

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

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Abstract

We have made a magnetic and specific heat characterization of five manganese samples. Ferromagnetic, antiferromagnetic and charge ordering transitions in our samples agree with previous reports. Each specific heat 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.

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Physical properties in charge ordering (CO) manganese perovskites arise from the strong competition among a ferromagnetic double exchange interaction, an antiferromagnetic superexchange interaction, and the spin-phonon coupling [1–7]. We report a general magnetic characterization and specific heat measurements in the full temperatures interval, between 2 and 300 K, for five manganese perovskites.

Polycrystalline samples of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ were prepared by the sol–gel method [8]. Polycrystalline samples of $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ were prepared by standard solid-state reaction method. Magnetization measurements were done with a Quantum Design MPMS-5S SQUID magnetometer. Specific heat measurements were done with a Quantum Design PPMS calorimeter.

Fig. 1 shows the temperature dependence of magnetization, measured with a 5 T applied magnetic field in field cooling conditions, in all polycrystalline samples. Charge ordering transition temperatures (T_{CO}) are indicated by arrows at 160, 250, 270, 280 and 271 K. The antiferromagnetic transition temperatures (T_{N}) were between 150 and 160 K in the samples of Fig. 1a. These temperatures are associated to peaks in the magnetization curves, in agreement with previous reports [9–12]. The $\text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

and $\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ 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. 1b. As shown ahead our high temperature measurements of specific heat present peaks at around the same temperature interval of the suggested charge ordered transition.

Fig. 2 shows specific heat measurements with a zero applied magnetic field from 2 to 300 K in the $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, $\text{Dy}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ samples. Specific heat measurements give information about both lattice and magnetic excitations. The magnetic contribution can be obtained approximately by subtracting the lattice part from the experimental values.

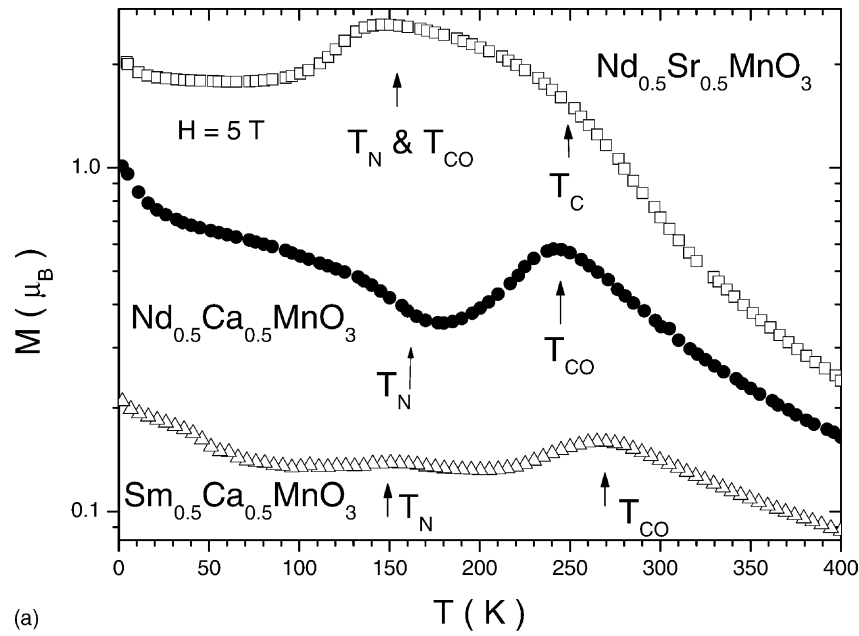
Continuous lines in Fig. 2 represent the fitting of the thermal background, in the interval from 30 to 300 K, by the Einstein model given by

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

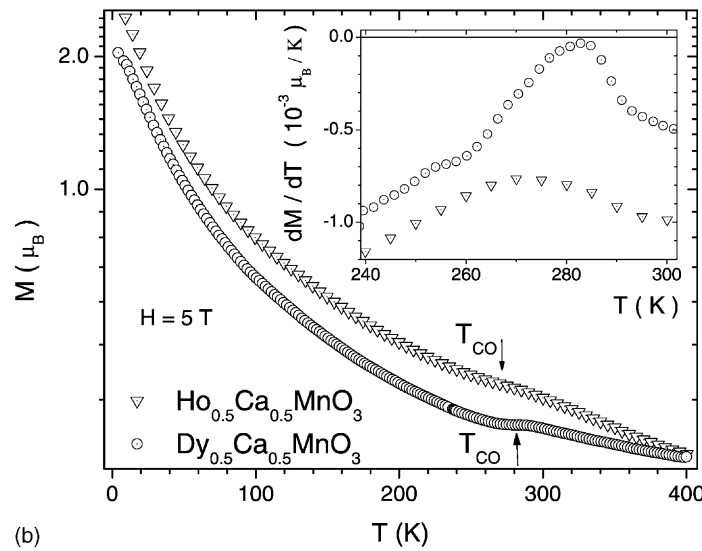
where $x_i = T_i/T$. We used three optical phonons ($i = 1, 2, 3$) with energies T_i (in Kelvin) and relative occupations a_i . The Einstein model for the specific heat considers the oscillation frequency (or energy) independently from the wave vector, which is a valid approximation for the optical part of the spectrum. The thermal background determination is

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(a)



(b)

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. The Curie (T_C), Néel (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 (b) represents the temperature derivative of the magnetization close to the charge ordering transition.

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. The values of temperatures and relative occupations are shown in Table 1 and are similar to other reports [13,14]. Specific heat variations due to the antiferromagnetic order are small compared to those induced in the charge ordering and ferromagnetic transitions. More details about the interpretation of the experimental data will be published elsewhere.

In conclusion, we have made a magnetic characterization of five manganese samples. Ferromagnetic,

Table 1

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

Samples	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

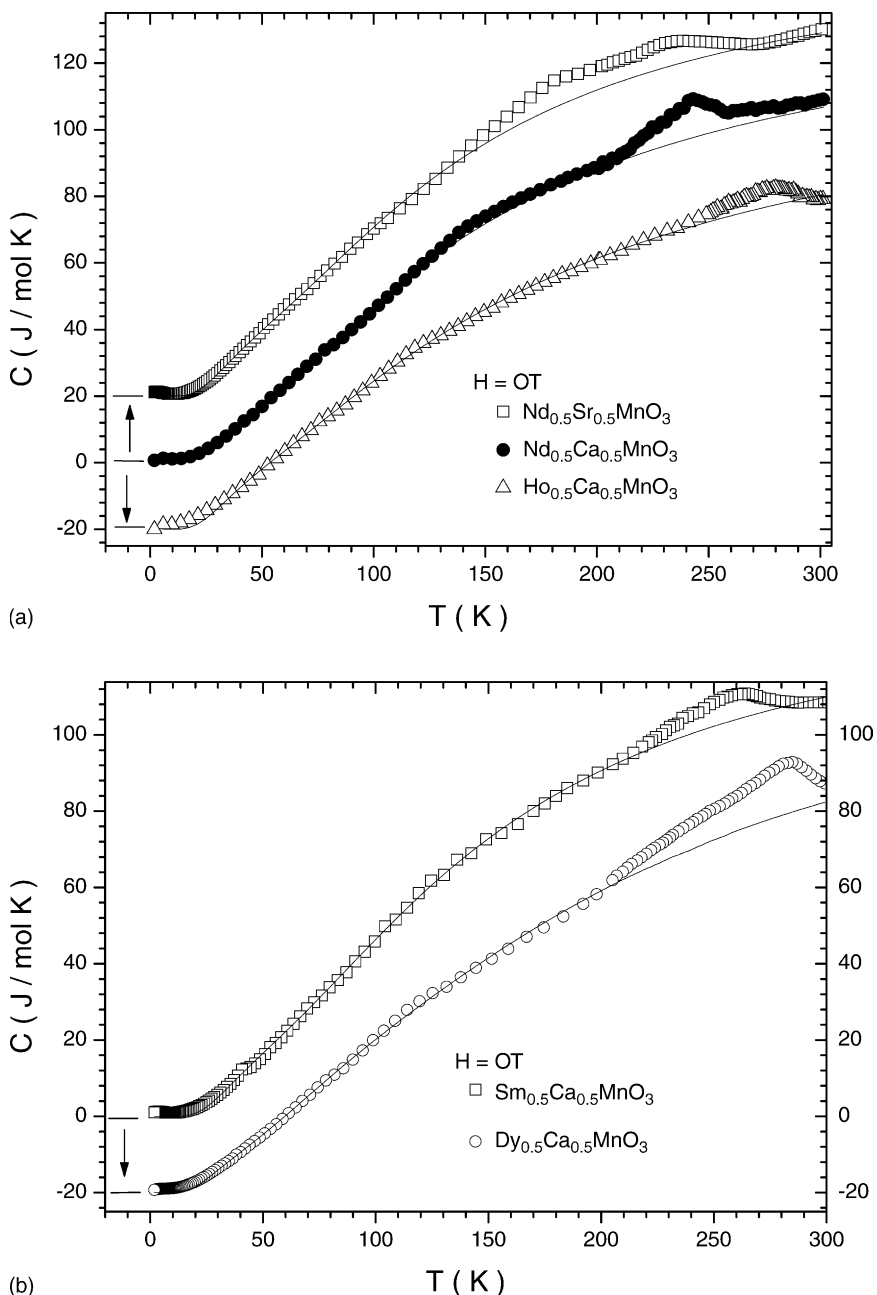


Fig. 2. Specific heat measurements between 2 and 300 K and $H = 0$ T in the five measured samples. Continuous lines represent the fitting of the phonon background to the Einstein model. The $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ curves in (a) were displaced 20 J/mol K upside and downside, respectively, the $\text{Ho}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ curve in (b) was displaced 20 J/mol K downside.

antiferromagnetic and charge ordering transitions in our samples agreed with previous papers. We also reported specific heat measurements with zero applied magnetic field and temperatures between 2 and 300 K in all 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. We thank Dr. P.N. Lisboa-Filho for the partial preparation of

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