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# Specific heat at low temperatures and magnetic measurements in $Nd_{0.5}Sr_{0.5}MnO_3$ and $R_{0.5}Ca_{0.5}MnO_3$ ($R=$Nd, Sm, Dy, and Ho) samples

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We studied the magnetization as a function of temperature and magnetic field in the compounds $Nd_{0.5}Sr_{0.5}MnO_3$, $Nd_{0.5}Ca_{0.5}MnO_3$, $Sm_{0.5}Ca_{0.5}MnO_3$, $Dy_{0.5}Ca_{0.5}MnO_3$, and $Ho_{0.5}Ca_{0.5}MnO_3$. Ferromagnetic, antiferromagnetic, and charge ordering transition in our samples agreed with previous reports. We also did specific-heat measurements with applied magnetic fields between 0 and 9 T and temperatures between 2 and 30 K in all five samples. Below 10 K the specific-heat measurements evidenced a Schottky-like anomaly for all samples. However, we could not successfully fit the curves to either a two level or a distribution of two-level-Schottky anomaly.

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## I. INTRODUCTION

Compounds like $La_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$ present a real-space ordering of $Mn^{3+}$ and $Mn^{4+}$ ions, named as charge ordering (CO). Close to the charge ordering temperature ($T_{CO}$), these materials show anomalies in resistivity, magnetization, and lattice parameters as a function of temperature, magnetic field, and isotope mass.[1,2] At low temperatures, both ferromagnetic and antiferromagnetic phases could coexist.[3] However, a relatively small external magnetic field can destroy the CO phase and enforces a ferromagnetic orientation of the spins.[4]

Moreover, electron microscope analysis has revealed convincing evidence that CO is accompanied by orientational ordering of the $3d^3$ orbitals on the $Mn^{3+}$ ions, called orbital ordering.[5] The physical properties in CO manganese perovskites are thought to arise from the strong competition among a ferromagnetic double exchange interaction, an antiferromagnetic superexchange interaction, and the spin-phonon coupling. These interactions are determined by intrinsic parameters such as doping level, average cationic size, cationic disorder, and oxygen stoichiometry. Microscopically, CO compounds are particularly interesting because spin, charge, and orbital degrees of freedom are at play simultaneously and classical simplifications that neglect some of these interactions do not work. More detailed information on the physics of manganites can be found in a review paper by Salamon and Jaime.[6]

We have shown that polycrystalline samples of $La_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$ presented an unusual magnetic relaxation behavior close to each critical temperature.[7,8] However, a clear understanding of all these features has not been reached yet. An alternative to a bulk characterization like magnetization would be to perform specific-heat measurements. In contrast to magnetization, which has a vector character, the specific heat is a scalar. Therefore, a comparison between both types of data could give valuable information.

Ghivelder *et al.*[9] reported specific-heat measurements in $LaMnO_{3+\delta}$ samples and they found that the specific heat at low temperature is very sensitive to small variations of $\delta$, similar to results found by Schnelle *et al.*[10] in a $Nd_{0.67}Sr_{0.33}MnO_{3-\delta}$ sample. In this latter work and also in a work by Gordon *et al.*[11] a Schottky-like anomaly was found at low temperatures in samples with similar compositions. They associated this result to the magnetic ordering of $Nd^{3+}$ ions and to the crystal-field splitting at low temperatures. Bartolomé *et al.*[12] also found a Schottky-like anomaly in a closely related compound of $NdCrO_3$. They proposed a crystal-field energy-level scheme in agreement with neutron-scattering studies in the same sample. In two papers Smolyaninova *et al.*[13,14] studied the low-temperature specific heat in $Pr_{1-x}Ca_xMnO_3$ ($0.3<x<0.5$) and $La_{1-x}Ca_xMnO_3$ ($x=0.47$, 0.5, and 0.53). They found an excess specific heat, $C'(T)$, of nonmagnetic origin associated with charge ordering. They also reported that a magnetic field sufficiently high to induce a transition from the charge ordered state to the ferromagnetic metallic state did not completely remove $C'(T)$. However, no Schottky anomaly was found in any of these compounds.

Here, we report a general magnetic characterization and specific-heat measurements with applied magnetic fields between 0 and 9 T and temperatures between 2 and 30 K for $Nd_{0.5}Sr_{0.5}MnO_3$, $Nd_{0.5}Ca_{0.5}MnO_3$, $Sm_{0.5}Ca_{0.5}MnO_3$, $Dy_{0.5}Ca_{0.5}MnO_3$, and $Ho_{0.5}Ca_{0.5}MnO_3$ samples. All these compounds presented a Schottky-like anomaly at low temperatures. We have already reported a short version of preliminary results about these topics.[15] However, as far as we know, detailed specific-heat measurements in these compounds have not been published yet.

## II. EXPERIMENTAL METHODS

Polycrystalline samples of $Nd_{0.5}Sr_{0.5}MnO_3$, $Nd_{0.5}Ca_{0.5}MnO_3$, and $Ho_{0.5}Ca_{0.5}MnO_3$ were prepared by the sol-gel method.[16] Stoichiometric parts of $Nd_2O_3$ ($Ho_2O_3$) and $MnCO_3$ were dissolved in $HNO_3$ and mixed to an aqueous citric acid solution, to which $SrCO_3$ or $CaCO_3$ was added. The mixed metallic citrate solution presented the ratio citric acid/metal of 1/3 (in molar basis). Ethylene glycol was added to this solution to obtain a citric acid/ethylene glycol ratio 60/40 (mass ratio). The resulting solution was neutralized to $p$H~7 with ethylenediamine. This solution was turned into a gel and subsequently decomposed to a solid by heating at 400 °C. The resulting powder was heat treated in vacuum at 900 °C for 24 h, with several intermediary grindings, in order to prevent the formation of impurity phases. This powder was pressed into pellets and sintered in air at 1050 °C for 12 h.

Polycrystalline samples of $Sm_{0.5}Ca_{0.5}MnO_3$ and $Dy_{0.5}Ca_{0.5}MnO_3$ were prepared from stoichiometric amounts of $Sm_2O_3$ or $Dy_2O_3$, CaO, and $MnO_2$ by standard solid-state reaction method. Purity of these starting materials was more than 99.99%. All the powders were mixed and grinded for a long time in order to produce a homogeneous mixture. First, the mixture was heated at 927 °C for 24 h and after that it was grinded and heated at 1327 °C (72 h) and 1527 °C (48 h). X-ray-diffraction measurements indicated high-quality samples in all the five cases.

The magnetization measurements were done with a quantum design MPMS-5S superconducting quantum interference device magnetometer. Specific-heat measurements were done with a quantum design PPMS calorimeter. The PPMS used the two-relaxation-time technique and data were always collected during sample cooling. The intensity of the heat pulse was calculated to produce a variation in the temperature bath between 0.5% (at low temperatures) and 2% (at high temperatures). Experimental errors during the specific-heat and magnetization measurements were lower than 1% for all temperatures and samples.

## III. RESULTS AND DISCUSSION

### A. Magnetization measurements

Figure 1 shows the temperature dependence of magnetization, measured with a 5 T applied magnetic field and zero-field cooling conditions, in polycrystalline samples of $Nd_{0.5}Sr_{0.5}MnO_3$, $Nd_{0.5}Ca_{0.5}MnO_3$, $Sm_{0.5}Ca_{0.5}MnO_3$, $Dy_{0.5}Ca_{0.5}MnO_3$, and $Ho_{0.5}Ca_{0.5}MnO_3$. The curves are plotted with a logarithmic scale in the $y$ axis to allow the comparison of the samples. Charge ordering transition temperatures ($T_{CO}$) are indicated by arrows at 160, 250, 270, 280, and 271 K, respectively. These temperatures are associated to peaks in the magnetization curves, in agreement with previous reports.[17–20] It is interesting to note that the relation between the charge ordering temperature and the antiferromagnetic ordering temperature ($T_N$) changes from one sample to the other.[17–20] In the first case they are approximately coincident, in the second and third cases the charge ordering temperatures are much higher, and in the fourth and fifth cases a long-range antiferromagnetic transition is not observed.

The $Nd_{0.5}Sr_{0.5}MnO_3$ sample presented a ferromagnetic transition at $T_C \approx 250$ K and an antiferromagnetic transition at $T_N \approx 160$ K. The $Nd_{0.5}Ca_{0.5}MnO_3$ compound presented a strong maximum near $T_{CO}$, but showed an unexpected minimum close to the antiferromagnetic transition temperature $T_N \approx 160$ K. Usually an antiferromagnetic transition is accompanied by a maximum in the temperature dependence of the magnetization. For temperatures lower than 10, 20, and 50 K the $Nd_{0.5}Sr_{0.5}MnO_3$, $Nd_{0.5}Ca_{0.5}MnO_3$, and $Sm_{0.5}Ca_{0.5}MnO_3$ samples showed a sharp increase in the magnetization. However, no long-range ferromagnetic order of the $Nd^{3+}$ ions was found in neutron diffraction measurements at these low temperatures.[17,18] The increase in magnetization at low temperatures was associated by Mathieu *et al.*[21] to a short-range magnetic ordering of the intrinsic magnetic moment of $Nd^{3+}$ ions. Nonetheless, a short-range

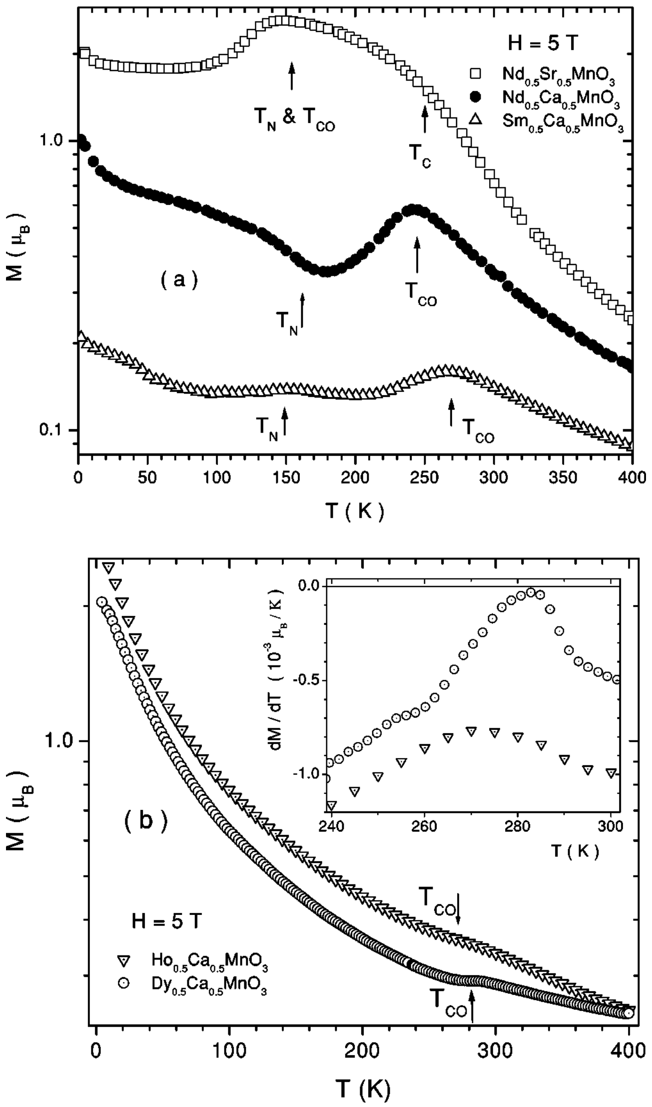

FIG. 1. Temperature dependence of the magnetization, with a 5 T applied magnetic field, in field cooling-warming condition for the five polycrystalline samples studied. Magnetization is given in Bohr magnetons per manganese ion. The Curie ($T_C$), Neél ($T_N$), and charge ordering ($T_{CO}$) temperatures are indicated for each curve. The curves are plotted with a logarithmic scale in the $y$ axis to allow the comparison of all samples. The inset in (b) represents the temperature derivative of the magnetization close to the charge ordering transition.

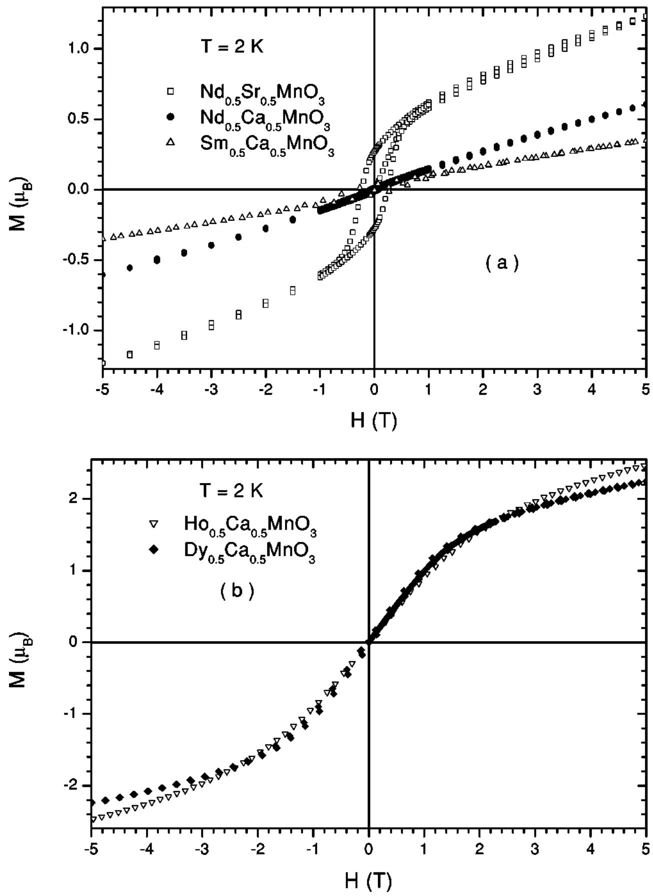

FIG. 2. Magnetization vs applied magnetic field at 2 K for the five samples studied. After a zero-field cooling the magnetic field was increased from 0 to 5 T, decreased from 5 T to $-5$ T and increased again from $-5$ T to 5 T. Magnetization is given in Bohr magnetons per manganese ion.

magnetic ordering should not produce the Schottky-like anomaly.

Differently from the three previous samples, the $Dy_{0.5}Ca_{0.5}MnO_3$ and $Ho_{0.5}Ca_{0.5}MnO_3$ compounds do not present a strong maximum at the charge ordering temperature in the magnetization versus temperature curve. However, a clear inflection is observed at $T_{CO}$ for both samples, as revealed by the temperature derivative shown in the inset of Fig. 1(b). The existence of charge ordering in $Dy_{0.5}Ca_{0.5}MnO_3$ and $Ho_{0.5}Ca_{0.5}MnO_3$ was suggested by Terai *et al.*[20] after studies of magnetization and resistivity curves. Our high-temperature measurements of specific heat (not shown) presented peaks at around the same temperature interval of the suggested charge ordered transition. These results will be published elsewhere.

Figure 2 shows the magnetization hysteresis loops at 2 K for the five studied samples. The applied magnetic field was increased from 0 to 5 T, decreased to $-5$ T, and then increased back to 5 T again. The $Nd_{0.5}Sr_{0.5}MnO_3$ curve is characteristic of a two-phase mixture: one ferromagnetic and another antiferromagnetic. The ferromagnetic part is easily oriented at low magnetic-field values and shows a hysteretic behavior. The almost linear and reversible dependence for magnetic fields higher than $\approx 1$ T, indicates a gradual destruction of the antiferromagnetic phase.[8] Mahendiran *et al.*[22] reported, in a sample with the same composition and measured at 50 K, that for magnetic fields higher than $\approx 5$ T the magnetization started to increase rapidly, and for magnetic fields above 10 T, it slowly approached the ferromagnetic saturation value. Because at 2 K these transition fields are expected to be much higher than 5 T, we were unable to see them.

The $Nd_{0.5}Ca_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$ curves only showed a small trace of ferromagnetic component at very low fields. Beyond this region the curves are linear and reversible for the whole magnetic-field interval. As before, this linearity characterizes the gradual destruction of the antiferromagnetic phase. Millange *et al.*[18] reported for a $Nd_{0.5}Ca_{0.5}MnO_3$ sample a set of $M$ versus $H$ curves with applied magnetic fields up to 22 T. They found sharp transitions and a large hysteresis at 130 K between applied magnetic fields of 12 and 18 T. Their results were interpreted as evidence of the existence of a spin-flop transition. Tokura and Tomioka[19] reported the phase diagram ($H$ versus $T$) for several charge ordered compounds and found that the $Sm_{0.5}Ca_{0.5}MnO_3$ sample required the largest magnetic fields to destroy the charge ordering state. For example, at about 10 K the transition fields were $\approx 39$ T and 65 T. In the $M$ versus $H$ curves for the $Dy_{0.5}Ca_{0.5}MnO_3$ and $Ho_{0.5}Ca_{0.5}MnO_3$ samples, shown in Fig. 2(b), two characteristics are well noticed. One that there is no hysteresis at all and the other that the magnetization values at 5 T are well below the theoretical saturation values of $8.73\mu_B$ and $8.70\mu_B$, respectively.[18]

### B. Specific heat at low temperatures

Figure 3 reproduces the specific-heat measurements for temperatures between 2 and 30 K in the samples of (a) $Nd_{0.5}Sr_{0.5}MnO_3$, (b) $Nd_{0.5}Ca_{0.5}MnO_3$, (c) $Sm_{0.5}Ca_{0.5}MnO_3$, (d) $Dy_{0.5}Ca_{0.5}MnO_3$, and (e) $Ho_{0.5}Ca_{0.5}MnO_3$. Measurements were made in the presence of applied magnetic fields of 0 T (squares), 5 T (circles), 7 T (up triangles), and 9 T (down triangles). Note that close to 5 K all curves show a Schottky-like anomaly.[23]

It is important to stress that high values of specific heat were found at low temperatures for the five samples presented here. These values are similar to those reported by Gordon *et al.*[11] in a sample of $Nd_{0.67}Sr_{0.33}MnO_3$. However, the absolute values of specific heat at 2 K, reported by Hamilton *et al.*[24] in samples of $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.80}Ca_{0.20}MnO_3$, were more than 100 times smaller. Similarly, Hardy *et al.*,[25] in a single crystal of $Pr_{0.63}Ca_{0.37}MnO_3$, found values approximately equal to those reported by Hamilton *et al.*[24] The high values of specific heat found in our work indicate enhanced excitations and could be due to an increase in the effective mass of the electrons caused by localization. This interpretation is consistent with the insulating behavior revealed by electrical resistivity measurements.[17–20] The fact that the resistivity is increasing with decreasing temperatures is associated with localization of charge carriers, which lead to the increase of their effective mass.

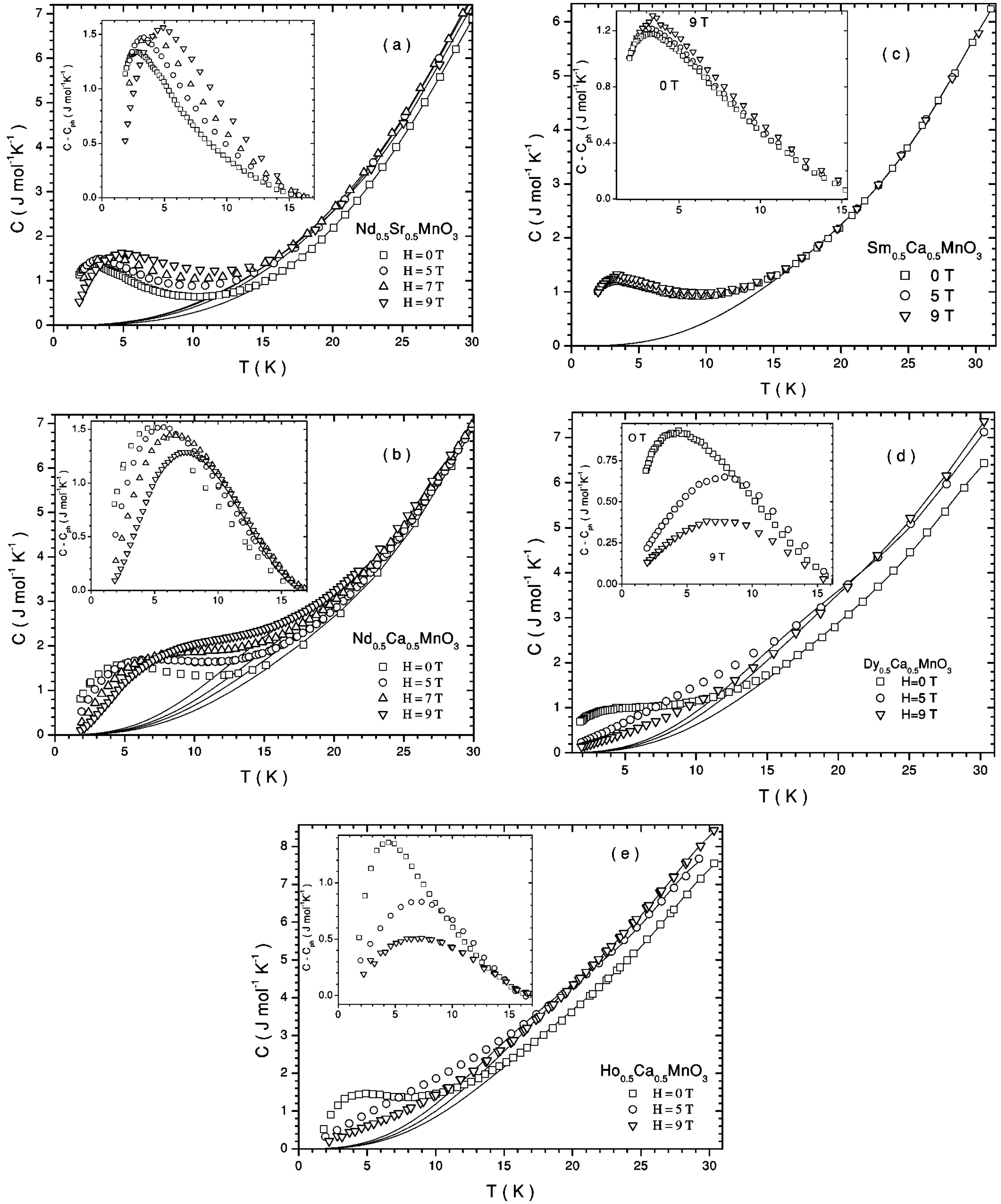

FIG. 3. Specific-heat measurements between 2 and 30 K in the samples of (a) $Nd_{0.5}Sr_{0.5}MnO_3$, (b) $Nd_{0.5}Ca_{0.5}MnO_3$, (c) $Sm_{0.5}Ca_{0.5}MnO_3$, (d) $Dy_{0.5}Ca_{0.5}MnO_3$, and (e) $Ho_{0.5}Ca_{0.5}MnO_3$. Measurements were made in the presence of applied magnetic fields of 0 T (squares), 5 T (circles), 7 T (up triangles), and 9 T (down triangles). Continuous lines represent the fitting of the 15 to 30 K temperature interval data by the phonon contribution, as explained in the text. The graphs in the insets show the difference between the experimental values and the extrapolation of the phonon contribution to temperatures lower than 15 K.

Continuous lines in Fig. 3 indicate the fitting of the experimental data between 15 and 30 K by the following expression:[11]

$$C = \sum \beta_{2n+1} T^{2n+1}. \tag{1}$$

Here, $C$ is the specific heat, $T$ is the temperature, and the parameters $\beta_{2n+1}$ represent the contribution of phonon modes. Notice that we did not include the lowest-temperature interval to avoid the Schottky anomaly. To be able to fit the whole temperature interval we have chosen values of $n$ from 1 to 4. Nonetheless, this large number of free parameters turns difficult an unique determination of each one.

Since from resistivity measurements[26,18,20] all the studied samples show an insulating behavior at low temperatures and the applied magnetic fields are not strong enough to destroy this characteristic, one should not expect the linear contribution from the free electrons to the specific heat. However, other kind of excitations could also lead to a linear contribution. This can imply an implicit error of the fitting model. Moreover, we could not resolve in our data a term of type $T^{3/2}$, usually interpreted as an evidence to the occurrence of ferromagnetic interactions. However, previous studies in samples clearly identified by other techniques as ferromagnetic, have not found this term in the specific heat either.[14,24] We also tried to include the hyperfine contribution with a $T^{-2}$ dependence, but the fitting did not improve. Gordon *et al.*[11] fitted the hyperfine contribution below 1.5 K, a temperature interval that we are not able to measure at the moment.

The influences of the external magnetic field on the specific heat are not clear for all samples. Almost no dependence was found for the $Sm_{0.5}Ca_{0.5}MnO_3$ sample, while in the other cases the specific heat increases with the external magnetic field. Even though the magnetic interactions do exist between 15 and 30 K and considering that there is not a long-range magnetic phase transition in this interval, we believe that the relative contribution of the magnetic excitations in this temperature interval, compared with the lattice vibrations, should be small. The external magnetic field could be primarily affecting the lattice vibrations, due to lattice distortions induced by the field, rather than affecting the antiferromagnetic or ferromagnetic spin waves. As a comparison, recently Lavrov *et al.*[27] described an unexpected magnetic effect on crystal shape in which the directions of the crystal's axes were swapped and the shape changed when a magnetic field was applied; this in turn induced curious memory effects in resistivity and magnetic susceptibility of an antiferromagnet, $La_{2-x}Sr_xCuO_4$.

The values of $\beta_3$ change between 0.28 mJ/(mol K$^4$) at $H=0$ T in $Nd_{0.5}Sr_{0.5}MnO_3$ to 1.57 mJ/(mol K$^4$) at $H=5$ T in $Ho_{0.5}Ca_{0.5}MnO_3$. The corresponding Debye temperatures ($T_D$), obtained from $\beta_3$, are plotted in Fig. 4(a). The graphs in the insets of Fig. 3 show the differences between the specific-heat experimental data and the phonon contribution to the specific heat, extrapolated to low temperatures from the fitting in the temperature interval between 15 and 30 K.

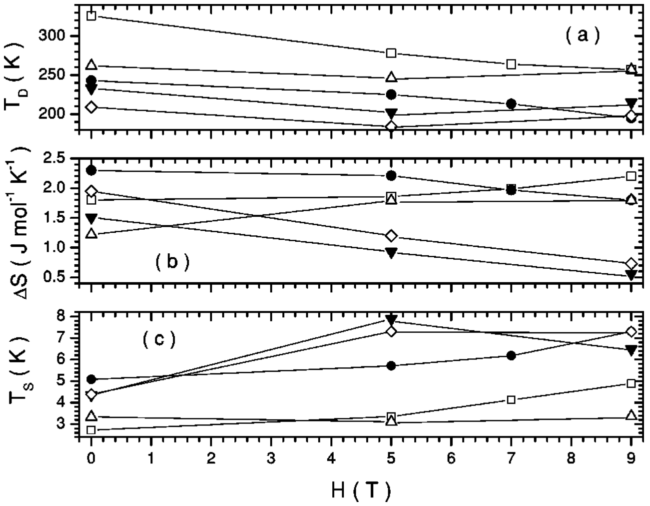

FIG. 4. Debye temperature ($T_D$), entropy variation between 2 and 20 K ($\Delta S$), and Schottky temperature ($T_S$) as a function of the applied magnetic field in $Nd_{0.5}Sr_{0.5}MnO_3$ (open squares), $Nd_{0.5}Ca_{0.5}MnO_3$ (closed circles), $Sm_{0.5}Ca_{0.5}MnO_3$ (open up triangles), $Dy_{0.5}Ca_{0.5}MnO_3$ (closed down triangles), and $Ho_{0.5}Ca_{0.5}MnO_3$ (open diamond).

Figure 4 shows (a) the magnetic-field dependence of the Debye temperature, (b) the variation of magnetic entropy between 2 and 20 K ($\Delta S$), and (c) the Schottky temperature ($T_S$) in the five studied samples. The Debye temperature was calculated using the values of $\beta_3$ and the following equation:[23]

$$T_D = \left( \frac{12\pi^4 n R}{5\beta_3} \right)^{1/3}, \tag{2}$$

where $n$ is the number of atoms in the unit cell and $R$ is the ideal-gas constant. We should point out that the Debye temperature was estimated from the low-temperature data. This procedure leads to values that are slightly different than the actual values of $T_D$ for which the specific heat saturates. As shown in Fig. 4(a) our $T_D$ values in general decrease with the increase of the applied magnetic field. We have also made specific-heat measurements with a 9 T magnetic field, at high temperatures, for several charge ordered compounds,[28] and they are in agreement with the magnetic-field dependence of the Debye temperatures shown here. Other authors[11] have made an initial assumption that the Debye temperature is magnetic-field independent, which is not supported by our experimental results.

To calculate the variation in entropy ($\Delta S$), associated to the Schottky anomaly, we used the definition

$$\Delta S = \int_{Ti}^{Tf} \frac{(C - C_{ph})}{T} dT, \tag{3}$$

where $T_i$ and $T_f$ are two temperatures conveniently chosen to delimitate the interval of interest and $C_{ph}$ is the specific heat due to the lattice oscillations.

The entropy variation, associated to the Schottky anomaly, grows as a function of magnetic field in the samples of $Nd_{0.5}Sr_{0.5}MnO_3$ and $Sm_{0.5}Ca_{0.5}MnO_3$. The same result is clearly visualized from the height of the Schottky anomaly in the insets of Figs. 3(a), 3(c), and 3(e). Gordon *et al.*[11] also reported a similar increase in a sample of $Nd_{0.67}Sr_{0.33}MnO_3$. However, the Schottky entropy variation decreases with the increase of magnetic field in the $Nd_{0.5}Ca_{0.5}MnO_3$, $Dy_{0.5}Ca_{0.5}MnO_3$, and $Ho_{0.5}Ca_{0.5}MnO_3$ samples. In these three cases, the $C$ versus $T$ curves in Figs. 3(b), 3(d), and 3(e) indicate that the local minimum, at a temperature above the Schottky anomaly, disappears with the increase of the external magnetic field. This is also reflected in the decrease of the height of the peak with the increase of the applied magnetic field [insets of Figs. 3(b), 3(d), and 3(e)].

The expected entropy variation from the magnetic ordering of $Nd^{3+}$, $Sm^{3+}$, $Dy^{3+}$, or $Ho^{3+}$ ions could be estimated[11] as $\Delta S = 0.5R\,\ln(2)$, where $R$ is the ideal-gas constant. The actually found variation corresponds to values from 63 to 77 % of the expected ones in the $Nd_{0.5}Sr_{0.5}MnO_3$ sample, 80 to 62 % in the $Nd_{0.5}Ca_{0.5}MnO_3$ sample, 42 to 62 % in the $Sm_{0.5}Ca_{0.5}MnO_3$ sample, 52 to 19 % in the $Dy_{0.5}Ca_{0.5}MnO_3$ sample, and 68 to 25 % in the $Ho_{0.5}Ca_{0.5}MnO_3$ sample, for magnetic fields between 0 and 9 T, respectively. Gordon *et al.*[11] found that the entropy variation associated to the ordering of $Nd^{3+}$ ions in $Nd_{0.67}Sr_{0.33}MnO_3$ was $\approx 85\%$ of the expected value.

Figure 4(c) shows that $T_S$, determined from the maxima in the insets of Fig. 3, grows with the increase of the external magnetic field in most of the cases. $T_S$ in the $Dy_{0.5}Ca_{0.5}MnO_3$ sample first increased and later slightly decreased. The growth of $T_S$ seems to be saturated for a magnetic field of 5 T in the sample of $Ho_{0.5}Ca_{0.5}MnO_3$ and it is almost constant in the $Sm_{0.5}Ca_{0.5}MnO_3$ sample. It is also interesting to note here the relative low $T_S$ values. For the reagent compounds of $Nd_2O_3$, $Sm_2O_3$, $Dy_2O_3$, and $Ho_2O_3$ the peaks in the specific heat, measured in zero magnetic field, were found at $\approx 10$, 7, 7, and 9 K, respectively.[29] The fact that $T_S$ is lower in the manganese compounds suggests that the collective charge ordered phase could be determining a smaller splitting in the energy levels. It also indicates that an interpretation of the Schottky-like anomaly based only on the ion total angular momentum or degeneracy is not adequate and one should consider the sample crystalline structure in detail.

Let us consider that Nd (Ho) ions be oriented by a molecular-field interaction ($H_{mf}$), and not by the exchange interaction between pairs of Nd-Nd ions (Ho-Ho).[11] Assuming that $H_{mf}$ does not change with the external magnetic field, it is possible to estimate it using a mean-field model and the peak temperature in the specific heat. Considering a two-level energy splitting $\Delta(H)$, due to a magnetic moment $m$ in an external magnetic field $H$, one finds in zero applied field $\Delta(0) = 2mH_{mf}$, and in $H = 9$ T the value changes to $\Delta(9\text{ T}) = 2m[H_{mf} + 9\text{ T}]$. One can also use that the energy splitting could be related to the peak temperature in the specific heat by $\Delta = k_B T_S/0.418$, a relation valid for a two-level-Schottky function.[23] Solving this system of two linear equations we found that $H_{mf} = 11.4$ T and $m = 0.43\mu_B$ in $Nd_{0.5}Sr_{0.5}MnO_3$, $H_{mf} = 20.6$ T and $m = 0.44\mu_B$ in $Nd_{0.5}Ca_{0.5}MnO_3$, $H_{mf} = 18.3$ T and $m = 0.42\mu_B$ in $Dy_{0.5}Ca_{0.5}MnO_3$, and $H_{mf} = 13.6$ T and $m = 0.58\mu_B$ in $Ho_{0.5}Ca_{0.5}MnO_3$. These values of $m$ are smaller than those obtained from susceptibility measurements at high temperatures.[18] However, they are similar to the ones found by Gordon *et al.*[11] using the same method ($H_{mf} = 10$ T and $m = 0.8\mu_B$ in $Nd_{0.67}Sr_{0.33}MnO_3$). This model could not be applied to the $Sm_{0.5}Ca_{0.5}MnO_3$ sample because $T_S$ did not change very much with the applied magnetic field.

The ground state of the $Nd^{3+}$, $Sm^{3+}$, $Dy^{3+}$, and $Ho^{3+}$ ions are usually denoted as ${}^4I_{9/2}$, ${}^6H_{5/2}$, ${}^6H_{15/2}$, and ${}^5I_8$, where $I$ or $H$ stands for an orbital angular momentum $L = 6$ or $L = 5$, the superprefix specifies the total spin as $2S + 1$ and the subscript the total angular momentum $J$. The number of the lowest energy levels is given by $2J + 1$, which leads to five, three, and eight Kramers doublets in the ground state of the first, second, and third ion, respectively. The $Ho^{3+}$ ions have a singlet and eight Kramers doublets.[30] Bartolomé *et al.*[12] showed that the second doublet in the $Nd^{3+}$ ion was $\approx 120$ K (in energy) above the lowest doublet. As this temperature is about ten times higher than the temperature where the Schottky anomaly appears, the contribution of the second doublet is expected to be small. The second doublet is even higher in temperature for the $Dy^{3+}$ and $Ho^{3+}$ ions and slightly lower for the $Sm^{3+}$ ion in comparison with the $Nd^{3+}$ ion.

In a previous report[15] we showed that a two-level-Schottky function (only one doublet) did not fit properly our experimental data at low temperatures. The same result was verified for all the experimental data presented here. One alternative, justified by the existence of several different grains in polycrystalline samples, is to consider a distribution of energy splitting around the value that would correspond to a single crystal in the same two-level-Schottky model. Although the fitting results using this second approach improved a little bit, we found that they still remained unsatisfactory.

At first sight someone might be tempted to correlate the existence of the Schottky anomaly with the presence of an intrinsic magnetic moment in $Nd^{3+}$ and $Ho^{3+}$ ions (in contrast with $La^{3+}$ ions without magnetic moment and no Schottky anomaly in the manganite). However, specific-heat measurements reported by Hardy *et al.*[25] in a compound of $Pr_{0.63}Ca_{0.37}MnO_3$ ($Pr^{3+}$ ions have approximately the same magnetic moment as $Nd^{3+}$ ions) did not show any Schottky anomaly. Moreover, $Ho^{3+}$ ions have an intrinsic magnetic moment almost three times bigger than $Nd^{3+}$ ions, but the Schottky temperatures at zero magnetic field were 2.73 K in $Nd_{0.5}Sr_{0.5}MnO_3$, 5.08 K in $Nd_{0.5}Ca_{0.5}MnO_3$, and 4.39 K in $Ho_{0.5}Ca_{0.5}MnO_3$.

Probably the existence of the Schottky anomaly is related with the Kramers theorem. It states that an ion possessing an odd number of electrons, no matter how unsymmetrical the crystal field, must have a ground state that is at least doubly degenerate.[30] This could lead to the thermal depopulation that produces the Schottky anomaly in the specific heat. Ions of Ce, Nd, Sm, Gd, Dy, Er, and Yb all have an odd number of electrons and their respective oxides present a Schottky anomaly in the specific heat. However, the Kramers theorem does not exclude that ions with an even number of electrons might also have a doubly degenerate ground state. For instance, someone might be tempted to state that Ho ions are equivalent to Pr ions and therefore no Schottky-like anomaly should be expected, however, experiments prove this analogy to be wrong. Furrer *et al.*[31] used inelastic neutron scattering to study the crystalline electric-field interaction at the Ho site in the high-temperature superconductor $HoBa_2Cu_3O_{7-\delta}$. They concluded that this interaction lifted the degeneracy of the ground-state *J* multiplet. Similar effects in the case of $Ho_{0.5}Ca_{0.5}MnO_3$ may be leading to a Schottky-like anomaly.

## IV. CONCLUSIONS

We have made a magnetic characterization of $Nd_{0.5}Sr_{0.5}MnO_3$, $Nd_{0.5}Ca_{0.5}MnO_3$, $Sm_{0.5}Ca_{0.5}MnO_3$, $Dy_{0.5}Ca_{0.5}MnO_3$, and $Ho_{0.5}Ca_{0.5}MnO_3$ polycrystalline samples. Ferromagnetic, antiferromagnetic, and charge ordering transitions in our samples agreed with previous reports. We also reported, to our knowledge for the first time, specific-heat measurements with applied magnetic fields between 0 and 9 T and temperatures between 2 and 30 K in all those five samples. Absolute values of specific heat close to 2 K were about 100 times higher in our samples than in other charge ordering samples like $Pr_{0.63}Ca_{0.37}MnO_3$. At low temperatures the specific-heat curve, in all five studied samples and measured magnetic fields, showed a Schottky-like anomaly. In almost all cases an increase in the applied magnetic field moves the Schottky peak to higher temperatures. However, the position of the peak is almost independent of the applied magnetic field in the $Sm_{0.5}Ca_{0.5}MnO_3$ sample. We could not successfully fit the curves by either assuming a single or a distribution of the two-level-Schottky anomaly. The physics discussed here do not allow us to separate a single variable like: degeneracy of the rare-earth ion ground state, effective magnetic moment of rare-earth ions, or even talk of the rare-earth ion instead of the sample crystalline structure, to explain the observed results. In other words, all these variables, considered individually, cannot explain the experiments. More experiments are clearly necessary to unambiguously identify the origin of the Schottky anomaly and its possible correlation with the charge ordered phase.

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