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Structure and Magnetic Properties of Double Perovskites SrCaLnRuO_6 ($Ln = \text{La, Pr, Nd}$)

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Abstract

Double perovskite compounds SrCaLnRuO_6 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) were prepared as a single phase. X-ray diffraction measurements show that Ca^{2+} and Ln^{3+} ions are partially disordered at the A site and half of the B site of the perovskite ABO_3 , and that $\text{Ca}^{2+}/\text{Ln}^{3+}$ and Ru^{5+} ions are regularly ordered at the B site. These compounds should be represented by $\text{SrCa}_{1-x}\text{Ln}_x[\text{Ln}_{1-x}\text{Ca}_x]\text{RuO}_6$ and $x = 0.83 - 0.93$ for $\text{Ln} = \text{La}, \text{Pr}, \text{and Nd}$. Magnetic and specific heat measurements show that any of these compounds orders antiferromagnetically at $10 - 12 \text{ K}$, which is due to the magnetic interactions between Ru^{5+} ions. The analysis of the magnetic entropy change indicates that the ground states of Ru^{5+} and Ln^{3+} ions are both doublet.

1. Introduction

The perovskite-type oxides have the general formula ABO_3 , in which A represents a large metal cation and B represents a small one. The perovskite structure can be described as a framework of corner-shared BO_6 octahedra, which contain A cations at 12-coordinate sites. Double perovskite-type oxides have the formula $A_2B'B''O_6$, in which the primes indicate the different ions in different oxidation states, and B' and B'' cations are regularly ordered, i.e., 1:1 arrangement of B' and B'' ions has been observed over the six-coordinate B sites [1]. Since the B cations generally determine the physical properties of perovskites, different kinds of B' and B'' ion should show a variety of the physical properties of double perovskite oxides.

The preparation, crystal structures and magnetic properties of double perovskite oxides containing Ru ion, A_2LnRuO_6 (A = alkali-earth metals), where Ln represents a rare earth ion, have been studied [2-14]. The electronic structure of Ru^{5+} is $[Kr]4d^3$ ([Kr]: krypton electronic core), which means that it has the largest spin ($S = 3/2$). Such highly oxidized cations from the second or third transition series sometimes show quite unusual magnetic behavior. Any of the double perovskites Ba_2LnRuO_6 (Ln = La ~ Lu) [2, 4, 5, 9-12] and Sr_2LnRuO_6 (Eu ~ Lu) [3, 4, 6-8, 12-14] showed an antiferromagnetic transition at low temperatures, and the transition temperature is higher than that for the compounds in which the magnetic ion at the B site is Ru^{5+} ion only. Among them, the transition temperature for Ba_2PrRuO_6 was astonishingly as high as

117 K [10], and $\text{Ba}_2\text{NdRuO}_6$ transformed to the antiferromagnetic state at 57 K [9].

In the case of $\text{Ca}_2\text{LnRuO}_6$, its crystal structure is different from that of $\text{Ba}_2\text{LnRuO}_6$ and $\text{Sr}_2\text{LnRuO}_6$ compounds in which both the rare earth ion and the ruthenium ion occupy B sites [2, 4, 6]. For $\text{Ca}_2\text{LnRuO}_6$, smaller Ln ions should occupy the B site of the perovskite ABO_3 , while larger Ln ions may replace the Ca ions of the A site. Previously, we prepared a series of $\text{Ca}_2\text{LnRuO}_6$ compounds (Ln = Y, La–Lu) and studied systematically their crystal structures [15, 16]. The X-ray diffraction measurements showed that for larger Ln ions Ca^{2+} and Ln^{3+} ions were partially disordered at the A site and half of the B site of the perovskite ABO_3 , and that $\text{Ca}^{2+}/\text{Ln}^{3+}$ and Ru^{5+} ions located at the B site were regularly ordered. Therefore, these compounds should be represented by $\text{Ca}_{2-x}\text{Ln}_x[\text{Ln}_{1-x}\text{Ca}_x]\text{RuO}_6$ [16]. The ratio of the Ln^{3+} ion located at the B site varied with its ionic radius. In the $\text{Ca}_2\text{LnRuO}_6$, the small size of the A site cation results in the large distortion of the perovskite from the cubic symmetry. As a result, the magnetic transition temperatures of $\text{Ca}_2\text{LnRuO}_6$ were much lower than those of the corresponding $\text{Ba}_2\text{LnRuO}_6$ and $\text{Sr}_2\text{LnRuO}_6$, for example 10 K ($\text{Ca}_2\text{PrRuO}_6$) and 11.5 K ($\text{Ca}_2\text{NdRuO}_6$) [15].

We focused our attention on the high antiferromagnetic transition temperatures for $\text{Ba}_2\text{PrRuO}_6$ and $\text{Ba}_2\text{NdRuO}_6$ [9, 10]. The corresponding strontium compounds $\text{Sr}_2\text{PrRuO}_6$ and $\text{Sr}_2\text{NdRuO}_6$ were not prepared [7]. Although $\text{Ca}_2\text{PrRuO}_6$ and $\text{Ca}_2\text{NdRuO}_6$ compounds were

formed, they were actually $\text{CaLn}[\text{CaRu}]\text{O}_6$, i.e., the Pr and Nd ions are located not at the B site, but at the A site [16].

In this study, we tried to prepare $\text{SrCa}[\text{LnRu}]\text{O}_6$ type compounds. In such compounds, since the larger Sr ion is situated at the A-site, the distortion of these double perovskites from the cubic symmetry should be smaller than that for the $\text{Ca}_2\text{LnRuO}_6$ (actually $\text{CaLn}[\text{CaRu}]\text{O}_6$). If the Pr and Nd ions were situated at the B site of the perovskite ABO_3 , i.e., the $\text{SrCa}[\text{PrRu}]\text{O}_6$ and $\text{SrCa}[\text{NdRu}]\text{O}_6$ were formed, the effect of the A site cations on the magnetic properties of Pr (Nd) and Ru ions will be elucidated by comparing the magnetic properties of SrCaLnRuO_6 with those of $\text{Ba}_2\text{LnRuO}_6$. We performed X-ray diffraction measurements to determine their crystal structures, and measured their magnetic susceptibility and specific heat down to 1.8 K.

2. Experimental

Polycrystalline samples of SrCaLnRuO_6 were prepared by firing the appropriate amounts of CaCO_3 , SrCO_3 , Ln_2O_3 ($\text{Ln} = \text{La}, \text{Nd-Gd}, \text{Dy-Lu}$) or Pr_6O_{11} , and RuO_2 , at 1373–1473K for 24 hr with frequent grindings and pelletings. X-ray powder diffraction measurements were performed on a Rigaku RINT 2100 diffractometer. The structure and lattice parameters were refined with a Rietveld program RIETAN 2000 [17]. Magnetic susceptibility measurements were performed under both the zero-field-cooled (ZFC) and field-cooled (FC) conditions with a

SQUID magnetometer (Quantum Design MPMS model). The former was measured on heating the samples to 300 K after zero-field cooling to 1.8 K. The applied magnetic field was 0.1 T. The latter was measured on cooling the samples from 300 to 1.8 K at 0.1 T. The specific heat measurements were carried out using a relaxation technique supplied by the commercial heat capacity measurement system (Quantum Design, Model PPMS). The sample in the form of a pellet (~ 10 mg) was mounted on an alumina plate with apiezon for better thermal contact. The specific heat and magnetic susceptibility were measured in the temperature range from 1.8 to 300 K.

3. Results and discussion

3.1. Crystal structure

Measurements of the X-ray diffraction patterns show that Ln = La, Pr, and Nd compounds crystallize as the perovskite phase. For Ln = Sm, Eu, and Gd, Ru-rich perovskite-phases $\text{Sr}_3\text{CaRu}_2\text{O}_9$ were formed [18], in which Ln ions are solid-solved and a small amount of the impurity phase was also observed. For smaller Ln ions, the desired compounds were not obtained. The stable Ln_2O_3 did not react well with the other starting materials.

Figure 1 shows the X-ray diffraction profile for SrCaLaRuO_6 . All the powder X-ray diffraction patterns for the compounds prepared as a monoclinic single phase were indexed with

the space group $P2_1/n$. The total intensity for (0 0 2) and (1 1 0) appeared at $2\theta \sim 22^\circ$ is significantly small, compared with the compounds in which both Ln and Ru ions are occupied completely at the B site. This fact reflects that Ca^{2+} ions partially occupy the B sites. The present case is the same with that for $\text{Ca}_2\text{LnRuO}_6$ (Ln = La ~ Gd) [16]. In addition, the (0 1 1) and (1 0 1) peaks observed at $2\theta \sim 19^\circ$ indicate the structural cation ordering between B' and B'' sites. In order to clarify the exact cation distribution in this SrCaLnRuO_6 series, the X-ray diffraction data were analyzed by the Rietveld method with using RIETAN 2000 program [17]. The results of this analysis show that Ca^{2+} ions partially occupy the B site, i.e. the SrCaLnRuO_6 is represented as $\text{SrCa}_{1-x}\text{Ln}_x[\text{Ln}_{1-x}\text{Ca}_x]\text{RuO}_6$. In addition, they show that the B' and B'' ions are regularly ordered in the NaCl-type. The B'' site is occupied by only the Ru^{5+} ion and the B' site is randomly occupied by Ca^{2+} and Ln^{3+} ions. Figure 2 shows the schematic crystal structure for SrCaLnRuO_6 , and the structural parameters determined for SrCaNdRuO_6 are listed in Table 1.

Figure 3 shows the variation of the occupancy x (the ratio of the Ca^{2+} ions at the B' site) with the Ln^{3+} ionic radius. It is revealed that the x value depends on the Ln^{3+} radius. For the compounds with Ln = La, the Ca^{2+} ion mainly occupies the B' site ($x \sim 0.93$). From Ln = Pr to Nd, the ratio of the Ca^{2+} ion at the B' site is gradually decreased. The cation disorder of the B' and A sites found in this SrCaLnRuO_6 series is also due to the fact that the ionic radius of Ca^{2+} (1.00 Å) is near to that of Ln^{3+} . In the same figure, the x values for $\text{Ca}_2\text{LnRuO}_6$ compounds

were also shown. It is clear that the x values for SrCaLnRuO_6 are smaller than those for $\text{Ca}_2\text{LnRuO}_6$, which is due to the fact that larger Sr ions stably occupy the A site and increase the average ionic radius of the A-site cations.

The lattice parameters and reliability factors for SrCaLnRuO_6 ($\text{Ln} = \text{La, Pr, Nd}$) are listed in Table 2. The lattice parameters a , b and c tend to decrease with decreasing the Ln^{3+} ionic radius. The values of β increase with decreasing the Ln^{3+} ionic radius, indicating that these double perovskites (actually $[\text{SrLn}][\text{CaRu}]\text{O}_6$) distort greatly from the cubic symmetry, because of its smaller difference in the ionic radius between A-site and B-site cations.

3.2. Magnetic properties of SrCaLaRuO_6

The magnetic susceptibilities of SrCaLaRuO_6 are plotted as a function of temperature in Fig. 4. It is found that an antiferromagnetic transition occurs at $T_N = 10$ K. The magnetic properties of SrCaLaRuO_6 are due to the Ru^{5+} ion because La^{3+} ion is diamagnetic. Its reciprocal magnetic susceptibility versus temperature curve (the inset of Fig. 4) was fitted with the Curie–Weiss law in the temperature range between 100 and 300 K. The effective magnetic moment and Weiss constant were obtained to be $3.89 \mu_B$ and -134 K, respectively. The effective magnetic moment is close to the spin-only value for the Ru^{5+} ion with $S = 3/2$ ($3.87 \mu_B$). The large negative Weiss constant indicates the antiferromagnetic interaction between Ru^{5+} ions.

The large divergence between the ZFC and FC susceptibilities has been found. This result indicates that SrCaLaRuO_6 is not an ideal antiferromagnet. This should be due to the contribution of the weak ferromagnetic component to the magnetic properties. In the case of the compound with low crystal symmetry such as monoclinic symmetry, the Dzyaloshinsky-Moriya (D-M) interaction can exist between the ordered moments, which results in the existence of a weak ferromagnetic component in its magnetic susceptibilities.

Figure 5 (a) shows the temperature dependence of the specific heat C_p for SrCaLaRuO_6 . The specific heat data also show a λ -type anomaly at the same temperature, 10 K. To calculate the magnetic contribution to the specific heat, we have to subtract the contribution of lattice specific heat from the total specific heat. They were estimated by using a polynomial function of the temperature, $f(T) = aT^3 + bT^5 + cT^7$ [19], in which the constants a , b and c were determined by fitting this function to the observed specific heat data above 30 K. Figure 5 (b) shows the temperature dependence of the magnetic specific heat divided by temperature (C_{mag}/T). From the temperature dependence of the magnetic specific heat, the magnetic entropy change of SrCaLaRuO_6 is calculated by the relation $S_{\text{mag}} = \int (C_{\text{mag}}/T) dT$. It is also shown in Fig. 5 (b). The magnetic entropy change due to the antiferromagnetic ordering of Ru^{5+} ions in the SrCaLaRuO_6 is about $4.8 \text{ J mol}^{-1} \text{ K}^{-1}$.

In an octahedral crystal field environment, the ground state of the Ru^{5+} ion ($4d^3$, the state

$^4F_{3/2}$) is the four-fold degenerate state. The magnetic entropy change of Ru^{5+} is calculated to be $R \ln (2S+1) = 11.5 \text{ J mol}^{-1} \text{ K}^{-1}$, where R and S are the molar gas constant and the spin quantum number, respectively. In the case of lower symmetry, this state splits into two Kramers doublet states. For such a case, the magnetic entropy change is expected to be $R \ln 2 = 5.76 \text{ J mol}^{-1} \text{ K}^{-1}$. The result of the magnetic entropy change indicates that the degeneracy of the ground state for the Ru^{5+} ion in SrCaLaRuO_6 should be doublet. These results for SrCaLaRuO_6 are quite similar to those for $\text{Ca}_2\text{LaRuO}_6$ (more precisely, $[\text{CaLa}][\text{CaRu}]\text{O}_6$), which means that the difference in the crystal structure between SrCaLaRuO_6 and $\text{Ca}_2\text{LaRuO}_6$ is negligible in their magnetic properties. This result is plausible, because the magnetic ion at the B-site is only the Ru^{5+} ion for both the SrCaLaRuO_6 and $\text{Ca}_2\text{LaRuO}_6$.

3.3. Magnetic properties of SrCaPrRuO_6

The magnetic susceptibility for SrCaPrRuO_6 is plotted as a function of temperature in Fig. 6. This compound shows an antiferromagnetic transition at 12 K. Compared with the antiferromagnetic transition temperature for SrCaLaRuO_6 , the transition temperature for SrCaPrRuO_6 increased, which may reflect the contribution of paramagnetic Pr^{3+} to the antiferromagnetic interaction. Another anomaly in the ZFC magnetic susceptibility was found at 5 K.

In the inset of Fig. 6, the reciprocal susceptibility was plotted against temperature. The fitting of the Curie-Weiss law gives $5.07 \mu_B$ and -69 K , respectively. Since the theoretical magnetic moments of Ru^{5+} and Pr^{3+} are 3.87 and $3.58 \mu_B$, respectively, the expected effective magnetic moment ($5.27\mu_B$) is estimated from the relation $\mu_{\text{eff}} = \sqrt{\mu_{\text{Ru}^{5+}}^2 + \mu_{\text{Pr}^{3+}}^2}$. The value obtained from the experiment is a little lower than the calculated value. This result may suggest that the magnetic ions in this compound are affected by the crystal field to some extent. The negative Weiss constant indicates that the predominant magnetic interaction in SrCaPrRuO_6 is antiferromagnetic.

3.4. Magnetic properties of SrCaNdRuO_6

Figure 7 shows the temperature dependence of the magnetic susceptibility for SrCaNdRuO_6 . This compound also shows an antiferromagnetic transition at 12 K . Below this temperature, the ZFC and FC susceptibilities diverged. Another anomaly in the ZFC susceptibility is observed at ca. 2 K . These results are quite similar to those for SrCaPrRuO_6 . The magnetic susceptibility obeys the Curie–Weiss law in the temperature range between 80 and 300 K . The effective magnetic moment and Weiss constant were obtained to be $5.15 \mu_B$ and -76 K , respectively. Since the theoretical magnetic moments of Ru^{5+} and Nd^{3+} are 3.87 and $3.62 \mu_B$, respectively, the effective magnetic moment for SrCaNdRuO_6 is calculated to be $5.30\mu_B$.

The experimental value is close to the moment estimated from this calculation.

In order to clarify the two magnetic anomalies at low temperatures, specific heat measurements were performed down to 1.8 K. The temperature dependence of the specific heat for SrCaNdRuO_6 is shown in Fig. 8 (a). Figure 8 (b) shows the dependence of the magnetic specific heat divided by temperature (C_{mag}/T) below 40 K. The magnetic specific heat (C_{mag}) is obtained from the specific heat data in the same way as is the case for SrCaLaRuO_6 . It is found that both the C_p vs. T and C_{mag}/T vs. T curves show two anomalies at 12 and 5 K. The anomaly at 12 K seems to correspond to the antiferromagnetic behavior found in the magnetic susceptibility measurements. Comparing the fact that the SrCaLaRuO_6 shows an antiferromagnetic transition at 10 K, the magnetic behavior observed for SrCaNdRuO_6 at 12 K is also due to magnetic interactions between Ru^{5+} ions. The higher magnetic transition temperature for SrCaNdRuO_6 than that for SrCaLaRuO_6 should be due to the contribution of paramagnetic Nd^{3+} ion to this antiferromagnetic interaction.

For the specific heat anomaly at 5 K, the corresponding anomaly is not observed in the magnetic susceptibility measurements. As shown in Fig. 7, both the ZFC and FC susceptibilities still increased with decreasing temperature, and below 2.0 K, the ZFC susceptibility began to decrease with decreasing temperature. Namely, the Nd^{3+} ion is still in the paramagnetic state at 5 K. We consider that the observed anomaly in the specific heat is due to not the magnetic

ordering, but the Schottky-type anomaly of the Nd^{3+} ion, as is the case for $\text{Ca}_2\text{NdRuO}_6$ [15].

Figure 8 (b) also shows the temperature dependence of the magnetic entropy change for SrCaNdRuO_6 . The total magnetic entropy change due to these two anomalies is approximately $8.3 \text{ J mol}^{-1} \text{ K}^{-1}$. Owing to the difficulty in dividing the magnetic entropy data into two anomalies, we cannot determine the individual ΔS_{mag} values. Since the magnetic entropy change due to the antiferromagnetic ordering of Ru^{5+} ions in the SrCaLaRuO_6 is experimentally obtained to be $4.8 \text{ J mol}^{-1} \text{ K}^{-1}$, the rest of the magnetic entropy change is estimated to be $3.5 \text{ J mol}^{-1} \text{ K}^{-1}$. The ground multiplet $^4\text{I}_{9/2}$ of Nd^{3+} ion splits into five Kramers' doublets in a crystal field with low symmetry. The ground doublet is selectively populated at low temperatures, and the magnetic entropy is expected to be $R \ln 2 = 5.76 \text{ J mol}^{-1} \text{ K}^{-1}$. Although the estimated value ($3.5 \text{ J mol}^{-1} \text{ K}^{-1}$) is smaller than the value $5.76 \text{ J mol}^{-1} \text{ K}^{-1}$, this result indicates that the ground state of the Nd^{3+} ion should be a Kramers' doublet. The reason for the smaller magnetic entropy change obtained experimentally is that we do not include the magnetic entropy change at very low temperatures due to still offset of the magnetic ordering of Nd^{3+} ions.

4. Summary

X-ray diffraction measurements on SrCaLnRuO_6 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) show that Ca^{2+} and Ln^{3+} ions are partially disordered at the A site and half of the B site of the perovskite ABO_3 , and

that $\text{Ca}^{2+}/\text{Ln}^{3+}$ and Ru^{5+} ions are regularly ordered at the B site. These compounds order antiferromagnetically at 10 – 12 K, due to the magnetic interactions between Ru^{5+} ions.

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FIGURE CAPTIONS

Fig.1 Powder x-ray diffraction profiles for SrCaLaRuO_6 . The calculated and observed profiles are shown on the top solid line and cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities.

Fig.2 The schematic crystal structure for SrCaLnRuO_6 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$).

Fig.3 The ratio of the Ca^{2+} ions at the B' site of the double perovskite $\text{A}_2\text{B}'\text{RuO}_6$. For comparison, the data for $\text{Ca}_2\text{LnRuO}_6$ were also shown.

Fig.4 Temperature dependence of the magnetic susceptibility for SrCaLaRuO_6 . The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the Curie-Weiss fitting.

Fig.5 (a) Temperature dependence of the specific heat C_p for SrCaLaRuO_6 . The inset shows the detailed temperature dependence below 40 K. The solid line is the calculation results for the lattice specific heat (see text). (b) Temperature dependences of the magnetic specific heat divided by temperature C_{mag}/T and the magnetic entropy change S_{mag} for SrCaLaRuO_6 below 40 K.

Fig.6 Temperature dependence of the magnetic susceptibility for SrCaPrRuO_6 . The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the

Curie-Weiss fitting.

Fig.7 Temperature dependence of the magnetic susceptibility for SrCaNdRuO_6 . The inset shows the detailed temperature dependence below 40 K.

Fig.8 (a) Temperature dependence of the specific heat C_p for SrCaNdRuO_6 . The inset shows the detailed temperature dependence below 40 K. The solid line is the calculation results for the lattice specific heat (see text). (b) Temperature dependences of the magnetic specific heat divided by temperature C_{mag}/T and the magnetic entropy change S_{mag} for SrCaNdRuO_6 below 40 K.

Table 1 Atomic positional parameters for SrCaNdRuO₆

Atom	site	occupancy	x	y	z	$B(\text{\AA}^2)^*$
Sr1	4e	0.5	0.5197(5)	0.550(3)	0.253(6)	0.55
Ca1	4e	0.085(4)	0.5197(5)	0.550(3)	0.253 (6)	0.55
La1	4e	0.415(4)	0.5197(5)	0.550(3)	0.253 (6)	0.55
Ru1	2d	1.0	1/2	0	0	0.22
Ca2	2c	0.830(7)	0	1/2	0	0.43
La2	2c	0.170(7)	0	1/2	0	0.43
O1	4e	1.0	0.205(3)	0.229(4)	−0.023 (4)	1.08
O2	4e	1.0	0.318(3)	0.718(4)	−0.070(3)	1.08
O3	4e	1.0	0.384(3)	−0.036(3)	0.211 (3)	1.08

* The values for B are fixed to the values for Ca₂LaRuO₆ [16].

Table 2 Lattice parameters and reliability factors for SrCaLnRuO₆

<i>Ln</i>	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	β/°	<i>V</i> / Å ³	<i>R</i> _{wp} /%	<i>R</i> _l /%
La	5.7187(3)	5.8498(3)	8.1562(4)	90.241(2)	272.85(2)	11.67	5.43
Pr	5.6714(3)	5.8475(3)	8.1090(5)	90.268(2)	268.92(3)	11.09	3.89
Nd	5.6716(9)	5.8450(9)	8.0979(11)	90.2724(6)	268.45(7)	14.82	3.54

Note. Definition of reliability factors *R*_{wp} and *R*_l are given as follows:

$$R_{\text{wp}} = \left[\sum w \left(|F(o)| - |F(c)| \right)^2 / \sum w |F(o)|^2 \right]^{\frac{1}{2}} \text{ and } R_l = \sum |I_k(o) - I_k(c)| / \sum I_k(o).$$