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Account/Revue

Transition metal oxides with triangular metallic sublattices: From multiferroics to low-dimensional magnets

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ABSTRACT

The very recent studies of two classes of transition metal oxides with a triangular metallic sublattice are reported. The first class of materials concerns the swedenborgite $\text{CaBaCo}_4\text{O}_7$ family, which is shown to be a ferrimagnetic multiferroic with a gigantic-induced electrical polarization, and the second one deals with the spin chain oxides of the $\text{Sr}_4\text{Mn}_2\text{CoO}_9$ type, which have been found to behave as single chain magnets and single ion magnets. These materials that exhibit a potential for applications in the field of memory devices and quantum computation pave the way for future investigations in these systems.

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Transition metal oxides characterized by a triangular geometry of their metallic sublattice have received considerable attention because of their complex magnetic behavior. However, the ability of these lattices to generate properties in view of applications has not been fully developed as compared with square-like lattices such as those of perovskites, which are used as ferroelectrics, high T_c superconductors, magnets, or colossal magnetoresistive materials. We report herein on recent studies of two classes of oxides with attractive properties either as multiferroics or as low-dimensional magnets.

1. Swedenborgite $\text{CaBaCo}_4\text{O}_7$ family: promising ferrimagnetic ferroelectrics

In the first class of oxides, the metallic cations form MO_6 octahedra or MO_4 tetrahedra and are displayed generally on a three-dimensional (3D) M_T sublattice built up of M_4 tetrahedra and M_3 triangles. This configuration

induces geometric magnetic frustration, as shown in the numerous studies of the pyrochlore oxide family [1], and in a more general way produces frustrated magnets such as in kagome lattices of the spinel structure and in garnets [2–4].

Recently, complex magnetic transitions correlated to structural and/or electric transitions were observed and studied in pure tetrahedral kagome frameworks of the swedenborgite-type “114” $\text{LnBaCo}_4\text{O}_7$ cobaltates [5–21]. The room temperature hexagonal $P31c$ structure of these oxides (Fig. 1a) consists of a 3D framework of corner-shared CoO_4 tetrahedra, built up of two sorts of layers, kagome layers (K) and triangular layers (T) as shown in Fig. 2. As a consequence, the metallic $[\text{Co}_4]$ sublattice of these oxides is built up of “ Co_5 ” bitetrahedra interconnected through “ Co_3 ” triangles (Fig. 3). It results in a 2D geometric frustration in the $(001)_H$ plane, which strongly competes with the 1D magnetic ordering along c in the original hexagonal cell. Thus, these oxides have been considered as a new class of frustrated magnets, which out-of-plane magnetic coupling acts as an external magnetic field with respect to the in-plane 2D magnetic frustration [15].

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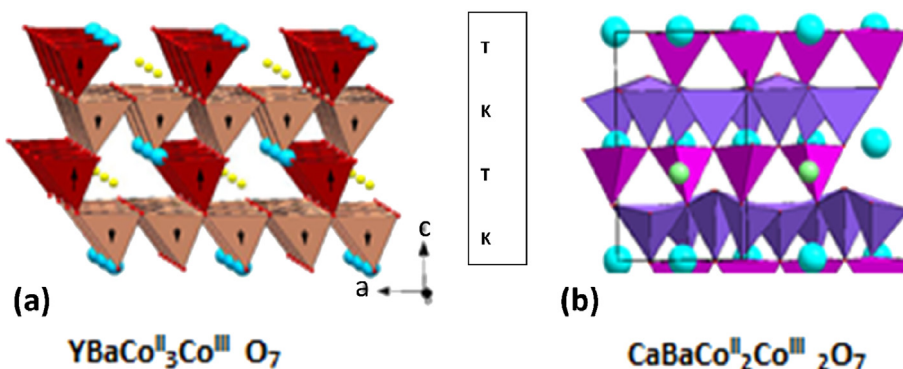


Fig. 1. Structure of the “114” cobalt oxides: (a) hexagonal $\text{LnBaCo}_4\text{O}_7$ and (b) $\text{CaBaCo}_4\text{O}_7$. Both consist of the stacking along c of triangular (T) and kagome (K) layers.

To modify the competition between this geometric 2D frustration and 1D magnetic ordering the possibility to replace the trivalent lanthanide by a divalent cation, calcium, was considered. The synthesis of the cobaltate $\text{CaBaCo}_4\text{O}_7$ [22,23] allows the mixed valence $\text{Co}^{2+}/\text{Co}^{3+}$ to be strongly modified, with an increase in the Co^{3+} content up to 50% with respect to $\text{LnBaCo}_4\text{O}_7$. This leads to a dramatic

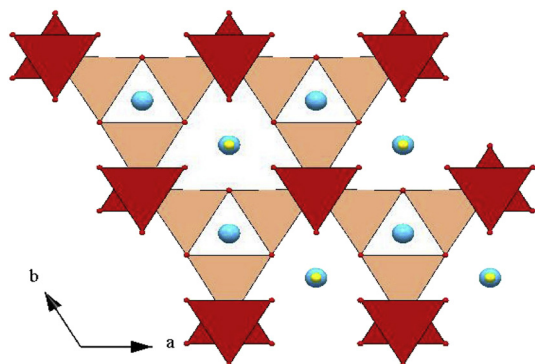


Fig. 2. View of the structure along c of the triangular layers (T) as isolated CoO_4 tetrahedra (red) and of the kagome layers (K) as corner-shared CoO_4 tetrahedra (pink) in the “114” cobalt oxides.

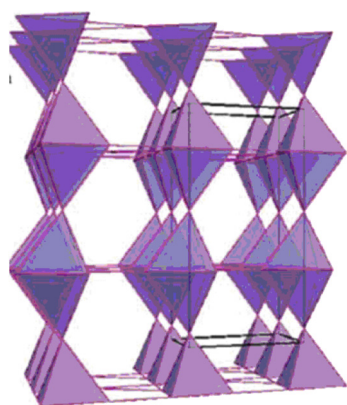


Fig. 3. Cobalt $[\text{Co}_4]$ sublattice of hexagonal $\text{LnBaCo}_4\text{O}_7$ and orthorhombic $\text{CaBaCo}_4\text{O}_7$ oxides.

change in both structural and magnetic properties. Although closely related to $\text{LnBaCo}_4\text{O}_7$ oxides, the structure of $\text{CaBaCo}_4\text{O}_7$ (Fig. 1b) differs by a strong buckling of the kagome layers, the triangular layers remaining flat [23]. The first important structural character of this oxide deals with the very large orthorhombic distortion of its cell, which lifts the geometric frustration. It results in the appearance of charge and magnetic ordering. A complex ferrimagnetic structure is indeed observed at less than 64 K [23] (Fig. 4): it consists of ferromagnetic Co^{2+} zigzag chains, which are antiferromagnetically coupled with isolated mixed valent cobalt species $\text{Co}^{3+}/\text{Co}^{2+}3d^6/3d^7L$. The second remarkable feature concerns the fact that the structure of $\text{CaBaCo}_4\text{O}_7$ is noncentrosymmetric, with the $Pbn2_1$ space group, a necessary condition for the coexistence of ferroelectricity and ferrimagnetism, for the realization of multiferroic properties.

On the basis of the aforementioned considerations, the dielectric properties of this cobaltate were first investigated on polycrystalline samples [24,25]. The dielectric permittivity and loss curves versus temperature measured at 100 kHz on these samples clearly show a peak at the same temperature as the ferrimagnetic transition $T_C = 64$ K (Fig. 5a), which was interpreted as spin–charge coupling. Measurements of the electric polarization versus temperature with an electric field of 111 kV/m (Fig. 5b) performed on the same polycrystalline samples evidence also a transition around T_C and importantly a sign change in the polarization by reversing the electric field. This behavior was then attributed to spin-driven ferroelectricity [24,25]. The study of large crystals of $\text{CaBaCo}_4\text{O}_7$ allowed us to confirm the multiferroic character of this oxide and showed that it is a remarkable magnetoelectric material [26] (Fig. 6). One indeed observes a sharp transition of the magnetization along b at 64 K, which coincides perfectly with the sharp peak of ϵ' measured along c . Importantly, this oxide exhibits a gigantic variation in its induced electric polarization along c , $\Delta P = 17,000 \mu\text{C}/\text{m}^2$, a value never reached for magnetically induced ferroelectric polarization in multiferroic oxides, six times larger than that obtained for the perovskite $\text{CaMn}_7\text{O}_{12}$ [27,28]. However, Caignaert et al. could not observe switching of the electric polarization by reversing the electrical field for the crystal [26] in contrast to the polycrystalline samples [24,25].

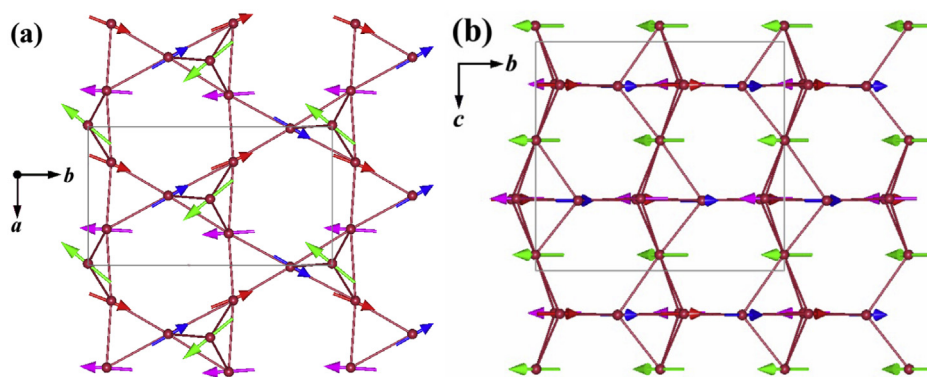


Fig. 4. Ferrimagnetic structure of $\text{CaBaCo}_4\text{O}_7$: (a) Co^{2+} zigzag chains running along b (red and blue arrows) are antiferromagnetically coupled with isolated mixed valent cobalt $\text{Co}^{3+}/\text{Co}^{2+}3d^6/3d^7L$ (green and pink arrows) and (b) bitetrahedral cobalt chains running along c .

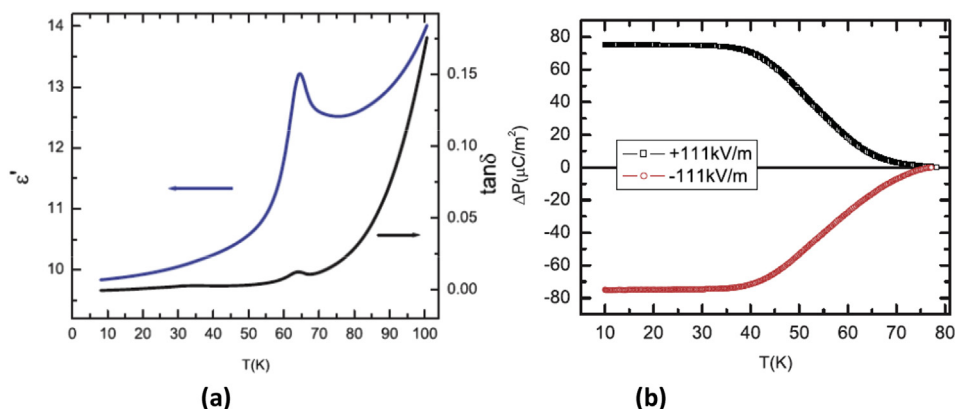


Fig. 5. Polycrystalline $\text{CaBaCo}_4\text{O}_7$: (a) dielectric permittivity and loss vs T at 100 kHz and (b) electric polarization vs T showing a transition around T_C with sign change of P by reversing E (111 kV/m).

From the latter results, Johnson et al. [29] reinvestigated the magnetoelectric coupling in $\text{CaBaCo}_4\text{O}_7$, using *ab initio* calculations and Landau theory; these authors showed that the observed giant variation in polarization is also compatible with exchange striction and that the strong magnetoelectric coupling close to T_C originates from magnetoelastic coupling. From the fitting of their model with the crystal data extracted from Ref. [26], Johnson et al. concluded that $\text{CaBaCo}_4\text{O}_7$ is not a ferroelectric but a ferrimagnetic pyroelectric [29]. Unfortunately this latter study does not explain the switching behavior of the polarization observed on polycrystalline samples [24,25]. The recent investigation of this multiferroic by Fishman et al. [30] sheds light on this issue. Upon rotating a $\text{CaBaCo}_4\text{O}_7$ crystal about c in a fixed magnetic field applied along a , these authors showed, from the threefold splitting of the spin wave frequencies, that the latter is not a single crystal but a hexagonally twinned crystal. Magnetization measurements on crystals, combined with powder neutron and terahertz absorption spectroscopy allowed magnetic domains with a complex spin order in each domain to be evidenced [30]. Describing the cobalt framework as bitetrahedral chains parallel to c and ferrimagnetically coupled with each other in the ab plane Fishman et al. [30]

concluded that the lifting of the geometric frustration in $\text{CaBaCo}_4\text{O}_7$ allows ferrimagnetism and ferroelectricity to coexist [30]. On the basis of the previously observed large changes in spin-induced polarization [26], these authors suggest that this oxide may have important technological applications, when a modest magnetic field less than 1 T is applied along b [30] close to T_C . The high sensitivity of the magnetic properties of this swedenborgite to the doping of the cobalt sites with different cations such as Zn, Ga, Li, Al, Fe, and to the doping of Ba sites with Sr or Ln [31–39] offers many possibilities for tuning the characteristics of this multiferroic. The recent study of the ferroelectric Ni-doped $\text{CaBaCo}_4\text{O}_7$, which exhibits an enhanced ordering temperature at 82 K [40], supports this statement.

2. Spin chain oxides $\text{Sr}_{4-x}\text{Ca}_x\text{Mn}_2\text{CoO}_9$: toward low-dimensional magnets

The second class of oxides belongs to the triangular spin chain oxide family. Their hexagonal structure consists of single chains of face-sharing MO_6 octahedra and trigonal prisms displayed at the corners of a triangular lattice. The $\text{Ca}_3\text{Co}_2\text{O}_6$ cobaltate, whose $[\text{Co}_2\text{O}_6]$ chains exhibit a 1:1 ordering of the CoO_6 prisms and CoO_6 octahedra (Fig. 7a), is

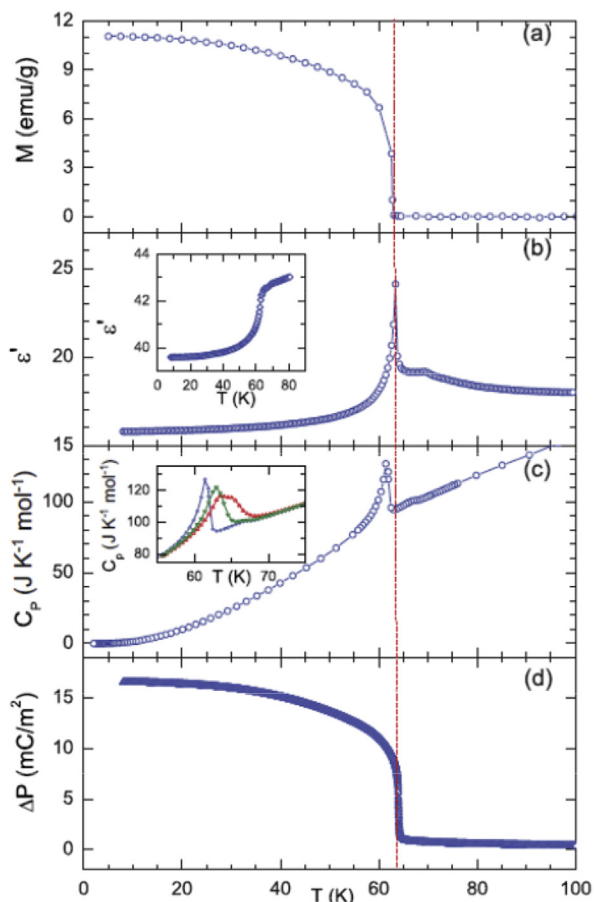


Fig. 6. “Single” crystal data of $\text{CaBaCo}_4\text{O}_7$: (a) $M(T)$ along b , (b) $\chi'(T)$ along c , (c) specific heat $C_p(T)$, and (d) variation in polarization $\Delta P(T)$ along c .

the archetype of these spin-chain compounds. The latter was found to exhibit several original features [41–48] such as a strong Ising-like character due to antiferromagnetic interchain and ferromagnetic intrachain coupling, with

magnetization plateaus, originating from the close energy values of the cobalt moments in the triangular planes perpendicular to the cobalt chains. The isotopic $\text{Ca}_3\text{MnCoO}_6$ compound [49] also characterized by a 1:1 intrachain ordering of the MnO_6 octahedra and CoO_6 prisms was revealed to be a multiferroic with complex magnetic behavior [50–53]. For these $\text{Ca}_3\text{MM}'\text{O}_6$ oxides, partially disordered antiferromagnetism was often reported to describe the magnetic interactions between the Ising chains on the triangular lattice [54–58].

The oxides $\text{Sr}_4\text{Mn}_2\text{CoO}_9$ [59] and $\text{Sr}_3\text{CaMn}_2\text{CoO}_9$ [60] can be described as the second members of this spin chain oxide family: in this hexagonal structure (Fig. 7b), the $[\text{Mn}_2\text{CoO}_9]$ chains are also formed of face-sharing MnO_6 octahedra and CoO_6 prisms, but a 2:1 ordering “ Mn_2Co ” between the octahedra and the prisms within each chain is observed. The magnetism of the latter compounds has not been intensely studied in contrast to the first members, most probably because of the ill-defined glassy character of their magnetic properties. Indeed, $\text{Sr}_4\text{Mn}_2\text{CoO}_9$ [59] was found to exhibit a behavior close to a spin glass, whereas the enhancement of magnetic correlations was observed for $\text{Sr}_3\text{CaMn}_2\text{CoO}_9$ [60], but no long-range ordering could be reached. Bearing in mind that the interchain distances should significantly influence the magnetic interactions between the chains, the size effect of the $\text{Ca}^{2+}/\text{Sr}^{2+}$ cations was recently investigated in the oxides $\text{Sr}_{4-x}\text{Ca}_x\text{Mn}_2\text{CoO}_9$, by comparing the magnetic behavior of $\text{Sr}_4\text{Mn}_2\text{CoO}_9$ ($x = 0$) and $\text{Sr}_2\text{Ca}_2\text{Mn}_2\text{CoO}_9$ ($x = 1$) [61]. The $\chi'(T)$ curves of these phases (Fig. 8) showed that they both exhibit a frequency-dependent bump around 6 K (labeled as regime 2 in Fig. 8), but differ in their behavior at higher temperature. $\text{Sr}_2\text{Ca}_2\text{Mn}_2\text{CoO}_9$ is characterized by a frequency-independent maximum of χ' around 29 K (labeled as regime 3 in Fig. 8), whereas $\text{Sr}_4\text{Mn}_2\text{CoO}_9$ displays a strongly dependent frequency peak around 10–15 K (labeled as regime 1). The regime 3 observed for $\text{Sr}_2\text{Ca}_2\text{Mn}_2\text{CoO}_9$ could easily be attributed to the existence of long-range antiferromagnetic ordering (LRO) with $T_N = 29$ K in agreement with neutron diffraction data. The regime 1 observed for

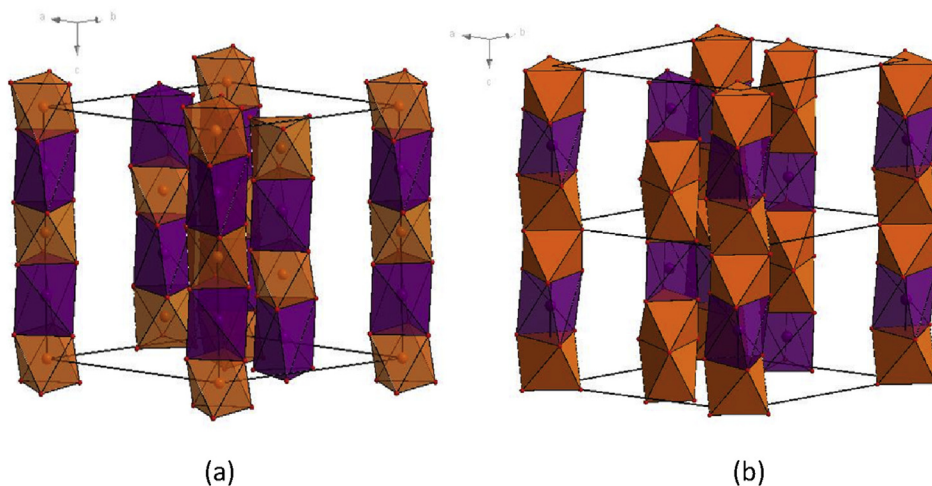


Fig. 7. Perspective view of the structure of the spin chain oxides (a) $\text{Ca}_3\text{MnCoO}_6$ and (b) $\text{Sr}_4\text{Mn}_2\text{CoO}_9$. Note the 1:1 and 2:1 ordering of the MnO_6 octahedra (rust colored) and CoO_6 trigonal prisms (purple). Ca^{2+} and Sr^{2+} cations are omitted for the sake of clarity.

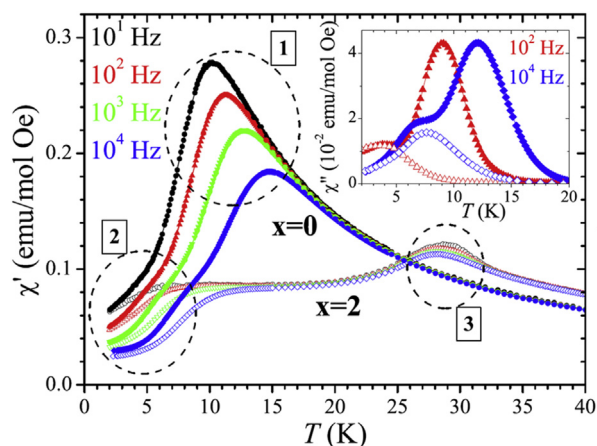


Fig. 8. $\text{Sr}_{4-x}\text{Ca}_x\text{Mn}_2\text{CoO}_9$: in-phase (main panel) and out-of-phase (inset) susceptibility of $x = 0$ (filled symbols) and $x = 2$ (open symbols). The dotted circles highlight the three regimes labeled 1, 2, and 3.

$\text{Sr}_4\text{Mn}_2\text{CoO}_9$ and the regime 2 observed for both compounds were clearly identified from $\chi''(T)$ curves and from Argand plots that were shown to be consistent with the Cole–Cole model.

The relaxation time curves $\tau_c(1/T)$ extracted from these investigations (Fig. 9) summarize these results. The temperature-independent character of τ_c observed for $\text{Sr}_2\text{Ca}_2\text{Mn}_2\text{CoO}_9$ (regime 3 in Fig. 9) originates from LRO. The Arrhenius-like evolution of τ_c versus $1/T$ observed for $\text{Sr}_4\text{Mn}_2\text{CoO}_9$ (regime 1 in Fig. 9) rules out the possibility of a spin glass behavior for this compound and is similar to that of a single chain magnet (SCM). Moreover, the values of $\tau_0 \sim 10^{-11}$ s and of $\Delta \sim 167$ K obtained from the maxima in $\chi''(T)$, close to those reported for SCM molecular

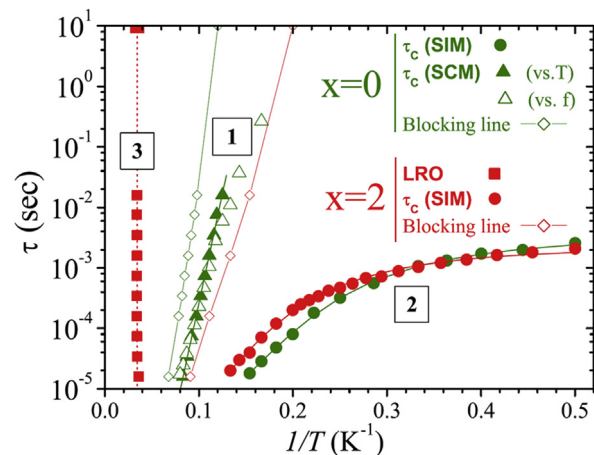


Fig. 9. $\text{Sr}_{4-x}\text{Ca}_x\text{Mn}_2\text{CoO}_9$: Arrhenius plot of the median relaxation times of regime 1 (SCM) in $x = 0$ and regime 2 (SIM) in both compounds ($x = 0$ and 2), with the corresponding fitting lines. Regime 3, derived from the high T maxima of $\chi_{dc}(T)$ in $x = 2$ is ascribed to the onset of LRO. The open diamonds delineate the domains where $\chi(T)$ starts being affected by spin blocking effects, i.e., SCM in $x = 0$ and SIM in $x = 2$. Also shown are dc data (associated with a characteristic time of 10 s) corresponding to regime 3 (midpoint of spontaneous magnetization) and to the blocking lines [start of the drop in $\chi_{dc}(T)$ zero field cooled (ZFC)].

compounds containing Co^{2+} [62–64] confirm this statement. The genuine SCM behavior of this phase was then demonstrated further by χ_{dc} measurements and from $M(H)$ hysteresis loops. In this way, it was shown that blocking effects associated with slow spin dynamics yield remanence and coercivity in the absence of LRO for $\text{Sr}_4\text{Mn}_2\text{CoO}_9$ [61]. The $\tau_c(1/T)$ evolution of regime 3 (Fig. 9), similar for both oxides, which coexists with SCM in $\text{Sr}_4\text{Mn}_2\text{CoO}_9$ and with LRO in $\text{Sr}_2\text{Ca}_2\text{Mn}_2\text{CoO}_9$ was attributed to the fact that Co^{2+} can act as a single ion magnet (SIM), in agreement with the behavior observed for SIM in Co^{2+} complexes [65–68].

These observations of SCM and SIM behaviors in purely anhydrous inorganic materials are quite unique. They show the possibility to realize low-dimensional magnets (0D or 1D) similar to those obtained for the large family of molecular compounds, which have been extensively studied for the generation of single molecule magnets [69,70] and SCMs [62,71]. In these oxides and especially in $\text{Sr}_4\text{Mn}_2\text{CoO}_9$, the Sr^{2+} cations because of their larger size allow the distances between the magnetic chains to be sufficiently increased to considerably weaken the 3D magnetism. In this way, they play the role of organic ligands or molecules that are generally used for shielding the magnetic interactions between the transition metal clusters or chains in molecular magnets. Bearing in mind that low-dimensional magnets have been the object of considerable interest for their potential applications in information storage [72,73] and in quantum computation [74], these oxides, which are highly stable as compared to molecular compounds, open the route for future investigations.

3. Conclusions

These recent studies show that transition metal oxides, which involve triangular metallic sublattices, exhibit besides magnetic frustration a great potential for the generation of materials with attractive properties in view of applications either as ferroelectric multiferroics or as low-dimensional magnets. Bearing in mind that the appearance of such properties stems from either the lifting of the geometric frustration or the weakening of chain interactions in triangular systems, this opens the route to the investigation of numerous alkaline earth-based transition metal oxides. In these systems the inter-related structural and chemical parameters such as distortion of the structure, valence of the transition element, oxygen stoichiometry, size of alkaline earth cation, and order–disorder phenomena have to be controlled carefully.

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