Study of itinerant electronic ferromagnetism in layered compounds $Ae_2ScO_3CoPn$ ($Ae = Sr, Ba$, $Pn = P, As$)

Hiroto Ohta, Shohei Ido, Shuku Hashizume, and Hiroko Aruga Katori

Institute of Engineering, Division of Advanced Applied Physics, Tokyo University of Agriculture and Technology, Nakacho 2-24-16, Koganei, Tokyo 184-8588, Japan

E-mail: h-ohta@cc.tuat.ac.jp

Abstract. We successfully synthesized polycrystalline samples of new layered compounds $Ae_2ScO_3CoP$ ($Ae = Sr, Ba$) and $Ba_2ScO_3CoAs$, members with $CoPn$ conduction layers, and measured magnetizations of them. As results, magnetic parameters, i.e. the Curie temperature and the Weiss temperature, are found not to be correlative with lattice parameters $a$ nor $c$ in the case of $Ae_2ScO_3CoPn$ compounds, including $Sr_2ScO_3CoAs$, unlike the case of three dimensional itinerant electronic ferromagnets. We suggested that structural parameters of $CoPn_4$ tetrahedron are good parameters to relate to magnetic parameters in the case of compounds with $CoPn$ layers.

1. Introduction

Itinerant electronic magnetism has been one of important topics not only in the field of magnetism but also in the field of strongly correlated electronic systems. Theory of itinerant electronic magnetism was developed by T. Moriya and his co-workers and the self-consistent renormalization (SCR) theory for spin fluctuations was established for itinerant electronic ferromagnetism (IEF). [1] The theory for IEF has been still developed by Y. Takahashi [2] and several important problems which Moriya’s theory have, e.g. critical phenomenon around the Curie temperature ($T_C$), magnetocaloric effect and so on, have been solved in Takahashi’s theory. [3] In the case of isotropic band structure, the understanding of IEF has grown from the viewpoint of theory and experiment while in the case of anisotropic band structure the understanding of IEF is not enough since experimental researches have not been done systematically.

Recently, layered compounds $LaCoPnO$ ($Pn = P$ or As), which have ZrCuSiAs-type crystal structure, were found to show IEF with $T_C$ being 30 K (for $Pn = P$) or 55 K (for $Pn = As$). [4] Since 3$d$ electrons of Co, which delocalize within Co$Pn$ layers, are responsible for magnetism in these compounds, $LaCoPnO$ have been thought as quasi two dimensional IEF compounds with anisotropic band structures. Spin fluctuations of $LaCoPnO$ were reported to actually have two dimensional nature in the paramagnetic state. [5, 6] $Sr_2ScO_3CoAs$, which has $Sr_2GaO_3CuS$-type crystal structure [7, 8], has CoAs conductive layers as well as $LaCoAsO$ but the distance between CoAs layers is about twice larger than that of $LaCoAsO$. [9] Although this compound does show ferromagnetic ordering at $T_C = 48$ K, there was reported that two dimensionality of
itinerant electrons in CoAs layers enhances in Sr$_2$ScO$_3$CoAs in comparison with LaCoAsO. [10] Among compounds with CoPn layers, those with Sr$_2$GaO$_3$CuS-type crystal structure have the most largest distance between CoPn layers for now, so we think such compounds are put on a good stage for studying IEF in anisotropic band structures. In addition, since compounds with Sr$_2$GaO$_3$CuS-type structure are composed of 5 elements, there seems to have the variety as the compounds which contain just Co as a magnetic element. For these reasons, we studied layered compounds $Ae_2$ScO$_3$CoPn ($Ae = Sr$, Ba, $Pn = P$, As) to clarify nature of itinerant electronic magnetism in anisotropic structures.

In this paper, we report results of synthesis and magnetic measurements of new layered compounds Ba$_2$ScO$_3$CoAs, $Ae_2$ScO$_3$CoP ($Ae = Sr$ or Ba). We also discuss relation between itinerant electronic ferromagnetism and crystal structure of layered compounds with CoPn ($Pn = P$ or As) conduction layers.

2. Experiments

Polycrystalline samples of Ba$_2$ScO$_3$CoAs, $Ae_2$ScO$_3$CoP ($Ae = Sr$ or Ba) were synthesized by a conventional solid state reaction method. First, powders of CoAs and CoP were synthesized by mixing powders of Co (purity: 99.9 %) and As (99.9 %) or P (99.9999 %) in the ratio of 1 : 1 and firing them at 800 °C for 12 hs in evacuated silica tubes. Then, obtained CoPn powders were mixed with $Ae$ (99 %), $Ae$O (99 %), and Sc$_2$O$_3$ (99.9 %) in the appropriate ratio and these mixtures were fired at 1,200 °C for 12 hs in evacuated silica tubes. This step was repeated once or twice to achieve good homogeneity. Samples were handled in a glove box filled with highly pure N$_2$ gas. Obtained samples were characterized by measuring powder X-ray diffraction (XRD) with Cu $K_a$ radiation. Magnetization of samples were measured by using vibrating sample magnetometer ($MagLab^{VSM}$, Oxford Instruments).

3. Results and Discussion

Figure 1 (a) shows the results of powder XRD measurements of the samples. As shown in the figure, we successfully synthesized each compound though Sr$_2$ScO$_3$CoP and Ba$_2$ScO$_3$CoP contain small amount of SrCo$_2$P$_2$ and BaCo$_2$P$_2$, respectively, as impurities. Since these impurities are paramagnets, [11, 12] their contribution to magnetization of each sample is thought to be negligible. From the data of XRD, we estimated lattice parameters along a and c-axes of each compound. The estimated values are listed in Table 1. For the case of Sr$_2$ScO$_3$CoP, our result is consistent with that reported by Okada et al. [13] We also shows the values of a and c for four compounds, i.e. Ba$_2$ScO$_3$CoAs, Sr$_2$ScO$_3$CoAs, Ba$_2$ScO$_3$CoP and Sr$_2$ScO$_3$CoP, in Fig. 1 (b). Both the parameters obviously depend primarily on ion size of alkali earth metal elements and secondly on that of pnictogen elements. By changing alkali earth metal elements from Sr to Ba and pnictogen elements from P to As, the values of a and c change about 4 % and 9 %, respectively. Such a large change in size of unit cell promises variation of magnetism in these compounds, since IEF strongly correlates to cell volume of the system in usual.

Figure 2 (a) shows temperature ($T$) dependence of magnetization ($M$) of Ba$_2$ScO$_3$CoAs measured at $H = 1$ T together with that of Sr$_2$ScO$_3$CoAs (denoted by Sr/As in the figure) for comparison. Clear ferromagnetic ordering was observed below about 40 K. Figure 2 (b) shows isothermal magnetization curves of Ba$_2$ScO$_3$CoAs at various temperatures. Below 40 K, spontaneous magnetizations were observed in consistency with the result of $T$ dependence of $M$. The Curie temperature ($T_C$) of this compound was estimated as 32 K, which is less than that of Sr$_2$ScO$_3$CoAs ($T_C = 48$ K).

Figure 3 (a) shows $T$ dependence of $M$ of Sr$_2$ScO$_3$CoP measured at $H = 1$ T. In the low temperature region, $M$ of the sample increases with decrease of $T$ and seems to show ferromagnetic ordering below about 10 K. Figure 3 (b) shows isothermal magnetization curves
at various temperatures. At $T = 2$ K, magnetic curve shows ferromagnetic enhancement as if the system is in ferromagnetic ordered state as the ground state. However, spontaneous magnetization was not observed at this temperature.

Figure 4 (a) shows $T$ dependence of $M$ of Ba$_2$ScO$_3$CoP measured at $H = 2$ T. In contrast with other samples, this sample does not show ferromagnetic ordering at all down to 2 K. Figure 4 (b) shows isothermal magnetization curves at various temperatures. Although magnetization curve at $T = 2$ K is convex upward, spontaneous magnetization does not observed down to 2 K consistent with the result of $T$ dependence of $M$.

Figure 5 shows temperature dependence of $H/M$ of the three samples together with that of Sr$_2$ScO$_3$CoAs for comparison. $H/M$ of all the compounds show linear temperature dependence, meaning that the Curie Weiss law holds. Magnetic parameters, i.e. the effective Bohr magneton number ($P_{\text{eff}}$) and the Weiss temperature ($\theta$), were estimated by fitting a function of the Curie Weiss law to the data and listed in Table 2. Almost constant value of $P_{\text{eff}}$ and systematic change of $\theta$ among these compounds are well explained by Moriya’s SCR theory for ferromagnetic spin fluctuations. [1] $P_{\text{eff}}$ of Ba$_2$ScO$_3$CoP is smaller compared with the others. Possibly, this is because an impurity phase exists in Ba$_2$ScO$_3$CoP. In the Moriya’s theory, $\theta$ has an important meaning. The absolute value of $\theta$ corresponds to the “distance” from a quantum critical point.

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**Figure 1.** (a) Results of powder XRD measurements of the samples. For each sample, upper and lower row show observed and calculated data, respectively. Peaks indicated by “+” and “*” correspond to the patterns of BaCo$_2$P$_2$ and SrCo$_2$P$_2$, respectively. (b) Lattice parameters along $a$ and $c$-axes for Ae$_2$ScO$_3$CoPn (abbreviated as Ae/Pn).

**Table 1.** Estimated lattice parameters from XRD measurements. $V$ is cell volume.

| Compound       | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) |
|----------------|---------|---------|-------------|
| Ba$_2$ScO$_3$CoAs | 4.170   | 16.773  | 291.7       |
| Sr$_2$ScO$_3$CoAs [10] | 4.049   | 15.557  | 255.0       |
| Ba$_2$ScO$_3$CoP  | 4.099   | 16.504  | 277.3       |
| Sr$_2$ScO$_3$CoP  | 4.020   | 15.412  | 249.1       |
Figure 2. (a) $T$ dependence of $M$ of Ba$_2$ScO$_3$CoAs measured at $H = 1$ T shown together with that of Sr$_2$ScO$_3$CoAs for comparison. (b) Isothermal magnetization curves at various temperatures.

Figure 3. (a) $T$ dependence of $M$ of Sr$_2$ScO$_3$CoP measured at $H = 1$ T. (b) Isothermal magnetization curves at various temperatures.

(QCP) and the sign of $\theta$ shows whether the system is in ordered state or disordered state: when $\theta > 0$ the system is in ferromagnetically ordered state while when $\theta < 0$ the system is in disordered (paramagnetic) state. As shown in Figure 6, electronic states of these compounds expressed by $U=W$ are located in the narrow region around QCP on the electronic phase diagram of IEF, and especially electronic state of Sr$_2$ScO$_3$CoP is in the vicinity of QCP of IEF.

In the case of compounds with isotropic band structure, enlargement of cell volume leads to decrease of $\theta$ or depression of ferromagnetism, since energy width of conduction band $W$ correlates to the cell volume: the larger cell volume corresponds to the smaller $W$ (larger $U/W$ and $\theta$) and vice versa. However, electronic systems of $Ae_2$ScO$_3$CoP$_n$ apparently do not have such a relationship between cell volume and $\theta$. In principle, strength of ferromagnetism, or $\theta$, should correlate to $U/W$, we think that $W$ does not simply relate to $V$ any more in the case of $Ae_2$ScO$_3$CoP$_n$. Such anomalous relationship has been reported in compounds with CoP$_n$ layers, [14, 15] indicating that this anomalous relationship is due to layered crystal structure.
Figure 4. (a) \( T \) dependence of \( M \) of \( \text{Ba}_2\text{ScO}_3\text{CoP} \) measured at \( H = 2 \, \text{T} \). (b) Isothermal magnetization curves at various temperatures.

Figure 5. \( T \) dependence of \( H/M \) of the samples together with that of \( \text{Sr}_2\text{ScO}_3\text{CoAs} \). \( \text{Ae/Pn} \) in the figure denote \( \text{Ae}_2\text{ScO}_3\text{CoPn} \).

Table 2. Magnetic parameters of the compounds: the effective Bohr magneton number \( P_{\text{eff}} \), the Weiss temperature \( \theta \) and the Curie temperature \( T_C \).

|                  | \( P_{\text{eff}} \) | \( \theta \) (K) | \( T_C \) (K) |
|------------------|----------------------|------------------|---------------|
| \( \text{Ba}_2\text{ScO}_3\text{CoAs} \) | 1.57                 | 56               | 32            |
| \( \text{Sr}_2\text{ScO}_3\text{CoAs} \) [10] | 1.34                 | 78               | 48            |
| \( \text{Ba}_2\text{ScO}_3\text{CoP} \)    | 1.04                 | -36              | -             |
| \( \text{Sr}_2\text{ScO}_3\text{CoP} \)    | 1.47                 | 6.8              | \( \sim 0 \)  |

In the case of Fe-analogue, relationship between superconducting transition temperature \( T_c \) and local structural parameters relating to \( \text{FeAs}_4 \) tetrahedron has been proposed. [16] In the
Figure 6. Schematic phase diagram of IEF around QCP. [1] Solid line shows a phase boundary while dotted lines just show cross over regions. $U$ and $W$ are the Coulomb repulsion energy and energy width of conduction band, respectively. $Ac/Pn$ in the figure denote $Ae_2ScO_3CoPn$.

Figure 7. (a) local structure of Co$Pn_4$ layer. (b)-(d) $T_C$ or $\theta$ plotted against (b) $d_{Co-Co}$, (c) $S$ and (d) $\gamma$. Data are after Ref. [4, 14, 17, 18, 19, 20]. In (b)-(d), red and orange markers show the data of arsenide and phosphide compounds, respectively.

track of the Fe-analogue, we checked relationship between $\theta$ and local structural parameters relating to Co$Pn_4$ tetrahedron. Among such parameters, we tentatively chose two parameters
layer and can be expressed by $\Delta T$ between two parameters. Figure 7 (c) and (d) show the $d$ in Figure 7 (a). Figure 7 (b) shows $T_c$ and $S$ structural parameters: the data of $T_c$ as shown by solid lines in each panel, strength of magnetism seems to correlate with local structural parameters: the data of $T_c$ or $\theta$ show a parabolic curvature against $\gamma$ while they show a monotonic decrease with increase of $S$. These correlations can roughly be understood as that energy width of conduction band $W$ depends on how $p$-orbitals of $Pn$ are hybridized with $d_{x^2-y^2}$ orbital of Co, since overlap integral of $p$-orbitals of $Pn$ and $d_{x^2-y^2}$ orbital of Co depends on both relative angle between these orbitals and distance between $Pn$ and Co. It should be noted that this conclusion must be verified experimentally by using more precise magnetic and structural parameters and also theoretically by doing precise band calculation and so on.

4. Summary
We successfully synthesized polycrystalline samples of new layered compounds Ba$_2$ScO$_3$CoAs and $Ae_2$ScO$_3$CoP ($Ae = $ Sr or Ba). We found that the Weiss temperatures of these compounds are ranging from about -40 to 60 K, indicating that these compounds are located in a narrow region around quantum critical point of itinerant electronic ferromagnetism. We proposed relationships between strength of magnetism and local structural parameters.

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