

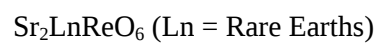


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Magnetic Interactions in Rhenium-containing Rare Earth Double Perovskites



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Abstract

The perovskite-type compounds containing both rare earth and rhenium $\text{Sr}_2\text{LnReO}_6$ ($\text{Ln} = \text{Y, Tb-Lu}$) have been prepared. Powder X-ray diffraction measurements and Rietveld analysis show that Ln^{3+} and Re^{5+} ions are structurally ordered at the B site of the perovskite SrBO_3 . Magnetic anomalies are found in their magnetic susceptibility and specific heat measurements at 2.6-20 K for $\text{Ln} = \text{Y, Tb, Dy, Yb, Lu}$ compounds. They are due to magnetic interactions between Re^{5+} ions. The results of the magnetic hysteresis and remnant magnetization measurements for Sr_2YReO_6 and $\text{Sr}_2\text{LuReO}_6$ indicate that the antiferromagnetic interactions between Re^{5+} ions below transition temperatures have a weak ferromagnetic component. The analysis of the magnetic specific heat data for $\text{Sr}_2\text{YbReO}_6$ shows that both the Yb^{3+} and Re^{5+} ions magnetically order at 20 K. For the case of $\text{Sr}_2\text{DyReO}_6$, magnetic ordering of the Re^{5+} moments occurs at 93K, and with decreasing temperature, the moments of Dy^{3+} ferromagnetically order at 5 K from the measurements of magnetic susceptibility and specific heat.

1. Introduction

The perovskite-type oxides have the general formula ABO_3 , in which A represents a large electropositive cation and B represents a small transition metal ions. This type of oxides are known to show interesting physical properties, such as ferroelectricity, electrical conductivity, superconductivity, and magnetoresistance, due to their diversity of crystal structure and electronic properties. We have been focusing our attention on the rare earth containing perovskite-type oxides. The rare earth ion is relatively large and tends to adopt a high coordination number. Therefore, the rare earth ion usually sits at the A site of the perovskite-type oxides ABO_3 . Not the A site ions but the B site ions normally determine the physical properties of the perovskites [1]. The perovskites have the flexibility of chemical composition and the possibility of combination of many kinds of ions. By selecting large alkaline earth elements such as Ba and Sr at the A site atoms, one finds that the rare earths occupy the 6-coordinate B sites [2-8]. 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 the cations at the B-sites, B' and B'' , are regularly ordered, i.e., 1:1 arrangement of B' and B'' ions has been observed over the six-coordinate B sites. Different kinds of B' and B'' ion should show a variety of the physical properties of double perovskite oxides. Since highly oxidized cations from the second or third transition series sometimes show quite unusual magnetic behavior, it attracts great attention to study the preparation and magnetic properties of double perovskite oxides containing both rare earth and such transition metals, A_2LnMO_6 ($A = Sr, Ba$; $Ln = \text{rare earths}$; $M = Ru, Os, Ir, Re$) [9-27].

Among them, magnetic properties of pentavalent ruthenium-containing perovskite oxides have aroused a great deal of interest, because the Ru^{5+} ion has the largest possible spin ($S = 3/2$). Double perovskite-type oxides A_2LnRuO_6 have been prepared for $A = Sr, Ba$, and the Ln and Ru ions are arranged in an alternating manner (NaCl-type) at the B-site position of the perovskite.

All the $A_2\text{LnRuO}_6$ compounds show an antiferromagnetic transitions at low temperatures (for $A = \text{Ba}$ compounds, $T_N = 30\text{-}117\text{ K}$ and for $A = \text{Sr}$, $T_N = 25\text{-}44\text{ K}$) [13, 17, 18, 20]. For $A = \text{Ba}$ and Sr compounds, the Néel temperatures of the $A_2\text{LnRuO}_6$ ($\text{Ln} \neq \text{Y, La, Eu}$) compounds are higher than those for $\text{Ln} = \text{Y, La, Eu}$ compounds. This fact indicates that the magnetic transition is mainly due to the magnetic cooperative phenomena between Ru^{5+} ($4d^3$) and Ln^{3+} ($4f^n$) ions. When the A-site cation is changed from Ba to Sr to Ca, the Néel temperature for $A_2\text{LnRuO}_6$ compounds decreases considerably. With decreasing the size of A-site cation, the alignment of Ln-O-Ru deviates from 180° , which results in weakening the magnetic super-exchange interaction between f and d electrons via oxygen ions [28, 29].

For iridium-containing double perovskites, $\text{Ba}_2\text{CeIrO}_6$, $\text{Ba}_2\text{PrIrO}_6$, $\text{Sr}_2\text{CeIrO}_6$, and $\text{Sr}_2\text{TbIrO}_6$ show antiferromagnetic transitions at 17, 71, 21, and 51 K, respectively [15, 19]. In these compounds, the Ce, Pr, Tb ions are not in the trivalent state, but are in the tetravalent state and the Ir ions are also tetravalent. The other compounds ($A_2\text{Ln}^{3+}\text{Ir}^{5+}\text{O}_6$) are paramagnetic down to 1.8 K [14].

Now, our attention has been focused on double perovskite oxides containing rhenium, $A_2\text{LnReO}_6$. In these compounds, the oxidation state of rhenium ions is expected to be in the pentavalent state. Their electronic configurations are $[\text{Xe}]5d^2$ ([Xe]: xenon electronic core), which is different from those for the above transition elements. Therefore, the magnetic properties of $A_2\text{LnReO}_6$ are expected to be quite different from those of other double perovskite oxides $A_2\text{LnMO}_6$, because in general, the effect of M^{5+} ions on the magnetic properties of $A_2\text{LnMO}_6$ is larger than that of Ln^{3+} ions. Previous studies on $\text{Ba}_2\text{LnReO}_6$ show that magnetic anomalies have been observed in their magnetic susceptibility and specific heat measurements, suggesting an antiferromagnetic ordering of Re^{5+} ions for $\text{Ba}_2\text{LnReO}_6$ ($\text{Ln} = \text{Y, Nd, Sm, Gd-Ho, Lu}$) at 27-100 K and that of Tb^{3+} ions for $\text{Ba}_2\text{TbReO}_6$ at 2.4 K [21]. Recently, magnetic properties of Ba_2YReO_6 have been discussed from the point of geometry frustrated structure [30].

In this study, we have paid our attention to the structural chemistry and magnetic properties of Sr-containing double perovskites $\text{Sr}_2\text{LnReO}_6$. Due to the smaller ionic radius of Sr^{2+} compared with that of Ba^{2+} , the alignment of Ln-O-Re is expected to deviate from linearity for the case of $\text{Sr}_2\text{LnReO}_6$ compounds. Therefore, comparing the magnetic properties of $\text{Sr}_2\text{LnReO}_6$ with those of $\text{Ba}_2\text{LnReO}_6$ will elucidate the effect of the alignment of Ln-O-Re on the magnetic interaction between Ln^{3+} and Re^{5+} ions.

From the standpoint of tolerance factor for the perovskite structure, the number of the double perovskite oxides containing both rare earth and rhenium ions at the B-site of the perovskite $\text{Sr}_2\text{LnReO}_6$ is expected to be limited. Therefore, it is important to systematically study the formation of the double perovskite $\text{Sr}_2\text{LnReO}_6$ and their crystal structures.

2. Experimental

2.1. Sample preparation

Polycrystalline samples of Re-bearing double perovskites $\text{Sr}_2\text{LnReO}_6$ were prepared by the standard solid-state reaction. Strontium peroxide SrO_2 , rare earth sesqui-oxides Ln_2O_3 (Ln = Y, La, Nd, Sm-Gd, Dy-Lu), rhenium metal (Re) and rhenium dioxide ReO_2 were used as starting materials. For the case of Ce, Pr, and Tb, CeO_2 , Pr_6O_{11} , and Tb_4O_7 were used, respectively. In order to remove any moisture, La_2O_3 and Nd_2O_3 were preheated in air at 1,173 K. The stoichiometric mixtures were well ground in an agate mortar in an inert dry box. The mixtures were pressed into pellets and enwrapped with platinum foils, and they were sealed in evacuated silica tubes. The mixtures were annealed at 1,073-1,373 K for 6-24 h with several intervening re-grinding and re-pelletizing.

2.2. X-ray diffraction analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with $\text{Cu-K}\alpha$ radiation equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of $10^\circ \leq 2\theta \leq 120^\circ$ at a 2θ step-size of 0.02° . The X-ray

diffraction data were analyzed by the Rietveld technique, using the program RIETAN-FP [31] and the crystal structure was drawn by VESTA program [32].

2.3. Magnetic susceptibility measurements

The temperature-dependence of the magnetic susceptibility was measured in an applied field of 0.1 T over the temperature range of $1.8 \text{ K} \leq T \leq 400 \text{ K}$, using a SQUID magnetometer (Quantum Design, MPMS5S). The susceptibility measurements were performed under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. The former was measured upon heating the sample to 400 K under the applied magnetic field of 0.1 T after zero-field cooling to 1.8 K. The latter was measured upon cooling the sample from 400 to 1.8 K in the applied field of 0.1 T.

2.4. Specific heat measurements

Specific heat measurements were performed using a relaxation technique by a commercial heat capacity measuring system (Quantum Design, PPMS) in the temperature range of 1.8-400 K. The sintered sample in the form of a pellet was mounted on a thin alumina plate with Apiezon for better thermal contact.

3. Results and Discussion

3.1. Crystal structure

The results of X-ray diffraction measurements show that $\text{Sr}_2\text{LnReO}_6$ ($\text{Ln} = \text{Y}, \text{Tb-Lu}$) compounds were formed as a single phase with perovskite-type structure. Due to the large ionic radius for $\text{Ln} = \text{La} \sim \text{Gd}$, the perovskite-type compounds were not obtained. The stability of perovskites is generally estimated by the tolerance factor t . For the double perovskite compounds $\text{A}_2\text{B}'\text{B}''\text{O}_6$, this factor is defined by Eq. (1)

$$t = (r_A + r_O) / \sqrt{2}((r_{B'} + r_{B''})/2 + r_O) \quad (1)$$

where r_A , $r_{B'}$, $r_{B''}$, and r_O are radii of the A, B', B'' metal ions and oxygen ions, respectively. For an ideal cubic perovskite structure, the value of t is equal to unity, whereas for structures distorted

from cubic symmetry, the value of t becomes <1 . The tolerance factors for $\text{Sr}_2\text{LnReO}_6$ with $\text{Ln} = \text{La} \sim \text{Gd}$ are calculated to be less than 0.93, which destabilizes the double perovskite-type structure.

Figure 1 shows the X-ray diffraction profile for $\text{Sr}_2\text{LuReO}_6$. The super lattice reflection appears at $2\theta \sim 19^\circ$, indicating that the compound is not single perovskite but double perovskite. The Rietveld analysis for the X-ray diffraction profile shows that the diffraction lines are indexed with the monoclinic structure with space group $P2_1/n$. This space group allows two crystallographically distinct octahedral sites in the double perovskite structure, thus permitting 1:1 ordered arrangement between Ln^{3+} and Re^{5+} ions. The relation between the lattice constants of this unit cell (a, b, c) with primitive perovskite unit cell (a_p) are given by $a \approx \sqrt{2}a_p$, $b \approx \sqrt{2}a_p$, and $c \approx 2a_p$. The atomic positional parameters for $\text{Sr}_2\text{LuReO}_6$ are tabulated in Table 1. Figure 2 shows the crystal structure of $\text{Sr}_2\text{LuReO}_6$. For other $\text{Sr}_2\text{LnReO}_6$ ($\text{Ln} = \text{Y}, \text{Tb-Yb}$) compounds, the unit cell parameters and the reliability factors are listed in Table 2.

Figure 3 shows the variation of lattice parameter for $\text{Sr}_2\text{LnReO}_6$ with the ionic radius of Ln^{3+} . As the ionic radius of Ln^{3+} increases, all the lattice parameters (a, b , and c) increase. The variation is nearly linear, so it is thought that the oxidation state of the rare earth is trivalent and that of rhenium is pentavalent for all the compounds $\text{Sr}_2\text{LnReO}_6$ ($\text{Ln} = \text{Y}, \text{Tb-Lu}$). In the case that some of the rare earth ion is in the tetravalent state, the deviation from the linear relationship between the lattice parameters and the ionic radius of Ln^{3+} has been observed for $\text{Sr}_2\text{LnIrO}_6$ [15] and $\text{Ba}_2\text{LnIrO}_6$ [19]. Figure 3 also shows that the lattice parameter β increases and the differences among a, b , and $c/\sqrt{2}$ spread with an increase of the Ln^{3+} ionic radius. This result indicates that the crystal structures of $\text{Sr}_2\text{LnReO}_6$ are more distorted from the cubic symmetry as the size of the Ln^{3+} ion becomes larger.

Figure 4 shows the variation of average bond lengths Ln-O and Re-O for the $\text{Sr}_2\text{LnReO}_6$ ($\text{Ln} = \text{Y}, \text{Tb-Lu}$). The average Ln-O length increases with the ionic radius of Ln^{3+} while the average Re-O bond length is nearly constant (1.94-1.94 Å). These bond lengths Ln-O and Re-O

are near to the bond lengths $\text{Ln}^{3+}\text{-O}^{2-}$ and $\text{Re}^{5+}\text{-O}^{2-}$ calculated from the Shannon' ionic radii [33]. The bond valence sums (BVS) are calculated from the interatomic distances [34, 35], and they are listed in Table 3. These values also indicate that the Ln and Re ions are in the trivalent and pentavalent, respectively.

3.2. Magnetic properties

The results of the magnetic susceptibility measurements for $\text{Sr}_2\text{LnReO}_6$ (Ln = Y, Tb-Lu) in the temperature range between 1.8 and 400 K are summarized in Table 4. The Curie-Weiss law is valid for the magnetic susceptibilities of $\text{Sr}_2\text{LnReO}_6$ in high temperature ranges (> 100 K). The effective magnetic moments (μ_{eff}) and Weiss constants (θ) of these compounds are also listed in Table 4. Magnetic exchange interaction has been observed for Ln = Y, Tb, Dy, Yb, and Lu compounds. The negative Weiss constant indicates that the predominant magnetic interactions observed for $\text{Sr}_2\text{LnReO}_6$ compounds are antiferromagnetic.

We will discuss magnetic properties of $\text{Sr}_2\text{LnReO}_6$ (Ln = Y, Tb-Lu) compounds in the followings.

3.2.1. Sr_2YReO_6 , $\text{Sr}_2\text{LuReO}_6$

Figures 5 and 6 depict the magnetic susceptibility vs temperature curves for Sr_2YReO_6 and $\text{Sr}_2\text{LuReO}_6$, respectively in the temperature range between 1.8 and 300 K. An antiferromagnetic behavior has been observed at 6.0 and 12 K, respectively. The ZFC and FC susceptibilities begin to diverge when the temperature is decreased through ca. 40 K, i.e., Sr_2YReO_6 and $\text{Sr}_2\text{LuReO}_6$ are not ideal antiferromagnets. Figures 7 (a) and (b) show the magnetic hysteresis curves measured at 5.0 K for Sr_2YReO_6 and $\text{Sr}_2\text{LuReO}_6$, respectively. Small magnetic hysteresis has been observed for both the compounds, and the remnant magnetization is estimated to be $0.003 \mu_B$ at 5 K. The remnant magnetization completely disappears when the temperature is increased above 40 K. That is, the antiferromagnetic interactions at low temperatures have a weak ferromagnetic

component. In these $\text{Sr}_2\text{LnReO}_6$ compounds with low crystal symmetry, the Dzyaloshinsky-Moriya (D-M) interaction can exist between the magnetically ordered elements, which results in the existence of a weak ferromagnetic moment in their susceptibilities. On the other hand, Ba_2YReO_6 and $\text{Ba}_2\text{LuReO}_6$ show no divergence between the ZFC and FC susceptibilities in the whole temperature range, because their crystal symmetry is cubic [21].

The inset figures of Figs. 5 and 6 show the temperature dependence of the reciprocal ZFC magnetic susceptibility for Sr_2YReO_6 and $\text{Sr}_2\text{LuReO}_6$, respectively. The Curie-Weiss law is valid in the temperature range between 90 and 300 K. The effective magnetic moments of Sr_2YReO_6 and $\text{Sr}_2\text{LuReO}_6$ are 2.27 and 2.68 μ_B , respectively. In these compounds, only the Re^{5+} ions are paramagnetic. Since the spin-orbit coupling cannot be ignored for the $5d^2$ ions, the expected moment of Re^{5+} should be lower than the spin-only value of 2.83 μ_B . Comparable lower effective magnetic moment of Re^{5+} has been observed in some Re-containing compounds [21, 36-39].

Figure 8 depicts the temperature dependence of the specific heat (C_p) for $\text{Sr}_2\text{LuReO}_6$ in the temperature range between 1.8 and 300 K, and the inset shows the specific heat divided by temperature (C_p/T) in low temperature region. A specific heat anomaly has been found at the same temperature at which the magnetic susceptibility shows the antiferromagnetic transition.

In this $\text{Sr}_2\text{LuReO}_6$ compound, only the Re^{5+} ions are magnetic. The magnetic entropy change (S_{mag}) associated with the magnetic ordering of Re^{5+} moments is estimated from the specific heat data. To evaluate the magnetic contribution to the specific heat (C_{mag}), we have to subtract the contribution of lattice specific heat (C_{lat}) from the total specific heat ($C_{\text{mag}} = C_p - C_{\text{lat}}$). The lattice specific heat was estimated by using the specific heat data for diamagnetic $\text{Sr}_2\text{LuTaO}_6$. From the temperature dependence of the magnetic specific heat, the magnetic entropy change (S_{mag}) for $\text{Sr}_2\text{LuReO}_6$ is calculated by integrating the magnetic specific heat divided by temperature (C_{mag}/T), i.e., $S_{\text{mag}} = \int (C_{\text{mag}}/T) dT$. The temperature dependence of S_{mag} is shown in Fig. 9. The obtained S_{mag} of $\text{Sr}_2\text{LuReO}_6$ at 40 K is 2.2 J/(mol K). In an octahedral

crystal field environment, the ground state of the Re^{5+} ion ($5d^2$, the state 3F_2) degenerates to five-fold ($\Gamma_3 + \Gamma_5$) [40]. In the case of lower symmetry, the degeneracy is lifted and the ground state becomes doublet (Γ_3). Thus the magnetic entropy change is calculated to be $R\ln 2 = 5.76$ J/(mol K). The magnetic entropy change S_{mag} obtained experimentally is lower than that calculated. This result may indicate that the magnetic ordering of Re^{5+} moments begins to occur at a higher temperature than the Néel temperature. Another reason for lower magnetic entropy change is due to inaccurate estimation for the lattice specific heat of $\text{Sr}_2\text{LuReO}_6$.

The results of the specific heat measurements for Sr_2YReO_6 are quite similar to those for $\text{Sr}_2\text{LuReO}_6$. A specific heat anomaly has been found at the same temperature at which the magnetic susceptibility shows the antiferromagnetic transition (Supplementary figure S1).

3.2.2. $\text{Sr}_2\text{YbReO}_6$

Figure 10 depicts the magnetic susceptibility vs. temperature curve for $\text{Sr}_2\text{YbReO}_6$. ZFC and FC susceptibilities begin to diverge when the temperature is decreased through 50 K. Magnetic anomaly has been observed in the ZFC susceptibility vs. temperature curve at 20 K.

The inset of Fig. 10 shows the temperature dependence of the reciprocal ZFC magnetic susceptibility for $\text{Sr}_2\text{YbReO}_6$. The Curie-Weiss law is valid in the temperature range between 90 and 300 K. The effective magnetic moment and Weiss constants are obtained to be $4.99 \mu_B$ and -131 K, respectively. In this compound, not only the Re^{5+} ions but also the Yb^{3+} ions are magnetic. When we assume that the magnetic moment of the Re^{5+} ion is $2.27 \mu_B$ (which is the moment of Sr_2YReO_6), the effective magnetic moment of $\text{Sr}_2\text{YbReO}_6$ is calculated to be $5.08 \mu_B$ from the equation $\mu_{\text{calc}} = \sqrt{\mu_{\text{Re}^{5+}}^2 + \mu_{\text{Yb}^{3+}}^2}$. Effective magnetic moment obtained experimentally for $\text{Sr}_2\text{YbReO}_6$ (μ_{eff}) agrees with this calculated moment (μ_{calc}).

Figure 11 shows the temperature dependence of the specific heat (C_p) for $\text{Sr}_2\text{YbReO}_6$. A clear λ -type specific heat anomaly has been observed at 20 K, which corresponds to the magnetic

anomaly observed by the magnetic susceptibility measurements. The magnetic specific heat (C_{mag}) of $\text{Sr}_2\text{YbReO}_6$ was estimated by subtracting the contribution of the lattice specific heat (C_{lat}) from the total specific heat (C_p). The magnetic entropy change (S_{mag}) associated with the magnetic ordering of $\text{Sr}_2\text{YbReO}_6$ is calculated by integrating the magnetic specific heat divided by temperature (C_{mag}/T), in the same way as is the case for $\text{Sr}_2\text{LuReO}_6$. The temperature dependence of the S_{mag} for $\text{Sr}_2\text{YbReO}_6$ is shown in Fig. 12. The obtained S_{mag} of $\text{Sr}_2\text{YbReO}_6$ at 40 K is 6.0 J/(mol K). In this compound, both Re^{5+} and Yb^{3+} ions are magnetic and contribute to the magnetic ordering. From the specific heat measurements for $\text{Sr}_2\text{LuReO}_6$, the magnetic entropy change S_{mag} is experimentally obtained to be 2.2 J/(mol K). Therefore, the entropy change for the magnetic ordering of Yb^{3+} ions is estimated to be 3.8 J/(mol K). In an octahedral crystal field environment, the ground state of the Yb^{3+} ion is doublet Γ_6 [41]. Thus the magnetic entropy change for the magnetic ordering of Yb^{3+} ions is calculated to be $R\ln 2 = 5.76$ J/(mol K). Although the magnetic entropy change S_{mag} obtained experimentally is lower than that calculated, we believe that both the Re^{5+} and Yb^{3+} ions magnetically order at the same temperature from considering the results of the temperature dependence of the magnetic susceptibility and specific heat.

3.2.3. $\text{Sr}_2\text{LnReO}_6$ (Ln = Ho, Er, Tm)

The results of the magnetic susceptibility measurements for Ln = Ho, Er, Tm compounds show that there exists no magnetic ordering down to 1.8 K. No divergence between ZFC and FC susceptibilities has been observed. No specific heat anomaly are found down to 1.8 K. Figure 13 shows the temperature dependence of the reciprocal magnetic susceptibilities for $\text{Sr}_2\text{LnReO}_6$ (Ln = Ho, Er, and Tm). The Curie-Weiss law is valid for the magnetic susceptibilities above 100 K. In these compounds, not only the Re^{5+} ions but also the Ln^{3+} ions are magnetic. In the same way as the case for $\text{Sr}_2\text{YbReO}_6$, the effective magnetic moments of $\text{Sr}_2\text{LnReO}_6$ (μ_{calc}) can be calculated

from the equation $\mu_{\text{calc}} = \sqrt{\mu_{\text{Re}^{5+}}^2 + \mu_{\text{Ln}^{3+}}^2}$, and they are also listed in Table 4. The moments experimentally obtained for $\text{Sr}_2\text{LnReO}_6$ (μ_{eff}) agree with those calculated moments.

3.2.4. $\text{Sr}_2\text{TbReO}_6$

Figure 14 depicts the magnetic susceptibility vs temperature curve for $\text{Sr}_2\text{TbReO}_6$, clearly indicating that $\text{Sr}_2\text{TbReO}_6$ is a typical antiferromagnet and that the Néel temperature (T_N) is 2.6 K. No divergence between ZFC and FC susceptibility has been observed below T_N . Figure 15 shows the temperature dependence of the specific heat for $\text{Sr}_2\text{TbReO}_6$, indicating the existence of the magnetic anomaly at the same temperature as that found by magnetic susceptibility measurements. The inset shows the specific heat divided by temperature (C_p/T) at low temperatures.

3.2.5. $\text{Sr}_2\text{DyReO}_6$

Figure 16 (a) shows the temperature dependence of the magnetic susceptibility for $\text{Sr}_2\text{DyReO}_6$. When the temperature is decreased through 5 K, the susceptibility steeply increases. The inset of Fig. 16 (a) shows the reciprocal susceptibility vs temperature curve in the temperature range between 1.8 and 100 K. If we apply the Curie-Weiss law below 50 K, the Weiss constant is obtained to be 10 K, which indicates the magnetic behavior at low temperatures is ferromagnetic.

Figure 17 shows the variation of magnetization as a function of magnetic field for $\text{Sr}_2\text{DyReO}_6$ at 5, 10, and 100 K. The magnetic moment is almost saturated to be $\sim 5 \mu_B$ at 5 K. The saturation moment is calculated to be $10 \mu_B$ from the ground state of Dy^{3+} ($^6H_{15/2}$, $g_J = 4/3$). The moment observed is much smaller than that calculated, indicating that the ground state of Dy^{3+} should be split by the crystal field and that the ordered moment is lowered.

Figure 18 shows the temperature dependence of the specific heat measured for $\text{Sr}_2\text{DyReO}_6$, indicating the existence of two λ -type specific heat anomalies at 5 and 93 K. The anomaly

observed at 5 K corresponds to the results by magnetic susceptibility measurements. Another clear specific heat anomaly has been observed at 93 K, although no magnetic anomaly behavior has been found in its magnetic susceptibility vs temperature curve (Fig. 16 (a)). Since the magnetic moment of Dy^{3+} is much larger than that of Re^{5+} , the magnetic ordering of Re^{5+} ions should be hindered by paramagnetic behavior of Dy^{3+} ions in the magnetic susceptibility vs temperature curve. Then, we performed the $d(\chi T)/dT$ plots against temperature in the temperature range between 40 and 200 K in Fig. 16 (b), following the method by Fisher [42]. A change of $d(\chi T)/dT$ has appeared when the temperature is decreased through 95 K, which accords with the specific heat measurements. We consider that the magnetic moments of Re^{5+} ions first order at 93 K, and then the moments of Dy^{3+} ions are ordered when the temperature is furthermore decreased through 5 K.

4. Summary

A series of perovskite-type compounds containing both rare earth and rhenium $\text{Sr}_2\text{LnReO}_6$ ($\text{Ln} = \text{Y}, \text{Tb} \sim \text{Lu}$) have been prepared. The Ln^{3+} and Re^{5+} ions are structurally ordered at the B site of the perovskite SrBO_3 . An antiferromagnetic transition has been observed at 2.6 ~ 20 K for $\text{Ln} = \text{Y}, \text{Tb}, \text{Dy}, \text{Yb},$ and Lu compounds. Their magnetic interactions are due to mainly interactions between Re^{5+} moments. The analysis of the specific heat data for $\text{Sr}_2\text{YbReO}_6$ shows that both the Yb^{3+} and Re^{5+} ions magnetically order at 20 K. For the case of $\text{Sr}_2\text{DyReO}_6$, it was found that magnetic ordering of the Re^{5+} moments occurs at around 90K, and with furthermore decreasing temperature, Dy moments ferromagnetically order from the magnetic susceptibility and specific heat measurements.

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Figure captions

Fig. 1 Powder X-ray diffraction profile for $\text{Sr}_2\text{LuReO}_6$. The calculated profiles based on the $P2_1/n$ model and the observed profiles are shown on the top solid line and cross markers, respectively. The bottom trace is a plot of the difference between calculated and observed intensities. The upper vertical marks in the middle show positions calculated for Bragg reflections. The lower vertical marks in the middle show positions calculated for Bragg reflections for Lu_2O_3 impurity. An arrow shows the super lattice reflection which is indexed to be 1 0 1 and 0 1 1.

Fig. 2 Crystal structure of double perovskite $\text{Sr}_2\text{LnReO}_6$. Red and black lines show cubic and monoclinic unit cells, respectively.

Fig. 3 Variation of lattice parameters for $\text{Sr}_2\text{LnReO}_6$ ($\text{Ln} = \text{Y}, \text{Tb-Lu}$) with Ln^{3+} radius.

Fig. 4 Bond lengths Ln-O and Re-O and bond angle Ln-O-Re for $\text{Sr}_2\text{LnReO}_6$ against Ln^{3+} radius.

Fig. 5 Temperature dependence of the magnetic susceptibility for Sr_2YReO_6 in the temperature range between 1.8 and 300 K. Filled circles are susceptibilities measured under ZFC conditions and open circles are those measured under FC conditions. The inset shows the temperature dependence of the reciprocal ZFC susceptibility for Sr_2YReO_6 . The red solid line is the Curie-Weiss fitting.

Fig. 6 Temperature dependence of the magnetic susceptibility for $\text{Sr}_2\text{LuReO}_6$ in the temperature range between 1.8 and 300 K. Filled circles are susceptibilities measured under ZFC conditions and open circles are those measured under FC conditions. The inset shows the temperature dependence of the reciprocal ZFC susceptibility for $\text{Sr}_2\text{LuReO}_6$. The red solid line is the Curie-Weiss fitting.

Fig. 7 Magnetic hysteresis curves for (a) Sr_2YReO_6 and (b) $\text{Sr}_2\text{LuReO}_6$ measured at 5 K.

Fig. 8 Temperature dependence of the specific heat (C_p) for $\text{Sr}_2\text{LuReO}_6$ in the temperature range between 1.8 and 300 K. The inset shows the specific heat divided by temperature (C_p/T) in low temperature region.

Fig. 9 Temperature dependence of the C_p below 40 K and magnetic entropy change (S_{mag}) for $\text{Sr}_2\text{LuReO}_6$. The red solid line is the specific heat data for $\text{Sr}_2\text{LuTaO}_6$ and the black solid line is the magnetic entropy change (S_{mag}).

Fig.10 Temperature dependence of the magnetic susceptibility for $\text{Sr}_2\text{YbReO}_6$ in the temperature range between 1.8 and 300 K. Filled circles are susceptibilities measured under ZFC conditions and open circles are those measured under FC conditions. The inset shows the temperature dependence of the reciprocal ZFC susceptibility for $\text{Sr}_2\text{YbReO}_6$. The red solid line is the Curie-Weiss fitting.

Fig.11 Temperature dependence of the specific heat (C_p) for $\text{Sr}_2\text{YbReO}_6$. The inset shows the specific heat divided by temperature (C_p/T) in low temperature region.

Fig.12 Temperature dependence of the C_p below 50 K and magnetic entropy change (S_{mag}) for $\text{Sr}_2\text{YbReO}_6$. The red solid line is the specific heat data for $\text{Sr}_2\text{LuTaO}_6$ and the black solid line is the magnetic entropy change (S_{mag}).

Fig. 13 Temperature dependence of the reciprocal magnetic susceptibilities for $\text{Sr}_2\text{LnReO}_6$ ($\text{Ln} = \text{Ho, Er, and Tm}$).

Fig.14 Temperature dependence of the magnetic susceptibility for $\text{Sr}_2\text{TbReO}_6$ in the temperature range between 1.8 and 100 K. Filled circles are susceptibilities measured under ZFC conditions and open circles are those measured under FC conditions. The inset shows the temperature dependence of the reciprocal ZFC susceptibility for $\text{Sr}_2\text{TbReO}_6$ in the temperature range between 1.8 and 300 K. The red solid line is the Curie-Weiss fitting.

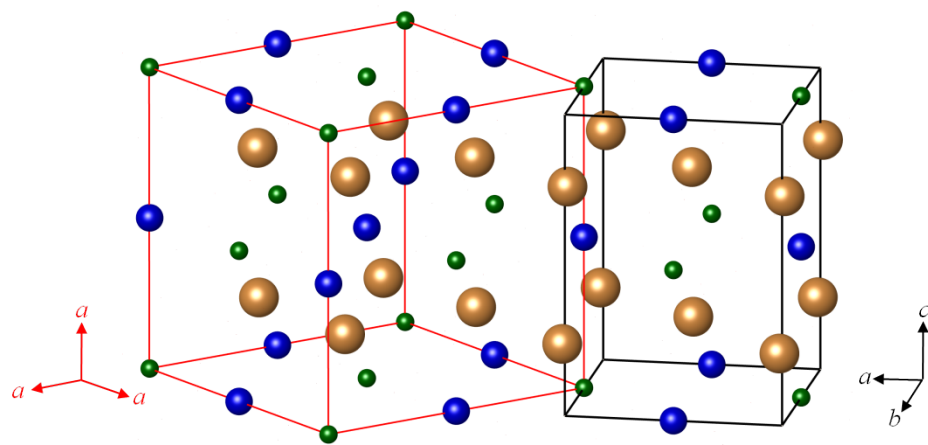
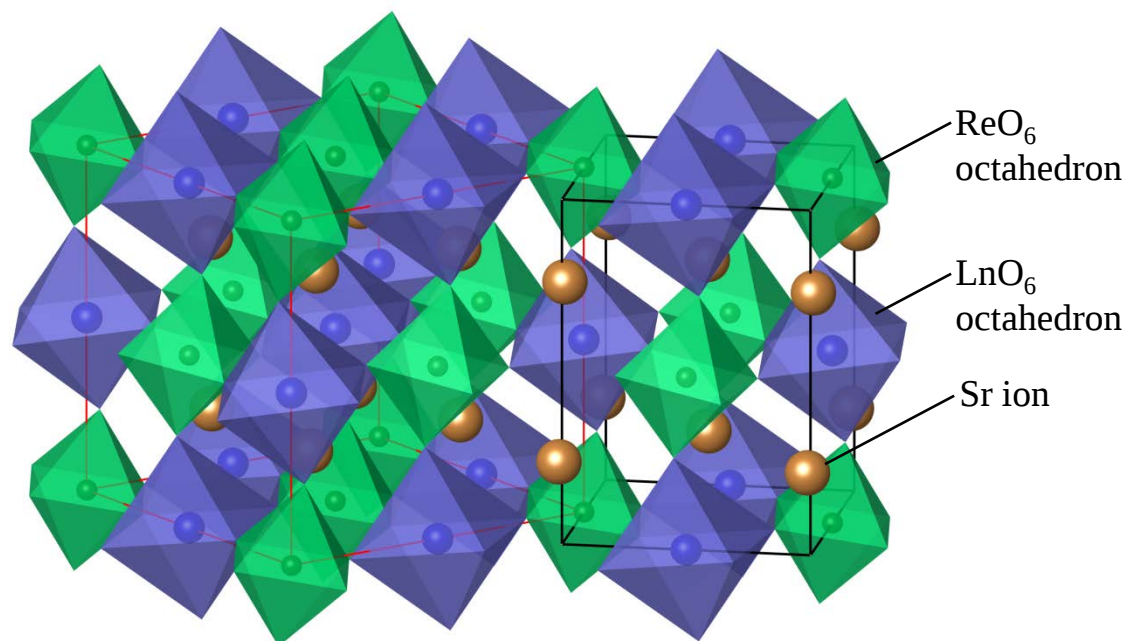
Fig.15 Temperature dependence of the specific heat (C_p) for $\text{Sr}_2\text{TbReO}_6$. The inset shows the specific heat divided by temperature (C_p/T) in low temperature region.

Fig.16 (a) Temperature dependence of the magnetic susceptibility for $\text{Sr}_2\text{DyReO}_6$ in the temperature range between 1.8 and 300 K. The inset shows the temperature dependence of the reciprocal ZFC susceptibility for $\text{Sr}_2\text{DyReO}_6$ in lower temperature region.

(b) Temperature dependence of the first derivatives of χT against temperature in the neighborhood of T_N .

Fig.17 Field dependence of the magnetization for $\text{Sr}_2\text{DyReO}_6$ at 5, 10, and 100 K.

Fig.18 Temperature dependence of the specific heat (C_p) for $\text{Sr}_2\text{DyReO}_6$. The inset shows the specific heat divided by temperature (C_p/T) in lower temperature region.



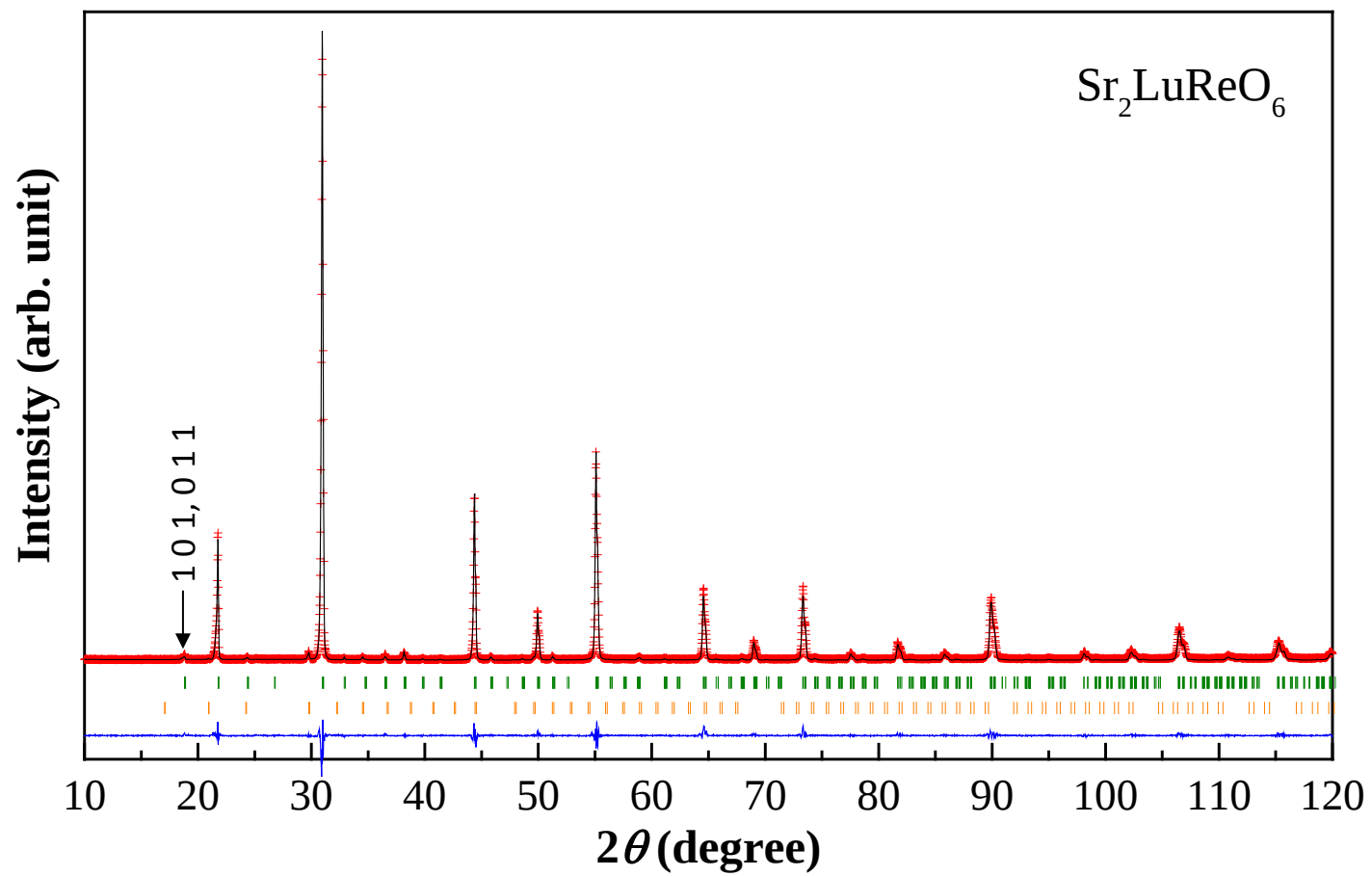


Fig.1

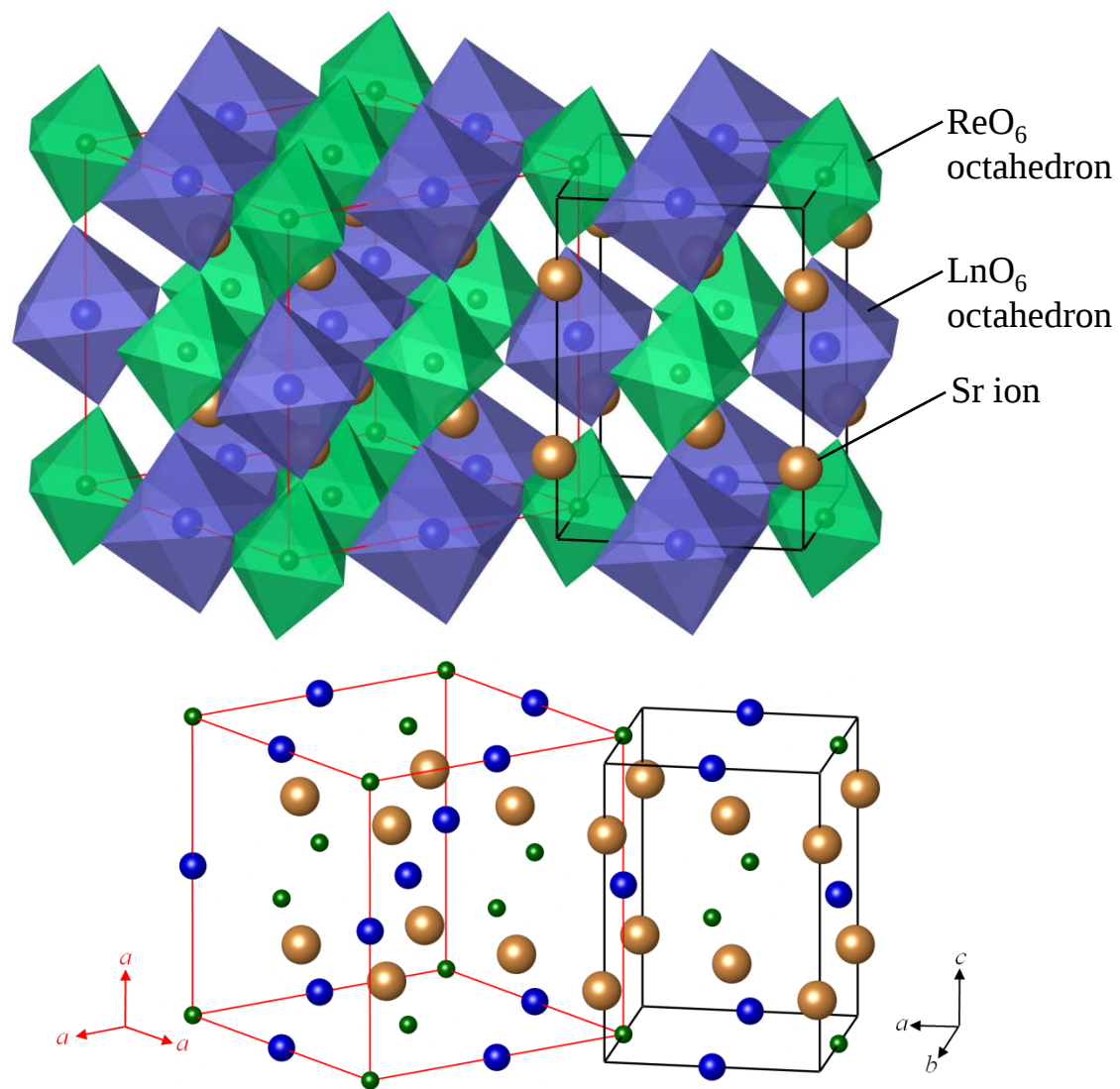


Fig. 2

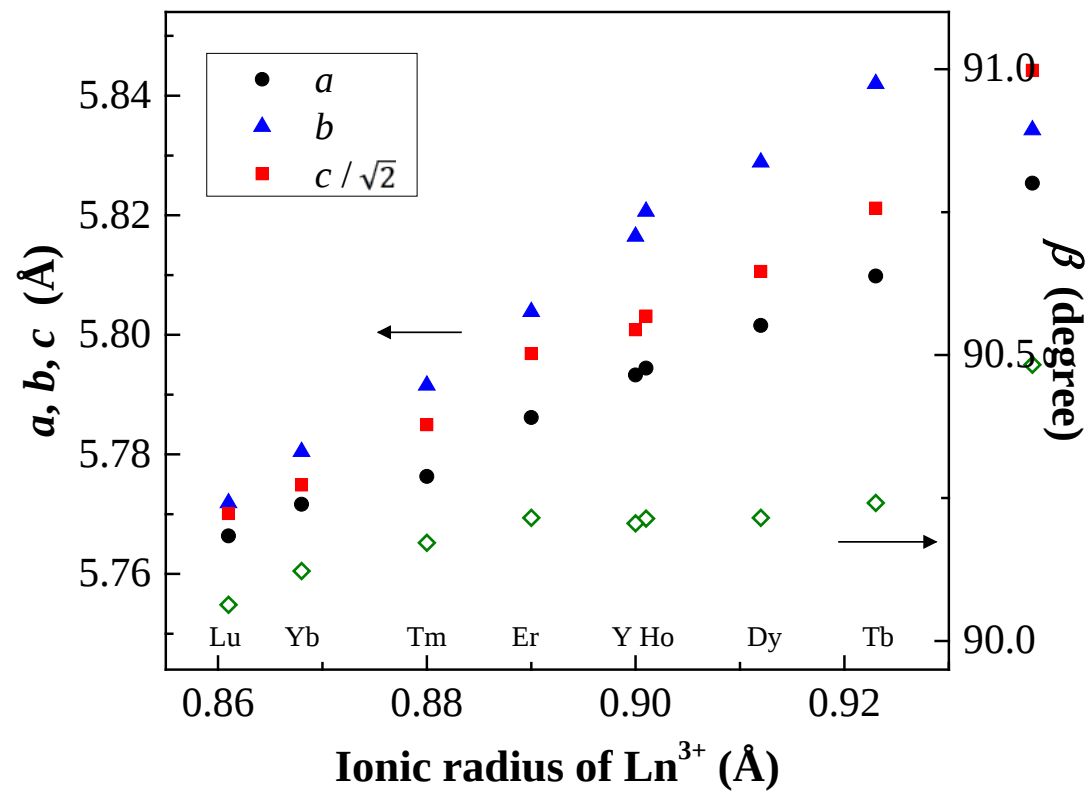


Fig. 3

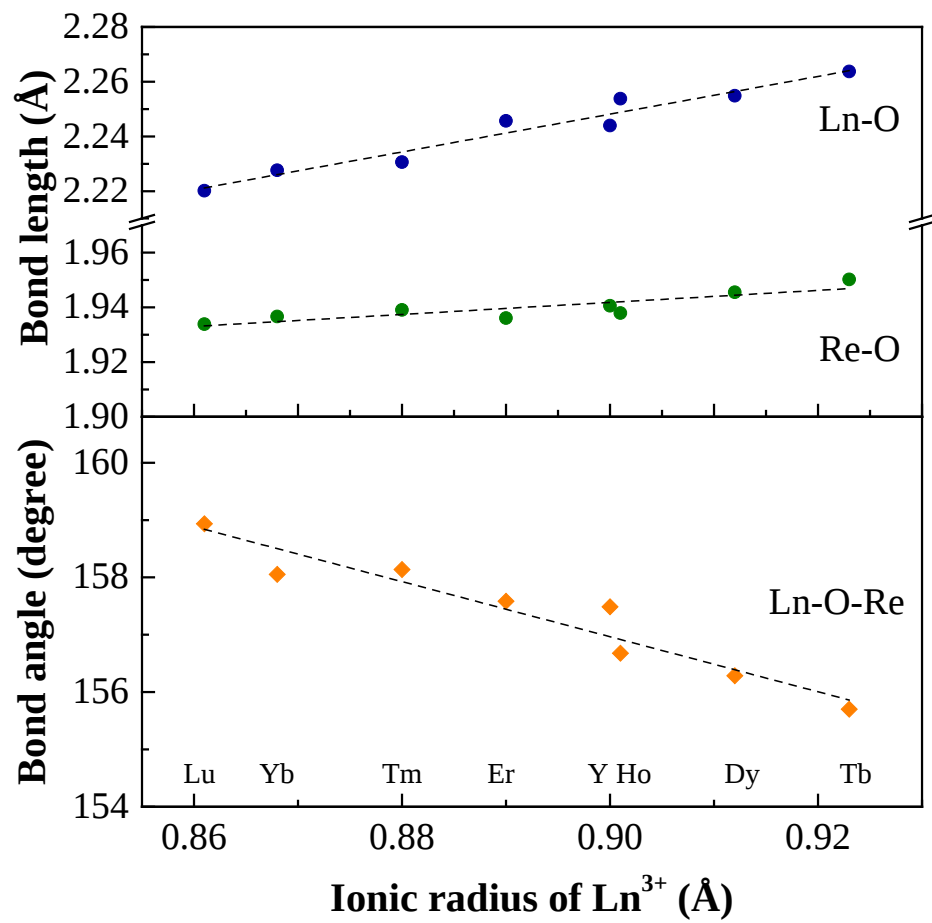


Fig. 4

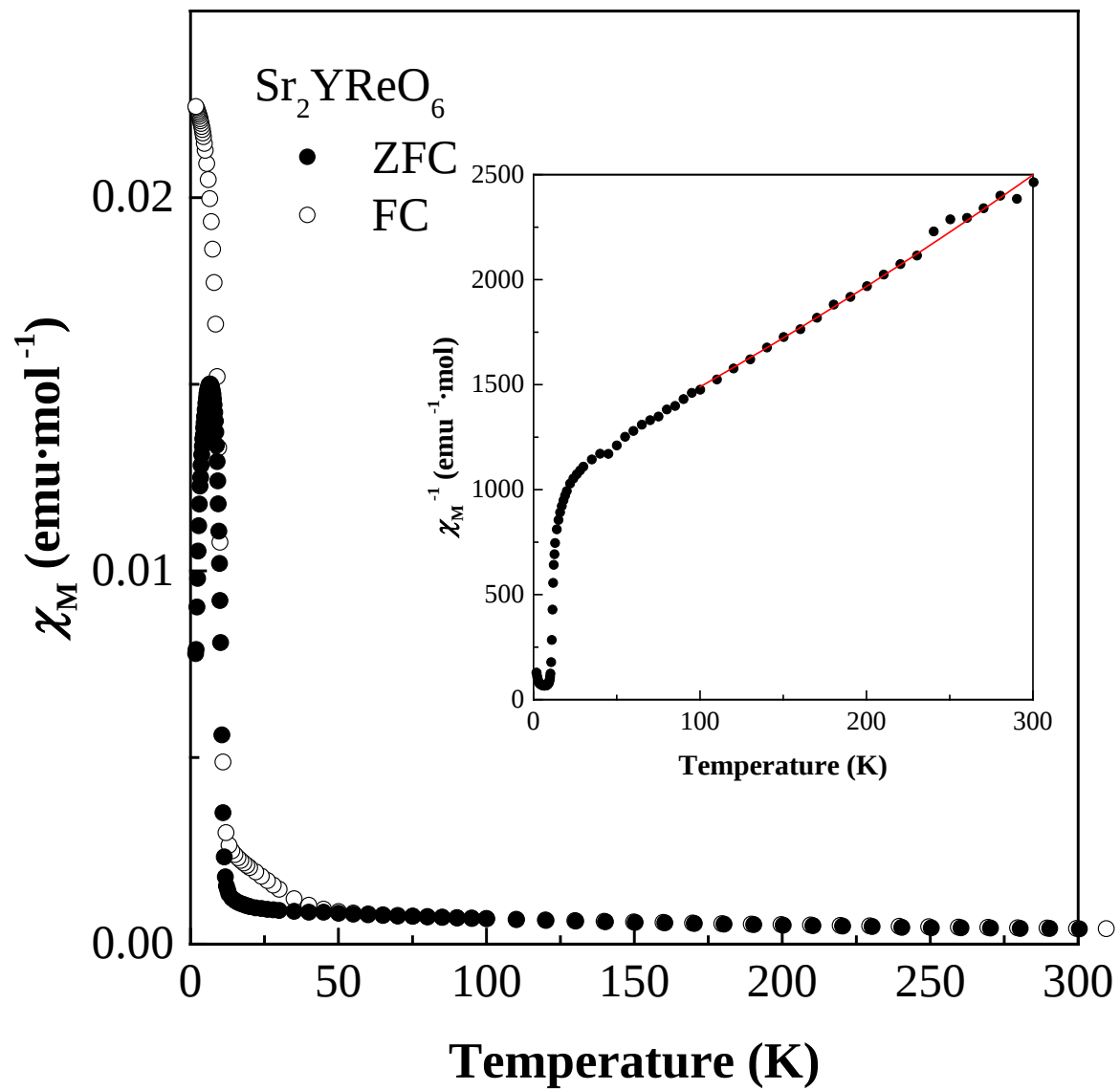


Fig. 5

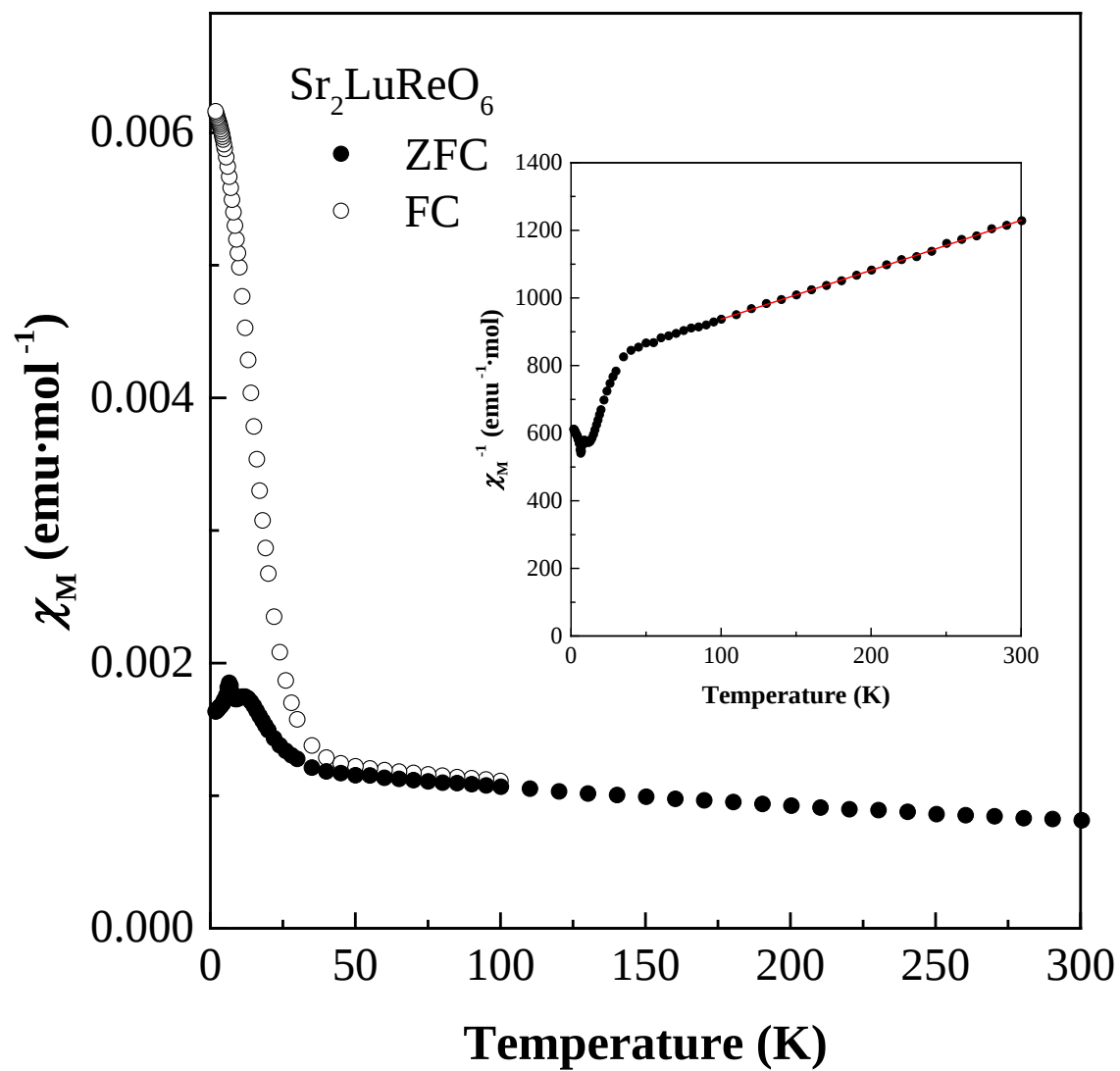


Fig. 6

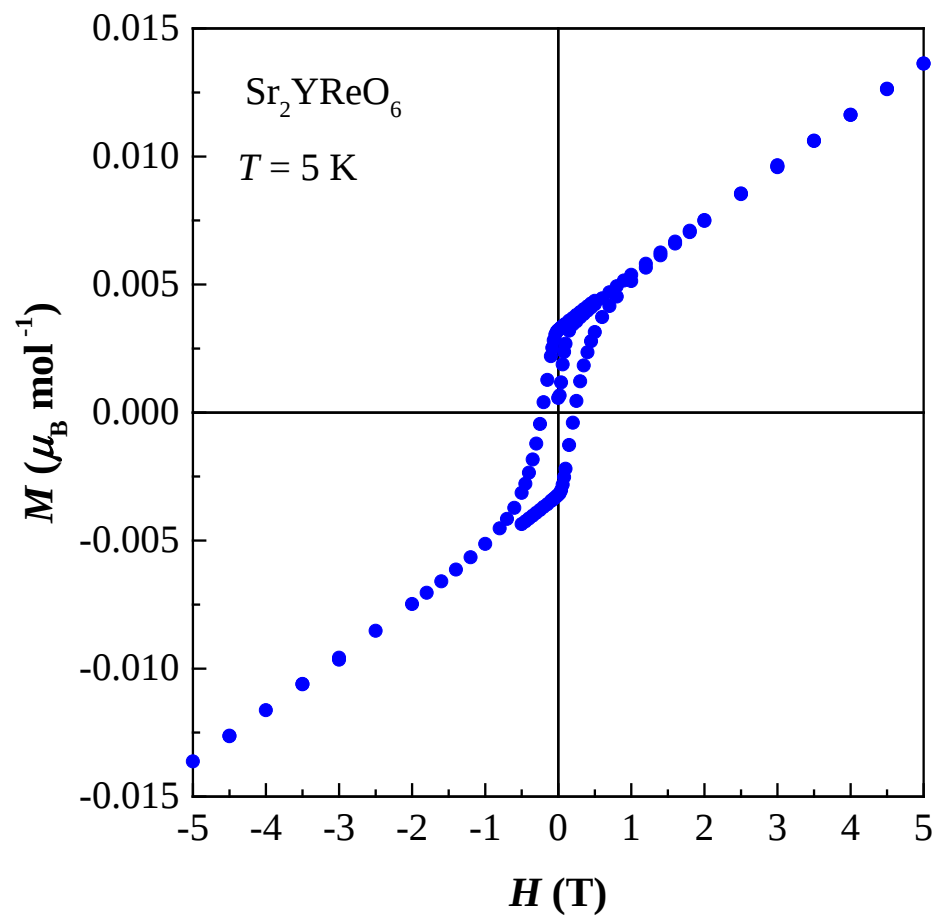


Fig. 7(a)

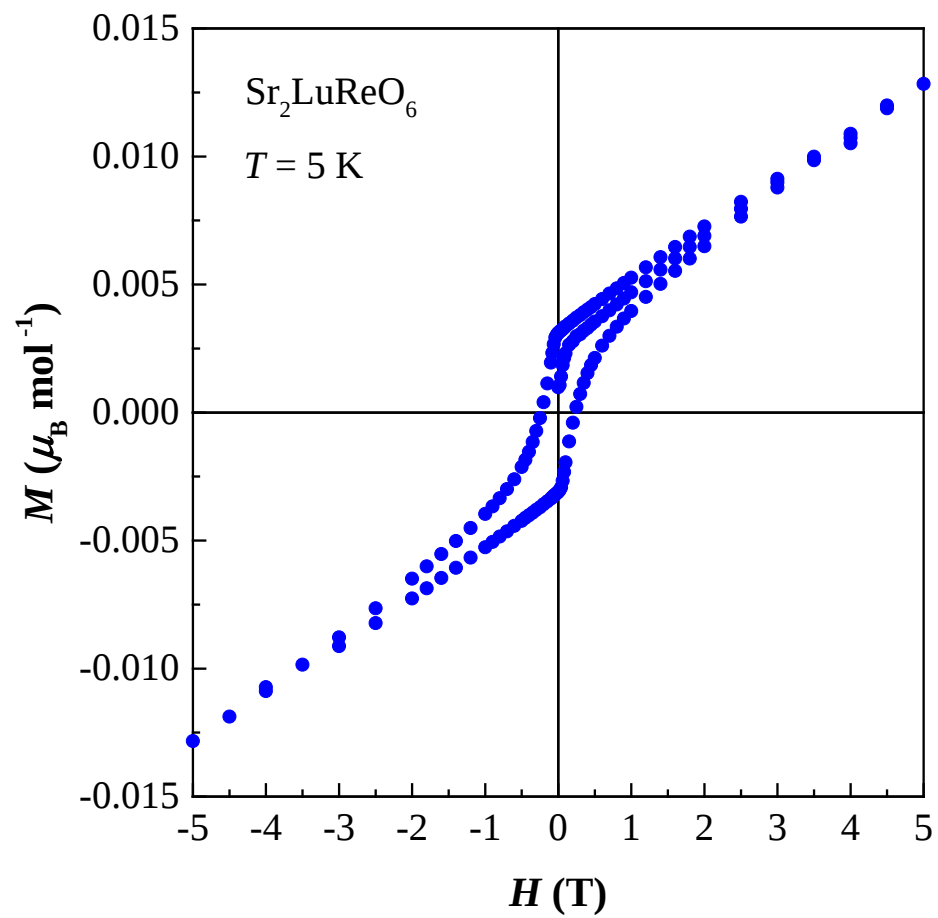


Fig. 7(b)

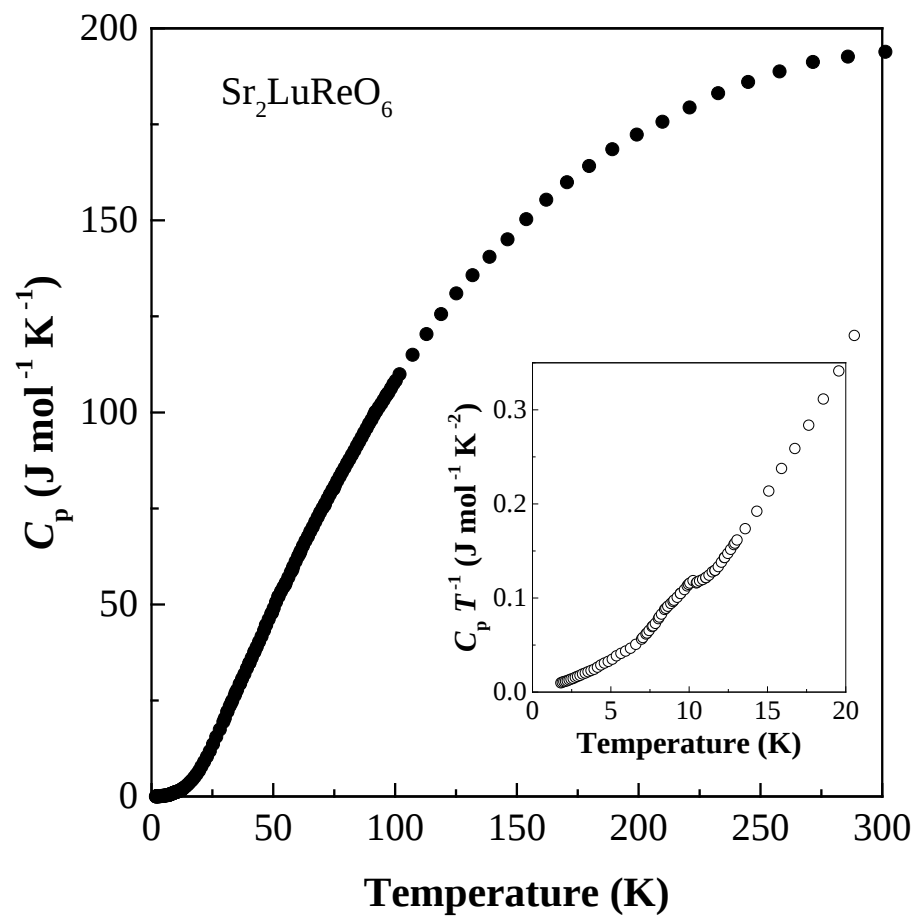


Fig. 8

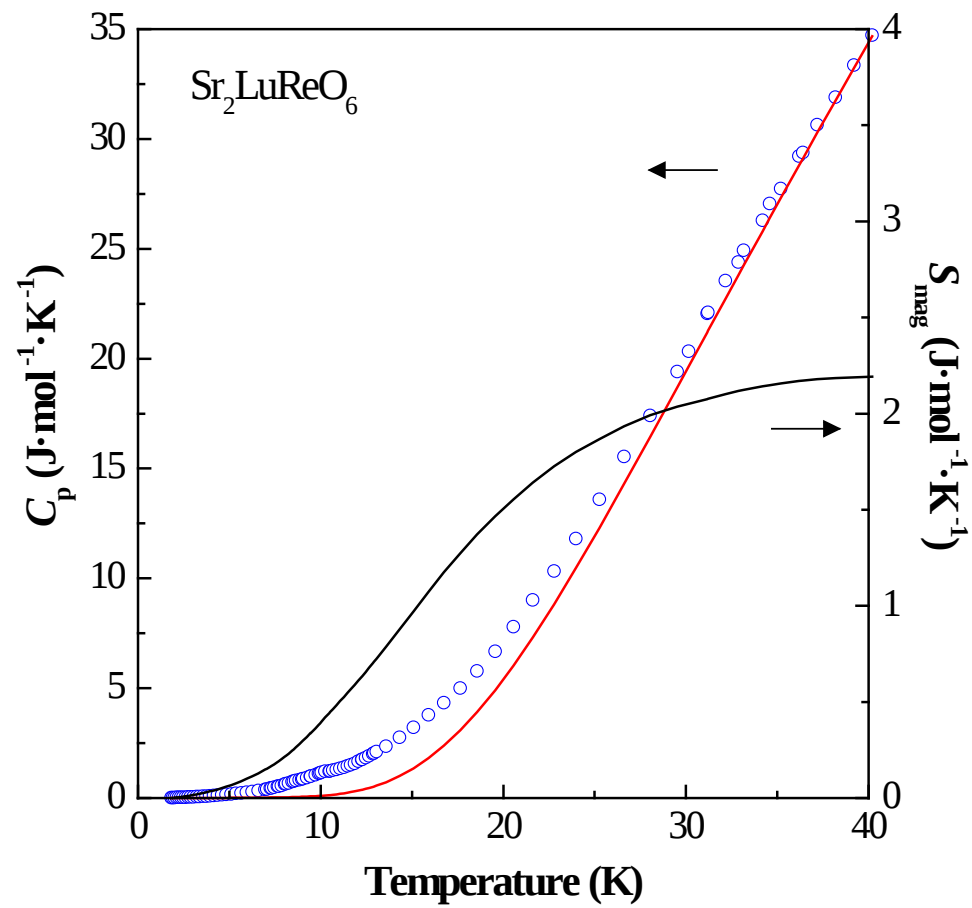


Fig. 9

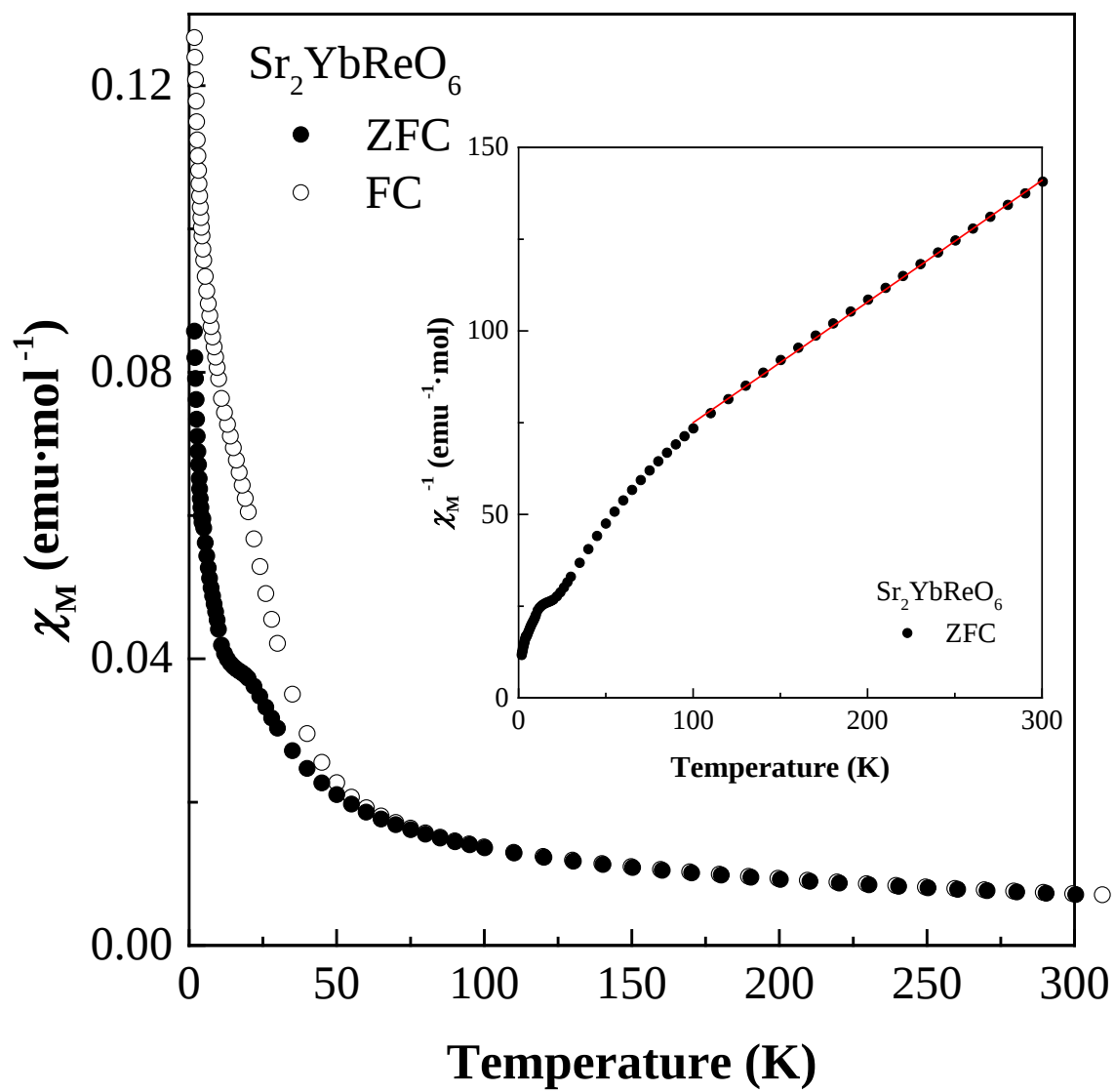


Fig. 10

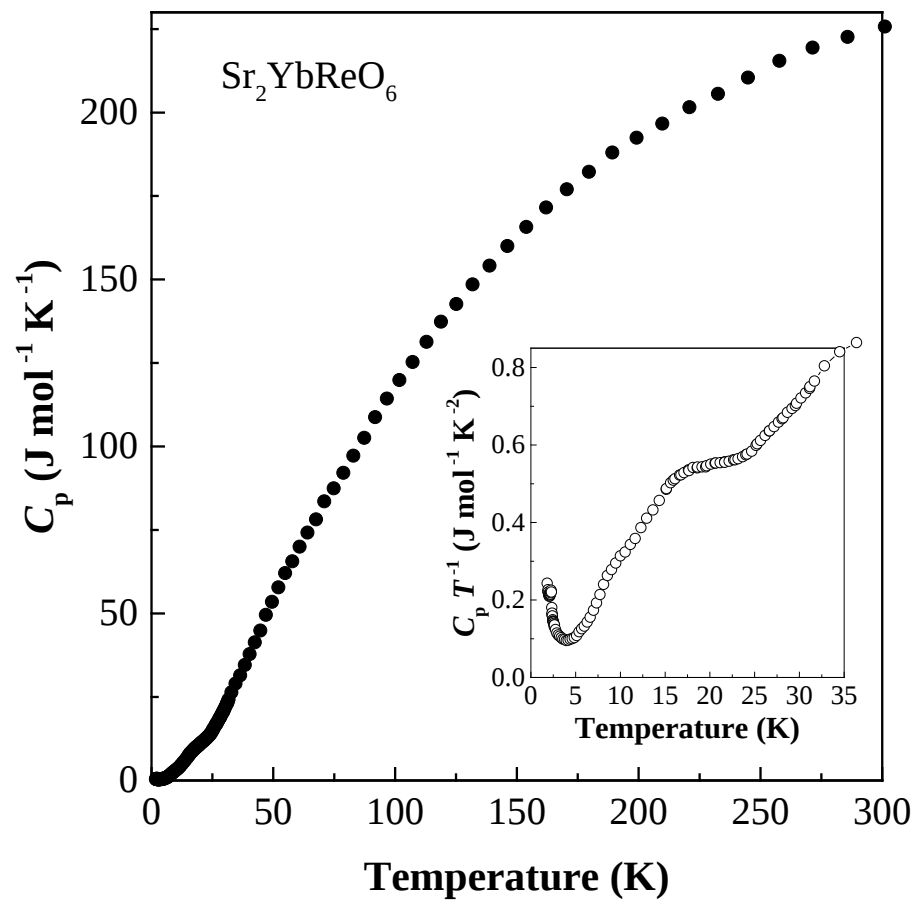


Fig. 11

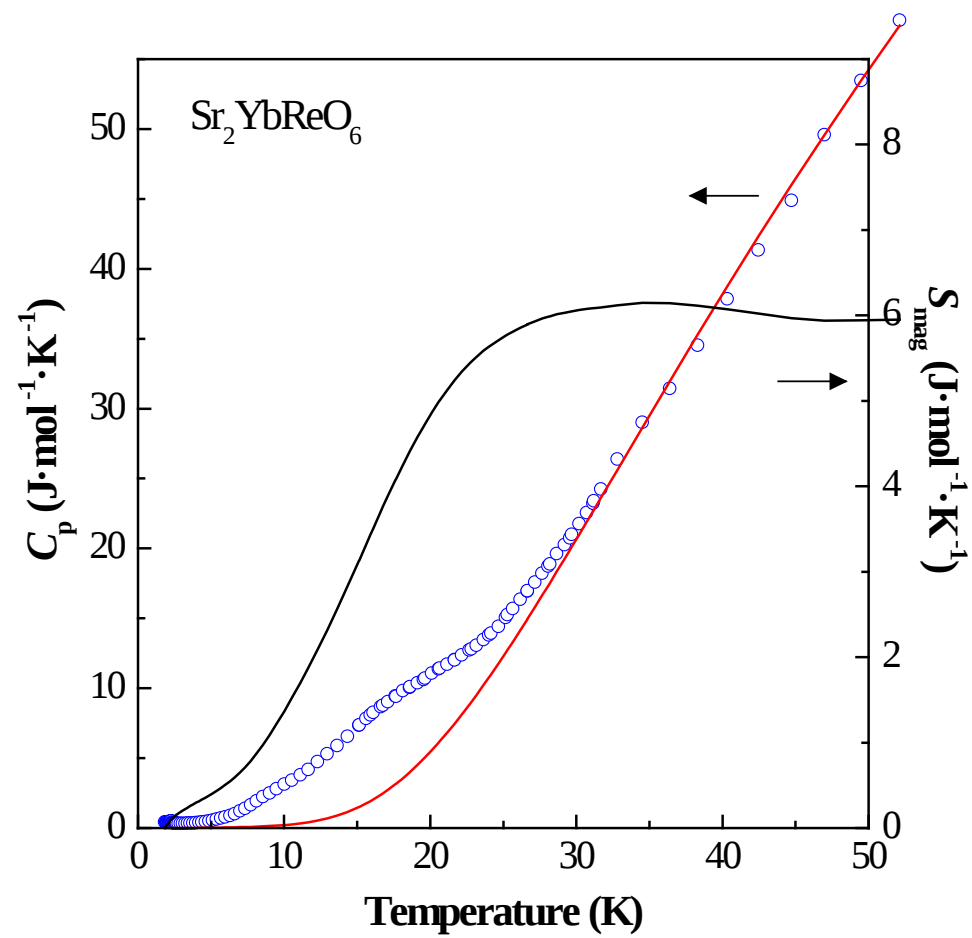


Fig. 12

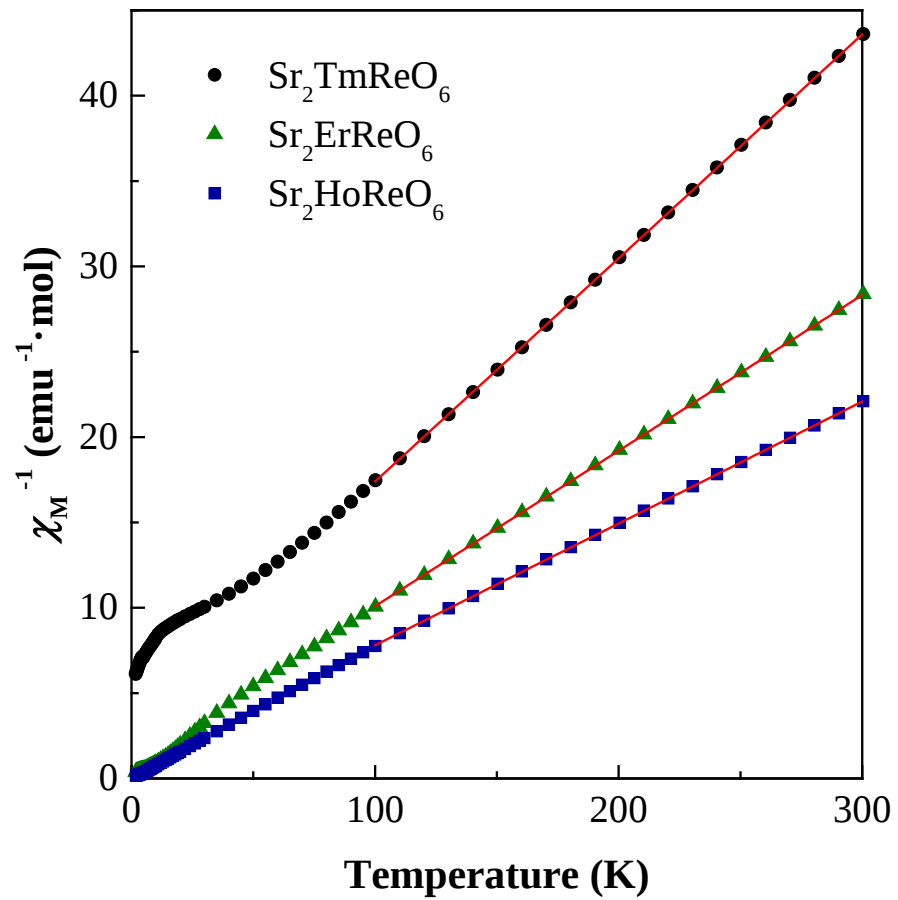


Fig. 13

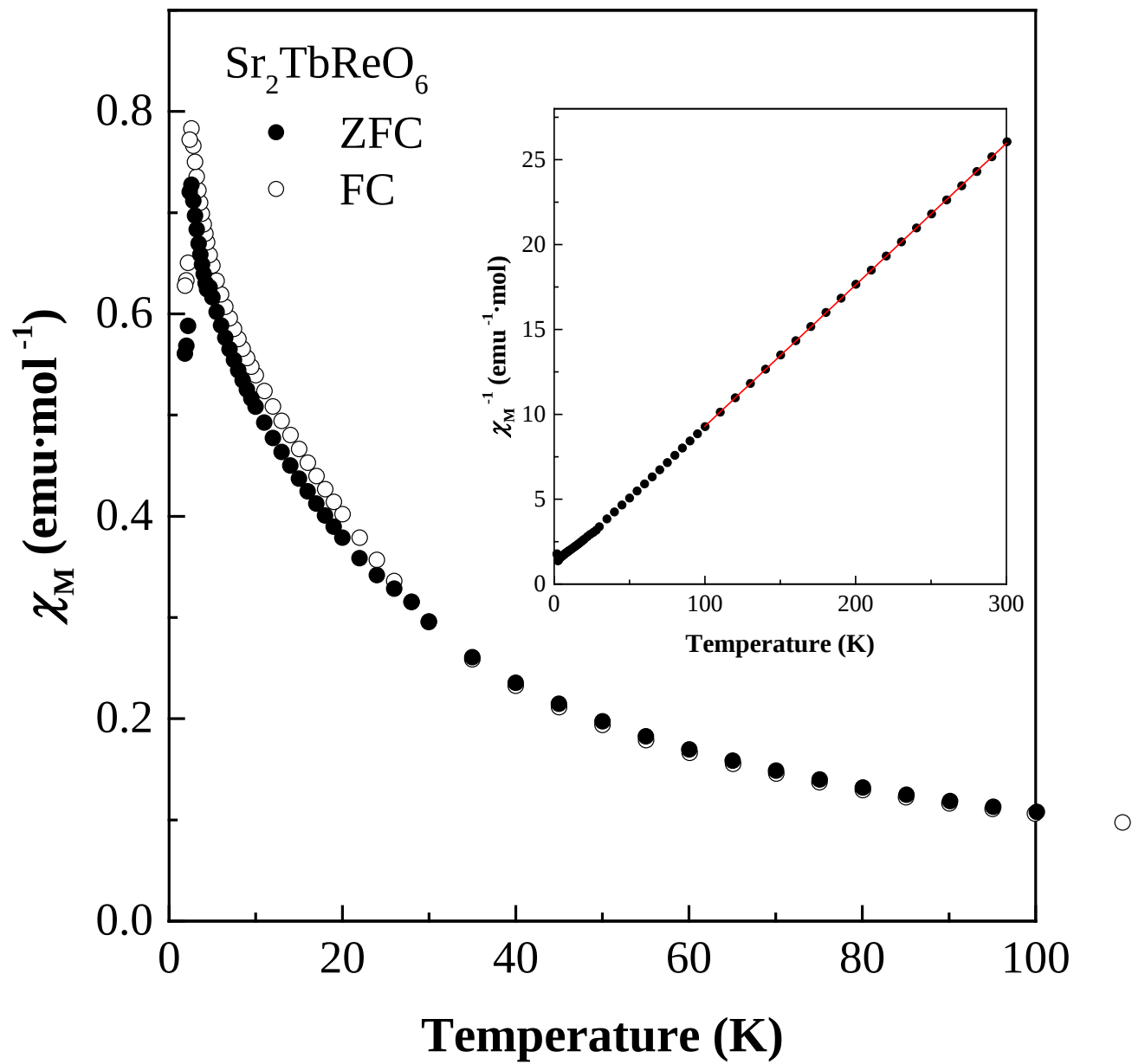


Fig. 14

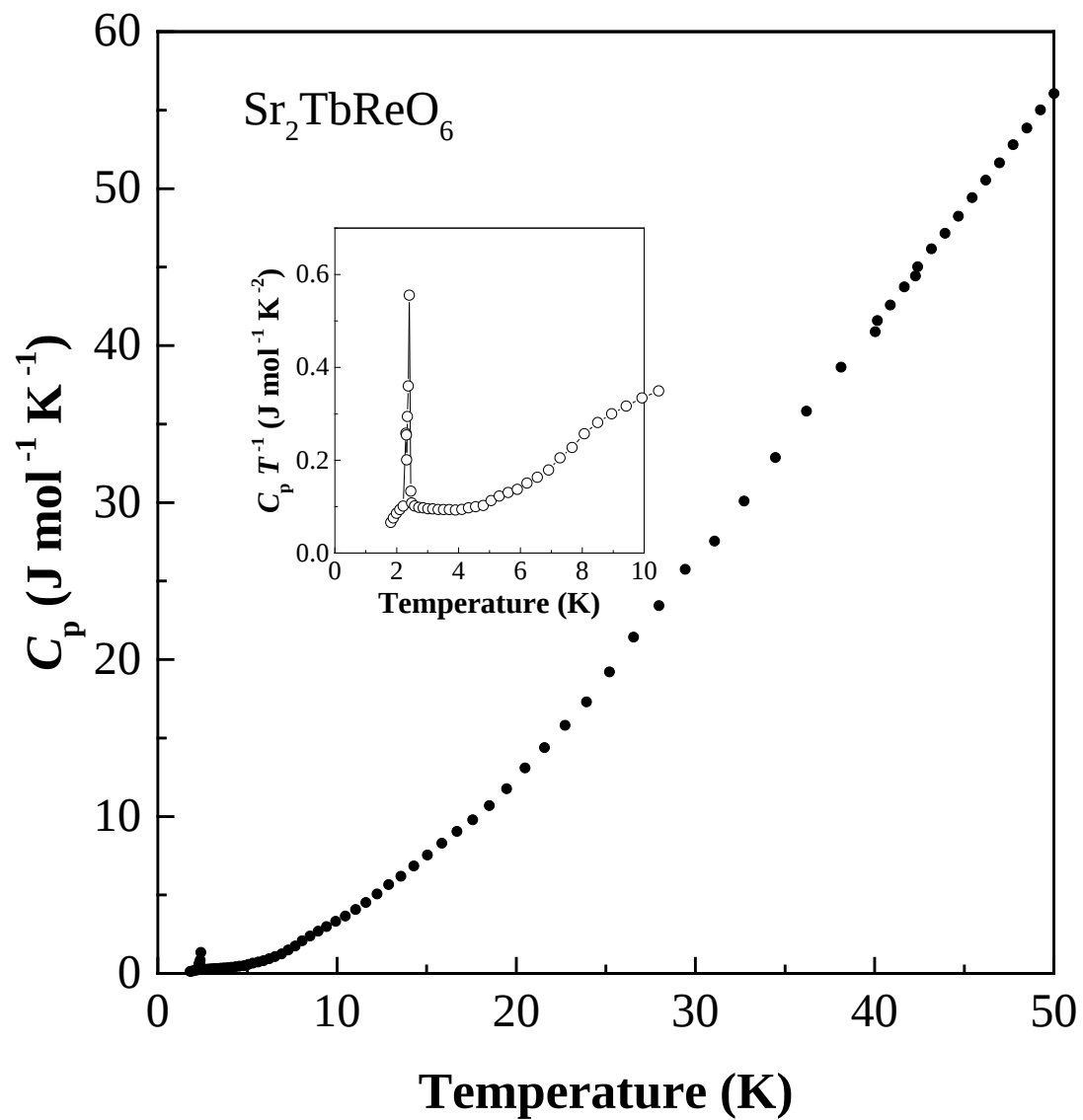


Fig. 15

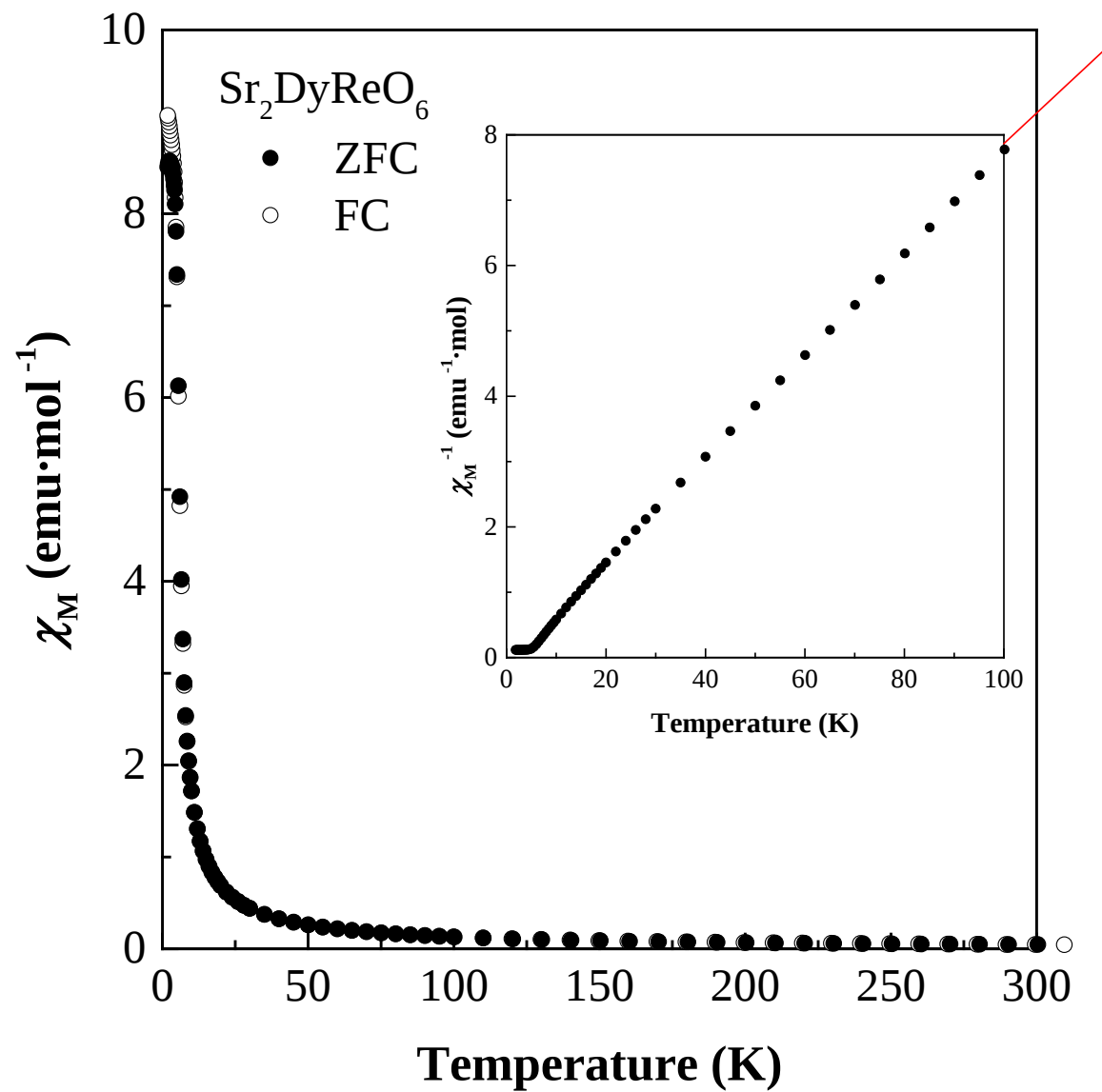


Fig. 16 (a)

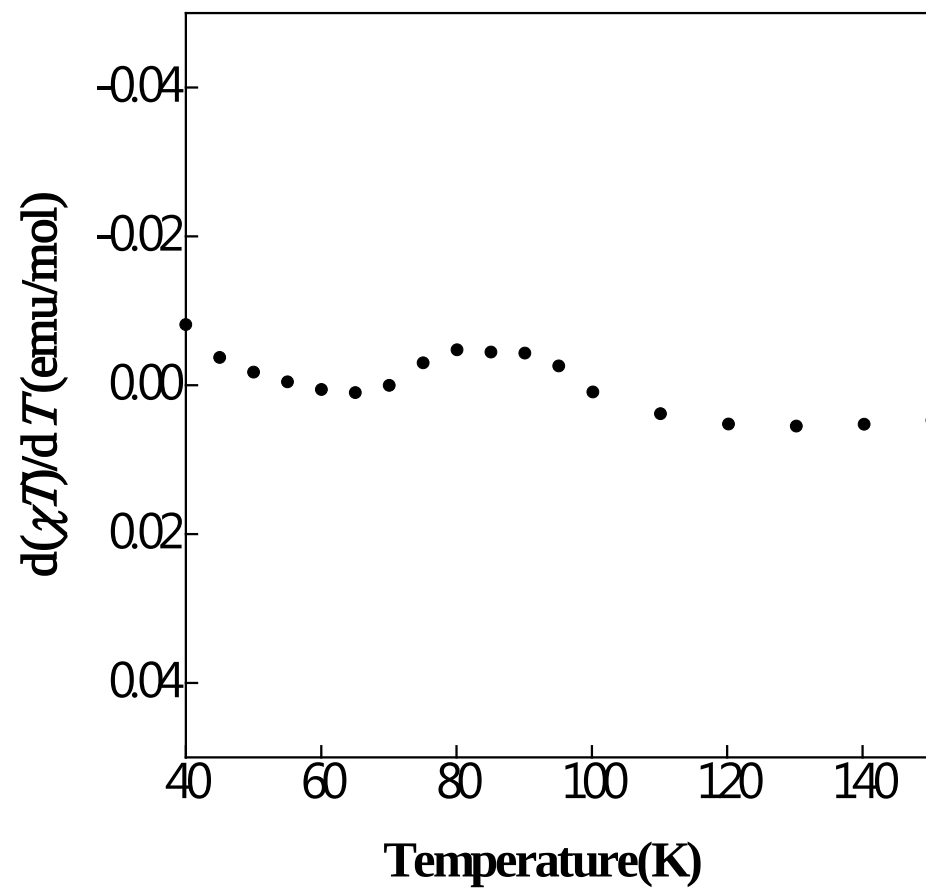


Fig. 16 (b)

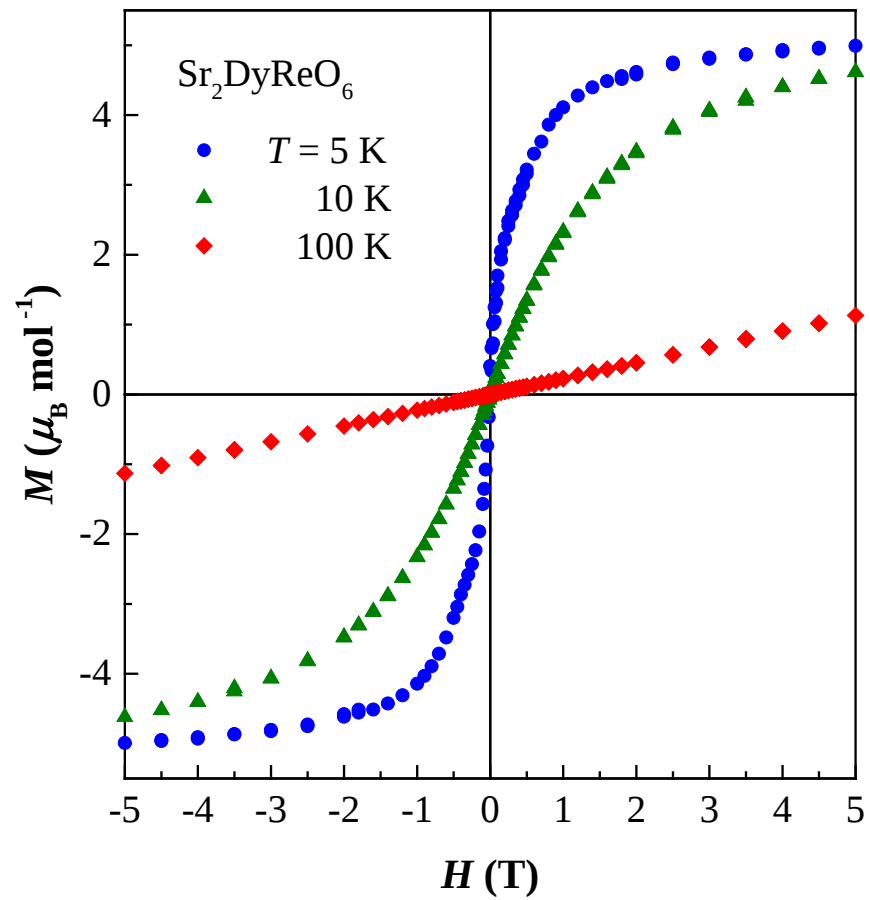


Fig. 17

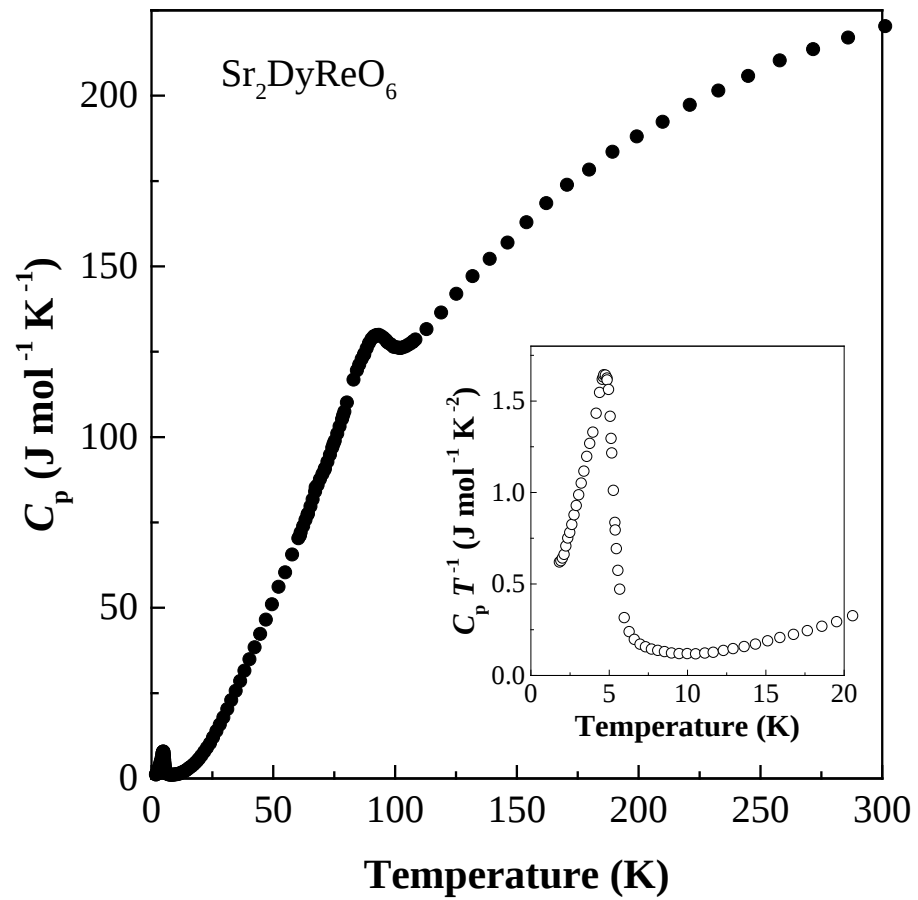


Fig. 18

Table 1. Structural parameters for $\text{Sr}_2\text{LuReO}_6$.

Atom	Site	x	y	z	$B / \text{\AA}^2$
Sr	$4e$	0.008(4)	0.025(1)	0.243(1)	0.37(6)
Lu	$2d$	1/2	0	0	0.3(1)
Re	$2c$	1/2	0	1/2	0.3(1)
O(1)	$4e$	0.255(2)	0.314 (2)	0.030(2)	1.0(2)
O(2)	$4e$	0.186(3)	-0.238(2)	0.0254(3)	1.0
O(3)	$4e$	0.052(3)	0.498(3)	0.236(3)	1.0

Note. Space group $P2_1/n$; $a = 5.7619(2) \text{ \AA}$, $b = 5.7709(1) \text{ \AA}$, $c = 8.1554(1) \text{ \AA}$, $\beta = 90.11(1)^\circ$, $V = 271.175(8) \text{ \AA}^3$, $R_{\text{wp}} = 13.33 \%$, and $R_e = 10.85 \%$, where

$$R_{\text{wp}} = \left[\sum_i w_i (y_i - f_i(\mathbf{x}))^2 / \sum_i w_i y_i^2 \right]^{1/2}, \text{ and } R_e = \left[(N - P) / \sum_i w_i y_i^2 \right]^{1/2}.$$

Table 2. Lattice parameters for $\text{Sr}_2\text{LnReO}_6$ (Ln = Y, Tb-Lu).

	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	R_{wp}
Sr_2YReO_6	5.7933(6)	5.8162(4)	8.2649(4)	90.22(1)	14.06
$\text{Sr}_2\text{TbReO}_6$	5.8099(6)	5.8419(4)	8.2322(4)	90.24(1)	14.06
$\text{Sr}_2\text{DyReO}_6$	5.8015(2)	5.8287(1)	8.2175(1)	90.22(1)	14.54
$\text{Sr}_2\text{HoReO}_6$	5.7942(4)	5.8205(2)	8.2068(2)	90.21(2)	13.39
$\text{Sr}_2\text{ErReO}_6$	5.7868(3)	5.8064(2)	8.1920(2)	90.21(2)	12.44
$\text{Sr}_2\text{TmReO}_6$	5.7785(3)	5.7919(2)	8.1777(2)	90.19(1)	11.34
$\text{Sr}_2\text{YbReO}_6$	5.7710(3)	5.7799(2)	8.1633(2)	90.16(2)	13.01
$\text{Sr}_2\text{LuReO}_6$	5.7619(2)	5.7709(1)	8.1554(1)	90.11(1)	13.33

Definition of reliability factors R_{wp} is given as follows:

$$R_{\text{wp}} = \left[\sum_i w_i (y_i - f_i(\mathbf{x}))^2 / \sum_i w_i y_i^2 \right]^{1/2}.$$

Table 3. The BVS for $\text{Sr}_2\text{LnReO}_6$

	Ln	Re
Sr_2YReO_6	3.22	4.83
$\text{Sr}_2\text{TbReO}_6$	3.31	4.70
$\text{Sr}_2\text{DyReO}_6$	3.02	4.76
$\text{Sr}_2\text{HoReO}_6$	3.23	4.86
$\text{Sr}_2\text{ErReO}_6$	2.99	4.89
$\text{Sr}_2\text{TmReO}_6$	3.22	4.85
$\text{Sr}_2\text{YbReO}_6$	3.12	4.88
$\text{Sr}_2\text{LuReO}_6$	3.06	4.92

Table 4. The effective magnetic moments (μ_{eff} : experimental, μ_{calc} : calculated) per formula unit and Weiss constants for $\text{Sr}_2\text{LnReO}_6$.

	$\mu_{\text{eff}}/\mu_{\text{B}}$	$\mu_{\text{calc}}/\mu_{\text{B}}$	θ/K	T_{N}/K
Sr_2YReO_6	2.27	2.83	-292	6.0
$\text{Sr}_2\text{TbReO}_6$	10.11	9.99	-17	2.6
$\text{Sr}_2\text{DyReO}_6$	10.13	10.88	10	5, 93
$\text{Sr}_2\text{HoReO}_6$	10.63	10.83	-11.0	para
$\text{Sr}_2\text{ErReO}_6$	9.39	9.86	-11.1	para
$\text{Sr}_2\text{TmReO}_6$	7.85	7.89	-33.6	para
$\text{Sr}_2\text{YbReO}_6$	4.99	5.08	-131	20
$\text{Sr}_2\text{LuReO}_6$	2.68	2.83	-649	12

*para: paramagnetic behavior in the whole temperature range.