

## Colossal magnetoresistance in $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$ double perovskites due to field-induced phase coexistence

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We have investigated the properties of the low-temperature magnetostructural transition in polycrystalline  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$  compounds. We have shown in a previous report that this kind of transition was present for  $x \geq 1$ . We have observed that the temperature dependence of the resistivity, the lattice parameters, and the magnetocrystalline anisotropy of the  $x=1.5$  compound mimics those of the  $x=2$  compound. Therefore, the coexistence of two monoclinic phases with different conductivities and crystallographic parameters, which is well reported for  $x=2$ , is suggested to occur also for  $x=1.5$ . Since the external applied field favors the high-temperature phase, we have performed magnetostriction and magnetoresistance experiments up to 25 and 45 T, respectively, in order to track macroscopically the phase coexistence. In the  $x=1.5$  compound, we find magnetoresistance above 2000%, which is an unexpected phenomenon in the field of double perovskites. Furthermore, the magnetostriction isotherms under high fields behave in a nonmonotonous way due to the different cell volumes of the coexisting phases. These results indicate that the field-induced phase coexistence is a general property in  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$  compounds showing large monoclinic distortion.

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### I. INTRODUCTION

$\text{A}_2\text{FeReO}_6$ -based double perovskites are attracting great interest for spintronics because they combine a theoretically half-metallic density of states<sup>1,2</sup> with Curie temperature well above 300 K.<sup>1,3</sup> Following the original description by Sarma *et al.*<sup>4</sup> for FeMo-based double perovskites, in these compounds the ferromagnetic ground state arises from a double-exchange-like mechanism that involves hopping interactions of the  $\text{Re}^{5+}(5d^2)$  delocalized electrons between the hybridized  $\text{Fe}(t_{2g})\text{-O}(2p_\pi)\text{-Re}(t_{2g})$  states. Since the Fe  $3d$  shell is half filled, the empty  $\text{Fe-}t_{2g}$  states are fully spin-down polarized (intraatomic Hund's coupling). Therefore, the electron hopping between Fe and Re sites can only occur if the delocalized electrons are antiparallel to the  $\text{Fe}^{3+}(3d^5, S=5/2)$  localized electrons. In consequence, the hopping interaction induces a nonzero magnetic moment antiparallel to the Fe one at the nonmagnetic Reatom,<sup>5-7</sup> as well as a  $\text{Fe}^{3+}/\text{Re}^{5+}\text{-Fe}^{2+}/\text{Re}^{6+}$  mixed valence state.<sup>8-10</sup> Similarly to the FeMo case, a metallic ground state with large spin polarization ( $P=-1$ ) at the Fermi level is expected. Indeed, the large spin polarization has been probed by means of inter-grain tunneling magnetoresistance (ITMR) in  $\text{A}_2\text{FeReO}_6$  polycrystalline compact pellets. ITMR is based on the spin-dependent electron tunneling probability across the insulating barriers formed between grain boundaries.<sup>1,11</sup> It has been shown that the following formula can account for the ITMR effect in double perovskites:<sup>12</sup>

$$MR = \frac{\rho(H) - \rho_0}{\rho(H)} = -P^2 m_{gb}^2, \quad (1)$$

where  $m_{gb}$  is the normalized magnetization in the vicinity of the grain boundary. Equivalently,

$$\frac{\rho(H)}{\rho_0} = \frac{1}{1 + P^2 m_{gb}^2}. \quad (2)$$

Nevertheless, FeRe-based compounds exhibit remarkable differences with respect to their FeMo-based analogs, in spite of their almost identical crystallographic properties.<sup>3,11,13</sup> Here we focus on the physical properties below room temperature. Contrary to the Mo-based double perovskites, in Re-based ones a strong magnetostructural coupling is observed at low temperatures (well below  $T_C$ ).<sup>3,14,15</sup> The driving mechanism is the interplay between the structural degrees of freedom and the unquenched Re orbital moment,<sup>14,16,17</sup> which is due to the large spin-orbit coupling constant of  $5d$  elements.<sup>13</sup> One of the consequences is the magnetostructural transition at  $T_{sm} < 150$  K, which was first reported for  $\text{Ca}_2\text{FeReO}_6$  (Refs. 6, 7, and 15) and later on it was shown to appear also in  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$  with  $x \geq 1$ .<sup>3</sup> The magnetostructural transition entails the transformation of the  $P2_1/n$  high-temperature (HT) phase showing soft ferromagnetism into another  $P2_1/n$  low-temperature (LT) phase with slightly different structural parameters, an enhanced magnetocrystalline anisotropy, and a new magnetic easy axis. Around  $T_{sm}$ , the two phases can coexist in a wide temperature range<sup>6</sup> or undergo a complete transformation,<sup>15</sup> which indicates that they must have very similar free energies. As a consequence, it is not surprising the fact that the phase fraction in the vicinity of  $T_{sm}$  were field dependent. In particular, it was found using neutron diffraction experiments that the HT phase in  $\text{Ca}_2\text{FeReO}_6$  is fairly favored under an external magnetic field of the order of several T.<sup>7</sup>

Furthermore, the LT and HT phases exhibit a rather more striking difference, which is the, respectively, insulating and metallic nature of the carrier transport. In the archetypal

complete phase transition of  $\text{Ca}_2\text{FeReO}_6$ , Iwasawa *et al.* reported the temperature dependence of the near- $E_F$  photoemission spectral weight.<sup>18</sup> A narrow insulating gap opens below  $T_{sm}$  in the  $\text{Re-}t_{2g}$  band ( $\sim 50$  meV), and the photoemission intensity at  $E_F$  undergoes an abrupt decrease below this temperature. This experiment confirms the insulating nature of the LT phase. This was proposed in an earlier work by means of resistivity and optical conductivity experiments, in which a metal to insulator transition is suggested to occur in  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$  for  $x > 0.4$ .<sup>19</sup> Therefore, the phase transition taking place at  $T_{sm}$  does not only involve a magnetostructural transition, but also a metal to insulator transition (MIT), in sharp contrast with the  $\text{Ca}_2\text{FeMoO}_6$  isostructural compound. The gap formation at the conduction band leading to the MIT could be explained by the opposite shift of the ground and first-excited bare  $\text{Re-}t_{2g}$  energy levels owing to an electrostatic effect.<sup>13</sup> The structural transition gives rise to a change of the  $\text{ReO}_6$  octahedra shape at  $T_{sm}$ , which modifies the crystal electric field produced by the negative oxygen ligands. Thus, the impact of the structural distortion on the density of states and the electron correlation of the multiple  $\text{Re } 5d$  electrons trigger the electronic localization below  $T_{sm}$ .<sup>13,18,19</sup>

The existence of two phases in Ca-rich  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$  having different structural, magnetic, and transport properties brings about an unexplored rich phenomenology. In the following we address the magnetoresistance and magnetostriction phenomena in the  $x=2$  and  $x=1.5$  compounds, which can be safely ascribed to the phase coexistence. The main issue of this paper is to explain their unique magnetoresistive behavior in the field of double perovskites. The samples transport properties exhibit an overall resistance change as a function of the magnetic field due to the prevalence of the conducting HT phase at the expense of the insulating LT phase. Such magnetoresistance mechanism, which is entirely unexpected, has been suggested from measurements up to 12 T.<sup>11</sup> In this work, the extension of the magnetic field range up to 45 T permits one to disclose the relationship between the magnetoresistance and the low-temperature magnetostructural transition for both  $x=2$  and  $x=1.5$  compounds. We show that the effect of the field on the sample macroscopic properties is much more prominent in the  $x=1.5$  case than in the  $x=2$  sample, and we discuss the differences. We first describe the similarities between the magnetostructural transition in  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$  to conclude that in both compounds the same kind of LT and HT phases are coexisting. Afterwards, we show resistance measurements up to 45 T that confirm the existence of a macroscopic phase separation leading to colossal-magnetoresistance-like behavior. Since the LT and HT phases possess different cell volumes, the field-dependent phase coexistence is further supported by magnetostriction measurements up to 25 T.

## II. EXPERIMENTAL DETAILS

Single-phase polycrystalline  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$  samples were prepared by the solid state reaction technique. Synthesis details are reported elsewhere.<sup>3</sup> Neutron powder diffraction on  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  was performed at the D2B ( $\lambda$

$= 1.594$  Å) high resolution diffractometer in the Institute Laue Langevin (Grenoble, France). Complementary x-ray diffraction measurements were carried out in a D-max Rigaku system with rotating anode operated at 40 kV and 80 mA, and a graphite monochromator was used to select the  $\text{Cu } K\alpha_{1,2}$ . Magnetization and ac susceptibility measurements were performed by using a superconducting quantum interference device magnetometer from Quantum Design. The strain-gauge technique was used for the magnetostriction measurements. Magnetoresistance was measured within the four-probe geometry in dc mode for steady fields and in ac mode for pulsed fields. Two pulsed magnetic fields facilities were used. Magnetostriction experiments were performed at the long-pulse 31 T coil at the ICMA (Zaragoza, Spain) operating at a maximum voltage of 7.1 kV, with a field profile of about 1.5 s reaching 30 T at 150 ms. A Tektronix 3C66 Anderson bridge/oscilloscope with a working frequency of 25 kHz is used to collect the bridge unbalance between the active (sample) and passive (silica quartz) strain gauges as a function of the field. Magnetoresistance data were acquired at the 60 T coil of the LNCMP (Toulouse, France). The field profile has a duration of 400 ms with raising time of 46 ms up to 55 T. Signal processing is done by means of a SR560 Dual-phase lock-in amplifier from Stanford Research. For clarity reasons we only show data during the field falling. The use of pulsed fields entails the risk of faked measurements owing to the plausible appearance of electromotive forces, magnetocapacitance effects, or to the influence of the wiring. In order to rule out the presence of spurious signals coming from the fast field variation, pulsed field measurements were cross-checked with analogous measurements obtained at the 12 T steady-field facility.

## III. LOW TEMPERATURE MAGNETOSTRUCTURAL TRANSITION

In Fig. 1 we compare the temperature dependence of the lattice parameters of  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  with those reported by Oikawa *et al.*<sup>15</sup> for  $\text{Ca}_2\text{FeReO}_6$ . It is readily seen that at  $T_{sm} \approx 130$  K there is a cell distortion very similar to the one occurring in  $\text{Ca}_2\text{FeReO}_6$ . The  $a$  and  $c$  parameters become slightly expanded on cooling, whereas the  $b$  parameter undergoes a markedly shrinkage and the  $\beta$  monoclinic angle becomes bent. All these features are remarkably smoothed in the  $x=1.5$  compound as compared to the  $x=2$  one. This is probably due to the reduced pristine monotonic distortion in the  $x=1.5$  compound at room temperature.<sup>3</sup> Since the temperature spacing during neutron diffraction profiles acquisition was quite large, we also tracked more finely the crystallographic structure by means of x-ray diffraction experiments around  $T_{sm}$  in the  $x=1.5$  compound (not shown here). We find the same kind of temperature dependence of the cell volume as the one reported in Ref. 15 and we observe a sudden volume shrinkage between 135 and 125 K of  $\approx -700$   $\mu\text{st}$  ( $1$   $\mu\text{st} = 10^{-6}$  relative strain). The thermal evolution of the crystallographic structure in our  $\text{Ca}_2\text{FeReO}_6$  sample was earlier reported by some of us,<sup>3</sup> and the same kind of structural distortion was detected at  $T_{sm} \approx 115$  K. Thus, it seems clear that the LT phase appears in both  $x$

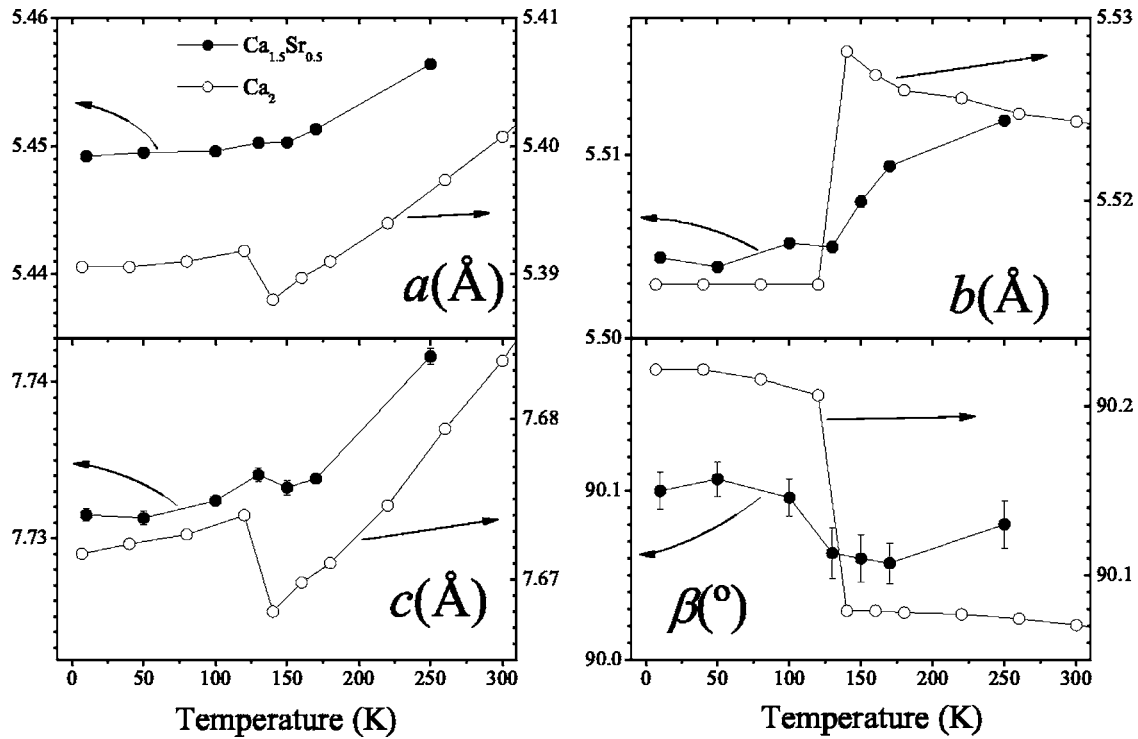


FIG. 1. Temperature dependence of the lattice parameters of  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  [filled circles, this work] and  $\text{Ca}_2\text{FeReO}_6$  (open circles, obtained by Oikawa *et al.* (Ref. 15)]. For the sake of comparison between the  $\text{Ca}_{1.5}\text{Sr}_{0.5}$  and  $\text{Ca}_2$  compounds, the spans of the left and right ordinate axes are the same.

$x=1.5$  and  $x=2$  compounds below 130 and 115 K, respectively. As explained above, the simultaneous MIT, magnetic and structural transition might be driven by correlation effects between the two  $5d$  Re electrons,<sup>15,18,19</sup> which can make energetically unstable the delocalized state in the presence of the LT  $\text{ReO}_6$  distortion.

Further proofs of the HT to LT-phase transition on cooling can be noticed in Fig. 2(a). The maximum  $\chi_{ac}$  versus temperature slope is attained at 115, 130, and 96 K for  $x=2$ , 1.5, and 1, respectively. Interestingly, those are the same temperatures at which the structural transition takes place. This is not surprising, since the new crystallographic environment of the Re atom brings about a change of the easy magnetization axis through the spin-orbit coupling.<sup>13,15</sup> Therefore, the  $\chi_{ac}$  anomaly can be associated to an abrupt change of the magnetocrystalline anisotropy due to the structural transition. As a consequence, the magnetization isofield runs are sensitive to this transition.<sup>3,19</sup> The hysteretic behavior of the magnetization versus temperature,<sup>19</sup> as well as the discontinuous volume change at  $T_{sm}$ , indicate that we are very likely facing a first order transition. However, without specific heat measurements around  $T_{sm}$ , one cannot safely elucidate the transition type, and this issue is beyond the scope of this paper.

Moreover, the magnetostructural transition is accompanied by a change of the transport properties. As done by Kato *et al.*,<sup>19</sup> we plot in Fig. 2(b) the parameter  $\partial \ln(\rho)/\partial(1/T)$  in order to track the MIT transition in  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$ . The cusplike behavior in the case of  $x > 1$  reflects the overall change of a metallic nature above  $T_{sm}$  to an insulating phase below this temperature. We point out that the anomalies associated to the LT(insulating)/HT(metallic) phase transition

vanish for Sr-rich compounds. Indeed,  $\chi_{ac}$  is monotonous in the entire ferromagnetic region for  $x \leq 0.5$  (see Ref. 3 and Fig. 2)

In order to search for the LT-HT phase coexistence, we have carried out a neutron diffraction study as a function of the magnetic field. Several authors have reported that

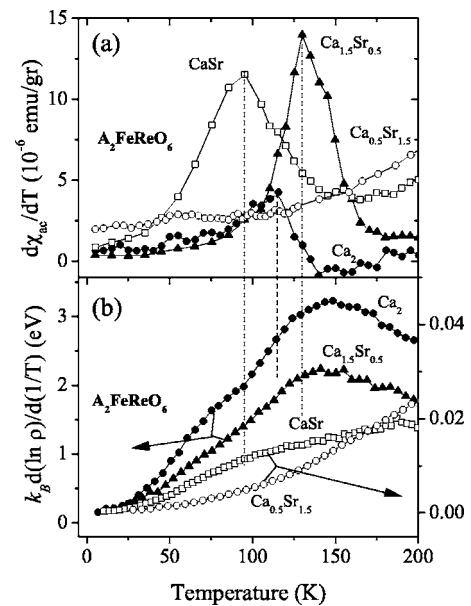


FIG. 2. (a) Derivative of the ac susceptibility with respect to the temperature. (b)  $\partial \ln(\rho)/\partial(1/T)$  as a function of the temperature, which is the parameter used by Kato *et al.* (Ref. 19) to track the metal-insulator transition in  $\text{A}_2\text{FeReO}_6$  compounds.

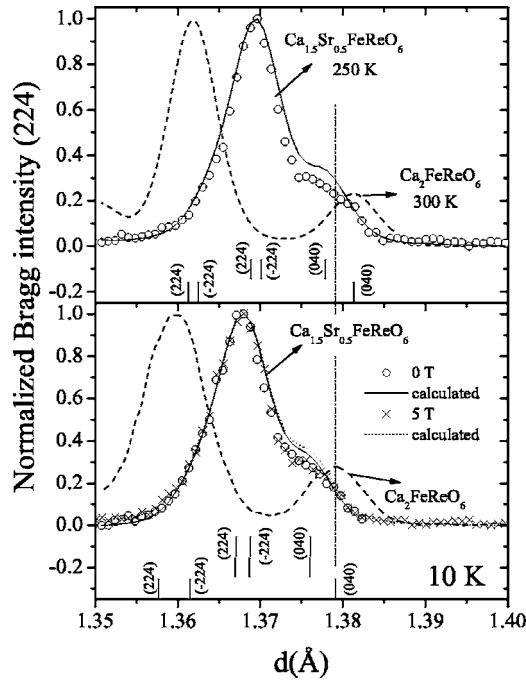


FIG. 3. Detail of the neutron powder diffraction profiles ( $1.35 \text{ \AA} \leq d \leq 1.40 \text{ \AA}$ ) at above  $T_{sm}$  (top panel, 300 K for  $\text{Ca}_2$  and 250 K for  $\text{Ca}_{1.5}\text{Sr}_{0.5}$ ) and below  $T_{sm}$  (bottom panel, 7 K for  $\text{Ca}_2$  and 10 K for  $\text{Ca}_{1.5}\text{Sr}_{0.5}$ ). The dashed line is the simulated pattern from the structural details published for  $\text{Ca}_2\text{FeReO}_6$  (Ref. 15) (see text). Open circles and crosses are the experimental patterns for  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  under applied fields of 0 and 5 T, respectively. The main (040), (-224), and (224) Bragg reflections are indicated.

when the LT and HT phases coexist, the monoclinic nuclear reflections broaden or even become split.<sup>6,7,15</sup> Hence, the observed neutron profiles can only be explained by the simultaneous presence of two monoclinic phases. The splitting is specially visible in the (040) Bragg peak.<sup>6,7</sup> In Fig. 3 the zoomed region of the diffraction profile corresponding to the (040) peak ( $1.35 \text{ \AA} \leq d \leq 1.40 \text{ \AA}$ ) is displayed for  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$ . In the same plot we have included the  $\text{Ca}_2\text{FeReO}_6$  diffraction pattern calculated from the structural data published by Oikawa *et al.*<sup>15</sup> For the simulation we have simply substituted our structural parameters by Oikawa's ones, and we have kept the background, Debye-Waller, peak-profile, and instrument-dependent parameters obtained for  $x = 1.5$ . The peak shift due to the structural transition from the HT phase (300 K, top panel) to the LT phase (10 K, bottom panel) is nicely seen in  $x = 2$  even under our experimental conditions. Nevertheless, the (040) reflection overlaps with the (224) one in the case of  $x = 1.5$ . The lower extent of the monoclinic distortion makes these two peaks overlap. This fact prevents us from discerning whether our sample at  $H = 0$  shows phase coexistence or a complete phase transition as a function of the temperature. The same reason can be invoked to explain that an applied field of 5 T does not modify the experimental diffraction profile at 10 K (see bottom panel of Fig. 3). Within the experimental error, the refined structural parameters are independent of the magnetic field up to 5 T. As discussed below, the LT phase is more stable in the  $x = 2$  compound than in  $x = 1.5$  but the magnetic

field required to induce a noticeable fraction of HT phase is still larger than 5 T. Therefore, when the (040) reflection is not well resolved, an applied field of 5 T is too small to observe the segregation of the HT-phase at low temperatures.

#### IV. MAGNETOSTRICTION

The origin of the magnetoelastic coupling in Re-based double perovskites is based on the existence of an unquenched orbital moment at the Re-atom, and therefore an anisotropic charge distribution around it.<sup>13,14</sup> The Re orbital moment, antiparallel to the Re spin moment<sup>16</sup> but parallel to the Fe one, tends to align parallel to the external magnetic field. This modifies the electronic charge distribution which interacts with the structural degrees of freedom via the crystal electric potential. The lattice must accommodate the new direction of the magnetic moment through the minimization of the magnetoelastic energy. In polycrystalline  $\text{A}_2\text{FeReO}_6$  double perovskites, a negative  $\lambda_{\parallel} = \delta L_{\parallel}/L_0$  is expected in the direction parallel to the applied field and positive  $\lambda_{\perp} = \delta L_{\perp}/L_0$  in the perpendicular direction, as actually found in  $\text{Ba}_2\text{FeReO}_6$  and  $\text{Ca}_2\text{FeReO}_6$ .<sup>13,14</sup> In  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$ ,  $\lambda_{\parallel}$  attains a maximum value of about  $-400 \mu\text{st}$  at 200 K and 25 T, and saturates above 20 T. The maximum  $\lambda_{\perp}$  at 25 T is achieved at 9 K with a value of  $350 \mu\text{st}$ , and it shows a linear dependence on the field with positive slope above 15 T. Both magnitudes show a striking nonmonotonic behavior as a function of the temperature around  $T_{sm}$ .

As previously done for  $\text{Ca}_2\text{FeReO}_6$ ,<sup>14</sup> we think that the lattice strain induced by the magnetization process, the so-called magnetostriction, is a good probe for the phase coexistence. By inspection of Fig. 1, one can realize that at  $T_{sm}$  there is a net volume change ascribed to the phase transition. The HT phase is thought to have a larger unit cell volume than the LT phase.<sup>14,15</sup> Therefore, magnetostriction effects additional to the above described mechanism are expected if the field induced phase-coexistence mechanism takes place in  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$ . We combine  $\lambda_{\parallel}$  and  $\lambda_{\perp}$  in order to obtain the overall volume and shape change as a function of the magnetic field. In a polycrystalline specimen, such magnitudes can be calculated, respectively, as the volume magnetostriction ( $\omega = \delta V/V_0 = \lambda_{\parallel} + 2\lambda_{\perp}$ ) and anisotropic magnetostriction ( $\lambda_r = \lambda_{\parallel} - \lambda_{\perp}$ ). Results for  $x = 1.5$  are displayed in Fig. 4 for selected temperatures. The volume magnetostriction is nearly linear for  $T > T_{sm} = 130 \text{ K}$ . Below this temperature, the initial  $\omega$  vs  $H$  slope is much smaller, and even becomes negative, which reflects the enhanced magnetocrystalline anisotropy of the LT phase. More interesting, above 12 T there is a more pronounced variation of  $\omega$ , which is illustrated in the inset of Fig. 4. Since the HT phase has a bigger unit cell, this additional volume contribution can be considered as a hint of the LT to HT phase transformation for high enough magnetic fields. According to the spontaneous magnetostriction measured by x-ray diffraction at  $T_{sm}$ , this contribution to  $\omega$  can be as large as  $700 \mu\text{st}$  in a single crystal. The impact of the magnetostructural transition and the phase-coexistence is also noticed in  $\lambda_r$ . The intrinsic  $\lambda_r$  of both the LT and HT phases must have a constant curvature sign as a function of the field because  $\lambda_r$  is produced by a magnetization or forced

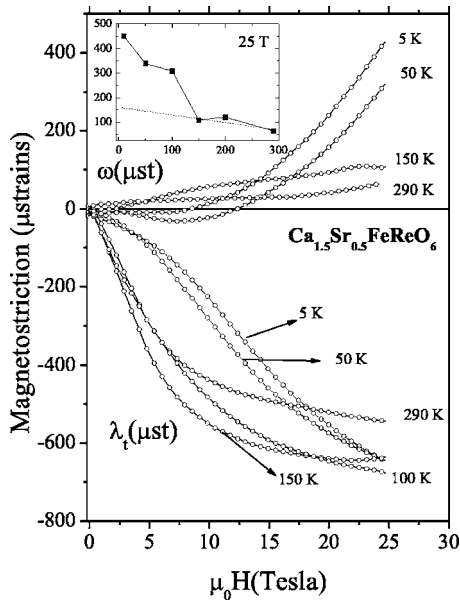


FIG. 4. Pulsed fields measurements of the volume ( $\omega$ ) and anisotropic ( $\lambda_t$ ) magnetostriction in the  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  compound. The inset in the top panel displays the  $\omega$  temperature dependence at 25 T.

magnetization process.<sup>20</sup> However, on cooling below  $T_{sm}$  there is a change of the upwards curvature to a downwards curvature at low fields ( $\mu_0 H < 10$  T), and subsequently the curvature changes again its sign for magnetic fields above 15 T. Under strong magnetic fields, the field-dependent-phase composition, together with the intrinsic mechanisms of each phase, contribute to the magnetostriction. The intrinsic magnetostriction must saturate at the bulk saturation magnetic field, which in Re based double perovskites can be as large as 20 T.<sup>21</sup> The features of the LT to HT phase transformation as the field increases are noticed in two facts. First,  $\omega$  does not saturate above the bulk saturation field and it keeps its linear behavior with large high-field slope. In addition, since the  $\omega$  high-field slope does not decrease as the temperature is lowered from 50 to 5 K, the single-ion type forced magnetostriction cannot be responsible for this behavior at high fields.<sup>22,23</sup> Second, the nonmonotonous behavior of the  $\lambda_t$  curvature below  $T_{sm}$  cannot be explained in terms of monotonous processes such as the magnetization trend to saturation or the forced magnetostriction. Instead, the only plausible explanation for the  $\lambda_t$  behavior is the gradual change of the overall magnetocrystalline anisotropy as the LT phase transforms into the HT phase, superimposed to the intrinsic  $\lambda_t$  of each phase.

## V. MAGNETORESISTANCE

As depicted in Fig. 5, above and around  $T_{sm}$ , the Ca-rich  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$  compounds retain the butterflylike shape of the MR (Ref. 11) typical of the ITMR effect described by Eq. (1). Such measurements exhibit a  $P^2 m_{gb}^2$  behavior, where  $m_{gb}$  can substantially differ from the bulk magnetization.<sup>12</sup>

In contrast, this model does no longer apply below  $T_{sm}$  if we extend the magnetic field range up to 45 T. We notice

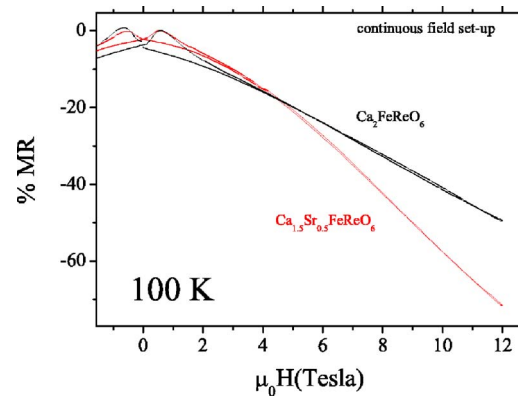


FIG. 5. (Color online) Magnetostriction isotherms at 100 K measured in the continuous field setup using the four-probe dc technique.

that the maximum ITMR value cannot exceed  $\text{MR} = -100\%$  [see Eq. (1)], or equivalently  $\rho(H)/\rho_0 > 0.5$ . However, Fig. 6 evidences that this threshold is surpassed by more than one order of magnitude in the  $x=1.5$  compound, the MR at 9 and 20 K being as large as  $-2180$  and  $-580\%$ , respectively. The MR increases rapidly on cooling because the LT-phase fraction at zero field grows and increases its resistivity as a result of its insulating nature.<sup>3,19</sup> Thus, when the low resistance HT phase is induced by the applied magnetic field, the relative resistance change becomes progressively larger. The saturation of the MR curves below 50 K indicates that the sample resistivity cannot be further decreased, thus suggesting that the LT phase can be completely melted by magnetic fields larger than 30 T. In the case of the CMR manganites, the magnetic field melts the insulating clusters in the paramagnetic phase or long-range insulating phases, giving rise to a similar MR response. In both cases, when the percolation limit is overcome, a steep resistance decrease takes place. By analogy with the manganites, the large negative MR in  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  can be viewed as a novel type of CMR effect in double perovskites.

Similarly to the  $x=1.5$  case, the ITMR limit is also exceeded in the  $x=2$  compound, as shown in Fig. 7. In this case, the steep resistance drop only takes place at 100 and 125 K, temperatures close to the magnetostructural transition

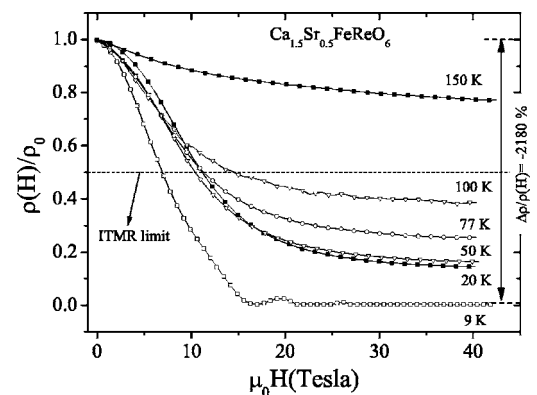


FIG. 6. Pulsed field magnetoresistance measurements of  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  using the four-probe ac lock-in technique.

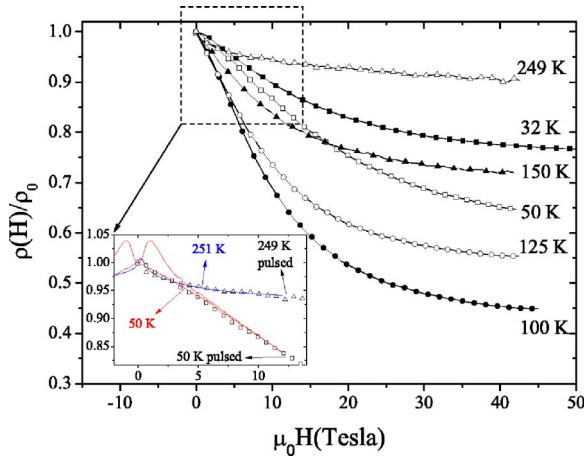


FIG. 7. (Color online) Pulsed field magnetoresistance measurements of  $\text{Ca}_2\text{FeReO}_6$  using the four-probe ac lock-in technique. The inset shows a comparison of the ac measurements under pulsed fields (circles 50 K, triangles 249 K) and the dc measurements under steady field (red line 50 K, blue line 251 K), where the ITMR contribution is nicely seen.

( $T_{sm} = 115$  K). The largest MR is  $-127\%$  at 100 K, although the coarse temperature interval at which MR has been measured does not permit to discard that the true maximum could be located at slightly different temperature. This fact indicates that in our  $\text{Ca}_2\text{FeReO}_6$  the phase coexistence can only occur in a narrow temperature range around  $T_{sm}$ , as was the case in Oikawa's work,<sup>15</sup> probably because the LT phase is energetically much more favorable than in the  $x=1.5$  compound. As a consequence, at 32 K the HT phase cannot even be formed under 53 T of applied magnetic field (see Fig. 7). Figure 7 also compares some selected measurements under pulsed and steady fields, whose agreement is perfect. Therefore, a significant difference between adiabatic (pulsed fields) and isothermal (steady fields) can be safely ruled out.

Figure 8 illustrates better the temperature region in which the CMR effect appears. Whereas for  $x=1.5$  the CMR effect sharply increases on cooling below  $T_{sm} = 130$  K, for  $x=2$  the region with noticeable CMR spans from 75 to 125 K. Therefore, we can conclude that the LT phase is much less stable in  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  than in  $\text{Ca}_2\text{FeReO}_6$ . Apart from the evolution that the  $T$ - $H$  projection of the phase diagram might have with  $x$  (for  $x=2$  see phase percentage versus magnetic field in Ref. 7), we put forward that this fact could be a consequence of the quenched chemical disorder induced by the Sr/Ca mixture at the A site, which is known to affect largely critical phenomena as for instance the ferromagnetic and charge-ordering transitions in manganites.<sup>24</sup> Following this reasoning, the LT phase in the CaSr compound should be even less stable than in the  $\text{Ca}_{1.5}\text{Sr}_{0.5}$  one, because not only is  $T_{sm}$  lower, but also the chemical disorder is larger. Pulsed field MR measurements on the  $x=0.5$  compound do not show any trace of CMR, and simply display the typical ITMR behavior given by Eq. (1).

Finally, despite the energy gap at the Fermi level of the LT phase in the  $x \geq 1$  compounds, the conduction band lying immediately above must retain some degree of spin polarization, since the presence of the ITMR effect at 50 K is obvious (see Fig. 5 and inset of Fig. 7).

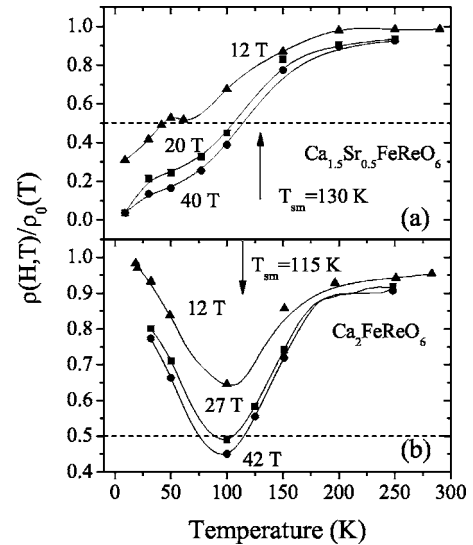


FIG. 8. Temperature dependence of the magnetoresistance [as defined in Eq. (2)] at several applied magnetic fields in the  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{FeReO}_6$  (a) and  $\text{Ca}_2$  (b) compounds. The dashed lines indicate the maximum magnetoresistance achievable within the ITMR model (Ref. 12).

## VI. CONCLUSIONS

In summary, a CMR mechanism has been proposed for  $\text{Ca}_x\text{Sr}_{2-x}\text{FeReO}_6$  double perovskites, which at low temperatures superimposes on the standard ITMR effect. In these compounds, the large monoclinic distortion ( $x \geq 1$ ) stabilizes a low temperature insulating phase that can coexist under strong magnetic fields with the high temperature metallic phase. First, we have highlighted the similarities between the magnetostructural transition undergone by the compounds with  $x=1.5$  and  $x=2$  at  $T_{sm}$ . Earlier evidences of field-dependent LT-HT phase composition below and around  $T_{sm}$  in  $\text{Ca}_2\text{FeReO}_6$ , together with the magnetostriction measurements shown in Sec. IV, indicates that the same kind of phase coexistence occurs in the  $1 \leq x \leq 2$  range, thus showing that the phase coexistence is not exclusive in  $\text{Ca}_2\text{FeReO}_6$ . The insulating character of the low-temperature phase relies on the extreme sensitivity of the near- $E_F$  density of states to the crystallographic environment of the Re atom.<sup>13,15,18</sup> On the basis of these assumptions, the large negative MR ( $>2000\%$ ) observed at low temperatures can be understood by the prevalence of the HT phase (metallic) at the expense of the LT phase (insulating). This MR effect resembles the CMR behavior of manganites around the paramagnetic to ferromagnetic transition. In the present case, both competing phases (one metallic, the other insulating) are ferromagnetic and the electronic localization has a purely electrostatic origin.

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- <sup>1</sup>K. I. Kobayashi, T. Kimura, Y. Tomioka, H. Sawada, K. Terakura, and Y. Tokura, *Phys. Rev. B* **59**, 11 159 (1999).
- <sup>2</sup>H. Wu, *Phys. Rev. B* **64**, 125126 (2001).
- <sup>3</sup>J. M. DeTeresa, D. Serrate, J. Blasco, M. R. Ibarra, and L. Morellon, *Phys. Rev. B* **69**, 144401 (2004).
- <sup>4</sup>D. D. Sarma, P. Mahadevan, T. Saha-Dasgupta, S. Ray, and A. Kumar, *Phys. Rev. Lett.* **85**, 2549 (2000).
- <sup>5</sup>N. Auth, G. Jakob, W. Weterburg, C. Ritter, I. Bonn, C. Felser, and W. Tremel, *J. Magn. Magn. Mater.* **272-276**, e607 (2004).
- <sup>6</sup>W. Westerburg, O. Lang, C. Ritter, C. Felser, W. Tremel, and G. Jakob, *Solid State Commun.* **122**, 201 (2002).
- <sup>7</sup>E. Granado, Q. Huang, J. W. Lynn, J. Gopalakrishnan, R. L. Greene, and K. Ramesha, *Phys. Rev. B* **66**, 064409 (2002).
- <sup>8</sup>J. Gopalakrishnan, A. Chattopadhyay, S. B. Ogale, T. Venkatesan, R. L. Greene, A. J. Millis, K. Ramesha, B. Hannoyer, and G. Marest, *Phys. Rev. B* **62**, 9538 (2000).
- <sup>9</sup>T. Alamelu, U. Varadaraju, M. Venkatesan, S. Douvalis, and J. Coey, *J. Appl. Phys.* **91**, 8909 (2002).
- <sup>10</sup>F. Sriti, N. Nguyen, C. Martin, A. Ducouret, and B. Raveau, *J. Magn. Magn. Mater.* **250**, 123 (2002).
- <sup>11</sup>J. M. DeTeresa, D. Serrate, J. Blasco, M. R. Ibarra, and L. Morellon, *J. Magn. Magn. Mater.* **290-291**, 1043 (2005).
- <sup>12</sup>D. Serrate, J. M. DeTeresa, P. A. Algarabel, M. R. Ibarra, and J. Galibert, *Phys. Rev. B* **71**, 104409 (2005).
- <sup>13</sup>D. Serrate, J. M. DeTeresa, and M. R. Ibarra, *J. Phys.: Condens. Matter* **19**, 023201 (2007).
- <sup>14</sup>D. Serrate, J. M. DeTeresa, P. Algarabel, C. Marquina, L. Morellon, J. Blasco, and M. R. Ibarra, *J. Magn. Magn. Mater.* **290-291**, 843 (2005).
- <sup>15</sup>K. Oikawa, T. Kamiyama, H. Kato, and Y. Tokura, *J. Phys. Soc. Jpn.* **72**, 1411 (2003).
- <sup>16</sup>M. Sikora, C. Kapusta, M. Borowiec, C. J. Oates, V. Prochazka, D. Rybicki, D. Zajac, J. M. DeTeresa, C. Marquina, and M. R. Ibarra, *Appl. Phys. Lett.* **89**, 062509 (2006).
- <sup>17</sup>P. Majewski, S. Geprags, O. Sanganas, M. Opel, R. Gross, F. Wilhelm, A. Rogalev, and L. Alff, *Appl. Phys. Lett.* **87**, 202503 (2005).
- <sup>18</sup>H. Iwasawa, T. Saitoh, Y. Yamashita, D. Ishii, H. Kato, N. Hamada, Y. Tokura, and D. D. Sarma, *Phys. Rev. B* **71**, 075106 (2005).
- <sup>19</sup>H. Kato, T. Okuda, Y. Okimoto, Y. Tomioka, K. Oikawa, T. Kamiyama, and Y. Tokura, *Phys. Rev. B* **65**, 144404 (2002).
- <sup>20</sup>E. Callen and H. Callen, *Phys. Rev.* **139**, A455 (1965).
- <sup>21</sup>J. Michalik, J. de Teresa, C. Ritter, J. Blasco, D. Serrate, M. Ibarra, C. Kapusta, J. Freudenberger, and N. Kozlova, *Europhys. Lett.* (to be published).
- <sup>22</sup>A. del Moral, C. Abadía, and B. García-Landa, *Phys. Rev. B* **61**, 6879 (2000).
- <sup>23</sup>A. del Moral and M. R. Ibarra, *J. Phys. Chem. Solids* **46**, 127 (1985).
- <sup>24</sup>D. Akahoshi, M. Uchida, Y. Tomioka, T. Arima, Y. Matsui, and Y. Tokura, *Phys. Rev. Lett.* **90**, 177203 (2003).