Octahedral tilting and emergence of ferrimagnetism in cobalt-ruthenium based double perovskites

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Abstract

Rare earth based cobalt-ruthenium double perovskites $A_2CoRuO_6$ ($A = La, Pr, Nd$ and Sm) were synthesized and investigated for their structural and magnetic properties. All the compounds crystallize in the monoclinic $P2_1/n$ structure with the indication of antisite disorder between Co and Ru sites. While La compound is already reported to have an antiferromagnetic state below 27 K, the Pr, Nd and Sm systems are found to be ferrimagnetic below $T_c = 46, 55$ and 78 K respectively. Field-dependent magnetization data indicate prominent hysteresis loop below $T_c$ in the samples containing magnetic rare-earth ions, however, magnetization does not saturate even at the highest applied fields. Our structural analysis indicates strong distortion in the Co–O–Ru bond angle, as La$^{3+}$ is replaced by smaller rare-earth ions such as Pr$^{3+}$, Nd$^{3+}$, and Sm$^{3+}$. The observed ferrimagnetism is possibly associated with the enhanced antiferromagnetic superexchange interaction in the Co–O–Ru pathway due to bond bending. The Pr, Nd and Sm samples also show the small magnetocaloric effect with the Nd sample showing the highest value of magnitude $\sim 3$ J kg$^{-1}$K$^{-1}$ at 50 kOe. The change in entropy below 20 K is found to be positive in the Sm sample as compared to the negative value in the Nd counterpart.

Keywords: double perovskite, ruthenates, ferrimagnetism

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the discovery of low field room temperature magneto-resistance in Sr$_2$FeMoO$_6$ [1], the double perovskites ($A_2BB'O_6$) have been intensely studied [2]. These quaternary compounds can be synthesized with varying combinations of cations at the A (alkaline earth or rare earth metals) and B/B' ($3d$, $4d$ or $5d$ transition metals) sites, which provide a scope to access diverse material properties within a similar crystallographic environment. Elements with partially filled $d$ level at the B/B' can give rise to a wealth of magnetic ground states including ferromagnetism, antiferromagnetism, ferrimagnetism as well as a glassy magnetic phase. Double perovskites are also associated with intriguing electronic properties [3] such as half-metallic behaviour [4], tunneling magneto-resistance [5], metal-insulator transition [6] and so on.

In the case of insulating $A_2BB'O_6$ double perovskites, the magnetic interaction between B and B' ions is primarily B–O–B' superexchange type and the Goodenough–Kanamori rule can predict the sign of the interaction [7]. Ideal double perovskites have cubic symmetry, but the presence of cations with small ionic radii at the A site can distort the structure. Such distortion lowers the lattice symmetry to tetragonal or monoclinic, where the BO$_6$/B'O$_6$ octahedra get tilted through the bending of the B–O–B' bond angle. It has been found that for two fixed B and B', the magnetic ground state is very much sensitive to this bond angle. Doping at the A site can change the bond angle and henceforth the nature of the ordered
magnetic state. For example, the substitution of Ca at the Sr site of Sr_{2}CoOsO_{6} drives the system from an antiferromagnetic (AFM) insulator to spin-glass (SG) and eventually to a ferromagnetic (FI) state on full replacement of Sr by Ca [8, 9]. There is also a report of drastic change in ferromagnetic coercivity in (Ca,Ba)_{2}FeReO_{6} under hydrostatic pressure due to the buckling of Fe–O–Re bond [10]. It has been argued that the magnetic ground state in these insulating systems is an outcome of the competition between the interactions along the paths B–O–B′ and B–O–B′–O–B (and similarly, B′–O–B–O–B′). When the octahedral tilting is minimal, the B–O–B′–O–B type interaction dominates, giving rise to strong AFM correlations within B sublattice [11]. However, with increasing distortion, B–O–B′ becomes stronger with the simultaneous weakening of B–O–B′–O–B coupling, and a simple FI state emerges (provided the magnetic moments at B and B′ ions are unequal) due to the strong AFM coupling between B and B′ ions. The intermediate spin-glass state possibly arises from these competing interactions.

Recently, La_{2}CoRuO_{6} compound has been shown to have an AFM ground state, which crystallizes in the distorted monoclinic structure [12]. Interestingly, the isostructural Y_{2}CoRuO_{6} shows ferrimagnetism and turns into a spin-glass on La doping at the Y site [13]. It is, therefore, worthwhile to study the magnetic states of A_{2}CoRuO_{6} with different rare-earth atoms at the A site. The ionic radius of rare-earth (in the ordering of rare-earth ion at the A-site [14].

2. Experimental details

Single phase polycrystalline A_{2}CoRuO_{6} samples (for A = La, Pr, Nd, and Sm) were synthesized by solid state technique. Stoichiometric amounts of A_{2}O_{3} (except Pr-sample, where Pr_{2}O_{11} was used), CoO_{2} and RuO_{2} were well mixed in an agate mortar pestle and calcined at 1073 K for 12 h and then sintered at 1473 K for 24 h in the pellet form with one intermediate grinding. The powder x-ray diffraction (PXRD) data were obtained in RIGAKU x-ray diffractometer with Cu-K_{α} radiation in the range 15° to 80°. Magnetization (M) measurements were carried out using a SQUID magnetometer (Quantum Design, MPMS-3) up to 70 kOe. High field magnetic measurements (up to 150 kOe) were performed on a vibrating sample magnetometer from Cryogenic Ltd., UK. The temperature dependence of the electrical resistivity (ρ) was measured by DC four-probe method in the temperature range between 50 K and 300 K.

3. Sample characterization

All four compositions, La_{2}CoRuO_{6} (LCRO), Pr_{2}CoRuO_{6} (PCRO), Nd_{2}CoRuO_{6} (NCRO), and Sm_{2}CoRuO_{6} (SCRO), crystallize in monoclinic rock-salt structure (space group P2_{1}/n) [15]. For double perovskite A_{2}BB′O_{6}, one can define a Goldschmidt tolerance factor t = \frac{r_{A} + r_{O}}{\sqrt{2}(r_{B} + r_{O})}, where r_{A}, r_{B}, and r_{O} are the ionic radii of A and O respectively, while r_{B}′ are the average radii of B and B′ ions. The radius for Co atom in (Co,O) octahedra is 0.745 \text{Å}, and the average radius of B and B′ type octahedra is 0.83 \text{Å} for four samples. Evidently, for these compositions, t is significantly lower than unity, and this explains the observed monoclinic symmetry rather than the ideal cubic one. This lower symmetry is associated with the tilting of the (B,B′)O_{6} octahedra. In order to determine the crystallographic parameters of our samples, we have performed Rietveld refinement on the room temperature PXRD data using the MAUD software package [16]. The data converges well with monoclinic space group P2_{1}/n for all the samples along with antisite disorder between Co and Ru sites (figures 1(a) and (b)). Our calculations show that there are 1%–5% antisite defects, i.e. the fractional occupancy of B site consists of 99%–95% Co and 1%–5% Ru. The antisite defect is found to be large in Nd and Sm compounds and it is low in the case of La and Pr counterparts. The refined crystallographic parameters are depicted in table 1, and they match well with the previously reported data [17]. We have also added the structural data of Y_{2}CoRuO_{6} (YCRO) from [13] for comparison. The crystal structure of LCRO, as obtained from the refinement of our PXRD data, is shown in the inset of figure 1(a). It is clearly evident that the (Co,Ru)O_{6} octahedra are tilted. The average tilting angle is defined as \langle Ψ \rangle = \frac{1}{2}[\pi – \langle Φ \rangle], where \langle Φ \rangle is the average inter-octahedral Co–O–Ru angle. Clearly, the tilt angle increases systematically as we move from La to Sm, which is the effect of the gradual binding of Co–O–Ru bond (see table 1). It is interesting to note that all the crystallographic parameters vary systematically with the ionic radius for La, Pr, Nd and Sm samples.

4. Results

4.1. Magnetic studies

Figures 2(a)–(d) depict the temperature (T) dependence of susceptibility (\chi = M/H) measured under different values of H for all the four samples, where both zero-field-cooled (ZFC) and field-cooled (FC) measurements were performed. LCRO (figure 2(a)) shows well-defined peak at the Neél temperature T_{N} = 27 K, indicating an AFM ground state and it matches well with the previous reports [7, 12, 19]. The T variation of susceptibility (\chi = M/H) of LCRO in the paramagnetic (PM)
state cannot be fitted with a simple Curie–Weiss law. However, the $\chi(T)$ data above 100 K can be fitted well with a modified Curie–Weiss law, $\chi^{\text{CW}}(T) = C/(T - \theta) + \chi_0$, where an additional $T$ independent term ($\chi_0$) is included. Here $C$ is the Curie constant and $\theta$ is the Curie–Weiss temperature. The effective PM moment, $\mu_{\text{eff}}$, obtained from Curie–Weiss fitting, is found to be 6.63 $\mu_B$ f.u.$^{-1}$. The value of $\theta$ is $-140$ K, signifying strong AFM correlations. The FC and ZFC data show weak divergence below $T_N$. We also observed an upward rise in the $\chi(T)$ data below 6 K. The observed value of $\mu_{\text{eff}}$ is higher than expected for a Co$^{2+}$-high-spin and Ru$^{4+}$-low-spin states [7], which was attributed to extended 4$d$-orbitals of Ru [19].

For PCRO, NCRO and SCRO, the $\chi(T)$ data are drastically different from that of LCRO (figures 2(b)–(d) respectively).

**Table 1.** Crystallographic lattice parameters ($a$, $b$, $c$, and $\beta$), average Co–O–Ru bond angle, average octahedral tilt angle ($\Psi$), the goodness of Rietveld refinement of XRD data ($R_{wp}$, $R_b$, $\sigma$), magnetic state, magnetic transition temperatures and coercivity are depicted for $A_2\text{CoRuO}_6$ ($A = \text{La, Pr, Nd, Sm, and Y}$). The parameters for Y compound are obtained from [13]. The ionic radii of rare-earth ions (in the 3$^+$ state with coordination number VI) at the A site are also shown [18].

| Parameters | LCRO | PCRO | NCRO | SCRO | YCRO |
|------------|------|------|------|------|------|
| $r_{A}^{3+}$ (Å) | 1.032 | 0.990 | 0.983 | 0.958 | 0.900 |
| $a$ (Å) | 5.575(2) | 5.497(1) | 5.440(5) | 5.390(2) | 5.266 |
| $b$ (Å) | 5.638(7) | 5.689(7) | 5.717(7) | 5.722(8) | 5.711 |
| $c$ (Å) | 7.886(2) | 7.802(4) | 7.739(2) | 7.685(7) | 7.558 |
| $\beta$ ($^\circ$) | 90.01(1) | 89.88(7) | 89.99(8) | 89.93(2) | 90.03 |
| $\langle \angle \text{Co–O–Ru } \rangle$ ($^\circ$) | 152.4 | 150.9 | 143.4 | 139.5 | 141.7 |
| $\langle \Psi \rangle$ ($^\circ$) | 13.8 | 14.6 | 18.3 | 20.3 | 19.7 |
| $R_{wp}$/%, $R_b$/%, $\sigma$ | 2.7/1.8/1.9 | 3.3/2.5/2.1 | 2.7/1.8/1.8 | 2.6/2.1/1.2 | — |
| Mag. state | AFM | FI | FI | FI | FI |
| Tran. temp. | $T_N = 27$ K | $T_c = 46$ K | $T_c = 55$ K | $T_c = 78$ K | $T_c = 82$ K |
| $H_{\text{coer}}$ | 9 kOe (2 K) | 8 kOe (2 K) | 22 kOe (2 K) | 22.5 kOe (5 K) | — |

**Figure 1.** (a) and (b) show powder x-ray diffraction data of LCRO and SCRO respectively collected at room temperature. The inset of (a) shows the crystal structure of the sample. Green, pink, blue and red spheres indicate La, Ru, Co and O atoms respectively. The bottom panel indicates the octahedral tilt of four compositions.
and it is quite eventful. $\chi$ shows a sharp rise below $T_c = 46$, 55 and 78 K for these magnetic rare-earth containing samples respectively. The FC and ZFC susceptibilities show strong irreversibility below $T_c$. The divergence exists even in measurement at $H = 1$ kOe (see inset of figure 2(c)), however, the extent of divergence reduces. The point of bifurcation also moves to lower $T$ with increasing $H$. The ZFC data show a well-defined peak at a temperature $T_P$, which lies below $T_c$. Notably, we observe a change in the value of $T_P$ with increasing $H$. The $H$ dependence of $T_P$ is particularly significant for SCRO, where we observe a shift of $T_P$ by 16 K when $H$ is changed from 100 Oe–1 kOe (see inset of figure 2(c)). A similar shift in the observed peak in ferrimagnetic Nd$_2$CoMnO$_6$ was also reported previously [8, 13, 21]. The origin of such a peak in the ZFC data is not fully understood, and some authors have attributed it to the formation of ferromagnetic (FM) clusters due to the presence of static antisite disorder [20, 21]. The FC susceptibility, on the other hand, rises monotonically for all the samples with decreasing $T$.

The susceptibility data of PCRO and NCRO can be well fitted with $\chi_{CW}(T)$ above 100 K, which gives $\mu_{\text{eff}} = 6.59$ and 6.47 $\mu_B$ respectively. $\theta$ is found to be $-25 \, (\sim -22)$ K for Pr(Nd) sample. These values of $\mu_{\text{eff}}$ are slightly lower than the expected value of 6.97 (7.01) $\mu_B$ with Pr$^{3+}$ (Nd$^{3+}$), Co$^{2+}$ (high-spin) and Ru$^{4+}$ (low-spin) states. This mismatch can be caused by the presence of antisite disorder. Such disorder is expected to cause a decrease in the magnetic moment, and empirically $M_{\text{actual}} = M_{\text{obs}}/(1 - 2D)$ [22] where $D$ is the degree of disorder between Co and Ru atoms. For example, in the case of NCRO with $D = 0.05$ and $M_{\text{obs}} = 6.47 \mu_B$, $M_{\text{actual}}$ is found to be 7.18 $\mu_B$, which is very close to the theoretically predicted value.

For SCRO, we failed to achieve a good fit using $\chi_{CW}(T)$ in the temperature range 100–315 K. The separation between ground ($J = 5/2$) and first excited ($J = 7/2$) multiplets in Sm$^{3+}$ is small, and their mixing can be responsible for the observed non-Curie–Weiss behaviour [23].

The isothermal $M$ versus $H$ data are shown in figures 3(a)–(d). For LCRO, a linear $M - H$ curve is obtained at 2 K (see figure 3(a)), indicating AFM state. On the other hand, Pr, Nd and Sm compounds show significant hysteresis with a large coercive field ($H_{\text{coer}}$). Non-zero $H_{\text{coer}}$ is observed for these FI systems just below $T_c$, and it increases with decreasing $T$. The values of $H_{\text{coer}}$ are found to be 9, 8 and 22 kOe at 2 K for PCRO, NCRO and SCRO respectively. However, $M$ does not saturate even at 70 kOe of field for any of the samples. We have also recorded high field magnetization for SCRO, as shown in the inset of figure 3(d). The $M - H$ curve at 5 K does
not fully saturate even at 150 kOe of applied field. $M$ attains a value close to $2 \mu_B$ at the highest $H$. The value of $H_{\text{coer}}$ for SCRO at 5 K is found to be 10.6 kOe, which is smaller than the value of $H_{\text{coer}}$ reported for Y$_2$CoRuO$_6$ ($\sim 22.5$ kOe) at the same $T$.

Considering non-zero coercivity and the presence of antisite disorder, we have recorded $M-H$ hysteresis loop at 2 K after the sample being field-cooled from room temperature. In the case of inhomogeneous magnetic systems, a shift in the hysteresis loop along the field axis may be observed due to the interfacial coupling of two magnetic phases, and it is referred as exchange bias effect [24]. Many double perovskites show exchange bias effect due to the presence of antisite disorder [25]. However, we failed to observe such exchange bias in NCRO and SCRO samples, which possibly rule out the existence of large magnetic inhomogeneity in the system.

In order to investigate the effect of external field on the magnetic state, we have measured magneto-caloric effect (MCE) of the samples in terms of entropy-change ($\Delta S_M$) by $H$. In the present work, we have obtained MCE from our isothermal magnetization data recorded at different constant temperatures. From the theory of thermodynamics,

$$\Delta S_M(0 \to H_0) = \int_0^{H_0} \left(\frac{\partial M}{\partial T}\right)_H \, dH,$$

where $\Delta S_M(0 \to H_0)$ denotes the entropy change for the change in $H$ from 0 to $H_0$ [27]. Figures 4(a)–(c) show $\Delta S_M(T, H_0)$ versus $T$ plot at different values of $H_0$ for PCRO, NCRO and SCRO samples respectively.

The magnitude of MCE is found to be low for all three samples, however, it shows several anomalies with $T$. For the Pr and Nd samples, $\Delta S_M(T)$ is mostly negative with its magnitude peaking around 12 and 8 K (peak magnitude: 1.7 and 2.9 J kg$^{-1}$ K$^{-1}$ at $H_0 = 50$ kOe) respectively. A broad feature is also observed in $\Delta S_M(T, H_0)$ data around 35 K. On the other hand, SCRO shows a contrasting behaviour as far as the MCE is concerned. $\Delta S_M(T)$ for SCRO is positive below 20 K, and increases with decreasing temperature (at least for $H_0 > 10$ kOe). $\Delta S_M$ attains a value of 3.1 J kg$^{-1}$ K$^{-1}$ for $H_0 = 50$ kOe at 2 K.

As already discussed, double perovskite systems can show glassy magnetic state [28]. An intermediate SG state is observed when the AFM state is transformed into an FI state by suitable A-site doping. In order to investigate the possibility of a glassy state, particularly those which lie across the AFM-FI boundary, field-cooled-field-stop memory
measurements were performed on Pr and Nd samples [29, 30]. In this protocol, the samples were cooled in 100 Oe of field down to 2 K with intermediate stops at several temperatures below $T_c$. Subsequently, the samples were heated back in 100 Oe and dc magnetization was measured. We do not observe any anomaly at the stopping temperatures during heating, which rules out the possibility of any glassy (spin glass or cluster glass) or super-paramagnetic state in PCRO and NCRO samples.

4.2. Electrical transport

Like many other $A_2BB'O_6$ compounds, LCRO, PCRO, NCRO, and SCRO show semiconducting behaviour as evident from the transport data depicted in figures 5(a)–(d) respectively. The values of $\rho$ at room temperature ($\sim 300$ K) are found to be 8.86, 8.81, 4.16 and 6.68 $\Omega \cdot$ cm for La, Pr, Nd, and Sm compounds respectively. Our analysis on the $\rho(T)$ data indicate that all four compositions show Mott Variable Range (VRH) hopping conduction, where $\rho(T) \sim \exp \left( \frac{C}{T} \right)^{1/4}$. This is also quite common among disordered double perovskite such as Sr$_2$MnRuO$_6$ [31] or Sr$_2$CoSbO$_6$ [32]. The VRH type conduction is quite clearly visible from the log $\rho$ versus $T^{-1/4}$ plots in the respective insets of figures 5(a)–(d). While for La and Nd compounds, the VRH nature is present almost over the full range of temperature (it deviates only below 65 K), Pr and Sm compounds show VRH conduction only in the range 160 to 60 K. The values of the parameter $T_0$ associated with the VRH conduction are found to be $6.9 \times 10^4$, $5.1 \times 10^4$, $8.8 \times 10^4$ and $6.8 \times 10^4$ K for La, Pr, Nd and Sm compounds respectively.

5. Discussions

It turns out that the magnetic properties of samples containing magnetic rare-earth are drastically different from that of LCRO. Naively, one can relate the FI state with the magnetic moment of A site. However, FI state is also observed in Y$_2$CoRuO$_6$, where A site contains nonmagnetic Y$^{3+}$ ions. In order to address the issue, let us first discuss various salient observations made on the studied samples.

(i) The Co–O–Ru bond distortion (and consequently, the octahedral tilt) is found to increase as we move from LCRO to heavier rare-earth-containing compounds. This is due to the reduction of the ionic radius at the A-site (lanthanide contraction), as we proceed from La to Sm. It has been already mentioned that the smaller radius of A-element leads to larger B–O–B’ bond distortion [2].

(ii) LCRO with relatively smaller bond distortion shows AFM ground state. On the other hand, PCRO, NCRO, and SCRO show a large increase in $M$ below the magnetic transition at $T_c$. Isothermal magnetization curves show large hysteresis with the presence of significant remanent magnetization. Isostructural Y$_2$CoRuO$_6$ shows similar magnetic behaviour and the Co–O–Ru superexchange interaction is found to be AFM in nature leading to a FI ground state (Co and Ru sublattices have different moment values) [13]. In analogy with the Y compound, we can conclude that the ground states of PCRO, NCRO, and SCRO are ferrimagnetic. Similar to Y compound, FI state in PCRO and subsequent compounds emerges possibly due to the Co–O–Ru bond distortion, rather than A-site magnetic moment formation.

(iii) All four studied compounds are found to be semiconducting with reasonably high resistivity ($\sim 10^4 \Omega \cdot$ cm) around the magnetic anomalies. Therefore, the magnetic interaction is likely to be mediated by the superexchange, rather than the double-exchange mechanism.

(iv) The coercivity associated with $M – H$ hysteresis loop is found to be much higher in the case of SCRO, however, it is lower than the value reported for Y$_2$CoRuO$_6$. It appears that the coercivity is not directly connected to the fact whether A site contains a magnetic (such as Pr, Nd or Sm) or nonmagnetic (here Y) ion.

(v) $\Delta S_M$ versus $T$ plots for PCRO, NCRO and SCRO show peak like anomaly around 10 K, which can be attributed to the rare-earth ordering. At low-$T$, $\Delta S_M$ turns positive, which is presumably due to the AFM phase of the rare-earth ions. The resulting magnetic moment from Co and Ru sublattices tends to align in the direction of the applied magnetic field. The low negative value of $\Delta S_M$ at higher temperatures ($T > 10$ K) is due to this alignment of spins.
As already mentioned, a transition from AFM to FI via a glassy magnetic state has been observed in several double perovskites with the bending of the B–O–B’ bond \[8–10, 13\], where the lattice distortion was created by systematic doping at the A site or by applying hydrostatic pressure. In the present case, we found a similar effect when one rare-earth ion is replaced by another one with smaller ionic radius. In analogy with the idea mooted in case of Sr2−xCa2xFeOsO6 and Sr2−xCa2xCoOsO6 \[8, 9\], the AFM state in LCRO is due to the strong AFM correlation along the long bonds Co–O–Ru–O–Co and Ru–O–Co–O–Ru when the Co–O–Ru bond distortion is low. Replacement of La by Pr initiates strong bending in Co–O–Ru bond (see table 1), which possibly strengthen the Co–O–Ru superexchange over the magnetic interaction on longer Co–O–Ru–O–Co and Ru–O–Co–O–Ru pathways leading to FI state. The bending further enhances in Sm compound, and a significantly large coercive field is observed.

The above argument is also supported by the drastic change in the values of paramagnetic Curie temperature \(\theta\) in Pr and Nd compounds (−25 and −22 K respectively) as compared to the antiferromagnetically ordered La counterpart. This may be an indication of the weakening of the exchange interaction along longer Co–O–Ru–O–Co and Ru–O–Co–O–Ru pathways. However, \(\theta\) still remains negative due to the presence of Co–O–Ru AFM interaction.

In case of SrCaCoOsO6 and La2−xYxCoRuO6 \((x \approx 0.25 – 1.5)\) SG states are observed \[8, 13\], when Ca(Y) is doped at the Sr(La) site, which has been assigned due to the frustration between long (B–O–B’–O) and short (B–O–B’’) exchange paths. However, neither of the Pr and Nd compounds shows a glassy magnetic state. For La1.25Y0.75CoRuO6 with tilt angle 15.5°, a prominent frequency dispersion is observed in the ac susceptibility data. On the other hand PCRO with lower tilt angle (14.6°) shows ordered FI state. Possibly, the emergence of a glassy state in doped samples is also connected with the doping induced disorder. Notably, La1.25Y0.75CoRuO6 has huge degree of antisite disorder (20%), as compared to 1% antisite disorder in PCRO.

In contrast to the presently studied A2CoRuO6 compounds, the Ni counterpart (namely, A2NiRuO6) are relatively insensitive to the change of rare-earth ion at the A site as far as the magnetic properties are concerned \[33\]. The Ni–Ru compositions mostly show AFM ground state irrespective of the rare-earth ion present at the A site.

It is now pertinent to address the role of 4f moment from the rare-earth present at the A site. In the case of isostructural Er2CoMnO6, rare-earth moment orders at a relatively lower \(T\) than the Co–Mn ordering temperature \[34\]. From our magnetization data, it is hard to identify the ordering of rare-earth moment. The \(\Delta S_M\) versus \(T\) data depicted in figure 4 show...
peak-like anomalies between 8 and 12 K in PCRO, NCRO and SCRO, and they can be probable ordering points of rare-earth moments. In order to shed more light on this issue, we have compared the moments of $A_2CoRuO_6$ ($A = Pr, Nd, Sm$ and $Y$), where the magnetic data of $Y_2CoRuO_6$ is obtained from [13]. The moments at 5 K ($M_K$), on applying 50 kOe of field, is found to be 2.3, 2.9, 1.4 and 0.8 $\mu_B$ f.u.$^{-1}$ on the virgin line of the $M - H$ curve for Pr, Nd, Sm and Y compounds. Y does not carry any moment, while the total angular momentum $J = 4, 9/2$ and $5/2$ for $Pr^{3+}$, $Nd^{3+}$ and $Sm^{3+}$ states respectively. The magnetic moments of these three ions are 3.58, 3.62 and 0.84 $\mu_B$ respectively. Clearly, the variation of $M_K$ corresponds well with the variation of rare-earth moment. This signifies that the A site rare-earth moment remains in ordered state at 5 K. It is important to perform a neutron diffraction study to ascertain the true magnetic structure of these compounds.

In summary, we have studied the structural, magnetic as well as transport properties of the double perovskites $La_2CoRuO_6$, $Pr_2CoRuO_6$, $Nd_2CoRuO_6$, $Sm_2CoRuO_6$. We observe a systematic change in the magnetic ground state as La is replaced by Pr, Nd and Sm. This matches well with the case of Fe–O$_5$ and Co–O$_5$ based double perovskites, where lattice distortion tunes the strength of the magnetic interactions in different exchange pathways.

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