Specific heat and magnetic measurements in \(\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3\) and \(\text{R}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) (R=Nd, Sm, Dy and Ho) samples

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Abstract

We have made a magnetic characterization of \(\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3\), \(\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\), \(\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\), \(\text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) and \(\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) polycrystalline samples. Ferromagnetic, antiferromagnetic and charge ordering transitions in our samples agree with previous reports. We also studied specific heat measurements with applied magnetic fields between 0 and 9 T and temperatures between 2 and 300 K in all cases. Each curve was successfully fitted at high temperatures by an Einstein model with three optical phonon modes. Close to the charge ordering and ferromagnetic transition temperatures the specific heat curves showed peaks superposed to the characteristic response of the lattice oscillations. The entropy variation corresponding to the charge ordering transition was higher than the one corresponding to the ferromagnetic transition. The external magnetic field seems to have no effect in specific heat of the CO phase transition.

65.40.Ba, 74.25.Ha, 75.60.-d
I. INTRODUCTION

The physical properties in charge ordering (CO) manganese perovskites are thought to arise from the strong competition involving a ferromagnetic double exchange interaction, an antiferromagnetic superexchange interaction, and the spin-phonon coupling\textsuperscript{1,2,3,4,5,6,7}. These interactions are determined by intrinsic parameters such as doping level, average cationic size, cationic disorder and oxygen stoichiometry. 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 Myron B. Salamon and Marcelo Jaime\textsuperscript{8}.

L. Ghivelder et al.\textsuperscript{9} reported specific heat measurements in LaMnO$_{3+\delta}$ samples and found that the specific heat at low temperature is very sensitive to small variations of $\delta$, similarly to results published by W. Schnelle et al.\textsuperscript{10} in a Nd$_{0.67}$Sr$_{0.33}$MnO$_{3-\delta}$ sample. In this latter work, and also in a paper by J. E. Gordon et al.\textsuperscript{11}, a Schottky-like anomaly was found at low temperatures. They associated this result to the magnetic ordering of Nd$^{3+}$ ions and to the crystal-field splitting. F. Bartolomé et al.\textsuperscript{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 V. N. Smolyaninova et al.\textsuperscript{13,14} studied the low temperature specific heat in Pr$_{1-x}$Ca$_x$MnO$_3$ (0.3<x<0.5) and La$_{1-x}$Ca$_x$MnO$_3$ (x=0.47, 0.5 and 0.53). They fitted the data with an excess specific heat, C′(T), of non-magnetic origin associated with charge ordering. They also showed 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.

We have already presented 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 pre-
presented a Schottky-like anomaly at low temperatures\textsuperscript{15,16}. Here, we report a general magnetic characterization and specific heat measurements in the full temperatures interval, between 2 and 300 K, for the same five samples. As far as we know, the high temperature interval of the specific heat measurements in these compounds have not been published yet.

II. EXPERIMENTAL METHODS

Polycrystalline samples of Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3}, Nd\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} and Ho\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} were prepared by the sol-gel method\textsuperscript{17}. Stoichiometric parts of Nd\textsubscript{2}O\textsubscript{3} (Ho\textsubscript{2}O\textsubscript{3}) and MnCO\textsubscript{3} were dissolved in HNO\textsubscript{3} and mixed to an aqueous citric acid solution, to which SrCO\textsubscript{3} or CaCO\textsubscript{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 pH\textasciitilde7 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 hours, with several intermediary grindings, in order to prevent formation of impurity phases. This powder was pressed into pellets and sintered in air at 1050 °C for 12 hours.

Polycrystalline samples of Sm\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} and Dy\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} were prepared from stoichiometric amounts of Sm\textsubscript{2}O\textsubscript{3} or Dy\textsubscript{2}O\textsubscript{3}, CaO, and MnO\textsubscript{2} by standard solid-state reaction method. All the powders were mixed and ground for a long time in order to produce a homogeneous mixture. First, the mixture was heated at 927 °C for 24 hours and after that it was ground and heated at 1327 °C (72 hours) and 1527 °C (48 hours). X-ray diffraction measurements indicated high quality samples in all cases.

The magnetization measurements were done with a Quantum Design MPMS-5S SQUID magnetometer. Specific heat measurements were done with a Quantum Design PPMS calorimeter. The PPMS used the two relaxation time technique, and data was 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 magnetization temperature dependence, measured with a 5 T applied magnetic field in 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-axes to facilitate comparisons. 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$^{18,19,20,21}$. 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$^{18,19,20,21}$. 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 $T_C \approx 244$ K and an antiferromagnetic transition at $T_N \approx 160$ K. The Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ compound presented a strong magnetization 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 magnetization. The antiferromagnetic transition in Sm$_{0.5}$Ca$_{0.5}$MnO$_3$ presented a maximum at $T_N \approx 150$ K. 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 respectively, showed a sharp increase in the magnetization. This trend have been associated to a short range magnetic ordering of the intrinsic magnetic
moment of Nd$^{3+}$ ions$^{22}$. However, no long range ferromagnetic order of the Nd$^{3+}$ ions was found in neutron diffraction measurements at these low temperatures$^{18,19}$.

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 magnetization maximum at the charge ordering temperature. However, a clear inflection is observed at $T_{CO}$ for both samples, as revealed by the temperature derivative shown in the inset of fig. 1b. 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 T. Terai et al.$^{21}$ after studies of magnetization and resistivity curves. As shown ahead our high temperature measurements of specific heat present peaks at around the same temperature interval of the suggested charge ordered transition.

B. Specific heat at high temperatures

Figure 2 shows specific heat measurements with a zero applied magnetic field from 2 to 300 K in the 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. In order to facilitate the visualization, the curves for Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and Ho$_{0.5}$Ca$_{0.5}$MnO$_3$ were displaced 20 J/mol K upside and downside in figure 2a, and the curve for Dy$_{0.5}$Ca$_{0.5}$MnO$_3$ was displaced 20 J/mol K downside in figure 2b. Specific heat measurements give information about both lattice and magnetic excitations. At high temperatures the excitations from the lattice vibrations are dominant and decrease as the temperature decreases. The magnetic contribution can be obtained approximately by subtracting the lattice part from the experimental values.

Continuous lines in figure 2 represent the fitting of the thermal background, in the interval from 30 to 300 K, by the Einstein model given by:

$$C_{Einstein} = 3nR \sum_i a_i \left[ \frac{x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} \right]$$  

(1)

where $x_i = T_i/T$. We used three optical phonons ($i = 1, 2, 3$) with energies $T_i$ (in Kelvin) and relative occupations $a_i$. The Einstein model for the specific heat considers the oscillation
frequency (or energy) independently of the wave vector, which is a valid approximation for the optical part of the spectrum. The values of temperatures (energies) and relative occupations are shown in table 1. These values are similar to those reported, using the same model, by A. P. Ramirez et al.\textsuperscript{23} in a La\textsubscript{0.37}Ca\textsubscript{0.63}MnO\textsubscript{3} sample and Raychaudhuri et al.\textsuperscript{24} in a Pr\textsubscript{0.63}Ca\textsubscript{0.37}MnO\textsubscript{3} sample. However, we should point out that the values found are not unique because there are six free parameters during the fitting (one energy and one occupation coefficient for each oscillation mode). Besides, the thermal background determination is risky, particularly because it could have a "tail" of any magnetic or charge ordering anomaly. Nonetheless, this seems to be the best possible trial to quantify the specific heat at high temperatures.

Figure 3 represents the differences between the experimental data and the fitted curves in figure 2. There is a maximum at 231 K for the Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} sample, which is correlated with the ferromagnetic transition at 250 K in the corresponding magnetization curve (figure 1). A second maximum, which could be partially associated to the antiferromagnetic and charge ordering transitions at 160 K, appears at 180 K. However, lattice parameters in this compound change rapidly between approximately 110 K and 250 K\textsuperscript{25}. The variation in lattice parameters changes the intensity of the interactions between the atoms and the oscillation frequency of the phonons mode, contributing to the specific heat in the second peak.

Figure 3 also shows that there is a maximum at 243 K for the Nd\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} sample. This maximum correlates with the corresponding charge ordering temperature at 250 K. Differently from the Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} compound, there is no magnetic ordering in this high temperature interval for the Nd\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} sample. However, in this latter case lattice parameters change very rapidly between approximately 200 and 250 K\textsuperscript{19}. An inflection point in the C vs. T curve (fig. 2a) appears at 141 K for the Nd\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} sample. Besides, there is a maximum at 141 K in figure 3, but its height is relatively small compared to the maximum at 243 K. The Neel temperature corresponding to this compound is 160 K. Therefore, these results lead us to conclude that the specific heat variations due to the
antiferromagnetic order are small compared to those induced in the charge ordering and
ferromagnetic transitions.

For the \( \text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \), \( \text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) and \( \text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) samples, the maxima were found at 254 K, 281 K and 276 K, respectively. These experimental results and the resistivity measurements reported by Y. Tokura et al.\textsuperscript{20} and T. Terai et al.\textsuperscript{21}, are strong evidences that indicate the existence of CO transitions in the \( \text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \), \( \text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) and \( \text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) samples. However, electron diffraction studies would be needed to unambiguously classify this transition as CO. The other small peaks, comparable to the experimental error, were not found to be correlated to any magnetic transition.

Results in figure 3 allow us to calculate the variation in entropy (\( \Delta S \)), within the limits of the model, associated to the charge ordering, ferromagnetic and antiferromagnetic transitions:

\[
\Delta S = \int_{T_i}^{T_f} \left( \frac{C - C_{ph}}{T} \right) dT
\]

(2)

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.

For the \( \text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) sample the entropy variation between 201 and 301 K, with \( H=0 \), was \( \Delta S(T_{CO}) = 2.0 \text{ J/(mol K)} \). Raychaudhuri et al.\textsuperscript{24} reported an entropy variation, close to the charge ordering transition in the compound \( \text{Pr}_{0.63}\text{Ca}_{0.37}\text{MnO}_3 \), of 1.8 J/(mol K) with zero applied magnetic field and 1.5 J/(mol K) with an 8 T magnetic field. On the other hand, Ramirez et al.\textsuperscript{23} found \( \Delta S(T_{CO}) = 5 \text{ J/(mol K)} \) in a \( \text{La}_{0.37}\text{Ca}_{0.63}\text{MnO}_3 \) sample. All these results correspond to those expected for a charge ordering transition\textsuperscript{24}. Besides, the entropy variation (not related with phonons), calculated between 118 and 201 K for the \( \text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) sample, was \( \Delta S(T_N) = 0.80 \text{ J/(mol K)} \). We associate this smaller \( \Delta S \) value to the antiferromagnetic order at \( T_N =160 \text{ K} \).

The entropy variation between 133 and 274 K for the \( \text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3 \) sample was \( \Delta S(T_{CO+FM}) = 3.6 \text{ J/(mol K)} \). Considering that the entropy variation associated to the charge ordering transition is the same as for the \( \text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) sample, one finds that the
entropy variation associated to the ferromagnetic transition is approximately 1.6 J/(mol K). Using a model proposed by J. E. Gordon et al.\textsuperscript{11} we estimate that the change in entropy needed to a full ferromagnetic transition in the Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} sample is 12.45 J/(mol K). Therefore, the fact that the entropy variation found is 13\% of the theoretical value, suggests that only a small part of the spins order ferromagnetically. J. E. Gordon et al.\textsuperscript{11} found also that the entropy variation associated to the ferromagnetic order in a Nd\textsubscript{0.67}Sr\textsubscript{0.33}MnO\textsubscript{3} sample was approximately 10\% of the theoretical value. The entropy variation, not associated to lattice oscillations, between 200 K and 300 K, for the Sm\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} and Dy\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} samples were $\Delta S(T_{CO}) = 1.15$ J/(mol K) and 2.80 J/(mol K); between 216 K and 294 K for the Ho\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} sample was $\Delta S(T_{CO}) = 0.78$ J/(mol K). The entropy variation for Sm\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} and Dy\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} are closer to the ones of the Nd\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} sample. The $\Delta S(T_{CO})$ for the Ho\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} sample is smaller than for the other samples, suggesting a different nature of the charge ordering transition.

Figure 4 shows the specific heat measurements, between 200 and 300 K, with a zero applied magnetic field (open symbols) and with $H = 9$ T (closed symbols) for the five measured samples. To allow comparisons the Nd\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} curve was displaced 20 J/mol K upside; the Sm\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3}, Dy\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} and Ho\textsubscript{0.5}Ca\textsubscript{0.5}MnO\textsubscript{3} curves were displaced 20, 40 and 60 J/mol K downside, respectively. The external magnetic field suppresses the peak around the ferromagnetic temperature in the Nd\textsubscript{0.5}Sr\textsubscript{0.5}MnO\textsubscript{3} sample. Although a 9 T magnetic field is much smaller than a thermodynamic field given by $k_B T_C / \mu_B$, near the ferromagnetic phase transition the system is in an unstable condition, which is very sensitive to the external magnetic field. This fact explains the suppression of the peak in the presence of field in the specific heat curve and the decrease in the slope of the magnetization curve (not shown).

On the other hand, the external magnetic field seems to have no effect in the specific heat of the other four compounds. This result indicates that, although the sample magnetization increases with temperature close to the charge ordering transition, the CO phase do not appear to depend thermodynamically on the application of an external magnetic field.
The increase of magnetization close to $T_{CO}$ is associated with an abrupt change in lattice parameters$^{20}$, affecting the distance among magnetic ions and hence their interactions. Our experiments show that an external magnetic field of 9 T is not strong enough to produce variations in the specific heat of the CO phase occurring in these samples.

**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 300 K in all these five samples. Each curve was successfully fitted at high temperatures by an Einstein model with three optical phonon modes. Close to the charge ordering and ferromagnetic transition temperatures the specific heat curves showed peaks superposed to the characteristic response of the lattice oscillations. The entropy variation corresponding to the charge ordering transition was higher than the one corresponding to the ferromagnetic transition. Near 160 K the specific heat curve showed an abrupt change in slope for the two compounds with Nd$^{3+}$ ions, which were correlated to the corresponding antiferromagnetic transition. However, an external 9 T magnetic field seems to have no effect in the specific heat of the CO phase transition.

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TABLES

TABLE I. Values of energies $T_i$ (in Kelvin) and relative occupations $a_i$ for the three optical phonons ($i = 1, 2, 3$) in an Einstein model for the specific heat in all the studied samples.

| Sample          | $T_1$(K) | $T_2$(K) | $T_3$(K) | $a_1$ | $a_2$ | $a_3$ |
|-----------------|----------|----------|----------|-------|-------|-------|
| Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ | 148      | 438      | 997      | 0.30  | 0.64  | 0.11  |
| Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ | 152      | 432      | 1035     | 0.27  | 0.62  | 0.18  |
| Sm$_{0.5}$Ca$_{0.5}$MnO$_3$ | 157      | 450      | 846      | 0.27  | 0.64  | 0.16  |
| Dy$_{0.5}$Ca$_{0.5}$MnO$_3$ | 126      | 351      | 821      | 0.17  | 0.41  | 0.51  |
| Ho$_{0.5}$Ca$_{0.5}$MnO$_3$ | 147      | 438      | 1023     | 0.27  | 0.51  | 0.25  |
FIGURES

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-axes to allow the comparison of all samples. The inset in fig.1b represents the temperature derivative of the magnetization close to the charge ordering transition.

FIG. 2. Specific heat measurements between 2 and 300 K in the five measured samples. Continuous lines represent the fitting of the phonon background to the Einstein model (see text). The Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and Ho$_{0.5}$Ca$_{0.5}$MnO$_3$ curves in fig.2a were displaced 20 J/mol K upside and downside, respectively; the Ho$_{0.5}$Ca$_{0.5}$MnO$_3$ curve in fig.2b was displaced 20 J/mol K downside.

FIG. 3. Differences between the experimental specific heat data and the corresponding background curves in 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.

FIG. 4. Specific heat measurements between 200 and 300 K with a zero applied magnetic field (open symbols) and with $H = 9$ T (closed symbols) in the five measured samples. To allow comparisons the Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ curves were displaced 20 J/mol K upside; the Sm$_{0.5}$Ca$_{0.5}$MnO$_3$, Dy$_{0.5}$Ca$_{0.5}$MnO$_3$ and Ho$_{0.5}$Ca$_{0.5}$MnO$_3$ curves were displaced 20, 40 and 60 J/mol K downside, respectively.
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Figure 1a

H = 5 T

Nd_{0.5}Sr_{0.5}MnO_3
Nd_{0.5}Ca_{0.5}MnO_3
Sm_{0.5}Ca_{0.5}MnO_3

M (\mu_B)

T (K)

T_N & T_{CO}

T_C

T_N

T_{CO}
Figure 1b

$M (\mu_B) vs. T (K)$

$H = 5 T$

$\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

$\text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

$T_{CO}$
Figure 2a

$H = 0 \ T$

- $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$
- $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$
- $\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

(a)

$C \ (J / \text{mol K})$

$T \ (K)$
Figure 2b

$H = 0 \text{T}$

- $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$
- $\text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

(b)

$C (\text{J/mol K})$

$T (\text{K})$
Figure 3a

$H = 0 \, T$

- $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$
- $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$
- $\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

$C - C_{\text{ph}} \, (\text{J} / \text{mol K})$

$T \, (\text{K})$
Figure 3b

H = 0 T
- \( \text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \)
- \( \text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \)

(b)

\[ C - C_{ph} \text{ (J/mol K)} \]

\[ T \text{ (K)} \]
Figure 4

\[
\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3
\]

\[
\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3
\]

\[
\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3
\]

\[
\text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3
\]

\[
\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3
\]

\[
\text{H} = 0 \text{ T}
\]

\[
\text{H} = 9 \text{ T}
\]