arised from conduction electron spin susceptibility. The spin susceptibility  $\chi_{\text{s}}$  is proportional to the density of states at the Fermi level  $\chi_{\text{s}} = \mu_{\text{B}}^2 D(E_{\text{F}})$ . The values of the Knight shift are positive and small in an entire temperature range, which suggests the small hyperfine coupling constant. Also, the magnitude decreases with increasing Fe content, which indicates the decrease of the density of states around the Fermi level.

### 3.2. Nuclear relaxation rate $1/T_1$

Figure 4 presents the recovery curves of the nuclear magnetization  $M(t)$  of  $^{31}\text{P}$  in  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  for (a)  $x = 0$  and (b)  $x = 0.8$  at  $T = 4.2$  K. The nuclear spin-lattice



**Figure 4.** Recovery curves of the nuclear magnetization of  $^{31}\text{P}$  in  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  for (a)  $x = 0$  and (b)  $x = 0.8$  at  $T = 4.2$  K. The solid lines are the best fit using the formula described in the text.



**Figure 5.** Temperature dependences of the nuclear spin-lattice relaxation rates divided by temperature  $1/T_1T$  of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  in a temperature range of 1.5 K–200 K measured at  $f=20.760$  MHz.

relaxation rate  $1/T_1$  was measured at the resonance peak maximum. The recovery of the nuclear magnetization  $M(t)$  is almost single component for the spin  $I = 1/2$  of  $^{31}\text{P}$  nuclei as  $M(t) = M_0[1 - \exp(-t/T_1)]$ , where  $M_0$  and  $M(t)$  are the nuclear magnetization in the thermal equilibrium and at a time  $t$  after the saturating pulse, respectively. As seen in the figure, the relaxation time  $T_1$  for the sample of  $x = 0.8$  is long more than one order compared to that for the sample of  $x = 0$ .

Figure 5 presents the temperature dependences the nuclear spin-lattice relaxation rates divided by temperature  $1/T_1T$  for  $^{31}\text{P}$  nuclei in  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  in a temperature range of 1.5 K – 200 K. For the sample of  $x = 0$ ,  $1/T_1T$  shows a weak temperature dependence at high temperatures, which suggests the existence of weak spin fluctuations. As further decreasing temperature,  $1/T_1T$  decreases with a small peak around  $\sim 40$  K and is almost independent of temperature at low temperatures. In contrast, for other samples,  $1/T_1T$ 's are roughly constant over the entire temperature range, as expected for simple metallic systems. Also, the magnitude of  $1/T_1T$  decreases with increasing the Fe content.

Generally,  $1/T_1T$  is expressed as  $1/T_1T \propto \lim_{\omega \rightarrow 0} \sum_q |A_q|^2 \frac{\chi''(q, \omega)}{\omega}$ , where  $\chi''(q, \omega)$  is the imaginary part of the dynamical susceptibility,  $\omega$  is the resonance frequency, and  $A_q$  is the Fourier  $q$  component of the hyperfine coupling constant. Thus,  $1/T_1T$  probes the  $q$ -sum of spin fluctuations  $\sum_q \chi(q, \omega \rightarrow 0)$ . If the  $q$  dependence of spin fluctuations is small,  $1/T_1T$  is given by  $1/T_1T \propto \int N^2(E) f(E) [1 - f(E)] dE$ , where  $f(E)$  is the Fermi distribution function and  $N(E)$  is the effective density of states around the Fermi level  $E_F$ . Thus, the decrease of  $1/T_1T$  with increasing the Fe content indicates the decrease of the density of states around the Fermi level, which is consistent with the results of the Knight shift.

#### 4. Summary

We have carried out the  $^{31}\text{P}$ -NMR experiments for  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  in order to understand the magnetic properties at low temperatures from the microscopic viewpoints. The NMR spectrum of  $\text{Sr}_2\text{ScCoPO}_3$  shows the uniaxially symmetric powder pattern due to the anisotropic

Knight shift at high temperatures. By substitution of Fe at an Co site, the spectrum changes to be symmetric. The  $^{31}\text{P}$ -Knight shift measured at the resonance peak maximum of  $\text{Sr}_2\text{Sc}(\text{Co}_{1-x}\text{Fe}_x)\text{PO}_3$  is  $T$ -independent and has a positive value in an entire temperature range, and the absolute value decreases with increasing Fe content. Also,  $1/T_1$  is almost proportional to the temperature at low temperatures., and the magnitude of  $1/T_1T$  decreases with increasing the Fe content, which suggests the decrease of the density of states around the Fermi level.

## References

- [1] Kamihara Y, Hiramatsu H, Hirano M, Kawamura R, Yanagi H, Kamiya T and Hosono H 2006 *J. Am. Chem. Soc.* **128** 10012
- [2] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
- [3] Yanagi H, Kawamura R, Kamiya T, Kamihara Y, Hirano M, Nakamura T, Osawa H and Hosono H 2008 *Phys. Rev. B* **77** 224431
- [4] Sugawara H, Ishida K, Nakai Y, Yanagi H, Kamiya T, Kamihara Y, Hirano M and Hosono H 2009 *J. Phys. Soc. Jpn.* **78** 113705
- [5] Majumder M, Ghoshray K, Ghoshray A, Bandyopadhyay B, Pahari B and Banerjee S 2009 *Phys. Rev. B* **80** 212402
- [6] Ohta H and Yoshimura K 2009 *Phys. Rev. B* **79** 184407
- [7] Ohta H and Yoshimura K 2009 *Phys. Rev. B* **80** 184409
- [8] Okada S, Kamihara Y, Ohkubo N, Ban S, Matoba M and Atou T 2012 *J. Phys.: Conf. Ser.* **400** 022091
- [9] Ogino H, Matsumura Y, Katsura Y, Ushiyama K, Horii S, Kishio K and Shimoyama J 2009 *Supercond. Sci. Technol.* **22** 075008
- [10] Okada S, Kamihara Y, Ohkubo N, Ban S and Matoba M 2014 *J. Phys.: Conf. Ser.* **568** 022034
- [11] Okada S, Kamihara Y, Ohkubo N, Ban S and Matoba M 2017 *Presented at the 28th Int. Conf. on Low Temperature Physics* (Gothenburg)